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Todaro, Louis J., Ph.D.

City University of New York, 1993

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IN THE IMAGE AND LIKENESS OF BENZENE:

Variable-temperature X-ray Studies of Substituted Barbaralanes and Semibullvalenes

by

Louis J. Todaro

Volume I

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirement for the degree of Doctor of Philosophy, The City University of New York.

1993

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ABSTRACT

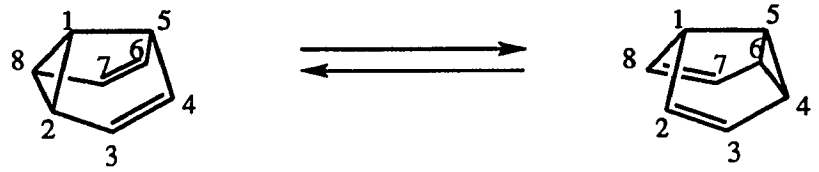
IN THE IMAGE AND LIKENESS OF BENZENE: Variable-temperature X-ray Studies of Substituted Barbaralanes and Semibullvalenes

by

Louis J. Todaro

Advisor: **Professor Klaus G. Grohmann**

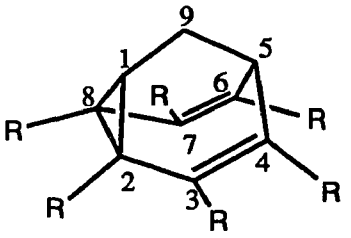
The **Cope rearrangement** involves the breaking of a **σ** bond, formation of a new **σ** bond, and migration of **π** bonds. A fast Cope rearrangement is a consequence of a low **activation energy**. Molecules, which rapidly change back and forth from one structure to an entirely equivalent structure via the Cope rearrangement, are called **fluxional** or **valence tautomers**. Among these molecules, **semibullvalene**, one of the fastest valence tautomer, and its derivatives have received particular attention.



Semibullvalene **Semibullvalene**

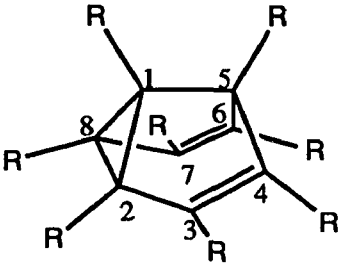
The existence of the Cope rearrangement in the solid state can be detected with various spectroscopic and diffraction methods. **Solid-state ^{13}C-NMR, ^{1}H-NMR**, and **single-crystal X-ray diffraction** have proved to be powerful tools in probing the nature of fluxional molecules.

We have undertaken a systematic, variable-temperature single-crystal X-ray study of substituted barbaralanes and semibullvalenes, which have a low activation energy for the Cope rearrangement. The compounds for this study are:



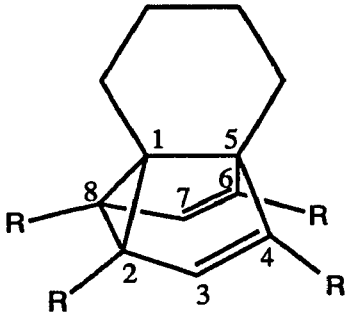
R = $COOCH_3$

2,4,6,8-Tetracarbomethoxybarbaralane
[Barbaralane-$(COOMe)_4$]



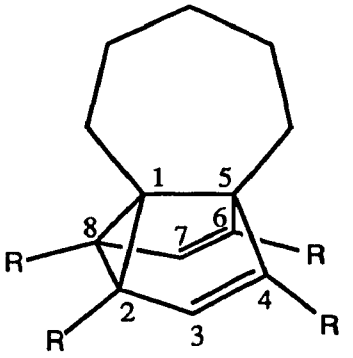
R = $COOCH_3$

Octacarbomethoxysemibullvalene
[Sb-$(COOMe)_8$]



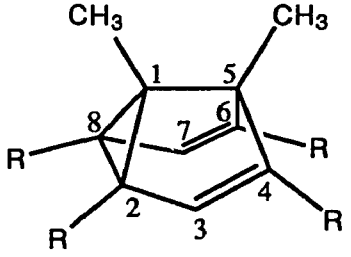
R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)



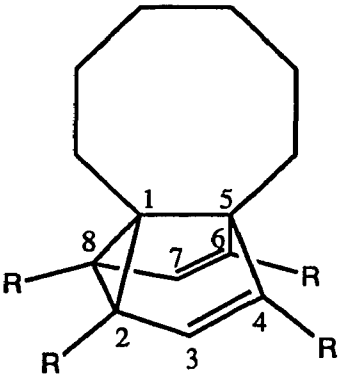
R = $COOCH_3$

1,5-Cycloheptano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-7)



R = $COOCH_3$

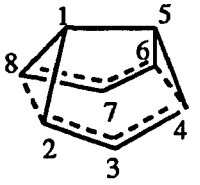
1,5-Dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-Me_2)



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

The data clearly indicate that these six molecules approach the bishomoaromatic transition state with increasing temperature (from 20 to 360 K), that is, **they become more and more like benzene.** In solution, these compounds undergo Cope rearrangement. In the solid state, however, no significant structural alterations take place in barbaralane $(COOMe)_4$ with temperature; gradual changes creep in Sb-$(COOMe)_8$; and spectacular transformations occur in Sb-8. These six compounds may be classified in an order of increasing dynamic behavior in the solid state: barbaralane-$(COOMe)_4$ being nearly static, while Sb-8 is the most dynamic. The rest fell between these two extremes. Stepping over one candidate to the next, we see that the trend toward the bishomoaromatic state intensifies. The climax is reached when Sb-8 achieves at room temperature the delocalized bishomoaromatic structure, where the single bonds in the semibullvalene ring, C2—C3 and C7—C8, and double bonds, C3—C4 and C6—C7 are all equal, along with the interatomic distances, C2—C8 and C4—C6.



Semibullvalene ring system in Sb-8 at room temperature

For the first time, we have characterized a neutral bishomobenzene molecule of the type which Hoffmann and Dewar had predicted more than twenty years ago. Even though Sb-8 at room temperature has the delocalized structure expected for a neutral bishomoaromatic compound, it is, nevertheless, static at temperatures below 90 K. We conclude that Sb-8 has not crossed the barrier between valence tautomerism ($\Delta G^{\ddagger} > 0$) to resonance ($\Delta G^{\ddagger} < 0$) as in benzene. The significance of low-temperature work is clear. It is indispensable in preventing misconceptions, which may be construed from examining just room-temperature data when characterizing compounds claimed to exhibit benzene-like behavior.

ACKNOWLEDGEMENTS

Words are often inadequate to express true feelings of gratitude. Nevertheless, I will attempt with these imperfect language tools to give credit to the many talented persons, who played a role in this project and who touched my life with their professionalism. But where do I begin to thank everyone responsible for the success of this research? Let me begin at the beginning. I am indebted to three special individuals at Hoffmann-La Roche, Drs. John Blount, Vince Madison, and Manfred Weigele, my superiors and friends, not only for taking the initiative in conceiving the idea to further my education but also for their encouragement. They offered me the opportunity, the time, the freedom, and Roche's resources at my disposal. Over the years, Dr. Blount has taught me a great deal of crystallography and has shown me many tricks of the trade. I have benefited from his programming skills and expertise. Dr. Madison has given me the freedom to manage the X-ray laboratory in my own way, like my own private business. That privilege has added substantially to my personal satisfaction. Early on, Dr. Weigele had the foresight to realize my potentials and presented me with the opportunity to remain in the company on a permanent basis. Under their tutelage, my success in this research was inevitable. Also, I thank Hoffmann-La Roche for its generous financial support and for providing the facilities to do the research. From all that Roche has done for me, there is no doubt that it certainly holds fast to its commitment of caring for its employees.

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My special thanks are in order to Dr. Charles Strousse, who helped me to collect and refine the 20 K data in his laboratory at UCLA. He treated me as family at his home and made my stay in California delightful.

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To My Family

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INTRODUCTION

SURVIVAL BASICS FOR THE FAST LANE

The Latin maxim, *Ex celeritate iuventus*, which translates as *From speed comes youth*, sums up basic notions dear to our hearts. One branch of chemistry, **reaction kinetics**, deals with one of these important concepts, namely, the **speed of a chemical reaction.**

0.1 DEFINITION OF REACTION RATE

The **speed** or **rate** of a chemical reaction denotes how fast reactants are converted to products. The rate, which is always considered to be a positive quantity, may be defined in several ways. It can be expressed in terms of the decrease in the amount of one of the reactants or, alternatively, in terms of the increase in the amount of a product in some time interval. Convenience dictates which chemical species is monitored to obtain the rate of reaction. Thus, for the general chemical reaction

$$A + B + \cdots \longrightarrow C + D + \cdots$$

or simply,

$$A + B \longrightarrow C + D$$

the rate in terms of the decrease in A is defined as

$$Rate \equiv -\frac{dn_A}{dt}$$

where n_A is the amount in moles of reactant A and t is time. Since the reactants are decreasing as the reaction proceeds to the right, the derivative, dn_A/dt, is negative;

hence, for a positive rate, a negative sign must precede this derivative. Similarly, in terms of the decrease in B, the rate is

$$Rate \equiv -\frac{dn_B}{dt}$$

Also, since one molecule of A and one molecule of B disappear at the same time to form one molecule of C and one molecule of D, the rate of disappearance for each of the reactants are equal, that is,

$$-\frac{dn_A}{dt} = -\frac{dn_B}{dt}$$

or

$$Rate = -\frac{dn_A}{dt} = -\frac{dn_B}{dt}$$

Alternatively, the rate in terms of the increase in the products C and D is

$$Rate = +\frac{dn_C}{dt} = +\frac{dn_D}{dt}$$

where n_C and n_D are the amounts in moles of products C and D, respectively. As reactants disappear, products are formed; and so, the rate of consumption of reactants equals the rate of product formation. Thus,

$$Rate = -\frac{dn_A}{dt} = -\frac{dn_B}{dt} = +\frac{dn_C}{dt} = +\frac{dn_D}{dt}$$

Of course, if transient-species build-up delays the formation of products relative to the disappearance of reactants, the rate of consumption of reactants does not equal the rate of product formation.

When the stoichiometric coefficients in a reaction are not all unity, the rate must still be expressed in a consistent fashion and must be the same regardless of which chemical species is monitored. For example, in the reaction

$$2A \longrightarrow C$$

two molecules of A disappear for each molecule of C formed. Thus, the rate of formation of C is half the rate of disappearance of A, that is,

$$-\frac{1}{2}\frac{dn_A}{dt} = +\frac{dn_C}{dt}$$

Therefore, for the reaction

$$aA + bB \longrightarrow cC + dD$$

the rate is expressed as,

$$Rate = -\frac{1}{a}\frac{dn_A}{dt} = -\frac{1}{b}\frac{dn_B}{dt} = +\frac{1}{c}\frac{dn_C}{dt} = +\frac{1}{d}\frac{dn_D}{dt}$$

As defined, the rate has the disadvantage of being an **extensive variable**, that is, it depends on the size of the reaction system. It would be better to have the rate as an **intensive quantity**, independent on the system's size. To accomplish this modification, the rate is divided by the volume of the system at a given instant, that is,

$$\frac{Rate}{V} = -\frac{1}{aV}\frac{dn_A}{dt} = -\frac{1}{bV}\frac{dn_B}{dt} = +\frac{1}{cV}\frac{dn_C}{dt} = +\frac{1}{dV}\frac{dn_D}{dt}$$

The rate per unit volume becomes the new rate of the reaction, that is,

$$rate \equiv \frac{Rate}{V}$$

or

$$\text{rate} = -\frac{1}{aV}\frac{dn_A}{dt} = -\frac{1}{bV}\frac{dn_B}{dt} = +\frac{1}{cV}\frac{dn_C}{dt} = +\frac{1}{dV}\frac{dn_D}{dt}$$

For a reaction system of constant volume, the new rate may be expressed in terms of concentrations, $c_j = n_j / V$,

$$\text{rate} = -\frac{1}{a}\frac{d(n_A/V)}{dt} = -\frac{1}{b}\frac{d(n_B/V)}{dt} = +\frac{1}{c}\frac{d(n_C/V)}{dt} = +\frac{1}{d}\frac{d(n_D/V)}{dt}$$

If the units of concentration are moles per liter, the new rate is written as

$$rate = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

0.2 THE RATE LAW AND RATE CONSTANT

Generally, the rate of reaction is a function of the concentrations of the reactants,[1] that is,

$$rate = f([A],[B])$$

For many reactions involving relatively low concentrations, at a fixed temperature and pressure, the rate is proportional to the product of concentrations raised to powers:

$$rate \propto [A]^{\alpha}[B]^{\beta}$$

where α and β are small integers or half-integers ($\frac{1}{2}$, $\frac{3}{2}$, ···), which are experimentally determined, temperature independent, and are not necessarily equal to a and b in the stoichiometric equation. The exponent α is the **order** of the reaction with respect to reactant A, and the exponent β is the **order** with respect to reactant B. The sum of the exponents, $\alpha+\beta$, is the **overall order** of the reaction. By introducing the proportionality constant k, the rate is written as

$$rate = k[A]^{\alpha}[B]^{\beta}$$

This idealized experimental result is known as the **rate law**. The proportionality constant k, called the **rate constant**, is characteristic for a given reaction. The rate constant is independent of concentrations but varies with temperature and pressure, as the functional notation shows

$$k = k(T,P)$$

where T is the absolute temperature and P is the pressure. Actually, a rate "constant" may depend somewhat on the concentrations of the reactants, solvent, pH, and/or other electrolytes. With every reaction, k increases strongly with increasing temperature. The pressure dependence of k, however, is small and is usually ignored. And so, the rate constant depends solely on temperature, that is,

$$k = k(T)$$

The rate constant then bears the brunt of the temperature dependence for the reaction rate. From the form of the rate law,

$$rate = k[A]^{\alpha}[B]^{\beta}$$

we can easily see that as the rate constant varies with temperature, so does the rate. Thus, a rise in temperature increases the rate and a decrease in temperature lowers the rate, regardless of whether the reaction is exothermic or endothermic. The next step is to discover the mathematical dependence of a rate constant on temperature, so that we can be a step closer in predicting reaction rates. Predicting the rate of a reaction is a primary aim of kinetics.

0.3 TEMPERATURE DEPENDENCE OF RATE CONSTANTS: A SEARCH FOR LINEARITY

For the narrow temperature range at which reaction rates are usually measured, a plot of k versus T in Figure 0–1 illustrates the trend how, for most reactions, the rate constant increases as the absolute temperature increases.

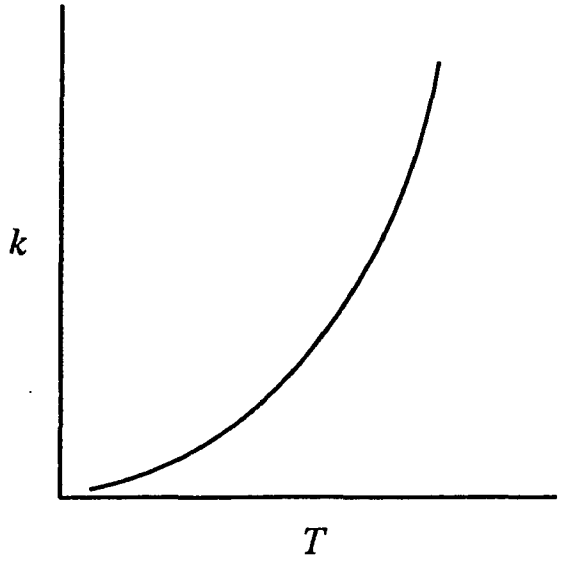


Figure 0–1. Rate constant as a function of absolute temperature for a typical reaction.

From this plot, it is not clear what the mathematical relation between k and T is. Is the graph parabolic? Is it exponential? Or is it something else? It is difficult to identify the nature of such a curve and assign to it the proper mathematical expression. If a graph is a straight line, however, we can easily recognize it as such and can correctly assign to it a linear function. The slope-intercept form of a linear equation in standard notation is

$$y = mx + b$$

where m is the constant slope and b is the y-intercept. And so, to successfully relate the rate constant k and the absolute temperature T, we must somehow transform these variables to obtain some function of k, $y(k)$ or possibly $y(k,T)$, and some function of the T, $x(T)$, so that a straight line emerges when $y(k)$is plotted against $x(T)$, that is,

$$x = x(T)$$
$$y = y(k)$$

such that,

$$y(k) = mx(T) + b$$

Remark!

The use of the letters m and b to represent the slope and the y-intercept in a linear equation probably originated from the definition of congruence in number theory. A congruence is a relationship between two integers with respect to another integer, called the **modulus**. More specifically, two integers, a and b, are congruent with respect to the modulus m iff their difference, $a - b$, is a multiple of m, that is,

$$a - b = mk$$

where k is an integer. After transposing,

$$a = mk + b$$

Thus, substituting a and k for y and x, we have the slope-intercept form of a linear equation in standard notation

$$y = mx + b$$

The congruence relationship is usually written in symbols as

$$a \equiv b \,(\mathrm{mod}\, m)$$

End of Remark!

Toward the latter part of the nineteenth century, it was discovered empirically, on the basis of numerous rate measurements, that a linear relation exists between $\ln k$ and 1/T, that is,

$$x(T) = \frac{1}{T}$$
$$y(k) = \ln k$$

such that,

$$\ln k = m\left(\frac{1}{T}\right) + b$$

and after letting $b = \ln A$,

$$\ln k = m\left(\frac{1}{T}\right) + \ln A$$

By differentiating with respect to $1/T$, we obtain the slope m as the derivative of $\ln k$ with respect to $1/T$,

$$\frac{d\ln k}{d(1/T)} = m$$

Figure 0–2 illustrates this linear relationship between $\ln k$ and 1/T for a typical kinetic data set. It is readily apparent from this figure that the straight-line graph has a negative slope.

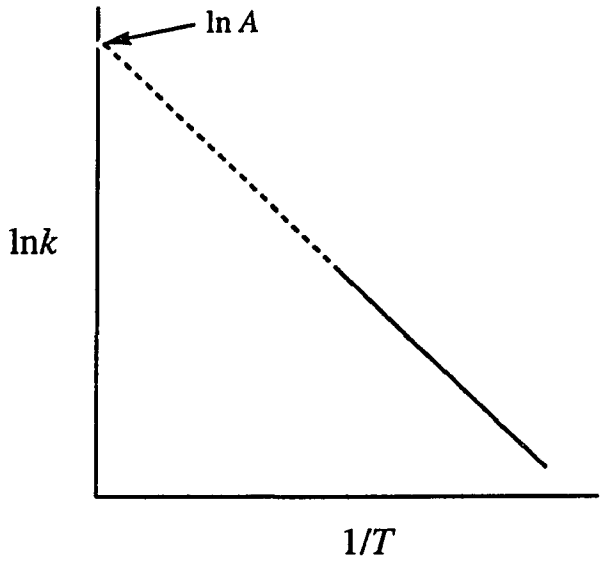


Figure 0–2. A plot of lnk versus 1/T for a typical chemical reaction.

The dashed extension of the graph is extrapolation toward higher temperatures, outside the experimental lower-temperature range. This long extrapolation toward the higher temperatures needed to locate the intercept, $\ln A$, is a considerable source of error in the constant A.[2]

The logarithmic form, which relates the rate constant and temperature, may be converted to the exponential form as follows:

$$\ln k = m\left(\frac{1}{T}\right) + \ln A$$

$$\ln k - \ln A = \frac{m}{T}$$

$$\ln\left(\frac{k}{A}\right) = \frac{m}{T}$$

$$\frac{k}{A} = e^{m/T}$$

$$k = Ae^{m/T}$$

Since the slope m is a negative constant, we may define the positive constant, m', such that,

$$k = Ae^{-m'/T}$$

This empirical equation summarizes the fact that the rate constant varies as the negative exponent of the reciprocal absolute temperature. According to this exponential equation, the rate constant decreases with decreasing temperature, increases as the temperature increases, and is bounded at the extreme temperatures. Since

$$k = Ae^{-m'/T}$$

or

$$k = \frac{A}{e^{m'/T}}$$

then, as the temperature decreases and approaches zero, the denominator increases without bounds,

$$\lim_{T \to 0} e^{m'/T} = \infty$$

and so the rate constant also decreases and tends to zero, that is,

$$\lim_{T \to 0} k = 0$$

As drawn, the graph in Figure 0–1 indicates this limiting behavior of the rate constant at temperatures close to zero. Similarly, as the temperature increases without bounds, the denominator approaches one,

$$\lim_{T \to \infty} e^{m'/T} = 1$$

and so the rate constant also increases but tends toward the value of the constant A, that is,

$$\lim_{T \to \infty} k = A$$

In 1889, the Swedish physical chemist Svandte Arrhenius attributed physical significance to the slope m of the plot $\ln k$ versus $1/T$. The reasoning behind his interpretation of m is in the discussion of the next section.

0.4 THE ARRHENIUS EQUATION: A TRIUMPHANT QUEST

Standing on the shoulders of his predecessors, Arrhenius justified the exponential relationship between the rate constant and temperature by analogy to the variation of the equilibrium constant with temperature. It was known then that the equilibrium constant, K, of a reaction depends on absolute temperature according to the van't Hoff equation,

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H}{RT^2}$$

where P is pressure, ΔH is the overall enthalpy change of the reaction, and R is the gas constant. A derivation of this equation is given in Appendix A. If constant pressure is understood, the van't Hoff equation is written as

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

Using the chain rule,

$$\frac{d \ln K}{d(1/T)} = \frac{d \ln K}{dT}\frac{dT}{d(1/T)}$$

and

$$\frac{dT}{d(1/T)} = -T^2$$

the van't Hoff equation may be expressed in the convenient slope form for the plot $\ln K$ versus $1/T$,

$$\frac{d \ln K}{d(1/T)} = \frac{d \ln K}{dT}\frac{dT}{d(1/T)}$$

$$= \left(\frac{\Delta H}{RT^2}\right)\left(-T^2\right)$$

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H}{R}$$

When $\ln K$ is plotted against $1/T$, the slope, $-\Delta H/R$, is nearly constant. This means that ΔH depends weakly on temperature and practically may be considered constant. With ΔH as a constant, the van't Hoff equation is easily integrated to give

$$\ln K = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \ln B$$

where $\ln B$ is the constant of integration. This logarithmic form may be converted to the exponential form in the usual manner,

$$\ln K = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \ln B$$

$$\ln K - \ln B = -\frac{\Delta H}{RT}$$

$$\ln\left(\frac{K}{B}\right) = -\frac{\Delta H}{RT}$$

$$\frac{K}{B} = e^{-\Delta H/RT}$$

$$K = Be^{-\Delta H/RT}$$

The rate constant expression of the previous section and the van't Hoff equation in their various forms can now be placed side by side and compared.

$$\ln k = m\left(\frac{1}{T}\right) + \ln A \qquad\qquad \ln K = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \ln B$$

$$k = Ae^{m/T} \qquad\qquad K = Be^{-\Delta H/RT}$$

The similarities are striking. Arrhenius marched on a little further and "derived" the relationship between the rate constant and temperature from the van't Hoff equation. He was familiar with the **law of mass action**, which had been proposed in 1864 by two Norwegian chemists, Cato Maximilian Guldberg and Peter Waage.[3] Consider the general chemical reaction

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + D$$

where k_1 and k_2 are the rate constants for the forward and reverse reaction, respectively. The law of mass action states that at equilibrium the ratio of product concentrations (each raised to some powers) to reactant concentrations (also raised to some powers) is a constant, that is,

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

K is known as the **equilibrium constant.** This experimental fact may be deduced directly from another experimental fact, namely, the **rate law.** For the forward reaction,

$$rate_{for} = k_1[A]^\alpha[B]^\beta$$

For the reverse reaction,

$$rate_{rev} = k_2[C]^\gamma[D]^\delta$$

At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction. Thus,

$$k_1[A]^\alpha[B]^\beta = k_2[C]^\gamma[D]^\delta$$

or

$$\frac{k_1}{k_2} = \frac{[C]^\gamma[D]^\delta}{[A]^\alpha[B]^\beta}$$

It is clear that the ratio of the two constants, k_1 and k_2, is always a constant; and in view of this last expression, this ratio, k_1/k_2, is truly the equilibrium constant K, that is,

$$K = \frac{k_1}{k_2}$$

Armed with this fact that the equilibrium constant K is equal to the ratio of the two rate constants k_1 and k_2, Arrhenius postulated that an energy barrier exists between reactants and products. He suggested that during the course of a reaction some reactant molecules must acquire a certain critical energy in order to react. This extra energy required to get over the barrier is called the **energy of activation** and molecules which have been activated with such extra energy are referred to as **activated complexes.** The activation

energy is then the difference between the average energy of the activated complexes and that of the reactants,

$$E_a \equiv \overline{E}^{\ddagger} - \overline{E}_r$$

The Arrhenius energy profile for the reaction is shown schematically in the diagram of Figure 0–3.[4] The activated complexes are designated with the *double dagger* (‡)

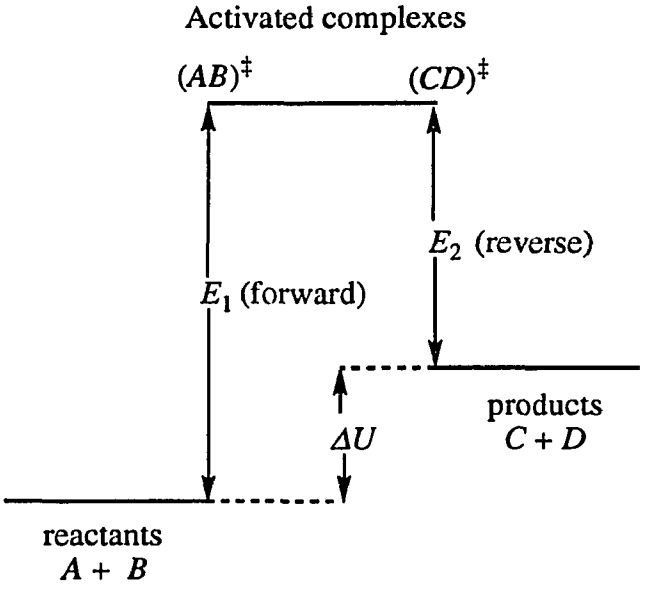


Figure 0–3. Arrhenius energy diagram for an endothermic reaction.

For the forward reaction, reactants A and B must acquire the activation energy E_1 to form the activated complex, $(AB)^{\ddagger}$, which then breaks up to yield C and D, that is,

$$A + B \xrightarrow{E_1} (AB)^{\ddagger} \longrightarrow C + D$$

Likewise, for the reverse reaction, C and D must acquire the activation energy E_2 to form the activated complex $(CD)^{\ddagger}$, which then breaks up to yield A and B, that is,

$$A + B \longleftarrow (CD)^{\ddagger} \xleftarrow{E_2} C + D$$

From inspection of the energy diagram, the internal energy change, ΔU, for the reaction may be expressed in terms of the activation energies of the forward and reverse reaction, E_1 and E_2, respectively, that is,

$$\Delta U = -(E_2 - E_1) = E_1 - E_2$$

For a system in which the initial state of pressure and volume is the same as the final state, the overall enthalpy change, ΔH, is equal to internal energy change, ΔU, that is,

$$\Delta H = \Delta U$$

This is justified from the definition of enthalpy, which is

$$H = U + PV$$

or

$$\Delta H = \Delta U + \Delta PV$$

If the initial pressure and volume are the same as the final pressure and volume, ΔPV is zero and

$$\Delta H = \Delta U$$

so that

$$\Delta H = -(E_2 - E_1) = E_1 - E_2$$

Since from above

$$K = \frac{k_1}{k_2} \quad \text{and} \quad K = Be^{-\Delta H/RT}$$

we have that

$$\frac{k_1}{k_2} = Be^{-(E_1 - E_2)/RT}$$

or

$$\frac{k_1}{k_2} = B\frac{e^{-E_1/RT}}{e^{-E_2/RT}}$$

which suggests that and is consistent with[5]

$$k_1 = A_1 e^{-E_1/RT}$$
$$k_2 = A_2 e^{-E_2/RT}$$

And so, a rate constant varies with the absolute temperature according to famous **Arrhenius equation**

$$k = Ae^{-E_a/RT}$$

where E_a is the usual symbol for the **Arrhenius activation energy** and A is known as the **pre-exponential** or **frequency factor.** The reason for calling A the pre-exponential factor is obvious; the use of the term *frequency factor* for A will become clear later in the discussion of the **hard-sphere collision theory** and the **transition-state theory**. The exponential nature of the Arrhenius equation is attested by statistical mechanics, which claims that according to the Maxwell-Boltzmann distribution, the exponential factor $e^{-E_a/RT}$ is equal to the fraction of activated molecules $N^{\ddagger}$ to the number of reactant molecules N_r, that is,

$$\frac{N^{\ddagger}}{N_r} = e^{-E_a/RT}$$

The method in deriving the Arrhenius equation is not peculiar just to this discussion nor is it an isolated event in science. Many attempts, aimed at discovering scientific principles, are really in disguise persistent *searches for linearity.*

Arrhenius then interpreted the slope, m, from the plot of $\ln k$ versus $1/T$ in terms of the activation energy, E_a, as follows. The logarithmic form of the Arrhenius equation is

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

After differentiating with respect to $1/T$,

$$\frac{d\ln k}{d(1/T)} = -\frac{E_a}{R}$$

When $\ln k$ is plotted against $1/T$, the slope m is equal to the derivative of $\ln k$ with respect to $1/T$, that is,

$$m = \frac{d\ln k}{d(1/T)}$$

Hence, we have the interpretation of the slope m in terms of the Arrhenius activation energy:

$$m = -\frac{E_a}{R}$$

The formal definition of the **Arrhenius activation energy** is

$$E_a \equiv -Rm$$

or

$$E_a \equiv -R\frac{d\ln k}{d(1/T)} = RT^2\frac{d\ln k}{dT}$$

Since the activation parameters, E_a and A, can be calculated from the slope and intercept of a plot $\ln k$ versus $1/T$, known as the **Arrhenius plot**, the Arrhenius equation fully describes a rate constant. The experimental magnitudes of E_a and A are our next concern.

0.5 RANGES OF ACTIVATION ENERGIES AND PRE-EXPONENTIAL FACTORS

The exponential form of the Arrhenius rate expression,

$$k = Ae^{-E_a/RT}$$

may be written as

$$k = \frac{A}{e^{E_a/RT}}$$

With this form of the Arrhenius equation, a qualitative assessment can be made on the variation of a rate constant with activation energy. Some reactions have a small energy of activation. A small activation energy diminishes the denominator and thus augments the rate constant, which implies that the reaction is fast. For other reactions, the energy of activation is large. A large value of E_a increases the denominator and thus reduces the value of k, which implies a slow reaction. Experimental values of E_a range form positive, zero, and even to negative values.

The magnitude of the energy of activation, E_a, depends on the nature of the reactants and is characteristic of each reaction. For most reactions, E_a is positive and the rate constant increases with temperature. Observed activation energies lie in the range of 0

to 100 kcal/mole for most elementary reactions. Unimolecular decomposition of compounds with strong bonds have very high E_a values. Reactions in solutions have E_a values in the range of 10 to 30 kcal/mole. A typical experimental error in E_a is 1 kcal/mole.[6]

The activation energy is zero for reactions in which no bonds are broken, as in the recombination of two radicals to form a stable molecule. For example,

$$\cdot CH_3 + \cdot CH_3 \longrightarrow C_2H_6$$

$$\cdot CH_3 + \cdot Cl \longrightarrow CH_3Cl$$

With zero activation energy, the rate constant is practically independent of temperature.[6]

For some reactions, E_a is negative and the rate constant decreases with temperature. Such reactions involve the formation of a weakly bound intermediate species, referred to as a **van der Waals complex**,[7] and occur as a single elementary step. An example is the recombination of iodine atoms in the presence of a third body M, which can be any atom or molecule, that is,

$$I + I + M \longrightarrow (I_2M)^{\ddagger} \longrightarrow I_2 + M$$

The observed rate law is for this reaction is

$$rate = k[I]^2[M]$$

The third party is needed to carry away the extra vibrational energy released in the formation of I_2. If this third body is not present to absorb such energy, the I_2 molecules dissociate back to iodine atoms. Ira N. Levine,[8] who vividly and elegantly described the mechanism of this trimolecular reaction, commented that increasing the temperature increases the trimolecular collision rate; however, as the energy of a trimolecular collision increases, the probability decreases that a given $I + I + M$ collision will result in transfer of energy to M and concomitant formation of I_2. The species M, he remarked, is

sometimes called a "chaperon," but this name is inappropriate since the commonly understood function of a chaperon is to prevent union rather than promote it. Dr. Klaus Grohmann suggested that this third body, *M*, which promotes the recombination of atoms by snatching away excess vibrational energy, should instead be referred to as a "madam".[9] Everyone knows that a madam promotes union and pockets cash as remuneration for services. A reaction like

$$\cdot CH_3 + \cdot CH_3 \longrightarrow C_2H_6$$

does not require a third body, since the extra vibrational energy attained on the formation of the C_2H_6 molecule can be distributed among vibrations of several bonds and no bond vibration need be energetic enough to break the bond. Levine concluded by saying that, in general, the activation energy for the recombination of atoms *X* and *Y* in the presence of a third party *M*,

$$X + Y + M \longrightarrow XY + M$$

is typically -1 to -4 kcal/mole, depending on the nature of *X*, *Y*, and *M*.

Values of Arrhenius pre-exponential factors, *A*, typically span from 10^8 to 10^{15} with proper units depending on the overall order of a reaction.[10] The **hard-sphere collision theory** in Section 0.8 justifies why the experimental numbers for *A* are so large by identifying the pre-exponential factor with the frequency of collisions between reactant molecules. A typical experimental error in *A* is a factor of 3 or 4. It was mentioned earlier in Section 0.3 that the long interpolation to find the intercept, $\ln A$, in the plot of $\ln k$ versus $1/T$ is a large source of error in *A*.

Nothing is perfect in life! In its persistent pursuit to disrupt ideals, reality has an unrelenting smoldering knack for tarnishing or even crippling every human endeavor, no matter how noble. The Arrhenius equation is no exception and also falls victim to the ravages of this stark reality!

0.6 DEVIATIONS FROM THE ARRHENIUS EQUATION: A TOUCH OF IMPERFECTION

Within the normal precision of measurements and within the usually narrow temperature ranges of most experiments, by and large, the Arrhenius equation fits kinetic data for elementary chemical reactions very well, that is, a plot of $\ln k$ versus $1/T$ is linear. Consequently, the activation parameters, E_a and A, are constants and thus temperature independent. When rate measurements have high precision and are performed over a wide range of temperatures, however, Arrhenius plots generally exhibit definite curvatures, **concave upward** or **concave downward**, as illustrated in Figures 0–4 and 0–5.[11]

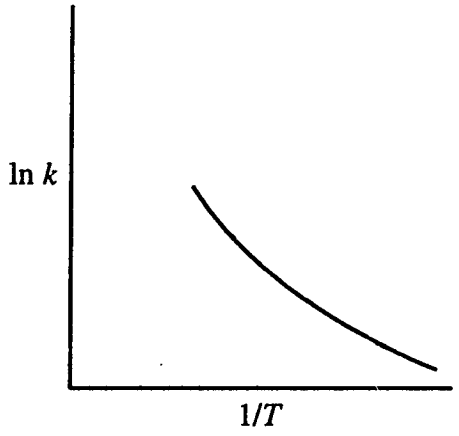


Figure 0–4. An Arrhenius plot. The graph is *concave upward.*

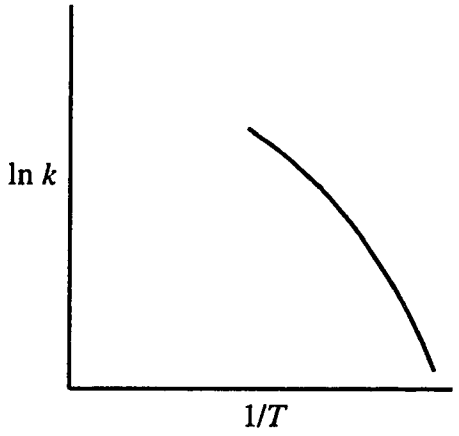


Figure 0–5. An Arrhenius plot. The graph is *concave downward.*

In general, the graph of a function is **concave upward** ("holds water") in an interval if its first derivative, $df(x)/dx$, increases with increasing x in that interval. An increasing first derivative implies that the second derivative, $d^2f(x)/dx^2$, is positive. Analogously, the graph of a function is **concave downward** ("spills water") in an interval if its first derivative, $df(x)/dx$, decreases with increasing x in that interval, which means that the

second derivative, $d^2 f(x)/dx^2$, is negative.[12] The second derivative test for concavity may be restated as,

$$\frac{d^2 f(x)}{dx^2} > 0 \quad \Rightarrow \quad \text{the graph is } \textit{concave upward.}$$

$$\frac{d^2 f(x)}{dx^2} < 0 \quad \Rightarrow \quad \text{the graph is } \textit{concave downward.}$$

$$\frac{d^2 f(x)}{dx^2} = 0 \quad \Rightarrow \quad \text{the graph is a } \textit{straight line.}$$

Some principal sources responsible for such nonlinearity in Arrhenius plots are:

- Systematic errors introduced in the measurements of the experiment.
- The Arrhenius activation parameters, E_a and A, are dependent on temperature.
- The reaction is complex, that is, composite and consists of competing pathways having different activation energies. It is interesting that some enzyme reactions show Arrhenius plots which not only curve but also wiggle.[13]
- Tunneling by particles of small mass, such as electrons and protons, becomes important in increasing reaction rates, especially at lower temperatures, where few molecules have sufficient energy to surmount the classical energy barrier. This quantum-mechanical tunnel effect tends to speed up a reaction because lighter particles, although they may have less energy than that required to go over the barrier, are able to leak through it and thus contribute in quickening product formation. On the other hand, particles of small mass can also be turned back even though their energy is greater than that required to overcome

the barrier height. The net effect, however, is an increase in the rate of reaction. The tunnel effect causes an Arrhenius plot to be concave upward.[14]

J. F. Bunnett,[15] K. A. Connors,[16] and J. R. Hulett[17] treat in detail the reasons why kinetic data fail to obey the Arrhenius law.

0.7 EXTENDING AND FINE-TUNING THE ARRHENIUS EQUATION

Instead of completely discarding the Arrhenius rate expression in light of the deviations, we opt to remedy the unpleasant situation by extending the Arrhenius equation so as to accommodate experimental data measured over a wider temperature range. For the Arrhenius equation to better fit kinetic data, we must relax the constraints that the Arrhenius activation parameters, E_a and A, be constants and allow them to vary with temperature. When the curvature of Arrhenius plots for elementary reactions is not due to experimental errors or tunneling, the major cause for the nonlinearity may be attributed to the temperature dependence of E_a and A. If E_a and A are no longer constants, we must attempt to discover their explicit dependence on temperature. As alluded earlier in Section 0.3, when a plot of $\ln k$ against $1/T$ has curvature, it is difficult, to assign the graph the proper mathematical expression. If, however, $\ln\left(k/T^n\right)$ is plotted against $1/T$, where the exponent n is a small positive or negative number, the graph is usually linear. In a manner analogous to that in Section 0.3, we have

$$x(T) = \frac{1}{T}$$

$$y(k,T) = \ln\left(\frac{k}{T^n}\right)$$

such that,

$$\ln\left(\frac{k}{T^n}\right) = m_0\left(\frac{1}{T}\right) + b_0$$

where m_0 is the constant slope and b_0 is the y-intercept. After letting

$$b_0 = \ln A_0$$

$$\ln\left(\frac{k}{T^n}\right) = m_0\left(\frac{1}{T}\right) + \ln A_0$$

we continue to convert to the exponential form,

$$\ln\left(\frac{k}{T^n}\right) - \ln A_0 = \frac{m_0}{T}$$

$$\ln\left(\frac{k}{A_0 T^n}\right) = \frac{m_0}{T}$$

$$\frac{k}{A_0 T^n} = e^{m_0/T}$$

$$k = A_0 T^n e^{m_0/T}$$

The similarity of this exponential expression to the Arrhenius equation suggests to interpret the constant slope m_0 in terms of another activation energy parameter E_0, just like what Arrhenius had done. Thus,

$$m_0 = -\frac{E_0}{R}$$

Substituting m_0 with $-E_0/R$ in

$$k = A_0 T^n e^{m_0/T}$$

we obtain a modified Arrhenius equation[18, 19]

$$k = A_0 T^n e^{-E_0/RT}$$

where E_0 and A_0 are both constants. We can now demonstrate that the Arrhenius activation parameters, E_a and A, are functions of T, and specifically

$$E_a = nRT + E_0$$

$$A = A_0 e^n T^n$$

The proof that

$$E_a = nRT + E_0$$

is as follows:

$$k = A_0 T^n e^{-E_0/RT}$$

We begin with the modified Arrhenius equation

$$k = A_0 T^n e^{-E_0/RT}$$

In logarithmic form,

$$\ln k = \ln A_0 + \ln T^n - \frac{E_0}{RT}$$

or

$$\ln k = \ln A_0 + n \ln T - \frac{E_0}{R}\left(\frac{1}{T}\right)$$

Differentiating both sides with respect to $1/T$,

$$\frac{d \ln k}{d(1/T)} = \frac{d \ln A_0}{d(1/T)} + \frac{d(n \ln T)}{d(1/T)} - \frac{E_0}{R}$$

or

$$\frac{d \ln k}{d(1/T)} = \qquad + n\frac{d \ln T}{d(1/T)} - \frac{E_0}{R}$$

Using the chain rule,

$$\frac{d \ln T}{d(1/T)} = \frac{d \ln T}{dT}\frac{dT}{d(1/T)}$$

$$= \left(\frac{1}{T}\right)\left(-T^2\right)$$

$$\frac{d \ln T}{d(1/T)} = -T$$

From above,

$$\frac{d \ln k}{d(1/T)} = n\frac{d \ln T}{d(1/T)} - \frac{E_0}{R}$$

Hence,

$$\frac{d \ln k}{d(1/T)} = -\ nT - \frac{E_0}{R}$$

Multiplying both sides by $-R$,

$$-R\frac{d \ln k}{d(1/T)} = nRT + E_0$$

The left side is the Arrhenius activation energy, which was previously defined as

$$E_a \equiv -R\frac{d\ln k}{d(1/T)}$$

Therefore,

$$E_a = nRT + E_0$$

Using this last result, we continue to show that the temperature dependence of the Arrhenius pre-exponential factor A is

$$A = A_0 e^n T^n$$

The proof is as follows:

$$E_a = nRT + E_0$$

or

$$-\frac{E_0}{RT} = n - \frac{E_a}{RT}$$

After substituting $-E_0/RT$ with $n - E_a/RT$ in

$$k = A_0 T^n e^{-E_a/RT}$$

we obtain

$$k = A_0 T^n e^{n-E_a/RT}$$
$$= A_0 T^n e^n e^{-E_a/RT}$$
$$k = \left(A_0 e^n T^n\right) e^{-E_a/RT}$$

Therefore,

$$A = A_0 e^n T^n$$

To check that these two expressions

$$E_a = nRT + E_0$$
$$A = A_0 e^n T^n$$

are reasonable and to get a feeling of the extent to which temperature effects the Arrhenius activation parameters, E_a and A, it is worthwhile to examine particular cases of n:

When $n = 0$, E_a and A, as expected, are constants and thus temperature independent, that is,

$$
\begin{aligned}
E_a &= nRT + E_0 \\
&= 0RT + E_0 \\
&= \ 0 \ + E_0 \\
&= E_0 \\
E_a &= -\frac{m_0}{R}
\end{aligned}
$$

$$
\begin{aligned}
A &= A_0 e^n T^n \\
&= A_0 e^0 T^0 \\
&= A_0 \cdot 1 \cdot 1 \\
A &= A_0
\end{aligned}
$$

When $n = 1$,

$$E_a = 1 \cdot RT + E_0 = RT + E_0 \quad \Rightarrow \quad E_a - E_0 = RT$$

$$A = A_0 e^1 T^1 \quad = A_0 eT \quad \Rightarrow \quad \frac{A}{A_0} = eT$$

At ordinary temperatures, in the neighborhood of 300 K, RT is approximately 0.6 kcal mole^{-1} (the gas constant R is 1.987 cal K^{-1} mole^{-1}). The difference between E_a and E_0 is less than the typical error of 1 cal mole^{-1}, inherent in these types of energies. This minimal energy difference indicates that the Arrhenius activation energy E_a is very weakly dependent on temperature. The effect of temperature on the pre-exponential factor A, however, is more pronounced; the ratio of A to A_0 is roughly 1000 for the same neighborhood of 300 K ($e \approx 2.718$).

When $n = -1$,

$$E_a = (-1) \cdot RT + E_0 = -RT + E_0 \quad \Rightarrow \quad E_a - E_0 = -RT$$

$$A = A_0 e^{-1} T^{-1} \quad = \frac{A_0}{eT} \quad \Rightarrow \quad \frac{A}{A_0} = \frac{1}{eT}$$

Again, in the same neighborhood of 300 K, the energy difference between E_a and E_0 has the same small magnitude of 0.6 kcal mole^{-1} as in the previous case. This difference

is almost negligible and reiterates the weak dependence of E_a on T. The pre-exponential factor A, however, is still sensitive to temperate; this time, the ratio A/A_0 is roughly 1/1000, the reciprocal of the previous case.

If the modified Arrhenius equation is to provide a good fit to experimental kinetic data, the curvature of the theoretical graph $\ln k$ versus $1/T$ must have at least the same direction of concavity as that of the Arrhenius plot. Hence, it is important to know in advance what factors in the modified Arrhenius equation determine the curvature of the theoretical graph $\ln k$ versus $1/T$. It turns out that the factor T^n in the modified Arrhenius equation controls completely the concavity of the theoretical curve $\ln k$ versus $1/T$. To prove this assertion, we begin again with the modified Arrhenius equation

$$k = A_0 T^n e^{-E_0/RT}$$

In logarithmic form,

$$\ln k = \ln A_0 + \ln T^n - \frac{E_0}{R}\left(\frac{1}{T}\right)$$

Differentiating both sides with respect to $1/T$,

$$\frac{d\ln k}{d(1/T)} = \frac{d\ln A_0}{d(1/T)} + \frac{d\ln T^n}{d(1/T)} - \frac{E_0}{R}$$

$$= \quad + \frac{d\ln T^n}{d(1/T)} - \frac{E_0}{R}$$

$$\frac{d\ln k}{d(1/T)} = \frac{d\ln T^n}{d(1/T)} - \frac{E_0}{R}$$

Differentiating again both sides with respect to $1/T$, we have

$$\frac{d^2 \ln k}{d(1/T)^2} = \frac{d^2 \ln T^n}{d(1/T)^2}$$

The equality of these two second derivatives, indicates that the theoretical curve $\ln k$ versus $1/T$ has the same curvature as the plot of $\ln T^n$ versus $1/T$. Moreover, the sign of

the parameter n, positive or negative, determines the direction of concavity, upward or downward, respectively; the magnitude of n determines the degree of concavity, that is,

$$\begin{aligned}\frac{d\ln T^n}{d(1/T)} &= \frac{d(n\ln T)}{d(1/T)} \\ &= n\frac{d\ln T}{d(1/T)} \\ &= n\frac{d\left(-\ln T^{-1}\right)}{d(1/T)} \\ &= -n\frac{d\ln(1/T)}{d(1/T)} \\ &= -n\left[\frac{1}{(1/T)}\right] \\ \frac{d\ln T^n}{d(1/T)} &= \frac{-n}{(1/T)}\end{aligned}$$

Differentiating both sides with respect to $1/T$, we have

$$\frac{d^2\ln T^n}{d(1/T)^2} = \frac{n}{(1/T)^2}$$

But

$$\frac{d^2\ln k}{d(1/T)^2} = \frac{d^2\ln T^n}{d(1/T)^2}$$

Hence,

$$\frac{d^2\ln k}{d(1/T)^2} = \frac{n}{(1/T)^2}$$

From all this , we can conclude that

- If the Arrhenius plot is *concave upward*, the second derivative of the theoretical curve, $d^2\ln k/d(1/T)^2$, must be positive; and therefore, the parameter n must also be positive.

- If the Arrhenius plot is *concave downward*, the second derivative of the theoretical curve, $d^2 \ln k/d(1/T)^2$, must be negative; and therefore, the parameter n must also be negative.

- If the Arrhenius plot is a *straight line*, the second derivative of the theoretical curve, $d^2 \ln k/d(1/T)^2$, must be zero; and therefore, the parameter n must also be zero, as expected.

The factor T^n in the modified Arrhenius equation does an excellent job in linearlizing the plot $\ln\left(k/T^n\right)$ versus $1/T$. But if, for some reason, T^n is too restrictive, we may express the modified Arrhenius equation in more general terms, that is,

$$k = A_0 B(T) e^{-E_0/RT}$$

where $B(T)$ is some function of T, not just T^n, which forces the graph $\ln[k/B(T)]$ versus $1/T$ to be a straight line. With the introduction of $B(T)$, the Arrhenius activation parameters, E_a and A, become

$$E_a = \Theta RT + E_0$$
$$A = A_0 e^{\Theta} B(T)$$

where Θ is a dimensionless parameter[20] defined as

$$\Theta \equiv \frac{d \ln B(T)}{d \ln T} = T \frac{d \ln B(T)}{dT} = -\frac{1}{T} \frac{d \ln B(T)}{d(1/T)}$$

To prove that

$$E_a = \Theta RT + E_0$$

where

$$\Theta \equiv \frac{d \ln B(T)}{d \ln T}$$

We begin with the modified Arrhenius equation in the general form

$$k = A_0 B(T) e^{-E_0/RT}$$

In logarithmic form,

$$\ln k = \ln A_0 + \ln B(T) - \frac{E_0}{R}\left(\frac{1}{T}\right)$$

Differentiating both sides with respect to $1/T$,

$$\frac{d\ln k}{d(1/T)} = \frac{d\ln A_0}{d(1/T)} + \frac{d\ln B(T)}{d(1/T)} - \frac{E_0}{R}$$

or

$$\frac{d\ln k}{d(1/T)} = \quad + \frac{d\ln B(T)}{d(1/T)} - \frac{E_0}{R}$$

Using the chain rule,

$$\frac{d\ln B(T)}{d(1/T)} = \frac{d\ln B(T)}{d\ln T}\frac{d\ln T}{d(1/T)}$$

But

$$\Theta \equiv \frac{d\ln B(T)}{d\ln T}$$

$$\frac{d\ln T}{d(1/T)} = -T$$

Thus,

$$\frac{d\ln B(T)}{d(1/T)} = -\Theta T$$

From above,

$$\frac{d\ln k}{d(1/T)} = \frac{d\ln B(T)}{d(1/T)} - \frac{E_0}{R}$$

Substituting $d\ln B(T)/d(1/T)$ with $-\Theta T$,

$$\frac{d\ln k}{d(1/T)} = -\Theta T - \frac{E_0}{R}$$

Multiplying both sides by $-R$,

$$-R\frac{d\ln k}{d(1/T)} = \Theta RT + E_0$$

The left side is the definition of E_a.

Therefore,

$$E_a = \Theta RT + E_0$$

With this last result, we continue to prove that the Arrhenius pre-exponential factor A is

$$A = A_0 e^{\Theta} B(T)$$

where

$$\Theta \equiv \frac{d \ln B(T)}{d \ln T}$$

The proof is as follows:

$$E_a = \Theta RT + E_0$$

or

$$-\frac{E_0}{RT} = \Theta - \frac{E_a}{RT}$$

After substituting $-E_0/RT$ with $\Theta - E_a/RT$ in

$$k = A_0 B(T) e^{-E_0/RT}$$

we obtain

$$\begin{aligned} k &= A_0 B(T) e^{\Theta - E_a/RT} \\ &= A_0 B(T) e^{\Theta} e^{-E_a/RT} \\ k &= \left[A_0 e^{\Theta} B(T)\right] e^{-E_a/RT} \end{aligned}$$

Therefore,

$$A = A_0 e^{\Theta} B(T)$$

When $B(T) = T^n$,

$$\begin{aligned} \Theta &\equiv \frac{d \ln B(T)}{d \ln T} \\ &= \frac{d \ln T^n}{d \ln T} \\ &= \frac{d(n \ln T)}{d \ln T} \\ &= n \frac{d \ln T}{d \ln T} \\ \Theta &= n \end{aligned}$$

Therefore, the equations

$$E_a = \Theta RT + E_0$$
$$A = A_0 e^{\Theta} B(T)$$

as expected, reduce to

$$E_a = nRT + E_0$$
$$A = A_0 e^n T^n$$

Just like the factor T^n, $B(T)$ also has total control on the curvature of the theoretical plot $\ln k$ versus $1/T$ from the modified Arrhenius equation in the more general form. In fact, the second derivative test demonstrates that the theoretical curve $\ln k$ versus $1/T$ has exactly the same curvature as the graph $\ln B(T)$ versus $1/T$. To prove this assertion, we begin again with the modified Arrhenius equation in the general form

$$k = A_0 B(T) e^{-E_0/RT}$$

In logarithmic form,

$$\ln k = \ln A_0 + \ln B(T) - \frac{E_0}{R}\left(\frac{1}{T}\right)$$

Differentiating both sides with respect to $1/T$,

$$\frac{d\ln k}{d(1/T)} = \frac{d\ln A_0}{d(1/T)} + \frac{d\ln B(T)}{d(1/T)} - \frac{E_0}{R}$$
$$= \quad + \frac{d\ln B(T)}{d(1/T)} - \frac{E_0}{R}$$
$$\frac{d\ln k}{d(1/T)} = \frac{d\ln B(T)}{d(1/T)} - \frac{E_0}{R}$$

Differentiating again both sides with respect to $1/T$, we have

$$\frac{d^2 \ln k}{d(1/T)^2} = \frac{d^2 \ln B(T)}{d(1/T)^2}$$

The equality of these two second derivatives, indicates that the theoretical curve $\ln k$ versus $1/T$ from the generalized Arrhenius equation has the same curvature as the

graph $\ln B(T)$ versus $1/T$. All this means that if, for example, we are trying to properly fit kinetic data, which has a concave-upward Arrhenius plot, the theoretical graph $\ln k$ versus $1/T$ must also be concave upward, and consequently, the plot $\ln B(T)$ versus $1/T$ is forced to have the same upward concavity if $B(T)$ is really a suitable candidate.

In conclusion, we can state unequivocally that the values of the Arrhenius activation parameters, E_a and A, can always be calculated from experimental data regardless of whether the Arrhenius plot, $\ln k$ versus 1/T, is concave upward, concave downward, or a straight line.

0.7 INTRODUCTION TO THEORIES OF ELEMENTARY REACTIONS

Even though the Arrhenius theory totally characterizes the rate constant of elementary reactions in terms of the activation parameters, E_a and A, it cannot, however, predict their values. Since much time and effort is spent obtaining values of E_a and A form experiments, it would be very practical and rewarding to extract such information from first principles, that is, theory. Two prominent theories, the **hard-sphere collision theory** and the **transition-state theory**, have made valiant attempts to predict values of the pre-exponential factor A from known properties of molecules. The activation energy E_a is still an elusive quantity for theoretical evaluations, except for very simple chemical processes which are amenable to quantum-mechanical calculations. Although experiment still reigns supreme in furnishing values for these indispensable activation parameters, theories have become essential tools not only to confirm, interpret, and correlate experimental findings but also to provide guidance and to shed insight necessary for the understanding of chemical processes. After all, even the concept of activation energy, which has proved to be very useful in interpreting, relating, and

systematizing a plethora of kinetic data, is itself a theoretical construct. Next, we examine the **hard-sphere collision theory**

0.8 THE HARD-SPHERE COLLISION THEORY

In 1918, twenty nine years after the Arrhenius's activation theory, W. C. McC. Lewis[21] formulated a satisfactory explanation for the magnitude of the frequency factor by proposing the **hard-sphere collision theory.**[22] It is reasonable to state that reacting molecules must first come together in order to form products, that is, reactants must collide. If every collision is successful in product formation, the rate of the reaction is equal to the number of collisions per unit time, that is,

$$Rate = \frac{\text{No. of collisions}}{\Delta t}$$

This rate is an **extensive variable** and thus depends on the size of the system. It would be better to have the rate as an **intensive variable**, independent on the system's size. For this task, we define a rate per unit volume as

$$rate \equiv \left(\frac{Rate}{V}\right)$$

or

$$rate = \frac{\text{No. of collisions}}{V\Delta t}$$

Usually, the letter Z is used to denote the number of collisions *per unit time* and *per unit volume*, that is

$$Z \equiv \frac{\text{No. of collisions}}{V\Delta t}$$

or

$$rate = Z$$

Z is called the **collision number** or **collision frequency.** In German, the word *zahl* means *number.* Since the rate of a reaction is usually expressed in units of mole-liter^{-1}-sec^{-1},

$$rate = -\frac{d[A]}{dt}$$

we must divide the number of collisions by Avogadro's constant N_O to convert to molar units, that is,

$$rate = \frac{\text{No. of collisions}/N_O}{\text{V}\Delta\text{t}}$$

or

$$rate = \frac{Z}{N_O}$$

In general, however, not all collisions, just a fraction of all collisions, lead to products. When reactant molecules collide so gently that there is no change in the identity of the colliding molecules after collision, no reaction occurs. Thus, the above rate must be attenuated by the fraction of collisions, N^*/N, having sufficient energy for reaction to occur, that is,

$$rate = \frac{Z}{N_O}\left(\frac{N^*}{N}\right)$$

where N^* is the number of collisions with energy greater than or equal to E_a' and N is the total number of collisions. According to the Maxwell-Boltzmann distribution, the fraction of colliding reactant molecules, N^*/N, having an energy E_a' equal to or greater than that required for product formation is

$$\frac{N^*}{N} = e^{-E_a'/RT}$$

Hence,

$$rate = \frac{Z}{N_O}\left(\frac{N^*}{N}\right) = \frac{Z}{N_O}e^{-E_a'/RT}$$

The **hard-sphere collision theory**, as its name implies, makes the basic assumptions that molecules, which are treated as hard spheres, must collide and must also have

sufficient energy before a chemical reaction can occur. Therefore, Lewis postulated that the rate of a reaction is a product of two factors,

$$rate = \begin{matrix}\text{collision}\\ \text{frequency}\\ \text{factor}\end{matrix} \times \begin{matrix}\text{energy}\\ \text{factor}\end{matrix}$$

or

$$rate = \frac{Z}{N_o} e^{-E_a'/RT}$$

Qualitatively, the collision theory quite satisfactorily accounts for three main factors which influence reaction rates:

- The rate of a chemical reaction depends the *nature* of the reactants, which determine the magnitude of the activation energy.

- The rate of a chemical reaction depends on the *concentration* of the reactants because the number of collisions increase as the concentrations are increased.

- The rate of a chemical reaction depends on the *temperature* because an increase in temperature makes molecules move faster and thus they collide more frequently with other reactant molecules. More importantly, as the temperature increases, collisions become more violent; consequently, more and more molecules acquire the critical energy, E_a', and thus more likely to cause reaction. The exponential energy factor incorporates this behavior with rising temperature. Its limit is 1 as the temperature increases, that is,

$$\lim_{T\to\infty} e^{-E_a'/RT} = \lim_{T\to\infty} \frac{1}{e^{E_a'/RT}} = 1$$

Therefore, the rate at very high temperatures becomes

$$rate = \frac{Z}{N_o} e^{-E_a'/RT} \approx \frac{Z}{N_o}(1)$$

or

$$rate \approx \frac{Z}{N_O}$$

Having acquired the critical energy at very high temperatures, almost every collision is effective in leading to products.

A goal of the *hard-sphere collision theory* is to develop a quantitative expression for the collision number Z by considering a relatively simple bimolecular reaction in the gas phase at low pressure between spherical reactants A and B, with radii r_A and r_B,

$$A + B \longrightarrow \text{Products}$$

Let's assume that this system has a volume V with N_A and N_B particles of reactants A and B, respectively. The simplest approach for deriving an expression for Z is to freeze the positions of all the particles except one, and then focus our attention on the moving particle A as it travels with a mean speed $\bar{v}_A$ for a time interval Δt.[23] The particle A collides with a particle B if their center-to-center distance is less than or equal to $r_A + r_B$ as depicted in Figure 0–6

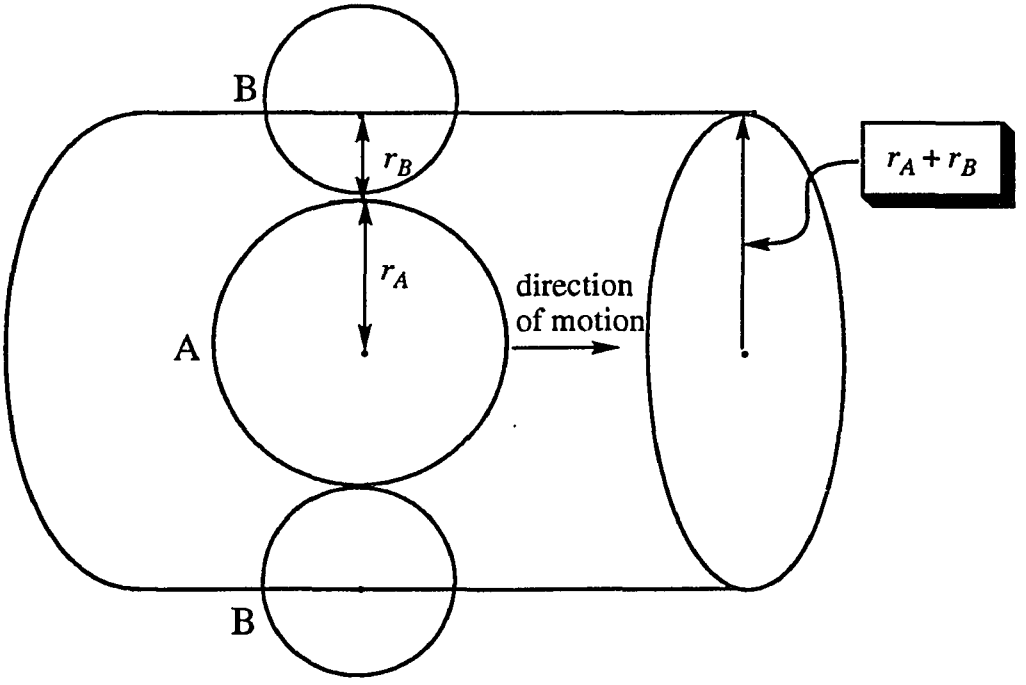


Figure 0–6. Collision cylinder.

As particle A moves, it sweeps out a **collision cylinder** of cross-sectional area σ,

$$\sigma = \pi(r_A + r_B)^2$$

The length, l, of the cylinder is the distance which particle A travels in the time Δt,

$$l = \bar{v}_A \Delta t$$

Therefore, the volume of the collision cylinder V_c is

$$V_c = \sigma l = \pi(r_A + r_B)^2 \bar{v}_A \Delta t$$

The number of B particles with centers in this collision cylinder is approximately the volume of the cylinder times the number density of B, N_B/V, that is,

$$\text{No. of } B \text{ particles in cylinder} = V_c\left(\frac{N_B}{V}\right)$$

The number of collisions that particle A makes with B particles within the collision cylinder is equal to this number of B particles having centers inside this cylinder, that is,

$$\text{No. of collisions in cylinder} = V_c\left(\frac{N_B}{V}\right)$$

After substituting V_c

$$\text{No. of collisions in cylinder} = \pi(r_A + r_B)^2 \bar{v}_A \Delta t\left(\frac{N_B}{V}\right)$$

For the *number of collisions per unit time*, ζ_{AB}, which particle A makes with B particles inside the collision cylinder, we must divide the number of collisions by the time interval Δt, that is,

$$\zeta_{AB} = \frac{\text{No. of collisions in cylinder}}{\Delta t} = \pi(r_A + r_B)^2 \bar{v}_A\left(\frac{N_B}{V}\right)$$

Since there are N_A particles of A, the *total number of collisions per unit time* is $N_A\zeta_{AB}$, or

$$N_A\zeta_{AB} = \pi(r_A + r_B)^2 \bar{v}_A\left(\frac{N_B}{V}\right)N_A$$

To obtain the *total number of collisions per unit time per unit volume*, Z_{AB}, we must divide $N_A\zeta_{AB}$ by the total volume V,

$$Z_{AB} = \frac{N_A \zeta_{AB}}{V}$$

or

$$Z_{AB} = \pi(r_A + r_B)^2 \bar{v}_A \left(\frac{N_B}{V}\right)\left(\frac{N_A}{V}\right)$$

This time, we rely heavily on one of the cardinal virtues, **Faith**, that the mean speed $\bar{v}_A$, which is the magnitude of the average velocity vector,

$$\bar{v}_A = |\bar{\mathbf{v}}_A|$$

according to kinetic theory is

$$\bar{v}_A = \left(\frac{8k_B T}{\pi m_A}\right)^{1/2}$$

where k_B is Boltzmann's constant, T is the absolute temperature, and m_A is the mass of particle A.[24] Actually, it is the relative speed between particles A and B which determines the frequency of collisions. The relative mean speed $\bar{v}_{AB}$ is the magnitude of the vector difference, $\bar{\mathbf{v}}_{AB}$, between the velocity vectors $\bar{\mathbf{v}}_A$ and $\bar{\mathbf{v}}_B$ of A and B, and depends on the angle between these vectors, that is,

$$\bar{\mathbf{v}}_{AB} = \bar{\mathbf{v}}_A - \bar{\mathbf{v}}_B$$
$$\bar{v}_{AB} = |\bar{\mathbf{v}}_{AB}| = |\bar{\mathbf{v}}_A - \bar{\mathbf{v}}_B|$$

But

$$\begin{aligned} |\bar{\mathbf{v}}_A - \bar{\mathbf{v}}_B|^2 &= (\bar{\mathbf{v}}_A - \bar{\mathbf{v}}_B)\cdot(\bar{\mathbf{v}}_A - \bar{\mathbf{v}}_B) \\ &= \bar{\mathbf{v}}_A \cdot \bar{\mathbf{v}}_A + \bar{\mathbf{v}}_B \cdot \bar{\mathbf{v}}_B - 2\bar{\mathbf{v}}_A \cdot \bar{\mathbf{v}}_B \\ &= |\bar{\mathbf{v}}_A|^2 + |\bar{\mathbf{v}}_B|^2 - 2|\bar{\mathbf{v}}_A||\bar{\mathbf{v}}_B|\cos\theta \\ |\bar{\mathbf{v}}_A - \bar{\mathbf{v}}_B|^2 &= v_A^2 + v_B^2 - 2v_A v_B \cos\theta \end{aligned}$$

Thus,

$$\bar{v}_{AB}^2 = \bar{v}_A^2 + \bar{v}_B^2 - 2\bar{v}_A \bar{v}_B \cos\theta$$

The angle θ between the velocity vectors $\bar{\mathbf{v}}_A$ and $\bar{\mathbf{v}}_B$ can have values form 0 to 180°. The average θ value is 90°. The average relative speed is then

$$\bar{v}_{AB}^2 = \bar{v}_A^2 + \bar{v}_B^2 - 2\bar{v}_A\bar{v}_B\cos\theta$$
$$\bar{v}_{AB}^2 = \bar{v}_A^2 + \bar{v}_B^2 - 2\bar{v}_A\bar{v}_B\cos 0$$
$$\bar{v}_{AB}^2 = \bar{v}_A^2 + \bar{v}_B^2 - 0$$
$$\bar{v}_{AB}^2 = \bar{v}_A^2 \quad + \bar{v}_B^2$$
$$= \frac{8k_BT}{\pi m_A} + \frac{8k_BT}{\pi m_B}$$
$$= \frac{8k_BT}{\pi}\left(\frac{1}{m_A} + \frac{1}{m_B}\right)$$
$$= \frac{8k_BT}{\pi}\left(\frac{m_B + m_A}{m_A m_B}\right)$$
$$= \frac{8k_BT}{\pi}\left(\frac{1}{\mu}\right)$$
$$\bar{v}_{AB}^2 = \frac{8k_BT}{\pi\mu}$$

or

$$\bar{v}_{AB} = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}$$

where,

$\bar{v}_A$ = the average speed of molecule A
$\bar{v}_B$ = the average speed of molecule B
$\bar{v}_{AB}$ = the relative average speed of molecule A with respect to molecule B
k_B = Boltzmann's constant
m_A = the mass of molecule A
m_B = the mass of molecule B
$\mu = \frac{m_A m_B}{m_A + m_B}$ is the reduced mass

Remark!

The parameter μ is called the reduced mass because it is less than either m_A or m_B, that is,

$$\mu < m_A$$
$$\mu < m_B$$

which may be proved from the definition of μ as follows:

$$\mu \equiv \frac{m_A m_B}{m_A + m_B}$$

Inverting,

$$\frac{1}{\mu} = \frac{m_A + m_B}{m_A m_B}$$

$$= \frac{m_A}{m_A m_B} + \frac{m_B}{m_A m_B}$$

$$\frac{1}{\mu} = \frac{1}{m_B} + \frac{1}{m_A}$$

Thus,

$$\frac{1}{\mu} > \frac{1}{m_A}$$

$$\frac{1}{\mu} > \frac{1}{m_B}$$

or

$$m_A > \mu$$

$$m_B > \mu$$

or equivalently

$$\mu < m_A$$

$$\mu < m_B$$

An alternate proof, again using the definition of μ, is as follows:

To prove that

$$\mu < m_A$$

we add and subtract the same quantity, m_A^2, in the numerator of the definition of μ,

$$\mu \equiv \frac{m_A m_B}{m_A + m_B}$$
$$= \frac{m_A m_B + m_A^2 - m_A^2}{m_A + m_B}$$
$$= \frac{m_A(m_B + m_A) - m_A^2}{m_A + m_B}$$
$$= \frac{m_A(m_B + m_A)}{m_A + m_B} - \frac{m_A^2}{m_A + m_B}$$
$$\mu = m_A - \frac{m_A^2}{m_A + m_B}$$

Therefore,

$$\mu < m_A$$

Similarly, to prove that

$$\mu < m_B$$

we add and subtract m_B^2 in the denominator of the definition of μ,

$$\mu \equiv \frac{m_A m_B}{m_A + m_B}$$
$$= \frac{m_A m_B + m_B^2 - m_B^2}{m_A + m_B}$$
$$= \frac{m_B(m_A + m_B) - m_B^2}{m_A + m_B}$$
$$= \frac{m_B(m_A + m_B)}{m_A + m_B} - \frac{m_B^2}{m_A + m_B}$$
$$\mu = m_B - \frac{m_B^2}{m_A + m_B}$$

Therefore,

$$\mu < m_B$$

End of Remark!

The collision number Z_{AB} in terms of the average relative speed is

$$Z_{AB} = \pi(r_A + r_B)^2 \bar{v}_{AB}\left(\frac{N_B}{V}\right)\left(\frac{N_A}{V}\right)$$

or after substituting $\bar{v}_{AB}$,

$$Z_{AB} = \pi(r_A + r_B)^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\left(\frac{N_B}{V}\right)\left(\frac{N_A}{V}\right)$$

Converting to molar concentrations with Avogadro's constant N_O, we have

$$Z_{AB} = N_O^2\pi(r_A + r_B)^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\left(\frac{N_B/N_O}{V}\right)\left(\frac{N_A/N_O}{V}\right)$$

or

$$Z_{AB} = N_O^2\pi(r_A + r_B)^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}[A][B]$$

But the form of the rate expression proposed by Lewis is

$$rate = \frac{Z_{AB}}{N_O}e^{-E_a'/RT}$$

After substituting Z_{AB}, the rate for a bimolecular reaction becomes

$$rate = N_O\pi(r_A + r_B)^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}[A][B]e^{-E_a'/RT}$$

Rearranging,

$$rate = N_O\pi(r_A + r_B)^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}e^{-E_a'/RT}[A][B]$$

But according to the rate law,

$$rate = k[A][B]$$

Therefore, the rate constant is

$$k = N_O\pi(r_A + r_B)^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}e^{-E_a'/RT}$$

which is of the form

$$k = A' T^{1/2}e^{-E_a'/RT}$$

Since values of r_A, r_B, and μ for many molecules are reasonably accessible, the pre-exponential factor $A'T^{1/2}$ for many reactions may now be calculated. The *a priori* calculation of pre-exponential factors for rate processes is the crowning glory and chief contribution of the hard-sphere collision theory!

The collision-theory rate constant expression is a particular case of the modified Arrhenius equation if $n = 1/2$,

$$k = A_0 T^n e^{-E_0/RT} = A_0 T^{1/2} e^{-E_0/RT}$$

Since the Arrhenius activation parameters, E_a and A, are related to those from the modified Arrhenius expression as

$$E_a = nRT + E_0$$
$$A = A_0 e^n T^n$$

In particular, for $n = 1/2$, the Arrhenius activation parameters are related to those from collision theory, E_a' and A' as

$$E_a = \frac{1}{2}RT + E_a'$$
$$A = A' e^{1/2} T^{1/2}$$

With these results, we can say that the hard-sphere collision theory confirms the experimental findings that both Arrhenius activation parameters are weakly dependent on temperature. The difference between E_a and E_a', $1/2RT$, is almost insignificant. The collision theory indicates that the Arrhenius pre-exponential factor A contains information on the frequency of reactant collisions. It's not too surprising that experimental values of A involve large numbers (from 10^8 to 10^{15} with units depending on the overall order of a reaction) and that A is also appropriately called the **frequency factor.**

The collision theory, like other theories, has shortcomings. Most experimental rate constants are generally much smaller than those calculated on the basis of collision theory. It's no surprise that some observed rates are larger than calculated rates. Besides

collision frequency and energy criteria, other factors must also be considered to improve the predictability of the rate expression from the simple collision theory. Molecules not only must collide with sufficient frequency and energy but also must be favorably oriented to produce effective collision leading to products. This steric requirement, which has been overlooked up to now, must also be factored in the rate expression of the collision model to close the gap between theory and experiment. Consequently, the theoretical rate must then be attenuated by the fraction, P, of sufficiently energetic collisions in which reactant molecules are also properly oriented to ensure product formation. The rate then becomes the product of three factors,[25] not just two,

$$rate = \begin{matrix}\text{orientation}\\ \text{factor}\end{matrix} \times \begin{matrix}\text{collision}\\ \text{frequency}\\ \text{factor}\end{matrix} \times \begin{matrix}\text{energy}\\ \text{factor}\end{matrix}$$

or

$$rate = P\frac{Z}{N_o}e^{-E_a/RT}$$

Of the three, the enegy factor is most sensitive to temperature changes due to its exponential nature. P is called the **probability** or **steric factor**. With the inclusion of this steric factor P, the rate constant of the hard-sphere collision theory becomes

$$k = PA'T^{1/2}e^{-E_a/RT}$$

Thus, the Arrhenius pre-exponential factor becomes

$$A = PA'e^{1/2}T^{1/2}$$

The Arrhenius A-factor now conveys not only information on the frequency of collisions but also on favorable geometry, conducive to the transformation of reactants to products. In other words, the Arrhenius frequency factor, A, may be interpreted with help from the collision theory as being the number of *effective collisions per unit time per unit volume.*

The idea that reactant molecules must be properly oriented for reaction to occur is not only reasonable but also valid. Unfortunately however, there is no simple way to calculate values for this steric factor from theory. In the final analysis, the *steric factor P* becomes nothing more that a *fudge factor* which brings theory in agrement with experiment. Another deficiency, perhaps even a more serious drawback, of the hard-sphere collision theory is that it treats reacting molecules as hard structureless blobs without regard to their internal *electronic* makeup, their *vibrational* or *rotational* degrees of freedom, and without reference to their intermolecular forces. The *translational* energy of moving molecules is not the only source of activation energy. Other forms of energy, such as, *rotational*, *vibrational*, and *electronic* also contribute in making a collision *effective* for product formation. We can summarize the major defects of the simple collision theory by simply saying that it is *inflexible* and cannot be tailored to meet the needs of a specific reaction. Another popular theory, the **transition-state theory**, first proposed in 1932 by H. Pelzer and E. Wigner,[26] and, later in 1935, extensively developed mainly by M. G. Evans and M. Polanyi,[27] and H. Eyring,[28] avoids these pitfalls and formulates reaction rates by describing the central role of a species, intermediate between reactants and products, in controlling these reaction rates. This approach leads to valuable interpretations and proves to be flexible enough in accommodating a variety of reactions.

0.9 THE TRANSITION-STATE THEORY AND A QUASI-THERMODYNAMIC DERIVATION OF THE EYRING EQUATION

To simplify the discussion on the transition-theory, we will consider a bimolecular reaction,

$$A + B \longrightarrow \text{Products}$$

even though this theory may be formulated more generally. The transition-state theory assumes that in passing from reactants to products sufficiently energetic reactant molecules must first form a well-defined and somewhat stable intermediate, $(AB)^*$, called the **activated complex** and designated by the *star* (*), that is,

$$A + B \longrightarrow (AB)^* \longrightarrow \text{Products}$$

The activated complex must then pass through a configuration of *maximum potential energy* (or equivalently of *minimum Gibbs free energy*) along the bond which will rupture as it decomposes to products. This region of maximum potential energy is referred to as the **transition state.** The *activated complex* in this idealized state of maximum potential energy along key bonds is also called the **transition state**, is said to have a **saddle-point configuration**, and is designated, following Eyring's convention,[29] by the *double dagger* (‡),

$$A + B \longrightarrow (AB)^* \longrightarrow (AB)^{\ddagger} \longrightarrow \text{Products}$$

Since the transition state is the chemical species in the lime light of this theory, we simply write,

$$A + B \longrightarrow (AB)^{\ddagger} \longrightarrow \text{Products}$$

Remark!

In most scientific literature, the terms "activated complex' and "transition state" are synonymous; and often they are used interchangeably. Thus, the transition-state theory is also called the **activated-complex theory**. The **absolute-reaction-rate theory** is also another name for this same theory. Even though the transition-state theory has chalked up many improvements over other kinetic theories, enthusiastic fans, however, should not be so eager as to call it by the title **absolute-rate theory** when in reality this theory is, at best, approximate and incomplete.[30]

End of Remark!

The transition-state theory describes a rate process by means of the **Eyring equation.** This fundamental equation, which contains energy information of the transition state with respect to the reactants, relates the rate constant k and the absolute temperature T, in a fashion very similar to the empirical Arrhenius equation. The Eyring rate expression may be formulated in terms of partition functions generated by the methods of statistical mechanics or in terms of the thermodynamic function, the **Gibbs free energy of activation** $\Delta G^{\ddagger}$, which is the difference between the free energy of the transition states, $G^{\ddagger}$, and G_r of the reactants,

$$\Delta G^{\ddagger} \equiv G^{\ddagger} - G_r$$

The statistical and thermodynamic approaches are complementary. Statistical mechanics analyzes a chemical process from the microscopic or molecular point of view, while the thermodynamic approach surveys the same chemical process from the macroscopic scenario. Often, the two approaches are intertwined. The Eyring equation in terms of the free energy of activation is

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT}$$

where,

k_B = Boltzmann's constant
h = Planck's constant
$\Delta G^{\ddagger}$ = Gibbs free enegy of activation
R = gas constant

A simple derivation of the Eyring equation given here utilizes concepts from both statistical mechanics and classical thermodynamics. The transition-state theory postulates that the rate of the reaction is equal to the product of the concentration of the transition state $(AB)^{\ddagger}$ formed from the reactants and the average frequency $\nu^{\ddagger}$ with which this species breakdown to form products, that is,

$$rate = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = [(AB)^{\ddagger}]\nu^{\ddagger}$$

From the **rate law**, we can say that

$$rate = k[A][B]$$

Therefore,

$$k[A][B] = [(AB)^{\ddagger}]\nu^{\ddagger}$$

and the rate constant is

$$k = \frac{[(AB)^{\ddagger}]}{[A][B]}\nu^{\ddagger}$$

or

$$k = \nu^{\ddagger}\frac{[(AB)^{\ddagger}]}{[A][B]}$$

The plan of attack in the discussion that follows is to transform the variables on the right-hand side of

$$k = \nu^{\ddagger}\frac{[(AB)^{\ddagger}]}{[A][B]}$$

into quantities which are more meaningful or experimentally more accessible. By classical statisitcal methods, it can be shown[31] that the frequency $\nu^{\ddagger}$ is

$$\nu^{\ddagger} = \frac{k_B T}{h}$$

and is thus a function of only temperature and is independent of the nature of reactants or transition state. Substituting the frequency $\nu^{\ddagger}$ with $k_B T/h$ in the rate-constant expression

$$k = \nu^{\ddagger}\frac{[(AB)^{\ddagger}]}{[A][B]}$$

we obtain

$$k = \frac{k_B T}{h}\frac{[(AB)^{\ddagger}]}{[A][B]}$$

Our next target is to manipulate the concentrations. Much of our knowledge of thermodynamics is really for processes which are at equilibrium. Before we can apply thermodynamic concepts to this problem, we need to *invent* an equilibrium between the reactants and the transition state, that is,

$$A + B \rightleftharpoons (AB)^{\ddagger} \longrightarrow \text{Products}$$

This equilibrium assumption is only a matter of convenience. More rigorous formulations of the transition state theory do not require this equilibrium.[32] The concentration of the transition state can now be formally related to the equilibrium constant $K^{\ddagger}$ as

$$K^{\ddagger} = \frac{[(AB)^{\ddagger}]}{[A][B]}$$

The ratio of the concentrations can now be replaced with the equilibrium constant $K^{\ddagger}$

$$k = \frac{k_B T}{h} K^{\ddagger}$$

The logarithmic equation,

$$\Delta G = -RT \ln K$$

relates free energy, ΔG, absolute temperature, T, and equilibrium constant, K.

$$\Delta G = -RT \ln K$$

In exponential form,

$$K = e^{-\Delta G/RT}$$

We can apply this expression to the "equilibrium" between the reactants and transition state, and affix K and ΔG with the *double dagger* (‡):

$$K^{\ddagger} = e^{-\Delta G^{\ddagger}/RT}$$

After replacing $K^{\ddagger}$ with the exponential factor in

$$k = \frac{k_B T}{h} K^{\ddagger}$$

we obtain the famous **Eyring Equation**

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT}$$

Often, it is convenient to express the Eyring equation in terms of the state functions, which define the Gibb's free energy. The definition of the Gibbs free energy, G,

$$G \equiv H - TS$$

where H is the enthalpy and S is entropy. If the temperature of the one state is the same as the temperature of another state, the free energy difference between two states is

$$\begin{aligned} G_2 - G_1 &= (H_2 - H_1) - (T_2 S_2 - T_1 S_1) \\ G_2 - G_1 &= (H_2 - H_1) - T(S_2 - S_1) \\ \Delta G &= \Delta H - T\Delta S \end{aligned}$$

in which $T = T_1 = T_2$. Since we are interested in energy differences between reactants and transition states, we tag the state functions which belong to transition states with the *double dagger* (‡) and those for the reactants with the subscript r, and we write

$$\begin{aligned} \Delta G^{\ddagger} &\equiv G^{\ddagger} - G_r \\ \Delta H^{\ddagger} &\equiv H^{\ddagger} - H_r \\ \Delta S^{\ddagger} &\equiv S^{\ddagger} - S_r \end{aligned}$$

so that

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

$\Delta H^{\ddagger}$ is the **enthalpy of activation** and $\Delta S^{\ddagger}$ is the **entropy of activation.** The Eyring equation may be rewritten as

$$\begin{aligned} k &= \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT} \\ &= \frac{k_B T}{h} e^{-(\Delta H^{\ddagger} - T\Delta S^{\ddagger})/RT} \\ k &= \frac{k_B T}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT} \end{aligned}$$

We are now ready to relate the transition-state activation parameters to those of Arrhenius. The Arrhenius activation parameters, E_a and A, are related to the enthalpy of activation, $\Delta H^{\ddagger}$, and the entropy of activation, $\Delta S^{\ddagger}$ as

$$E_a = \Delta H^{\ddagger} + RT$$

$$A = e\left(\frac{k_B T}{h}\right) e^{\Delta S^{\ddagger}/R}$$

The proof that

$$E_a = \Delta H^{\ddagger} + RT$$

is as follows,

$$k = \frac{k_B T}{h} K^{\ddagger}$$

$$\ln k = \ln\left(\frac{k_B T}{h} K^{\ddagger}\right)$$

$$= \ln\frac{k_B}{h} + \ln T + \ln K^{\ddagger}$$

$$\ln k = \ln\frac{k_B}{h} - \ln\frac{1}{T} + \ln K^{\ddagger}$$

After differentiating both sides with respect to $1/T$,

$$\frac{d\ln k}{d(1/T)} = \frac{d}{d(1/T)}\left(\ln\frac{k_B}{h} - \ln\frac{1}{T} + \ln K^{\ddagger}\right)$$

$$= \frac{d\ln(k_B/h)}{d(1/T)} - \frac{d\ln(1/T)}{d(1/T)} + \frac{d\ln K^{\ddagger}}{d(1/T)}$$

$$= \quad 0 \quad - \frac{1}{(1/T)} \quad + \frac{d\ln K^{\ddagger}}{d(1/T)}$$

$$\frac{d\ln k}{d(1/T)} = \quad - \quad T \quad + \frac{d\ln K^{\ddagger}}{d(1/T)}$$

The van't Hoff equation, first shown in Section 0.4, relates the equilibrium constant K and the enthalpy ΔH at constant pressure as

$$\frac{d\ln K}{d(1/T)} = -\frac{\Delta H}{R}$$

We can apply this expression to the "equilibrium" between the reactants and transition state, and tag K and ΔH with the *double dagger* (‡):

$$\frac{d\ln K^{\ddagger}}{d(1/T)} = -\frac{\Delta H^{\ddagger}}{R}$$

Thus,

$$\frac{d\ln k}{d(1/T)} = -T - \frac{\Delta H^{\ddagger}}{R}$$

Multiplying both sides with $-R$,

$$-R\frac{d\ln k}{d(1/T)} = RT + \Delta H^{\ddagger}$$

The left-hand side is the definition of the Arrhenius activation energy E_a. Therefore,

$$E_a = RT + \Delta H^{\ddagger}$$

or

$$E_a = \Delta H^{\ddagger} + RT$$

Using this result, we can prove that the Arrhenius exponential factor, A, is related to the entropy of activation, $\Delta S^{\ddagger}$, as

$$A = e\left(\frac{k_B T}{h}\right)e^{\Delta S^{\ddagger}/R}$$

We begin the proof with the Arrhenius equation and the Eyring expression:

$$k = Ae^{-E_a/RT}$$

$$k = \frac{k_B T}{h}e^{\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT}$$

Hence,

$$Ae^{-E_a/RT} = \frac{k_B T}{h}e^{\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT}$$

$$Ae^{-(\Delta H^{\ddagger}+RT)/RT} =$$

$$A\left(e^{-\Delta H^{\ddagger}/RT}\right)e^{-1} = \frac{k_B T}{h}e^{\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT}$$

$$Ae^{-1} = \frac{k_B T}{h}e^{\Delta S^{\ddagger}/R}$$

Therefore,

$$A = e\left(\frac{k_B T}{h}\right) e^{\Delta S^{\ddagger}/R}$$

We see from this equation that the Arrhenius exponential factor, A, incorporates frequency information, that is,

$$\nu^{\ddagger} = \frac{k_B T}{h}$$

$$A = e\left(\nu^{\ddagger}\right) e^{\Delta S^{\ddagger}/R}$$

In the transition-state theory, "frequency" refers to the *frequency of breakdown* of the transition state; in the collision theory, "frequency" refers to the *frequency of collisions*. Either way, this Arrhenius factor, A, is appropriately called the **frequency factor**, as mentioned in Section 0.4.

0.10 CALCULATIONS OF $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, AND $\Delta G^{\ddagger}$

There are a variety of ways to calculate the *enthalpy of activation*, $\Delta H^{\ddagger}$, the *entropy of activation*, $\Delta S^{\ddagger}$, and the *Gibbs free energy of activation*, $\Delta G^{\ddagger}$, from experimental data. The transition-state activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, are analogous to the Arrhenius activation parameters, E_a and A. Conceptually, the simplest procedure is to use these Arrhenius activation parameters, E_a and A, to derive values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$,. The enthalpy of activation, $\Delta H^{\ddagger}$, is accessible from the equation

$$E_a = \Delta H^{\ddagger} + RT$$

or

$$\Delta H^{\ddagger} = E_a - RT$$

Graphically, $\Delta H^{\ddagger}$ may be evaluated from the slope of the plot $\ln(k/T)$ against $1/T$, known as an **Eyring plot**,[33] analogous to an Arrhenius plot ($\ln k$ versus $1/T$). The slope of an Eyring plot is $-\Delta H^{\ddagger}/R$, that is,

$$\frac{d\ln(k/T)}{d(1/T)} = -\frac{\Delta H^{\ddagger}}{R}$$

which may be proved as follows,

$$k = \frac{k_B T}{h} K^{\ddagger}$$

$$\frac{k}{T} = \frac{k_B}{h} K^{\ddagger}$$

$$\ln\frac{k}{T} = \ln\frac{k_B}{h} + \ln K^{\ddagger}$$

Differentiating both sides with respect to $1/T$,

$$\frac{d\ln(k/T)}{d(1/T)} = \frac{d\ln(k_B/h)}{d(1/T)} + \frac{d\ln K^{\ddagger}}{d(1/T)}$$

$$= \quad 0 \quad + \frac{d\ln K^{\ddagger}}{d(1/T)}$$

$$\frac{d\ln(k/T)}{d(1/T)} = \frac{d\ln K^{\ddagger}}{d(1/T)}$$

The van't Hoff equation, first shown in Section 0.4, relates the equilibrium constant $K^{\ddagger}$ and the enthalpy of activation $\Delta H^{\ddagger}$ at constant pressure as

$$\frac{d\ln K^{\ddagger}}{d(1/T)} = -\frac{\Delta H^{\ddagger}}{R}$$

Therefore,

$$\frac{d\ln(k/T)}{d(1/T)} = -\frac{\Delta H^{\ddagger}}{R}$$

The entropy of activation, $\Delta S^{\ddagger}$, is obtained via

$$A = e\left(\frac{k_B T}{h}\right) e^{\Delta S^{\ddagger}/R}$$

which is transformed to logarithmic form

$$\ln A = \ln\left(\frac{ek_BT}{h}\right) + \frac{\Delta S^{\ddagger}}{R}$$

$$R\ln A = R\ln\left(\frac{ek_BT}{h}\right) + \Delta S^{\ddagger}$$

$$\Delta S^{\ddagger} = R\ln A - R\ln\left(\frac{ek_BT}{h}\right)$$

Finally, $\Delta G^{\ddagger}$ may be calculated from

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

with the known values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Of course, it may also be obtained directly from the Eyring equation

$$k = \frac{k_BT}{h}e^{-\Delta G^{\ddagger}/RT}$$

which may be converted to the convenient logarithmic form,

$$\Delta G^{\ddagger} = -RT\left(\ln\frac{k_B}{h} + \ln\frac{k}{T}\right)$$

We should not assume at this point that the free energy of activation, $\Delta G^{\ddagger}$, is temperature independent. The temperature dependence is already built in the definition of the Gibbs free energy,

$$G \equiv H - TS$$

and shows up also in $\Delta G^{\ddagger}$,

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

We hasten to add that tacitly we would like to believe that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are independent of temperature just like the Arrhenius activation parameters, E_a and A, once were thought to be.

In these modern times, the transition-state activation parameters, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ come mostly from line-shape analysis of dynamic NMR data.[34, 35, 36]

0.11 COMMENTS ON $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, AND $\Delta G^{\ddagger}$

Through the Eyring equation, the transition-state theory plays a variation of the same melody, which the Arrhenius and collision theories already have harped on. The Eyring equation is

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT}$$

where,

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

The smaller the $\Delta H^{\ddagger}$ and the larger the $\Delta S^{\ddagger}$, the smaller the $\Delta G^{\ddagger}$ is; the faster the reaction will go. Expressed in terms of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, the Eyring equation is

$$k = \frac{k_B T}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$$

This rate constant shares similar features with those from the Arrhenius and collision theories and is made up of three factors,

$$k = \begin{matrix}\text{frequency}\\ \text{factor}\end{matrix} \times \begin{matrix}\text{entropy}\\ \text{factor}\end{matrix} \times \begin{matrix}\text{energy}\\ \text{factor}\end{matrix}$$

We have already discussed in some detail the frequency and energy factors. We now say a few words on the entropy factor. Entropy is a measure of disorder. The *entropy of activation*, then, gauges the randomness of the transition states relative to the reactants. The fewer the restrictions which are placed on the arrangement of atoms in the transition state relative to the reactants, the bigger $\Delta S^{\ddagger}$ becomes; and consequently, the faster the reaction will proceed. The entropy of activation, which is analogous to the *steric factor* of the collision theory, provides valuable information in elucidating the nature of the transition state. $\Delta S^{\ddagger}$ can be *negative* or *positive*. Often, there is a *decrease* in entropy in passing from reactants to transition state if simple molecules are involved in the reaction. Generally, translational or rotational energy, which small molecules lose in forming a activated complex, is transferred to the vibrational modes of the complex. The

net effect is that two simple molecules, which were once freely roaming and tumbling, now become more constrained as an activated complex, just like when two people get married and lose some of their individual freedom. A transition state of complex molecules, however, may develop *more* degrees of freedom, such as *new* vibrational modes; and accordingly, the activation entropy *increases.*

0.12 THE EYRING EQUATION IN TERMS OF PARTITION FUNCTIONS

The partition function Q is defined as

$$Q \equiv \sum_{n=0}^{\infty} g_n e^{-\varepsilon_n/k_B T}$$

where g_n is the degeneracy of the energy level ε_n. It may be written in the expanded form

$$\begin{aligned} Q &\equiv \sum_{n=0}^{\infty} g_n e^{-\varepsilon_n/k_B T} \\ &= g_0 e^{-\varepsilon_0/k_B T} + g_1 e^{-\varepsilon_1/k_B T} + g_2 e^{-\varepsilon_2/k_B T} + \cdots \\ Q &= \frac{g_0}{e^{\varepsilon_0/k_B T}} + \frac{g_1}{e^{\varepsilon_1/k_B T}} + \frac{g_2}{e^{\varepsilon_2/k_B T}} + \cdots \end{aligned}$$

If the energy levels, $\varepsilon_0, \varepsilon_1, \varepsilon_2, \ldots$, are large when compared to $k_B T$, $\varepsilon_n >> k_B T$, and increase rapidly, the terms in the above expansion become successively very small; the expansion ceases to grow; and the value of Q thus remains small. To put it in another way, a large value of Q will result if the energy levels are highly degenerate and closely spaced. According to quantum mechanics and spectroscopy, the spacing in the translational, rotational, vibrational, and electronic energy levels are in this order,[37]

$$\varepsilon_t < \varepsilon_r < \varepsilon_v < \varepsilon_e$$

Since the translational energy levels are highly degenerate and closely spaced while the electronic levels have large gaps, the partition functions, corresponding to those energies, fall into this sequence,

$$Q_t >> Q_r > Q_v > Q_e$$

The translational partition function, Q_t, is the heavyweight; and the electronic partition function, Q_e, is in the bantam classification, that is, Q_t is the biggest and Q_e is the smallest.[38] Also, when the various degrees of freedom in a system are not interacting (not coupled), the wavefunction, Ψ, for that system may be expressed as the product of the individual wavefunctions,

$$\Psi = \psi_t \psi_r \psi_v \psi_e$$

the total energy, ε_n, of the nth level is the sum of the individual energy components,

$$\varepsilon_n = \varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e$$

and the degeneracy, g_n, of ε_n is then the product of the corresponding degeneracies,

$$g_n = g_t g_r g_v g_e$$

The total partition, Q, may be written as

$$Q \equiv \sum_{n=0}^{\infty} g_n e^{-\varepsilon_n/k_B T}$$

$$= \sum_{t,r,v,e=0}^{\infty} g_t g_r g_v g_e e^{-(\varepsilon_t+\varepsilon_r+\varepsilon_v+\varepsilon_e)/k_B T}$$

$$Q = \sum_{t,r,v,e=0}^{\infty} \left(g_t e^{-\varepsilon_t/k_B T}\right)\left(g_r e^{-\varepsilon_r/k_B T}\right)\left(g_v e^{-\varepsilon_v/k_B T}\right)\left(g_e e^{-\varepsilon_e/k_B T}\right)$$

Since *the sum of products* equals *the product of sums*, Q, becomes equal to the product of the partition functions, Q_t, Q_r, Q_v, and Q_e, that is,

$$Q = \sum_{t,r,v,e=0}^{\infty} \left(g_t e^{-\varepsilon_t/k_B T}\right)\left(g_r e^{-\varepsilon_r/k_B T}\right)\left(g_v e^{-\varepsilon_v/k_B T}\right)\left(g_e e^{-\varepsilon_e/k_B T}\right)$$

$$= \sum_{t=0}^{\infty} \left(g_t e^{-\varepsilon_t/k_B T}\right) \sum_{r=0}^{\infty} \left(g_r e^{-\varepsilon_r/k_B T}\right) \sum_{v=0}^{\infty} \left(g_v e^{-\varepsilon_v/k_B T}\right) \sum_{e=0}^{\infty} \left(g_e e^{-\varepsilon_e/k_B T}\right)$$

$$Q = Q_t Q_r Q_v Q_e$$

The equilibrium constant, $K^{\ddagger}$, may be expressed in terms of the partition functions and the molar energy difference, $\Delta E_0^{\ddagger}$, between the lowest energy level of the transition state and the sum of the lowest energy levels of the reactants,[39]

$$K^{\ddagger} = \frac{Q^{\ddagger}}{Q_A Q_B} e^{-\Delta E_0^{\ddagger}/RT}$$

The Eyring equation in terms of partition functions[40] becomes

$$k = \frac{k_B T}{h} K^{\ddagger}$$

$$= \frac{k_B T}{h} \left(\frac{Q^{\ddagger}}{Q_A Q_B} \right) e^{-\Delta E_0^{\ddagger}/RT}$$

$$k = \frac{k_B T}{h} \left(\frac{Q^{\ddagger}}{Q_A Q_B} \right)_t \left(\frac{Q^{\ddagger}}{Q_A Q_B} \right)_r \left(\frac{Q^{\ddagger}}{Q_A Q_B} \right)_v \left(\frac{Q^{\ddagger}}{Q_A Q_B} \right)_e e^{-\Delta E_0^{\ddagger}/RT}$$

in which the volume, V, is factored out from all the translational partition functions and the zero level of the vibrational partition function is usually set to zero.

The translational partition function is obtained from the energy levels of a particle in a box,

$$\varepsilon_n = \frac{n^2 h^2}{8ma^2}$$

where m is the mass of a particle in a one dimensional box of length a. The translational partition function for one dimension from this energy expression is[41]

$$Q_{trans} = \frac{(2\pi m k_B T)^{1/2} a}{h}$$

The total translational partition function is then the product of three factors,

$$Q_{trans} = \left(\frac{(2\pi m k_B T)^{1/2} a}{h} \right)^3 = \frac{(2\pi m k_B T)^{3/2} a^3}{h^3}$$

But the factor, a^3, is the volume, V, of the cubical box,

$$V = a^3$$

Hence,

$$Q_{trans} = \frac{(2\pi m k_B T)^{3/2} V}{h^3}$$

Thus,

$$Q_t = \frac{Q_{trans}}{V} = \frac{(2\pi m k_B T)^{3/2}}{h^3}$$

The energy levels of a linear molecule, behaving as a rigid rotator, are

$$\varepsilon_J = \frac{J(J+1)\hbar^2}{2I}$$

where,

$$J = 0,1,2,\cdots$$

$$I = \frac{m_A m_B}{m_A + m_B}(r_A + r_B)^2 = \mu(r_A + r_B)^2$$

$$g_J = 2J + 1$$

The rotational partition function from those rotational energies is[42]

$$Q_r = \frac{8\pi^2 I k_B T}{\sigma h^2}$$

where,

$\sigma = 1$ for unsymmetric linear molecule

$\sigma = 2$ for symmetric linear molecule

If the linear molecule is symmetric, two orientations which would otherwise be considered different become equivalent; and so, the *symmetry number*, σ, is needed to avoid too many indistinguishable orientations being taken into account.

The vibrational partition function, Q_{vib}, which is

$$Q_{vib} = \frac{e^{-h\nu/2k_BT}}{1 - e^{-h\nu/k_BT}}$$

may be derived as follows. For a harmonic oscillator of frequency ν, the quantum mechanical energy levels are given by

$$\varepsilon_n = (n + \tfrac{1}{2})h\nu$$

in which $n = 0,1,2,\cdots$. From this expression, we see that the vibrational energy levels are not degenerate. Therefore, the vibrational partition function, Q_{vib}, is

$$Q \equiv \sum_{n=0}^{\infty} g_n e^{-\varepsilon_n/k_B T}$$

$$Q_{vib} = \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})h\nu/k_B T}$$

where $g_n = 1$ since there is no degeneracy in the vibrational energy levels. This vibrational partition expression may be transformed into a more manageable form:

$$Q_{vib} = \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})h\nu/k_B T}$$

$$= \sum_{n=0}^{\infty} e^{-nh\nu/k_B T} e^{-h\nu/2k_B T}$$

$$Q_{vib} = e^{-h\nu/2k_B T} \sum_{n=0}^{\infty} e^{-nh\nu/k_B T}$$

The infinite series on the right-hand side, which is of the form

$$\sum_{n=0}^{\infty} e^{-nh\nu/k_B T} = \sum_{n=0}^{\infty} \left(e^{-h\nu/k_B T}\right)^n$$

may be summed in closed form with the aid of the identity

$$a^{n+1} - b^{n+1} \equiv (a-b)(a^n + a^{n-1}b + a^{n-2}b^2 + \cdots + b^n)$$

or after dividing by $(a-b)$

$$\frac{a^{n+1} - b^{n+1}}{a-b} = a^n + a^{n-1}b + a^{n-2}b^2 + \cdots + b^n$$

In particular for $a = 1$, we have

$$\frac{1-b^{n+1}}{1-b} = 1 + b + b^2 + \cdots + b^n$$

If $|b| < 1$, we see that $\lim_{n\to 0} b^{n+1} = 0$; thus,

$$\lim_{n\to\infty}\left(\frac{1-b^{n+1}}{1-b}\right)=\frac{\lim_{n\to\infty}\left(1-b^{n+1}\right)}{\lim_{n\to\infty}(1-b)}$$

$$=\frac{1-\lim_{n\to\infty} b^{n+1}}{1-b}$$

$$=\frac{1-0}{1-b}$$

$$\lim_{n\to\infty}\left(\frac{1-b^{n+1}}{1-b}\right)=\frac{1}{1-b}$$

Since

$$\frac{1-b^{n+1}}{1-b}=1+b+b^2+\cdots+b^n$$

and

$$\lim_{n\to\infty}\left(\frac{1-b^{n+1}}{1-b}\right)=\lim_{n\to\infty}\left(1+b+b^2+\cdots+b^n\right)$$

we have,

$$\lim_{n\to\infty}\left(1+b+b^2+\cdots+b^n\right)=\frac{1}{1-b}$$

Since

$$\sum_{n=0}^{\infty} b^n \equiv \lim_{n\to\infty}\left(1+b+b^2+\cdots+b^n\right)$$

then

$$\sum_{n=0}^{\infty} b^n=\frac{1}{1-b}$$

If

$$b=e^{-h\nu/k_BT}$$

then

$$\sum_{n=0}^{\infty}\left(e^{-h\nu/k_BT}\right)^n=\frac{1}{1-e^{-h\nu/k_BT}}$$

The vibrational partition function

$$Q_{vib}=e^{-h\nu/2k_BT}\sum_{n=0}^{\infty} e^{-nh\nu/k_BT}$$

then becomes

$$Q_{vib} = e^{-h\nu/2k_BT}\left(\frac{1}{1-e^{-h\nu/k_BT}}\right)$$

or

$$Q_{vib} = \frac{e^{-h\nu/2k_BT}}{1-e^{-h\nu/k_BT}}$$

If, however, in the vibrational partition function, the zero energy level

$$\varepsilon_0 = \frac{h\nu}{2}$$

is set to zero, we have, Q_v, that is,

$$Q_v = \frac{e^{-0}}{1-e^{-h\nu/k_BT}} = \frac{1}{1-e^{-h\nu/k_BT}}$$

This result may be obtained by dividing out from Q_{vib} the exponential factor which bears the zero energy level, that is,

$$Q_v = \frac{Q_{vib}}{e^{-h\nu/2k_BT}}$$

Since electronic energy levels are usually so large compared with k_BT, $\varepsilon_n >> k_BT$, only the ground level is mostly populated at normal temperatures; and hence, many reactions occur adiabatically, that is, without electronic excitations. Then, usually,

$$\left(\frac{Q^{\ddagger}}{Q_AQ_B}\right)_e \approx 1$$

and thus, electronic partition functions can often be conveniently ignored. When electronic effects become important, the electronic partition functions may be calculated from spectroscopic data

If we apply the transition-state theory to a reaction of two structureless particles of mass m_A and m_B, with the transition state having mass $m^{\ddagger} = m_A + m_A$, we obtain the interesting result,

$$k = \frac{k_B T}{h}\left(\frac{Q^{\ddagger}}{Q_A Q_B}\right)_t Q_r^{\ddagger} e^{-\Delta E_0^{\ddagger}/RT}$$

$$= \frac{k_B T}{h}\left[\frac{\frac{(2\pi m^{\ddagger} k_B T)^{3/2}}{h^3}}{\frac{(2\pi m k_B T)^{3/2}}{h^3}\frac{(2\pi m k_B T)^{3/2}}{h^3}}\right]\left[\frac{8\pi^2 k_B T}{h^2}\frac{m_A m_B}{m_A + m_B}(r_A + r_B)^2\right]e^{-\Delta E_0^{\ddagger}/RT}$$

$$k = \pi(r_A + r_B)^2\left(\frac{8\pi k_B T}{\pi\mu}\right)e^{-\Delta E_0^{\ddagger}/RT}$$

If we insist that the rate constant has molar units, we must insert Avogadro's constant,

$$k = N_O \pi(r_A + r_B)^2\left(\frac{8\pi k_B T}{\pi\mu}\right)e^{-\Delta E_0^{\ddagger}/RT}$$

This result is identical to that of the collision theory in Section 0.8.[43, 44]

Remark!

A nifty result from statistical mechanics is that the total energy, E, of a system at constant volume with N particles is related to the partition function, Q, as

$$E = -Nk_B\frac{d\ln Q}{d(1/T)} = Nk_B T^2\frac{d\ln Q}{dT}$$

The partition function Q is defined as

$$Q \equiv \sum_{n=0}^{\infty} g_n e^{-\varepsilon_n/k_B T}$$

where g_n is the degeneracy of the energy level ε_n. Since the Boltzmann's constant, k_B, is defined as

$$k_B = \frac{R}{N_o}$$

where R is the gas constant and N_o is Avogadro's constant, this energy expression may be rewritten as

$$E = -N\left(\frac{R}{N_o}\right)\frac{d\ln Q}{d(1/T)} = N\left(\frac{R}{N_o}\right)T^2\frac{d\ln Q}{dT}$$

or

$$E = -\left(\frac{N}{N_o}\right)R\frac{d\ln Q}{d(1/T)} = \left(\frac{N}{N_o}\right)RT^2\frac{d\ln Q}{dT}$$

The ratio N/N_o is the number of moles n. Hence,

$$E = -nR\frac{d\ln Q}{d(1/T)} = nRT^2\frac{d\ln Q}{dT}$$

Thus the energy per mole becomes

$$\frac{E}{n} = -R\frac{d\ln Q}{d(1/T)} = RT^2\frac{d\ln Q}{dT}$$

If we define the molar energy $\tilde{E}$ as

$$\tilde{E} \equiv \frac{E}{n}$$

then

$$\tilde{E} = -R\frac{d\ln Q}{d(1/T)} = RT^2\frac{d\ln Q}{dT}$$

It is very interesting that the form of this enegy expression resembles the definition of the Arrhenius activation energy, E_a, which is also a molar energy!

$$E_a \equiv -R\frac{d\ln k}{d(1/T)} = RT^2\frac{d\ln k}{dT}$$

End of Remark!

0.13 THE TRANSMISSION COEFFICIENT

The discussion on the Eyring equation would not be complete without mentioning the problematic *transmission coefficient* κ. As with the hard-sphere collision theory, some rates calculated on the basis of transition-state theory are greater than observed rates. A small number of calculated rates, such as in electron-transfer reactions, where quantum-mechanical tunneling effects become important and cannot be ignored, are even smaller than experimental rates. To equalize the disparity between theory and experiment, an empirical "fudge factor" κ, called the *transmission coefficient*, must be inserted in the Eyring equation,

$$k = \kappa \frac{k_B T}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$$

This transmission coefficient, usually $\kappa < 1$, is analogous to the *steric factor*, usually $P < 1$, of the old collision theory. For nonadiabatic reactions, that is, those that proceed with electronic excitation, the values of κ may be as low as 10^{-7}.[45] For ordinary chemical reactions, involving the breaking of bonds, κ is between 0.5 and 1.0. For all practical purposes, we may set $\kappa = 1$ and allow $\Delta S^{\ddagger}$ in the exponential factor to soak up[46] all discrepancies which the transmission coefficient is supposed to assimilate.

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CHAPTER 1

GENESIS

We are now entering the fascinating but enigmatic world of the **bullvalenes, barbaralanes, semibullvalenes,...,** molecules created in **the image and likeness of benzene.** ***Benzene*** is the **Molecule of molecules** in organic chemistry. It is the **dynamic molecular idol** to emulate.

1.1 BENZENE

Benzene (C_6H_6, m. p. 5.5 °C, b. p. 80.1 °C) may be considered the *stable* intermediate in the rapid *degenerate rearrangement* of the *unstable* **1,3,5-cyclohexatriene** molecule (Kekulé's structure) as illustrated in Figure 1–1. A rearrangement is **degenerate** if the product of rearrangement is structurally identical to the starting material. In a degenerate rearrangement, bonds may change positions but the new molecule has the same structure as the original one.

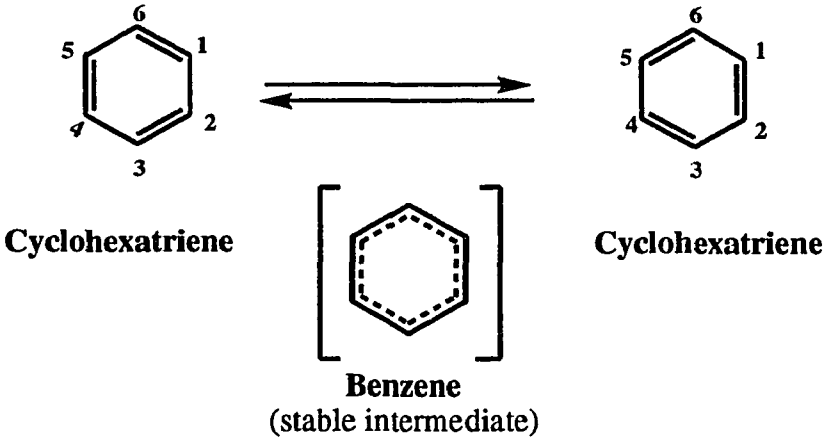


Figure 1–1. Degenerate rearrangement of 1,3,5-cyclohexatriene.

Remark!

The name "benzene" was given to this hydrocarbon because it may be synthesized from benzoic acid from the long-known gum **benzoin**. Benzene was discovered by Faraday in 1825 as one constituent of an oil collected in illuminating-gas lines. Monosubstituted products of benzene are often called "phenyl" compounds. The word "phenyl" comes from the Greek root *phainein*, which means "to appear," "to show," "to illuminate." Other familiar words, such as, *fantasy*, *photon*, also are derived from the same Greek root. The selection of this name "phenyl" for monosubstituted derivatives of benzene is then associated with the discovery of benzene in illuminating gas.[1]

End of Remark!

Cyclohexatriene and benzene have structural differences. In a cyclohexatriene molecule, single and double carbon-carbon bonds alternate; in the highly symmetrical and planar benzene, the carbon-carbon bonds are all of equal length (1.398 Å), longer than a double bond (1.33 Å) but shorter than a single bond (1.48—1.54 Å) as shown in Figure 1–2.

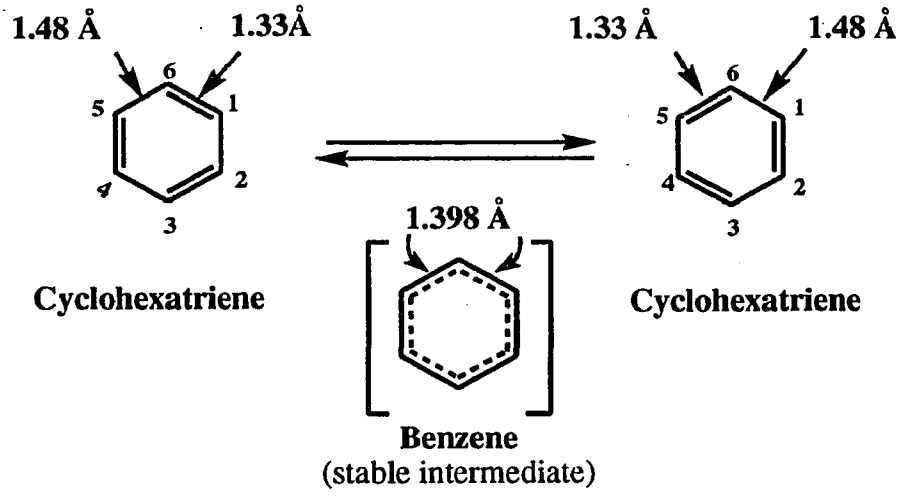


Figure 1–2. Degenerate rearrangement of 1,3,5-cyclohexatriene.

Structural information for benzene have come from various diffraction and spectroscopic techniques, such as, *neutron* diffraction, *X-ray* diffraction, *electron* diffraction, *NMR*, and *rotational spectroscopy*. Crystal data, atomic coordinates, thermal factors, bond distances of benzene from neutron and X-ray diffraction at various temperatures are summarized in Tables 1–1 to 5. Half of a benzene molecule is related to the other half by an inversion center.

Table 1–1. Diffraction Data for Benzene at Four Temperatures from Neutron and X-ray Diffraction

	Neutron diffraction[2]		**X-ray diffraction**[3,4]	
	138 K	**218 K**	**270 K**	**295 K** (high pressure)[a]
Formula	C_6H_6	C_6H_6	C_6H_6	C_6H_6
Formula weight	78.12	78.12	78.12	78.12
Crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic
Space group	*Pbca*	*Pbca*	*Pbca*	$P2_1/c$
a (Å)	7.39	7.44	7.46(0)	5.417(5)
b (Å)	9.42	9.55	9.66(6)	5.376(19)
c (Å)	6.81	6.92	7.03(4)	7.532(7)
β (°)	90	90	90	110.00(8)
Volume (Å^3)	474	492	507	295
Z	4	4	4	2
d_{calc} (g cm^{-3})	1.094	1.055	1.024	1.258
wavelength (Å)	1.08	1.08	2.291 (Cr Kα)	—
R	0.076	0.059	0.105	0.076
R_w	—	—	—	0.091

[a] The pressure is 25 kbar (1 atm = 1.01325 bar).

Table 1–2. Atomic Coordinates for Benzene at Four Temperatures from Neutron and X-ray Diffraction

Temperature	Atom	*x/a*	*y/b*	*z/c*
138 K	C1	–0.0607	0.1393	–0.0069
	C2	–0.1377	0.0447	0.1260
	C3	–0.0770	–0.0958	0.1325
	H1	–0.1046	0.2502	–0.0123
	H2	–0.2458	0.0781	0.2241
	H3	–0.1371	–0.1681	0.2360
218 K	C1	–0.0569	0.1387	–0.0054
	C2	–0.1335	0.0460	0.1264
	C3	–0.0774	–0.0925	0.1295
	H1	–0.0976	0.2447	–0.0177
	H2	–0.2409	0.0794	0.2218
	H3	–0.1371	–0.1631	0.2312
270 K	C1	–0.0508	0.1370	–0.0056
	C2	–0.1287	0.0476	0.1227
	C3	–0.0784	–0.0891	0.1295
295 K	C1	–0.2614	–0.0234	–0.1150
	C2	–0.0802	–0.2046	–0.1188
	C3	–0.1813	0.1812	0.0038
	H1	–0.4401	–0.0394	–0.1936
	H2	–0.1348	–0.3449	–0.2002
	H3	–0.3053	0.3055	0.0065

Table 1–3. Isotropic Thermal Parameters-*B's* (Å^2) for Benzene at Three Temperatures from Neutron and X-ray Diffraction

	Neutron		**X-ray**
Atom	**138 K**	**218 K**	**270 K**
C1	1.87	3.55	5.62
C2	2.00	3.79	5.61
C3	2.08	3.63	5.45
H1	3.42	6.45	—
H2	4.34	6.82	—
H3	3.82	6.21	—

The isotropic thermal parameter B in Table 1–3 is related to the mean-square displacement $\langle U^2 \rangle$ of an atom from its equilibrium position according to the equation

$$B = 8\pi^2 \langle U^2 \rangle$$

Table 1–4. Anisotropic Thermal Parameters (U_{ij}) for Benzene at Three Temperatures from Neutron and X-ray Diffraction

Temp.	Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
138 K	C1	0.040	0.040	0.055	–0.003	–0.004	–0.006
	C2	0.038	0.051	0.055	0.004	0.007	–0.004
	C3	0.043	0.050	0.045	–0.004	0.004	0.002
	H1	0.104	0.048	0.093	0.024	–0.011	–0.006
	H2	0.072	0.096	0.091	0.008	0.010	–0.001
	H3	0.077	0.077	0.082	0.008	–0.008	0.016
218 K	C1	0.023	0.022	0.026	0.001	–0.003	0.000
	C2	0.023	0.025	0.028	–0.001	0.005	–0.001
	C3	0.026	0.023	0.030	0.000	0.000	0.001
	H1	0.051	0.031	0.048	0.000	0.005	0.002
	H2	0.048	0.060	0.057	0.014	0.029	0.010
	H3	0.049	0.044	0.052	–0.004	0.014	0.015
270 K	C1	0.0633	0.0901	0.0601	-0.0057	-0.0004	0.0013
	C2	0.0830	0.0630	0.0672	-0.0196	-0.0029	0.0006
	C3	0.0918	0.0610	0.0542	0.0132	-0.0057	0.0025

Bond lengths in benzene from neutron and X-ray diffraction at four temperatures are reported in Table 1–5. In neutral atoms, neutrons are scattered by nuclei, while X-rays are scattered almost entirely by electrons.[5] Thus, if the center of gravity of electron distribution in an atom does not coincide with the position of a nucleus, the atomic positions determined by the two methods will differ. It is evident from the data in Table 1–5 that bond distances in benzene do not vary significantly with changes in temperature.

Table 1–5. Bond Lengths (Å) for Benzene at Four Temperatures

	Neutron diffraction		**X-ray diffraction**	
Bond	**138 K**	**218 K**	**270 K**	**295 K** (high pressure)
C1—C2	1.392(7)	1.394(10)	1.379	1.390
C2—C3	1.397(7)	1.387(9)	1.374	1.390
C3—C1	1.391(7)	1.389(9)	1.379	1.390
mean C—C	1.393(7)	1.390(9)	1.377(10)	1.390
C—C corrected for thermal motion	1.398	1.398	1.392	—
C1—H1	1.095(8)	1.059(15)	—	0.950
C2—H2	1.087(10)	1.085(17)	—	0.953
C3—H3	1.076(9)	1.072(16)	—	0.953
mean C—H	1.086(9)	1.072(16)	—	0.952
C—H corrected for thermal motion	1.090	1.077	—	—

The C—C and C—H lengths for benzene at four temperatures from various techniques are summarized in Table 1–6.

Table 1–6. Summary of Bond Lengths (Å) for Benzene from Various Techniques

Technique	Temperature	C—C	C—H	Comments
Neutron	**138 K**	1.393(7)	1.086(9)	Average
		1.398	1.090	Corrected for libration
	218 K	1.390(9)	1.072((16)	Average
		1.398	1.077	Corrected for libration
X-ray	**270 K**	1.377(10)	—	Average
		1.392	—	Corrected for libration
	295 K	1.390	0.952	
Electron diffraction (gas phase)[6,7]	—	1.397(1)	1.081	
		1.393(5)	1.08(2)	
Gas-rotational spectroscopy[8,9]	—	1.3964(2)		

From the data presented above, the agreement of the C—C and C—H bond distances from the various physical methods is truly remarkable! We conclude that the average C—C distances in benzene is the tight range of 1.390 to 1.400 Å

It is appropriate at this time, to explain the effect of thermal motion on bond distances and the meaning of "libration." The thermal anisotropic vibrations of atoms in a crystal may be described in terms of the anisotropic translational and rotational oscillations (**librations**) of the molecules. An important consequence of librational motion is that the maxima of the atomic peaks in the electron or nuclear density are closer to the center of rotation, and so, intramolecular distances appear to be foreshortened. This

may become clearer by examining the drawing in Figure 1–3, illustrating a simplified oscillation of atom B relative to atom A.[10]

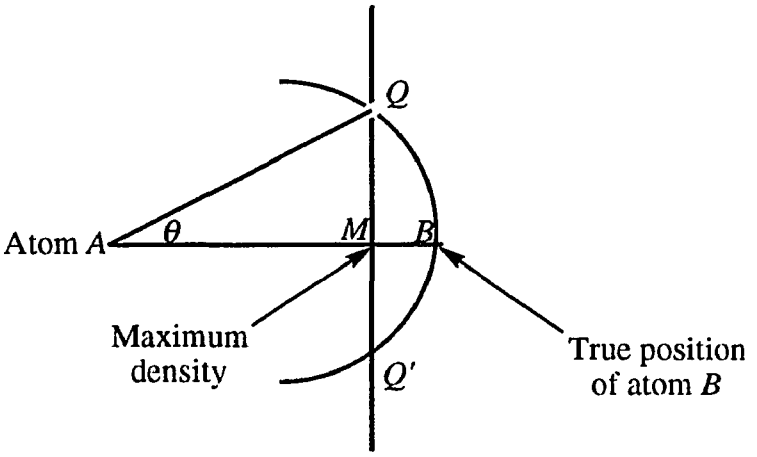


Figure 1–3. Peak displacements of atom *B* because of angular oscillations

If the atom *B* rocks relative to atom *A* between the points *Q* and *Q'*, its position calculated from the maximum electron or nuclear density seems to be at *M* and so the distance between the atoms *A* and *B* appears to be shorter than it actually is.

The carbon atoms in benzene are essentially planar as indicated by the 120 °C angles in Table 1–7. A least-square plane calculated from the positions of all twelve atoms in benzene clearly points out that benzene is indeed a planar molecule.

Table 1–7. Bond Angles (°) for Benzene at Four Temperatures from Neutron and X-ray Diffraction

	Neutron Diffraction		X-ray Diffraction	
Angle	**138 K**	**218 K**	**270 K**	**295 K** (high pressure)
C2—C1—C3	120.7	119.8	119.9	120.0
C2—C1—H1	120.8	122.9	—	120.0
C3—C1—H1	118.5	117.3	—	120.0
C1—C2—C3	119.7	119.5	120.7	120.0
C1—C2—H2	121.0	120.9	—	120.1
C3—C2—H2	119.3	119.5	—	119.9
C1—C3—C2	119.6	120.6	119.4	120.0
C1—C3—H3	121.2	120.3	—	120.1
C2—C3—H3	119.2	119.1	—	119.9

Table 1–8. Root-Mean-Square Amplitudes (Å) of Thermal Vibrations for Benzene at Three Temperatures from Neutron and X-ray Diffraction

Temp.	Atom	**Min.**	**Int'med.**	**Max.**
138 K	C1	0.144	0.150	0.167
(neutron)	C2	0.141	0.157	0.177
	C3	0.151	0.161	0.174
	H1	0.175	0.211	0.234
	H2	0.150	0.227	0.302
	H3	0.161	0.225	0.261
218 K	C1	0.186	0.207	0.240
(neutron)	C2	0.184	0.227	0.242
	C3	0.196	0.219	0.228
	H1	0.198	0.295	0.345
	H2	0.256	0.307	0.315
	H3	0.239	0.289	0.309
270 K	C1	0.245	0.249	0.302
(X-ray)	C2	0.226	0.259	0.309
	C3	0.225	0.244	0.312

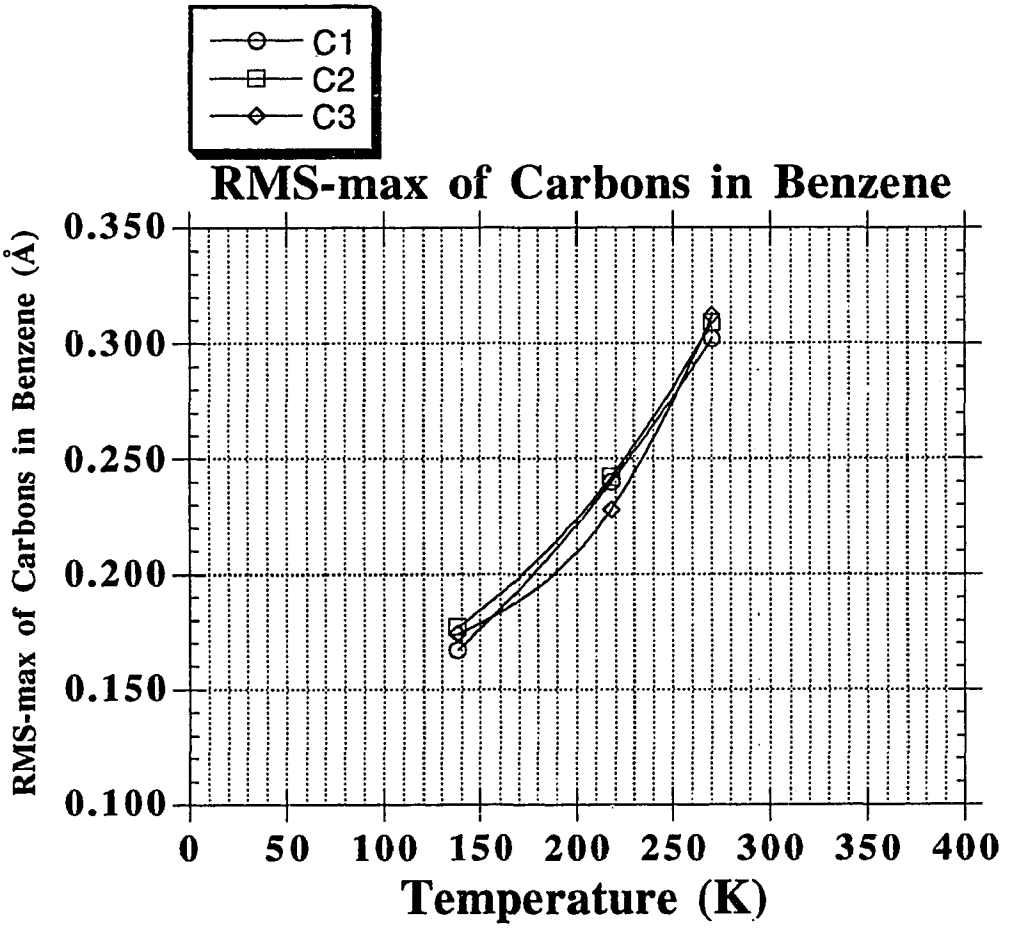


Figure 1–4. Plots of root-mean-square displacements of thermal vibrations of carbon atoms in benzene versus temperature.

From the diffraction data of the previous tables, we generate *ORTEP*[11] drawings of benzene as shown in Figures 1–4 through 6. Half of the molecule of benzene is related to the other half by an inversion center.

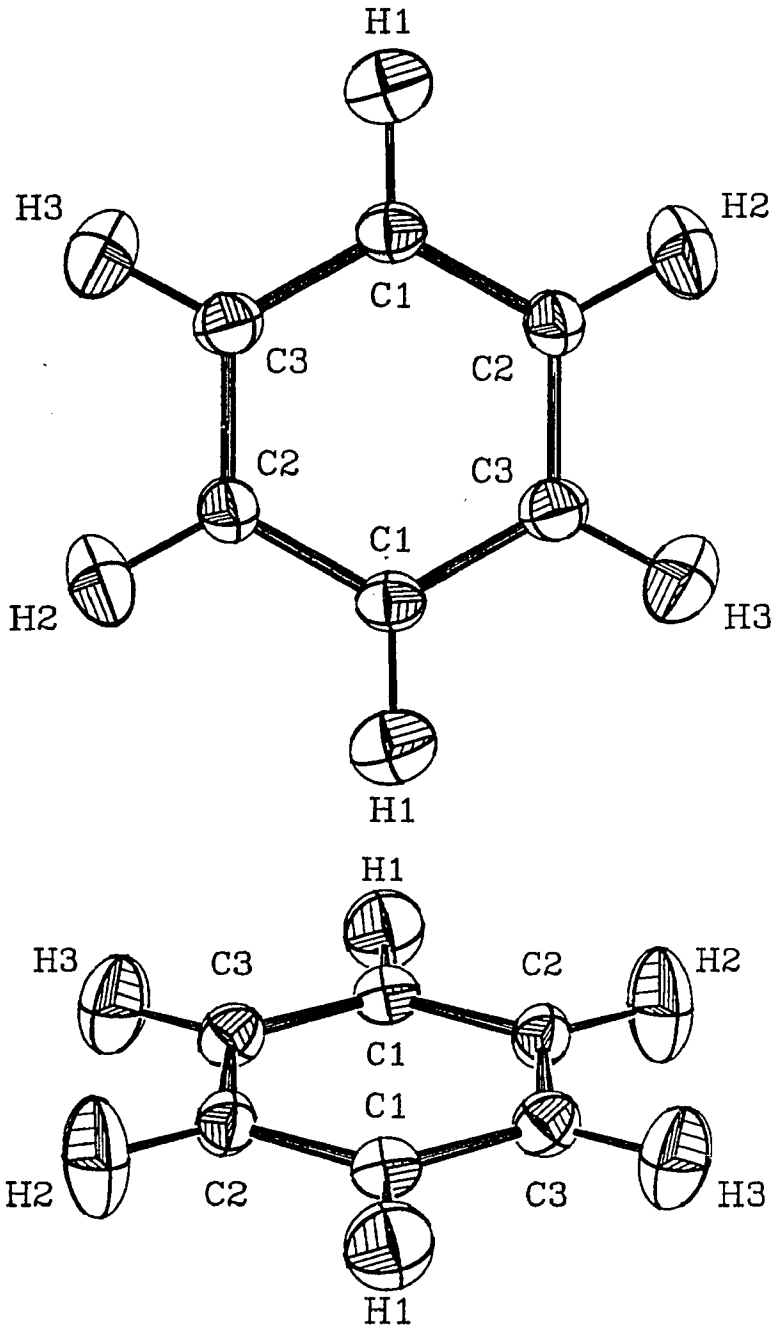


Figure 1–5. *ORTEP* drawings of benzene at **138 K** from neutron diffraction with 50% thermal ellipsoids.

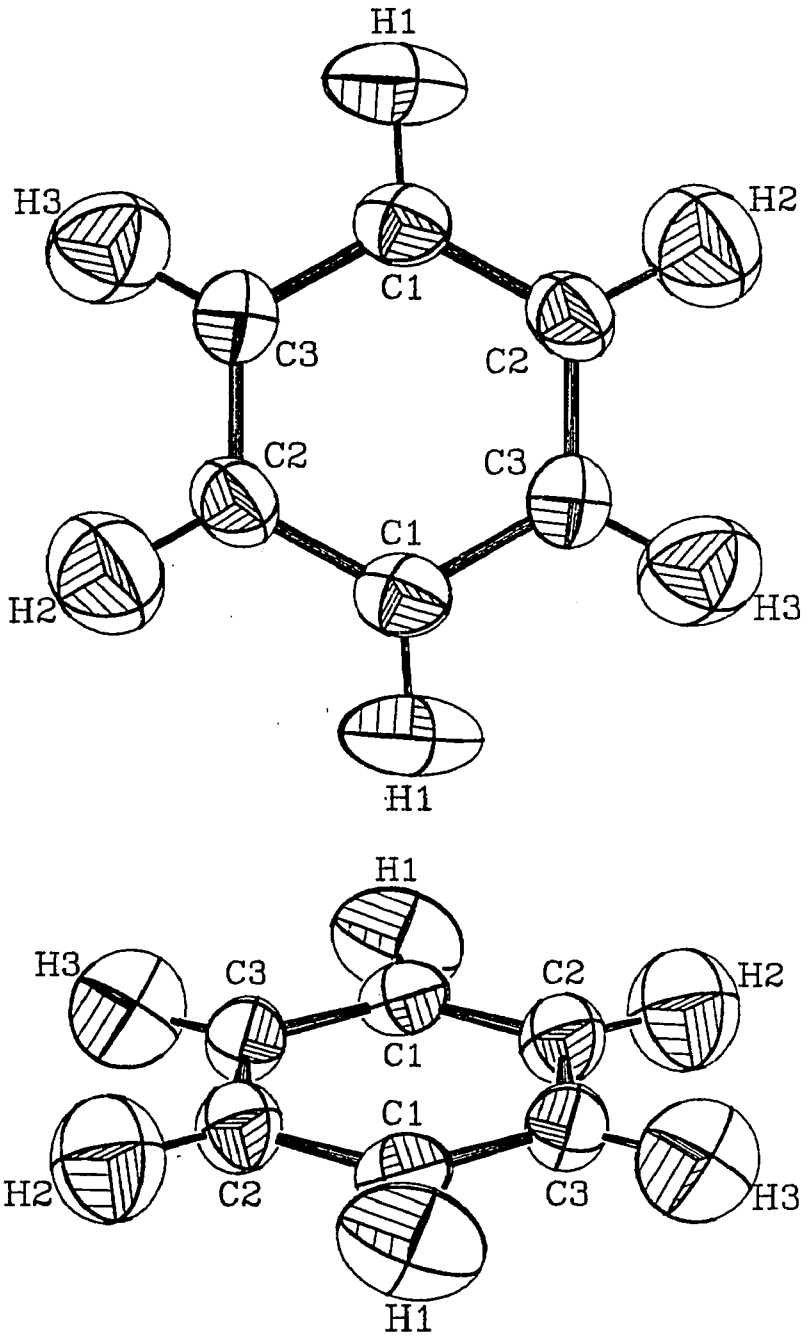


Figure 1–6. *ORTEP* drawings of benzene at **218 K** from neutron diffraction with 50% thermal ellipsoids.

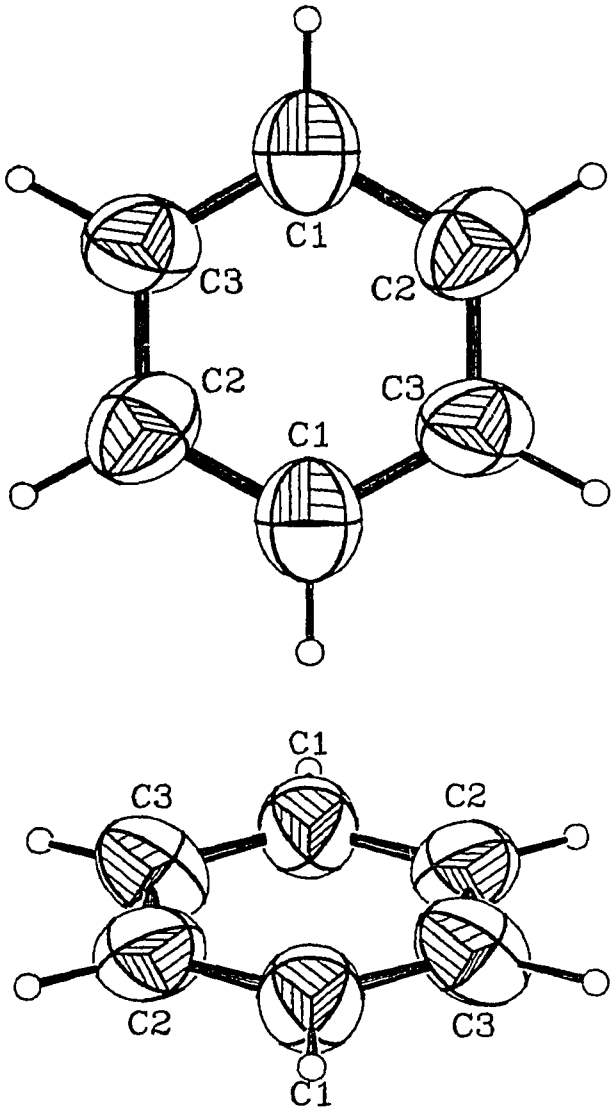


Figure 1–7. *ORTEP* drawings of benzene at **270 K** from X-ray diffraction with 50% thermal ellipsoids.

We now briefly turn to the energetics of benzene.

The **heat of hydrogenation** is the heat evolved when one mole of an unsaturated compound is hydrogenated. Generally, the heat of hydrogenation is approximately 28–30 kcal for each double bond present in a compound. Cyclohexene has one double bond and its heat of hydrogenation is 28.6 kcal; cyclohexadiene has two

double bonds and its heat of hydrogenation is approximately twice that value, 55.4 kcal.[12] For cyclohexatriene, which has three double bonds, we would expect that its heat of hydrogenation would be about three times that of cyclohexene, that is, $3 \times 28.6 = 85.8$ kcal. The experimental value for benzene is 49.8 kcal, which is *36 kcal less* than the expected amount of cyclohexatriene. In other words, benzene is more stable than cyclohexatriene by 36 kcal. The heat of combustion of benzene is also lower than the expected amount by about 36 kcal. This value of 36 kcal, which is usually called the **resonance energy** of benzene, may be identified with some form of activation energy for the rearrangement of cyclohexatriene. Since the various forms of activation energies (E_a, $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$) are similar, as alluded in the Introduction, we may conveniently equate this number to the Gibbs free energy of activation, $\Delta G^{\ddagger}$ for the degenerate rearrangement in Figure 1–7, that is,

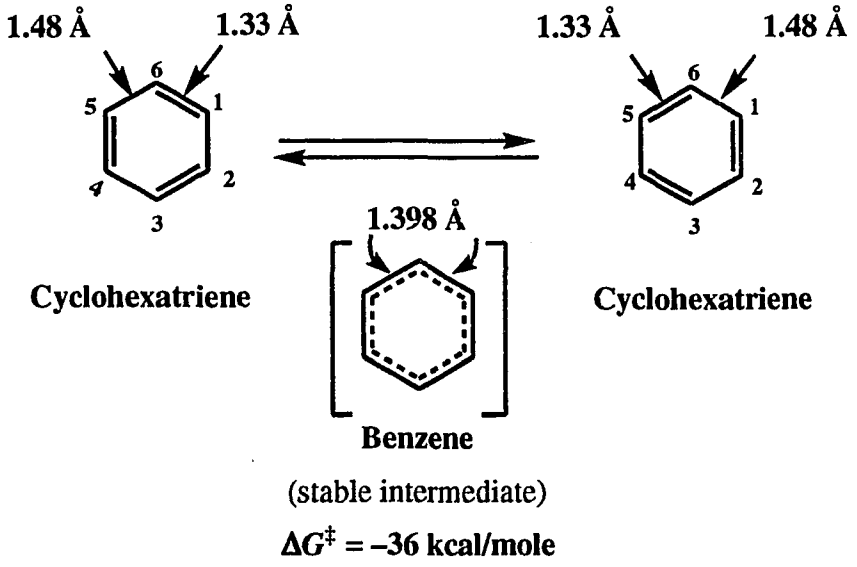
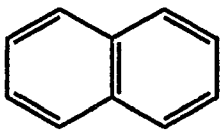


Figure 1–8. Degenerate rearrangement of 1,3,5-cyclohexatriene.

A negative value for $\Delta G^{\ddagger}$ means that benzene as a transition state is more stable than cyclohexatriene. Generally, most organic reactions have activation energy in the range of 10-35 kcal/mole. Reactions with activation energies less than 20 kcal/mole take place

spontaneously at room temperature or below, whereas those with higher energy barriers normally require heating.

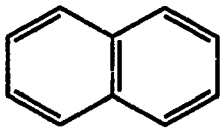
To better appreciate the structural nature of benzene, we focus our attention on benzene's next of kin, namely **naphthalene.**



Naphthalene

1.2 NAPHTHALENE

If two benzene molecules, so to speak, are joined at the hip, we obtain the planar **naphthalene** molecule ($C_{10}H_{10}$, m. p. 80 °C, b. p. 218 °C):



Naphthalene

The interest in naphthalene is for the purpose of comparing it with benzene. Even within the same family of molecular brotherhood, naphthalene does not measure up to the symmetry perfection of benzene. With naphthalene, the lesson to be learned here is that *more or bigger is not necessarily better!*

Again we turn to X-ray diffraction experiments of naphthalene for a glimpse of its structural characteristics. Brock and Dunitz have reported X-ray crystal data of naphthalene at five temperatures (Tables 1–9 to 15).[13]

Table 1–9. X-ray Diffraction Data for Naphthalene at Five Temperatures

	92 K	**109 K**	**143 K**	**184 K**	**239 K**
Formula	$C_{10}H_8$	$C_{10}H_8$	$C_{10}H_8$	$C_{10}H_8$	$C_{10}H_8$
Formula wt	128.18	128.18	128.18	128.18	128.18
Melting point (°C)	80	80	80	80	80
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$
a (Å)	8.108(5)	8.122(5)	8.143(4)	8.169(3)	8.213(2)
b (Å)	5.940(2)	5.943(2)	5.951(2)	5.962(1)	5.973(1)
c (Å)	8.647(5)	8.653(4)	8.659(3)	8.665(3)	8.675(2)
β (°)	124.38(4)	124.32(4)	124.13(3)	124.86(3)	123.39(2)
Volume (Å^3)	343.70	344.94	347.38	350.42	355.28
Z	2	2	2	2	2
d_{calc} (g cm^{-3})	1.238	1.234	1.225	1.215	1.198
μ (Mo $K\alpha$) (cm^{-1})	0.65	0.65	0.64	0.64	0.63
R	0.038	0.040	0.038	0.038	0.035
R_w	0.051	0.051	0.050	0.050	0.043

The asymmetric unit contains one-half independent molecule of naphthalene. One half of a molecule of naphthalene is related to the other half by a center of symmetry.

Table 1–10. Atomic Coordinates for Naphthalene at Five Temperatures from X-ray Diffraction

Temperature	Atom	*x/a*	*y/b*	*z/c*
92 K	C1	0.0824(2)	0.0189(2)	0.3288(5)
	C2	0.1132(2)	0.1638(2)	0.2233(5)
	C3	0.0479(1)	0.1055(1)	0.0371(5)
	C4	0.0770(1)	0.2521(2)	0.0756(5)
	C5	0.0134(2)	0.1906(2)	0.2545(5)
	H1	0.1229(35)	0.0572(38)	0.4471(47)
	H2	0.1798(29)	0.3066(34)	0.2726(39)
	H4	0.1412(30)	0.3883(36)	0.0253 (39)
	H5	0.0323(36)	0.2915 (41)	0.3289(51)
109 K	C1	0.0826(2)	0.0189(2)	0.32860(5)
	C2	0.1134(2)	0.1635(2)	0.22300(5)
	C3	0.0479(1)	0.1054(1)	0.03700(5)
	C4	0.0769(1)	0.2518(2)	-0.07580(5)
	C5	0.0131(2)	0.1903(2)	-0.25470(5)
	H1	0.1210(37)	0.0545(40)	0.4458(49)
	H2	0.1795(30)	0.3054(34)	0.2707(38)
	H4	0.1411(31)	0.3883(36)	-0.0243(39)
	H5	0.0309(36)	0.2912(42)	-0.3287(50)
143 K	C1	0.0828(2)	0.0184(2)	0.32800(1)
	C2	0.1137(1)	0.1629(2)	0.22280(1)
	C3	0.0481(1)	0.1051(1)	0.03700(1)
	C4	0.0766(1)	0.2511(2)	-0.07590(1)
	C5	0.0128(2)	0.1901(2)	-0.25450(2)
	H1	0.1207(40)	0.0538(44)	0.4435(38)
	H2	0.1782(31)	0.3050(36)	0.2707(28)
	H4	0.1400(30)	0.3883(35)	-0.0238(28)
	H5	0.0290(37)	0.2894(43)	-0.3269(35)

Table 1–10 (cont'd). Atomic Coordinates for Naphthalene at Five Temperatures from X-ray Diffraction

Temperature	Atom	*x/a*	*y/b*	*z/c*
184 K	C1	0.0832(2)	0.0180(2)	0.32730(2)
	C2	0.1139(2)	0.1618(2)	0.22220(1)
	C3	0.0481(1)	0.1047(1)	0.03670(1)
	C4	0.0766(1)	0.2502(2)	-0.07590(1)
	C5	0.0123(2)	0.1893(2)	-0.25450(2)
	H1	0.1198(47)	0.0508(52)	0.4404(45)
	H2	0.1797(36)	0.2980(42)	0.2712(33)
	H4	0.1395(31)	0.3858(37)	-0.0268(30)
	H5	0.0280(46)	0.2843(53)	-0.3281(43)
239 K	C1	0.0838(2)	0.0176(3)	0.32630(2)
	C2	0.1146(2)	0.1607(2)	0.22160(2)
	C3	0.0482(1)	0.1039(2)	0.03640(1)
	C4	0.0762(2)	0.2489(2)	-0.07670(2)
	C5	0.0116(2)	0.1884(3)	-0.25430(2)
	H1	0.1251(51)	0.0498(60)	0.4440(50)
	H2	0.1778(36)	0.3014(43)	0.2671()33
	H4	0.1381(37)	0.3856(45)	-0.0289(35)
	H5	0.0217(52)	0.2809(61)	-0.3334(50)

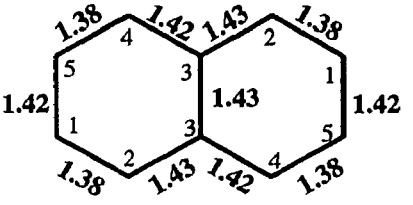
Table 1–11. Isotropic Thermal Parameters-*B's* ($Å^2$) for Napthalene at Five Temperatures from X-ray Diffraction

Atom	**92 K**	**109 K**	**143 K**	**184 K**	**239 K**
C1	1.30	1.47	1.88	2.50	3.58
C2	1.12	1.25	1.59	2.10	3.03
C3	0.89	0.97	1.21	1.59	2.25
C4	1.05	1.18	1.50	1.99	2.87
C5	1.28	1.44	1.82	2.41	3.49

Table 1–12. Anisotropic Thermal Parameters (U_{ij}) for Napthalene at Three Temperatures from X-ray Diffraction

Temp.	Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
92 K	C1	0.0165	0.0202	0.0140	0.0014	0.0094	0.0002
	C2	0.0136	0.0138	0.0157	-0.0009	0.0085	-0.0025
	C3	0.0100	0.0110	0.0144	0.0006	0.0079	0.0003
	C4	0.0128	0.0113	0.0183	-0.0001	0.0102	0.0015
	C5	0.0166	0.0179	0.0187	0.0018	0.0127	0.0040
109 K	C1	0.0186	0.0230	0.0158	0.0015	0.0105	0.0002
	C2	0.0154	0.0157	0.0168	-0.0010	0.0092	-0.0027
	C3	0.0113	0.0114	0.0157	0.0004	0.0086	0.0001
	C4	0.0144	0.0125	0.0207	0.0001	0.0115	0.0020
	C5	0.0187	0.0200	0.0209	0.0022	0.0141	0.0050
143 K	C1	0.0243	0.0290	0.0193	0.0019	0.0129	0.0003
	C2	0.0191	0.0199	0.0207	-0.0018	0.0107	-0.0040
	C3	0.0139	0.0142	0.0190	0.0004	0.0098	0.0001
	C4	0.0182	0.0155	0.0260	0.0000	0.0141	0.0026
	C5	0.0240	0.0249	0.0258	0.0028	0.0173	0.0062
184 K	C1	0.0321	0.0393	0.0249	0.0026	0.0166	0.0001
	C2	0.0259	0.0260	0.0262	-0.0023	0.0135	-0.0052
	C3	0.0182	0.0179	0.0251	0.0002	0.0126	-0.0003
	C4	0.0245	0.0205	0.0334	0.0000	0.0178	0.0034
	C5	0.0319	0.0336	0.0324	0.0031	0.0218	0.0081
239 K	C1	0.0471	0.0551	0.0355	0.0037	0.0237	-0.0002
	C2	0.0372	0.0372	0.0382	-0.0032	0.0192	-0.0073
	C3	0.0254	0.0251	0.0360	0.0002	0.0176	-0.0010
	C4	0.0354	0.0287	0.0490	-0.0007	0.0257	0.0039
	C5	0.0468	0.0472	0.0474	0.0044	0.0316	0.0122

The C—C bonds of a naphthalene molecule, listed in Table 1–13, are not fully hybrids as in benzene but retain some of their single and double-bond character. They have a tendency to alternate and, but like in benzene, do not change with temperature.



Naphthalene

Table 1–13. Bond distances (Å) for Naphthalene at Five Temperatures
(Values in parentheses are corrected for librational motion.)
(E.s.d.'s are about 0.002 Å for C—C and 0.03 Å for C—H.)

	92 K	109 K	143 K	184 K	239 K
C1—C2	1.376	1.376	1.374	1.372	1.368
	(1.377)	(1.378)	(1.377)	(1.375)	(1.373)
C4—C5	1.376	1.377	1.376	1.377	1.374
	(1.378)	(1.379)	(1.378)	(1.381)	(1.380)
C2—C3	1.425	1.424	1.425	1.423	1.425
	(1.426)	(1.426)	(1.428)	(1.428)	(1.431)
C3—C4	1.422	1.422	1.421	1.418	1.419
	(1.424)	(1.424)	(1.423)	(1.421)	(1.424)
C1—C5	1.415	1.414	1.412	1.409	1.407
	(1.417	(1.416)	(1.415)	(1.413)	(1.413)
C3—C3	1.422	1.423	1.423	1.423	1.420
	(1.424)	(1.425)	(1.426)	(1.427)	(1.426)
C1—H1	0.91	0.90	0.89	0.87	0.90
C5—H5	0.95	0.95	0.92	0.91	0.92
C2—H2	0.97	0.96	0.96	0.94	0.95
C4—H4	0.93	0.93	0.94	0.92	0.93

The bond angles in Table 1–14 deviate from the ideal planar angle of 120 °C, which indicates that a naphthalene molecule is not as flat as a benzene molecule. The difference in planarity is obvious but is nevertheless small.

Table 1–14. Bond Angles (°) for Naphthalene at Five Temperatures

	92 K	**109 K**	**143 K**	**184 K**	**239 K**
C2—C1—C5	120.52	120.55	120.70	120.75	120.85
C1—C2—C3	120.44	120.47	120.36	120.44	120.26
C2—C3—C3	118.93	118.91	118.93	118.80	118.92
C2—C3—C4	121.73	121.75	121.81	121.82	121.82
C3—C3—C4	119.34	119.34	119.26	119.38	119.26
C3—C4—C5	120.41	120.41	120.51	120.38	120.36
C1—C5—C4	120.36	120.31	120.23	120.24	120.34

These data clearly demonstrates that naphthalene does not have symmetric structural features which seem to be so prevalent in benzene.

The deviations of the carbon atoms in naphthalene (Table 1–15 and Figure 1–9) from their equilibrium positions are less than those in benzene (Table 1–6 and Figure 1–4).

Table 1–15 Root-Mean-Square Amplitudes (Å) of Thermal Vibrations for Naphthalene at Five Temperatures from X-ray Diffraction

	Atom	Min.	Int'med.	Max.
92 K	C1	0.112	0.127	0.144
	C2	0.110	0.115	0.132
	C3	0.091	0.105	0.120
	C4	0.098	0.109	0.136
	C5	0.103	0.125	0.150
109 K	C1	0.120	0.135	0.153
	C2	0.116	0.123	0.138
	C3	0.098	0.107	0.125
	C4	0.103	0.114	0.146
	C5	0.109	0.131	0.160
143 K	C1	0.134	0.154	0.173
	C2	0.127	0.140	0.157
	C3	0.113	0.120	0.138
	C4	0.116	0.129	0.163
	C5	0.125	0.147	0.178
184 K	C1	0.153	0.177	0.201
	C2	0.144	0.165	0.178
	C3	0.130	0.134	0.160
	C4	0.136	0.151	0.186
	C5	0.144	0.172	0.203
239 K	C1	0.182	0.214	0.239
	C2	0.174	0.197	0.214
	C3	0.153	0.159	0.192
	C4	0.162	0.182	0.224
	C5	0.172	0.207	0.245

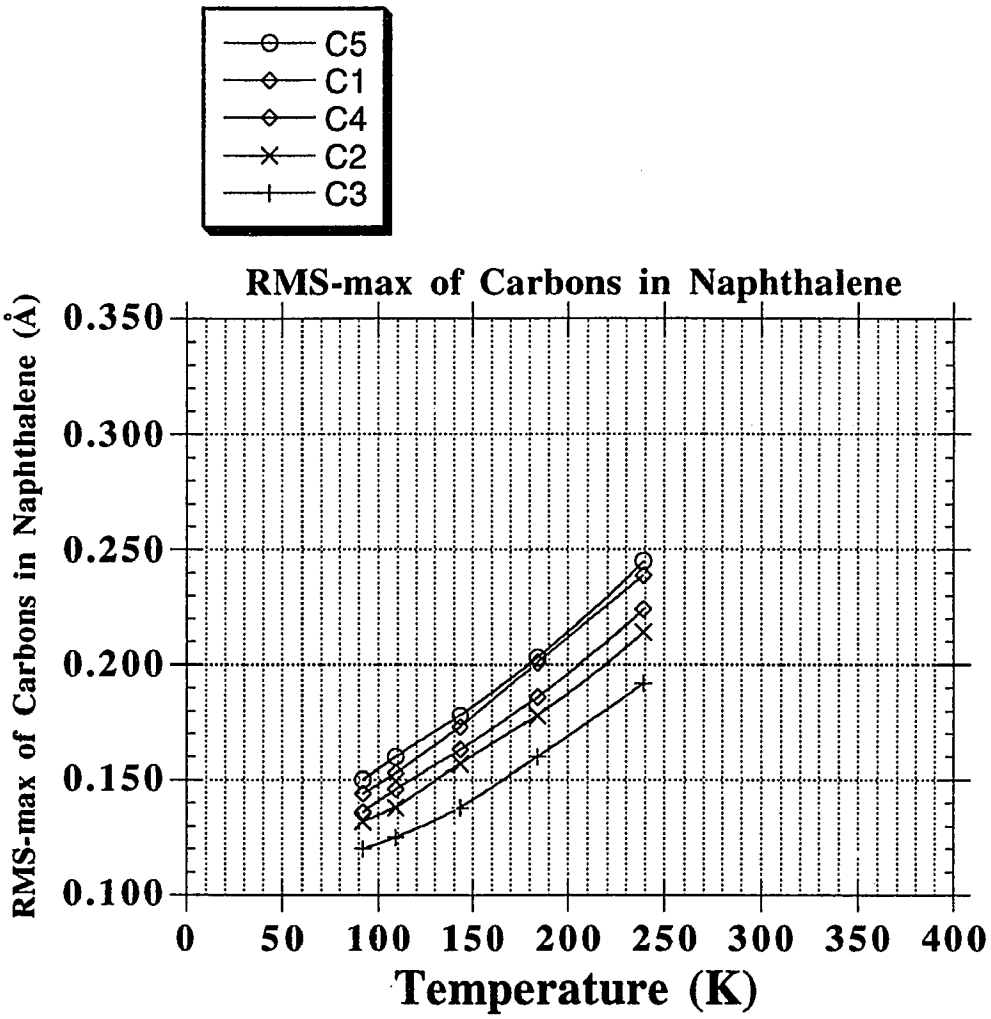


Figure 1–9. A plots of root-mean-square displacements of thermal vibrations of carbon atoms in naphthalene versus temperature.

From these X-ray diffraction data, we can generate *ORTEP* drawings of naphthalene. These *ORTEP* drawings indicate that generally, as in benzene, the major axes of thermal ellipsoids in the ring are aligned in the direction of the C—C bonds.

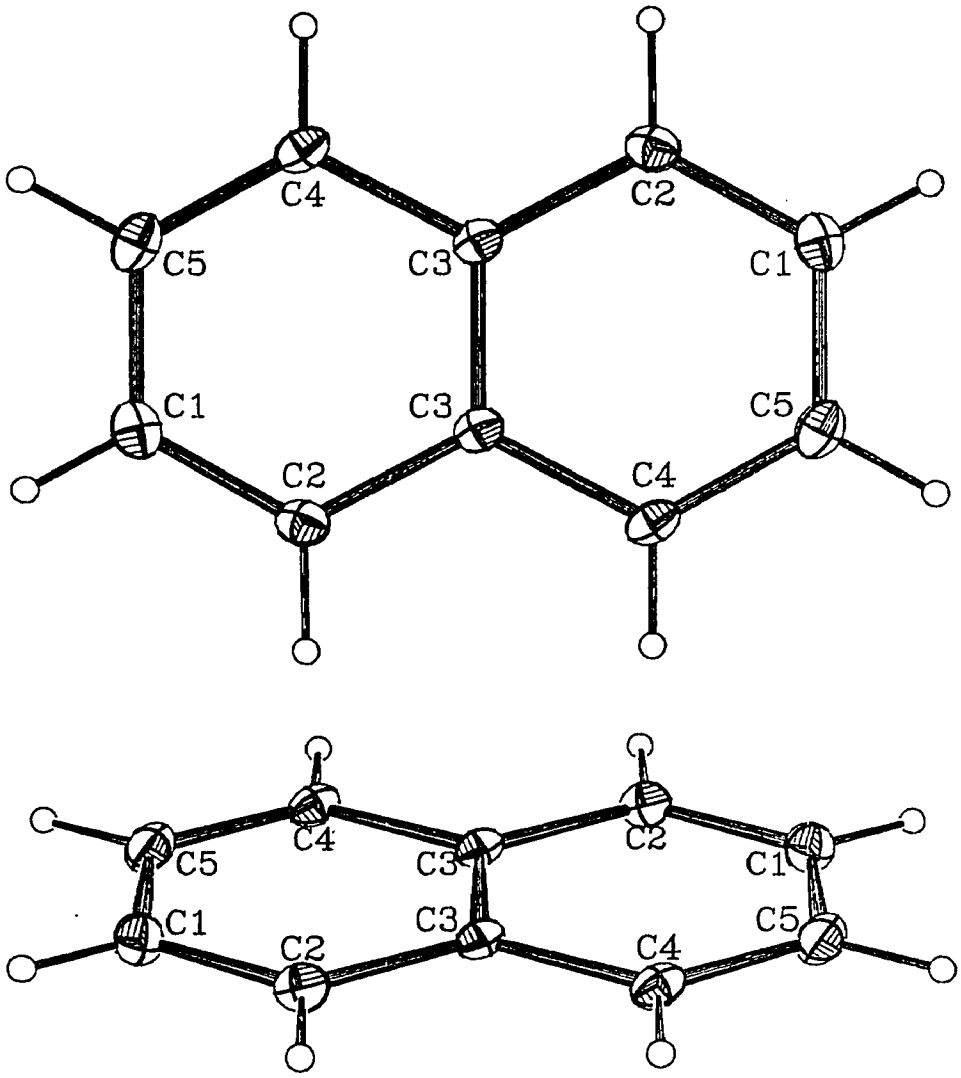


Figure 1–10. *ORTEP* drawings of naphthalene at **92 K** from X-ray diffraction with 50% thermal ellipsoids.

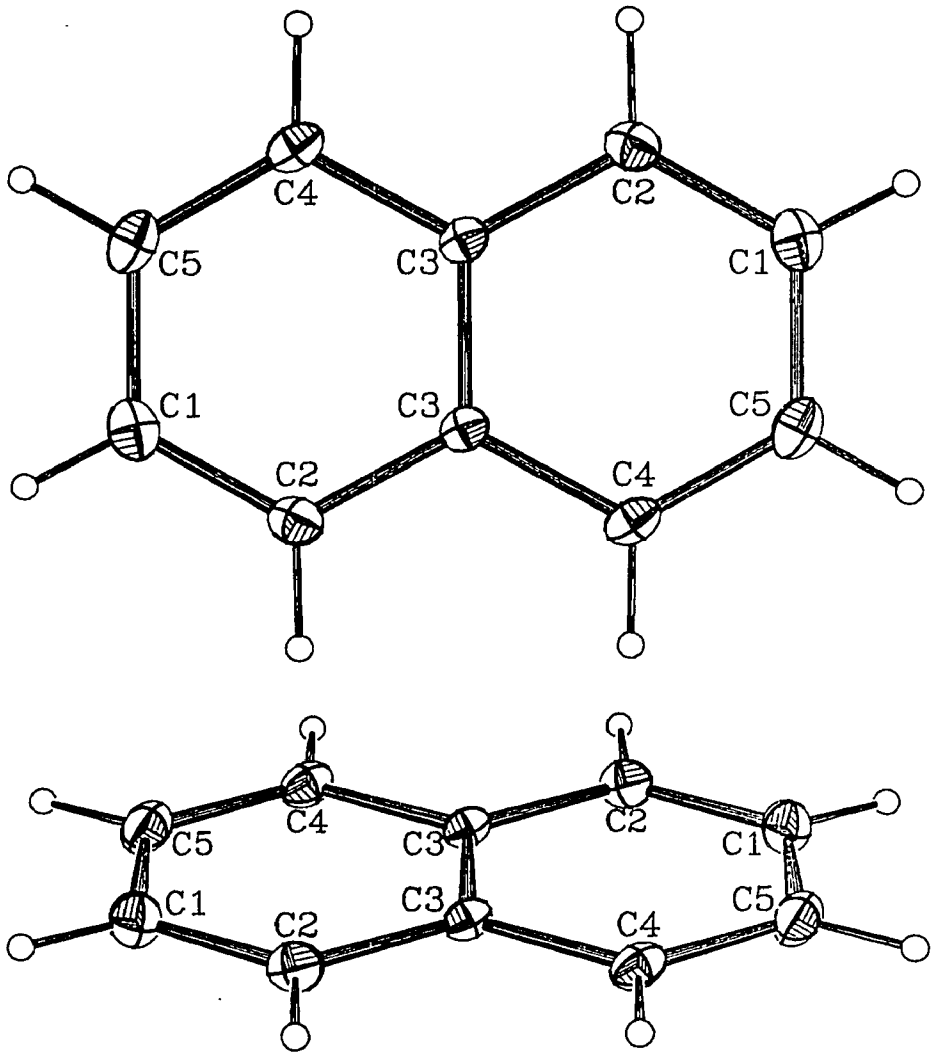


Figure 1–11. *ORTEP* drawings of naphthalene at **109 K** from X-ray diffraction with 50% thermal ellipsoids.

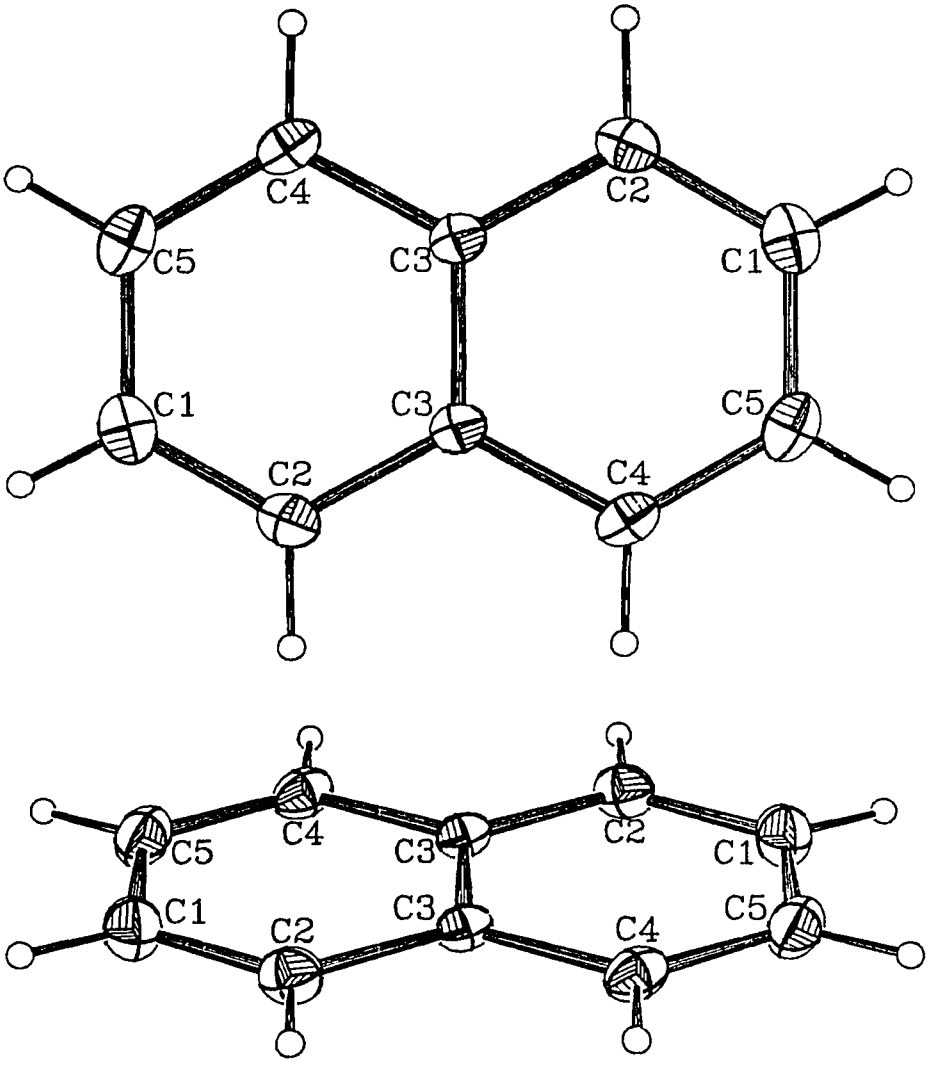


Figure 1–12. *ORTEP* drawings of naphthalene at **143 K** from X-ray diffraction with 50% thermal ellipsoids.

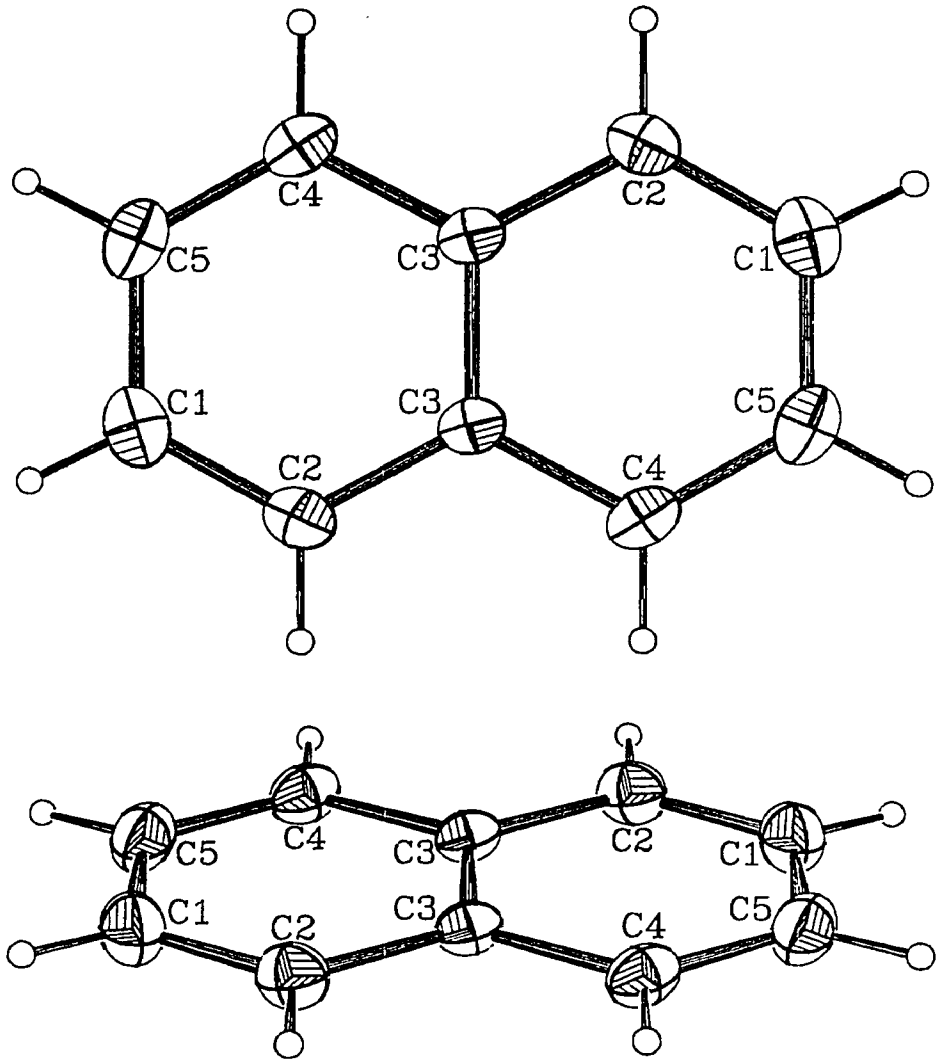


Figure 1–13. *ORTEP* drawings of naphthalene at **184 K** from X-ray diffraction with 50% thermal ellipsoids.

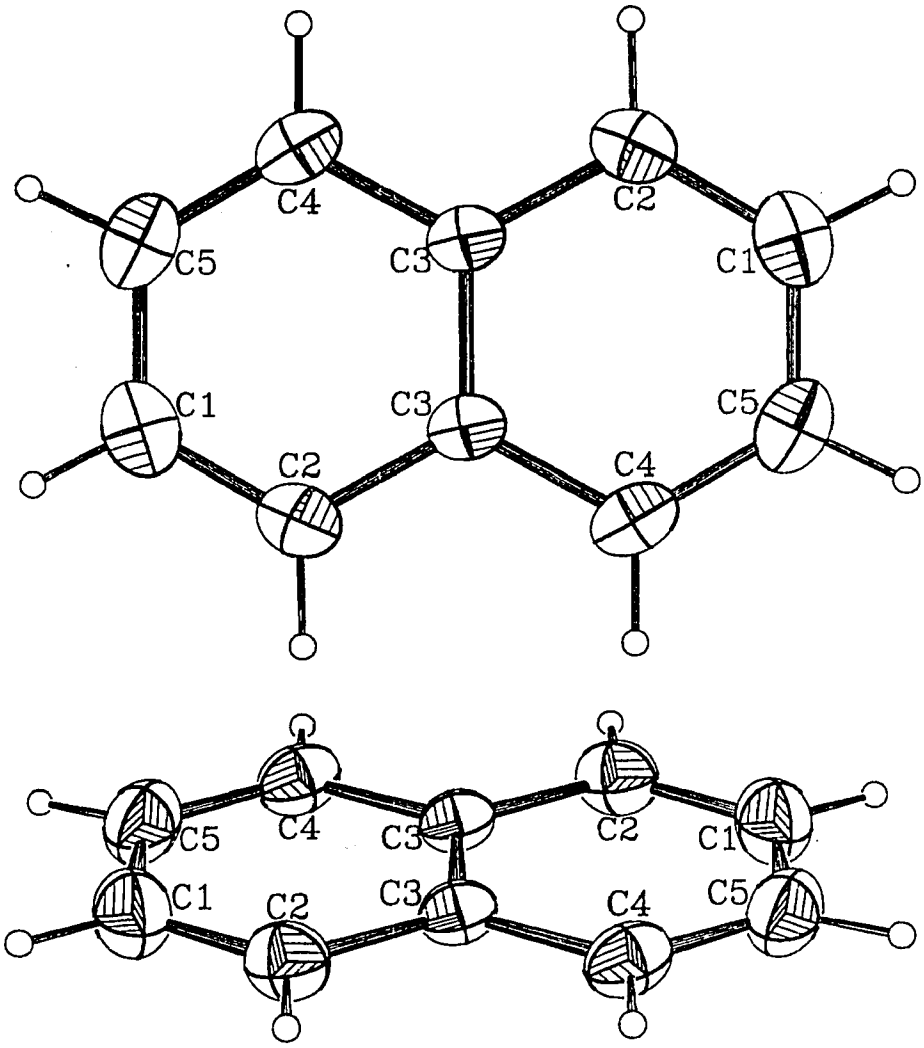
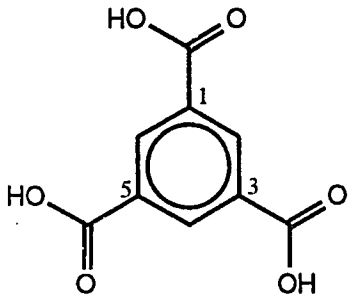


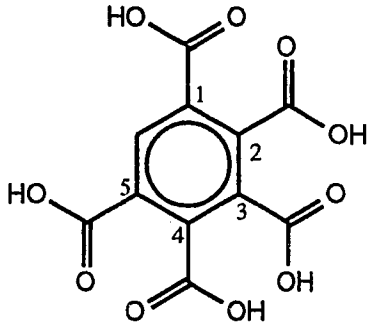
Figure 1–14. *ORTEP* drawings of naphthalene at **239 K** from X-ray diffraction with 50% thermal ellipsoids.

1.3 EFFECTS OF CARBOXYL GROUPS ON BOND DISTANCES IN BENZENE

Carboxylic groups have little effect on bond distances in the benzene rings. We examine **benzene-1,3,5-tricarboxylic acid**[14] (with common name **trimesic acid**) and **benzene-1,2,3,4,5-tetracarboxylic acid**:[15]



Benzene-1,3,5-tricarboxylic acid
(Trimesic acid)



Benzene-1,2,3,4,5-pemtacarboxylic acid

The X-ray crystal data for both of these compounds are presented in Table 1–16.

Table 1–16. X-ray Crystal Data for Benzene-1,3,5-tricarboxylic (**I**) and Benzene-1,2,3,4,5-tetracarboxylic acid (**II**) from X-ray Diffraction

	I	**II**
	295 K	**293 K**
Formula	$C_9H_6O_6$	$C_{11}H_6O_{10}$
Formula weight	210.15	298.16
Crystal system	monoclinic	monoclinic
Space group	*C2/c*	$P2_1/n$
a (Å)	26.520(2)	8.1104(4)
b (Å)	16.420(1)	8.8737(6)
c (Å)	26.551(2)	16.5061(5)
β (°)	91.53(1)	102.068(4)
Volume (Å^3)	11557.7	1161.68(6)
Z	48	4
d_{calc} (g cm^{-3})	1.449	1.705
wavelength (Å)	1.54056 (Cu $K\alpha$)	0.71073 (Mo $K\alpha$)
μ (cm^{-1})	10.6	1.47
R	0.068	0.037
R_w	—	0.039

The unit cell of benzene-1,3,5-tricarboxylic acid contains six independent molecules (designated as A trough F in Table 1–17), that is, six molecules not related by crystallographic symmetry.

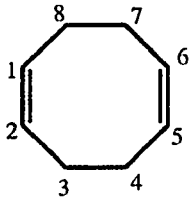
Table 1–17. Bond lengths (Å) in the Ring of Benzene-1,3,5-tricarboxylic acid (**I**) and Benzene-1,2,3,4,5-tetracarboxylic acid (II) from X-ray Diffraction

	I						**II**
Bond	A	B	C	D	E	F	
C1—C2	1.394	1.395	1.396	1.376	1.391	1.401	1.397
C2—C3	1.386	1.394	1.393	1.389	1.386	1.391	1.406
C3—C4	1.388	1.383	1.393	1.383	1.386	1.376	1.393
C4—C5	1.393	1.401	1.392	1.395	1.383	1.392	1.408
C5—C6	1.401	1.388	1.392	1.390	1.387	1.390	1.392
C6—C1	1.395	1.389	1.384	1.388	1.392	1.394	1.381
Mean C—C	1.392(8)	1.390(3)	1.390(6)	1.385(6)	1.393(5)	1.391(4)	1.395(4)

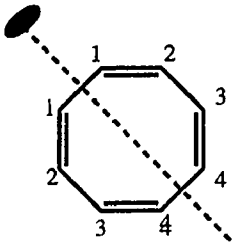
The bonds of the benzene ring in these compounds are within experimental errors the same as in benzene (Table 1–5). The average C—C ring distance of benzene-1,3,5-tricarboxylic acid is 1.390 Å and that of benzene-1,2,3,4,5-tetracarboxylic acid in Table 1–17 is 1.395 Å, which are essentially the same as the C—C bond distance of 1.398 Å in benzene itself.

1.4 CYCLOOCTA-1,5-DIENE AND SOME CYCLOOCTATETRAENE COMPOUNDS

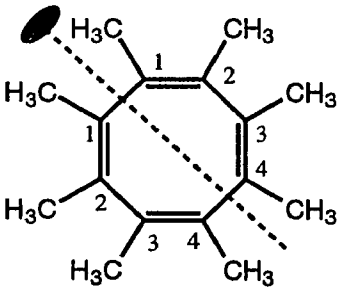
Cycloocta-1,5-diene and cyclooctatetraene compounds in Figure 1–15 are useful in assessing bond-distance variations of single and double bonds for the purpose of comparing them to the bond distances in benzene.



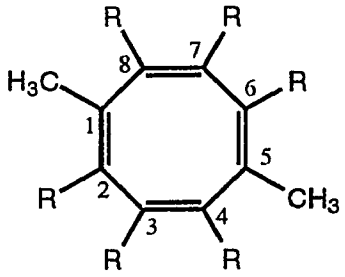
Cycloocta-1,5-diene
(COD)



Cyclooctatetraene
(COT)

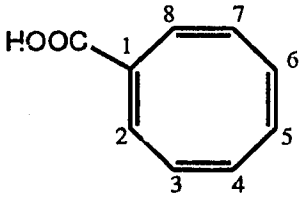


Octamethylcyclooctatetraene
(Me_8COT)

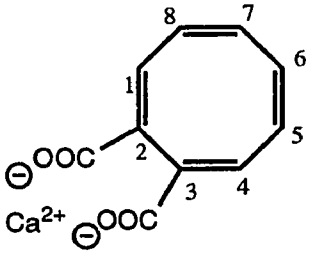


$R = COOCH_3$

1,5-Dimethyl-2,4,6,8-tetra-carbomethoxy-cyclooctatetraene
[$Me_2(COOMe)_4COT$]



Cyclooctatetraene carboxylic acid
(COT acid)



Calcium cyclooctatetraene-1,2-dicarboxylate
(CaCOT)

Figure 1–15. Cycloocta-1,5-diene and some cyclooctatetraene compounds. The symbol ⬮ refers to a two-fold rotation axis passing through the molecule of the X-ray structure.

Table 1–18. X-ray Crystal Data for Cycloocta-1,5-diene and Some Cyclooctatetraenes

	COD[16]	Me_8COT[17]	$Me_2(COOMe)_4$ COT[a]
	20 K	**295 K**	**295 K**
Formula	$C_{60}H_{52}N_4Zn$	$C_{16}H_{24}$	$C_{18}H_{20}O_8$
Formula weight	894.48	216.37	364.36
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$I\bar{1}$	*Pbcn*	*P*21/*c*
a (Å)	11.518(3)	12.774(3)	16.363(1)
b (Å)	13.289(4)	9.339(2)	15.733(1)
c (Å)	15.015(5)	12.217(2)	15.433(3)
α (°)	91.07(1)	90	90
β (°)	87.58(1)	90	109.73(1)
γ (°)	87.09(1)	90	90
Volume (Å^3)	229.8	1457.4	3739.6
Z	2	4	8
d_{calc} (g cm^{-3})	1.30	0.986	1.294
wavelength (Å)	0.7107 (Mo $K\alpha$)	1.54056 (Cu $K\alpha$)	1.54056 (Cu $K\alpha$)
R	0.050	0.086	0.049
R_w	0.067	—	0.063

[a] This work. The unit cell contains two independent molecules (designated as unprimed and primed).

Table 1–19. Bond distances (Å) for Cycloocta-1,5-diene and Some Cyclooctatetraenes from X-ray Diffraction

	COD	$Me_2(COOMe)_4$ COT		COT acid[18]	CaCOT[19]
	20 K	**295 K**		**295 K**	**295 K**
		unprimed	primed		
C1—C2	1.334	1.348	1.340	1.323	1.333
C2—C3	1.525	1.468	1.478	1.463	1.462
C3—C4	1.535	1.334	1.331	1.324	1.339
C4—C5	1.502	1.502	1.491	1.450	1.437
C5—C6	1.333	1.334	1.344	1.329	1.335
C6—C7	1.513	1.471	1.475	1.489	1.466
C7—C8	1.543	1.339	1.329	1.310	1.333
C8—C1	1.501	1.486	1.493	1.477	1.490
Standard. deviations from the averages are shown in parentheses.					
Mean C=C	1.334(1)	1.339(3)	1.336(7)	1.322(8)	1.335(3)
Mean C—C near C=C	1.511(11)	1.482(15)	1.484(9)	1.470(17)	1.464(22)
Mean C—C not near C=C	1.539(6)	—	—	—	—

Table 1–19 (cont'd). Bond distances (Å) for Cycloocta-1,5-diene and Some Cyclooctatetraenes from X-ray Diffraction

	COT[20]	Me_8COT
	295 K	**295 K**
C1 = C2	1.326	1.325
C2—C3	1.465	1.479
C3 = C4	1.335	1.327
C1—C1	1.439	1.487
C4—C4	1.454	1.488
Standard. deviations from the averages are shown in parentheses.		
Mean C=C	1.331(5)	1.326(1)
Mean C—C	1.456(12)	1.483(5)
Mean C=C e⁻ diffraction	1.334	—
Mean C—C e⁻ diffraction	1.462	—

The variation on the length of a double bond in these six compounds is extremely small. The average double-bond length in all these molecules is 1.33 Å, which is an accepted value of carbon-carbon double bond. The length of a single bond, however, varies dramatically in these compounds, from approximately 1.46 to 1.54 Å, depending on its environment. The electron diffraction interatomic distances agree with those from the X-ray.

ORTEP molecular drawings of just Me_8COT and $Me_2(COOMe)_4COT$ are shown in Figures 1–16 and 18, respectively.

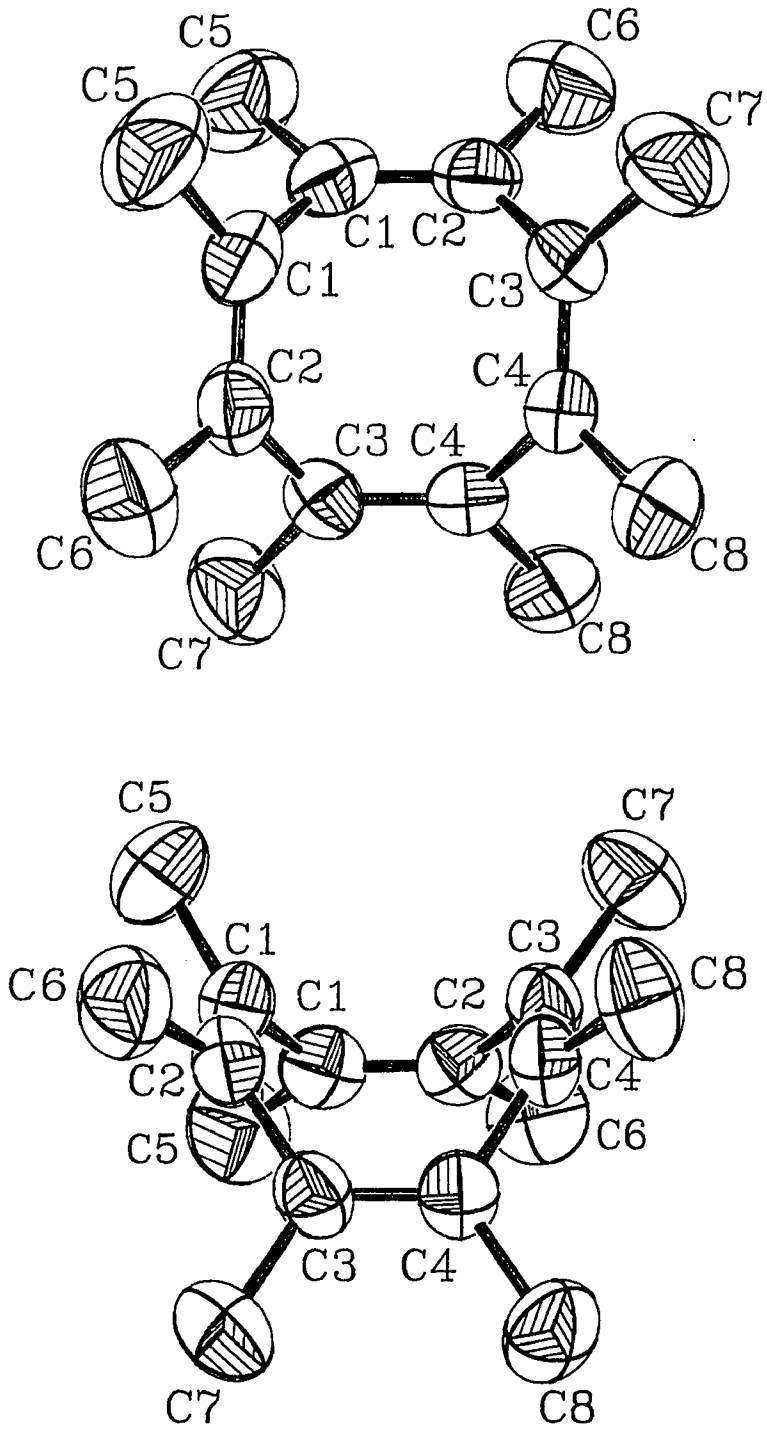


Figure 1–16. *ORTEP* drawings of octamethylcyclooctatetraene at **295 K** with 50% thermal ellipsoids. The two halves of the molecule are related by a two-fold axis parallel to the *b*-axis.

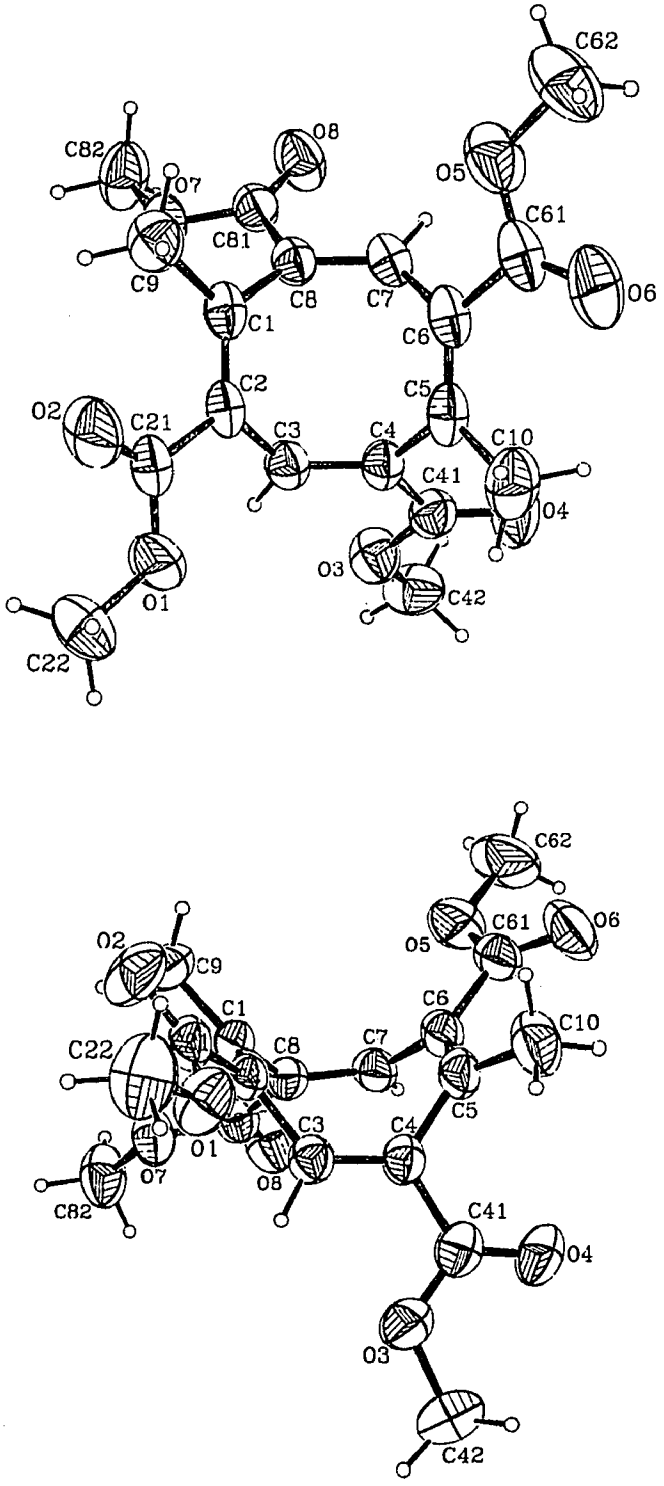


Figure 1–17. *ORTEP* drawings of 1,5-dimethyl-2,4,6,8-tetracarbomethoxycycloocta-tetraene (unprimed) at **295 K** with 50% thermal ellipsoids.

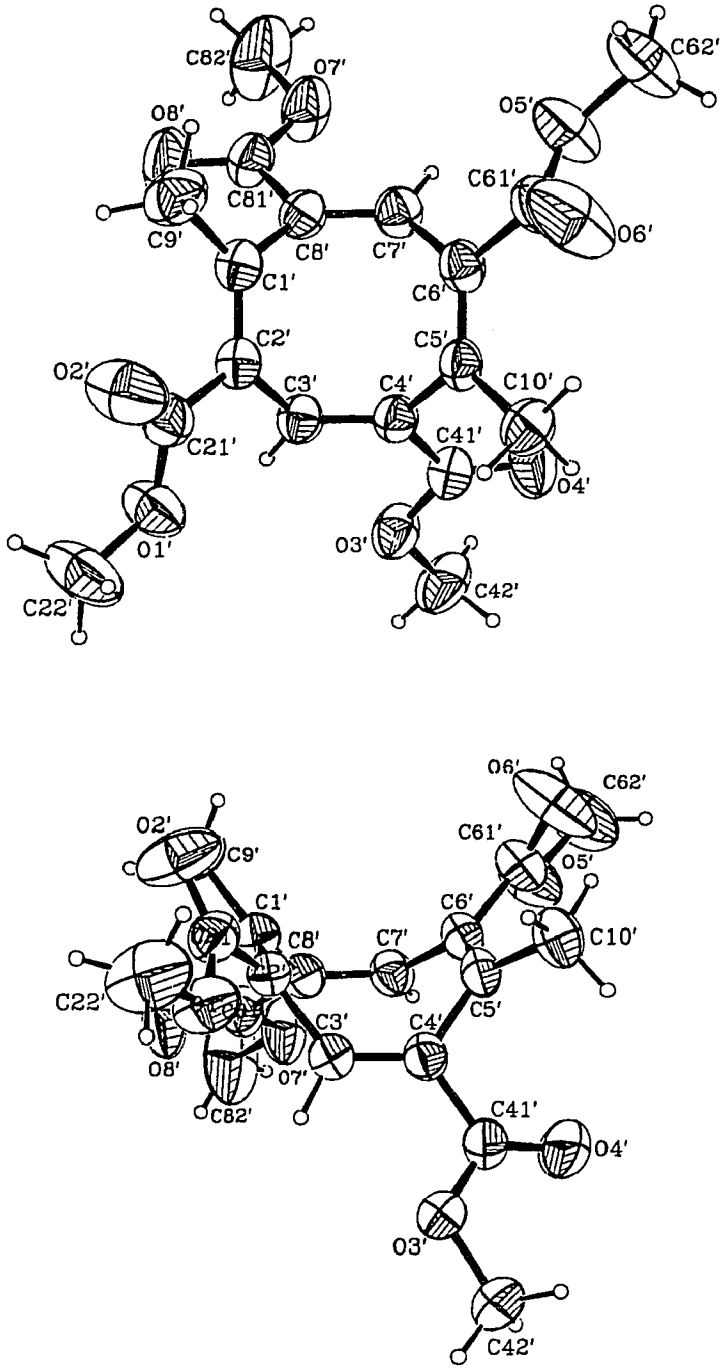
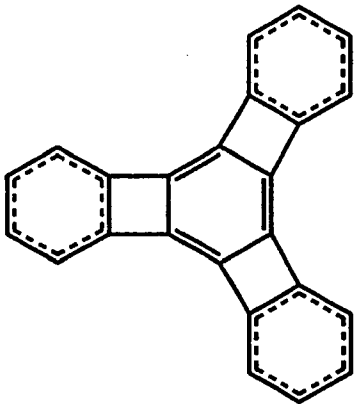


Figure 1–18. *ORTEP* drawings of 1,5-dimethyl-2,4,6,8-tetracarbomethoxycyclooctatetraene (primed) at **295 K** with 50% thermal ellipsoids.

1.4 TRIS(BENZOCYCLOBUTADIENO)BENZENE: THE TRIANGULAR [4]PHENYLENE WITH A COMPLETELY BOND-FIXED CYCLOHEXATRIENE RING

The isolation of the **1,3,5-cyclohexatriene**, the molecule which is supposed to exhibit *alternating* and *maximally localized* double bonds, has been an elusive quest up to now. The dream of trapping cyclohexatriene with its alternating double bonds in a highly localized state has been realized only in **tris(benzocyclobutadieno)benzene**, which was synthesized and characterized by Dierks and Vollhardt:[21]



Tris(benzocyclobutadieno)benzene

^{13}C NMR, ^{13}H NMR, and UV spectra indicate an extraordinary extent of single and double-bonds fixation in the central cyclohexatriene ring and a high degree of delocalization in the outer three benzene rings. A single-crystal X-ray analysis of the **hexa(trimethylsilyl)tris(benzocyclobutadieno)benzene**, shown in Figure 1–19 with bond distances and angles, also has corroborated the m*aximal localization* of single and double bonds in the inner cyclohexatriene ring but *delocalization* in the outer benzene rings.

Table 1–20. X-ray Crystal Data for Hexa(trimethylsilyl)-tris(benzocyclobutadieno)benzene at **160 K**

Formula	$C_{42}H_{60}Si_6 \cdot \frac{5}{2}C_3H_6O$
Formula weight	878.65
Crystal system	monoclinic
Space group	*I*2/*a*
a (Å)	26.597(4)
b (Å)	14.006(1)
c (Å)	29.123(2)
β (°)	112.45(1)°
Volume (Å^3)	10027(4)
Z	8
d_{calc} (g cm^{-3})	1.16
μ(Mo $K\alpha$)	2.0
R	0.044
R_w	0.060

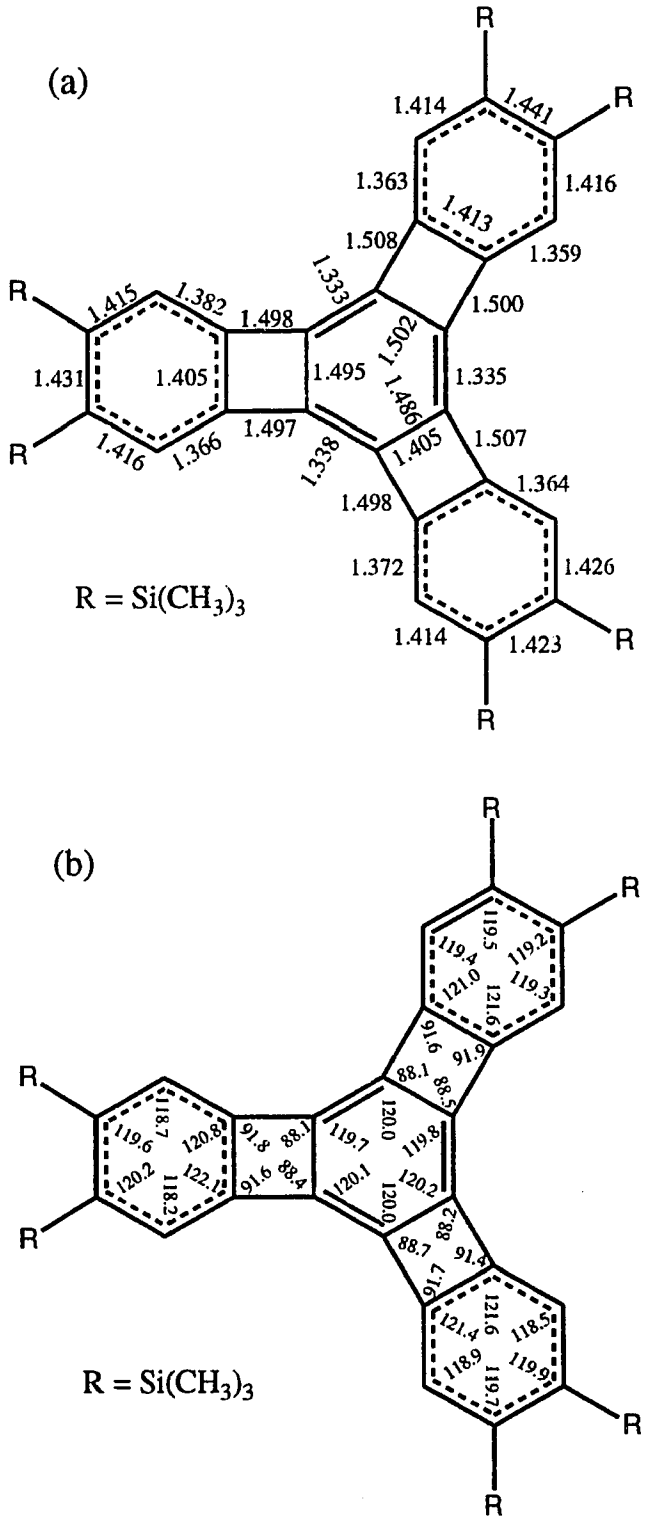
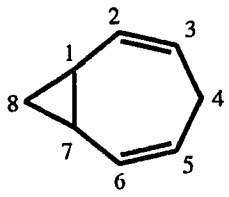


Figure 1–19. Hexa(trimethylsilyl)tris(benzocyclobutadieno)benzene (a) with bond distances (Å) and (b) with bond angles (°).

1.5 AN IDENTITY CRISIS

Even with molecules there are identity crises. They know who and what they are, but often we do not. The actual symmetry of benzene, the most important molecule in organic chemistry is still a toss up between D_{3h} or D_{6h}. Up to now, experiments have not conclusively determined the state of this distinguished molecule. Since cyclohexatriene has never been isolated or detected not even at low temperatures, its interconversion may be termed *hypothetical.* The controversy, then, whether benzene is actually a cyclohexatriene molecule with D_{3h} symmetry or whether it has really D_{6h} symmetry by being the stable intermediate of the degenerate rearrangement of cyclohexatriene still rages on![22]

Other similar rearrangements, however, which strive to that hypothetical state of *benzene-like perfection*, are experimentally verifiable. One such prominent case is the rearrangement of **bicyclo[5.1.0]octa-2,5-diene** to itself, more commonly known as **homotropilidene**,



Bicyclo[5.1.0]octa-2,5-diene
(Homotropilidene)

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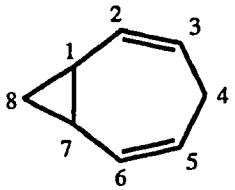
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CHAPTER 2

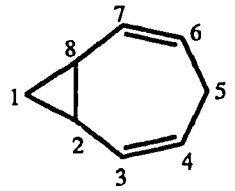
GREAT BEGINNINGS:
The Homotropilidene Story

The compound **bicyclo[5.1.0]octa-2,5-diene**, which is more commonly known as **homotropilidene**, has the following numbering system:



Bicyclo[5.1.0]octa-2,5-diene
(Homotropilidene)

For the purpose of comparing homotropilidene with other compounds of interest, however, we will adopt henceforth a new numbering scheme for this molecule, that is,

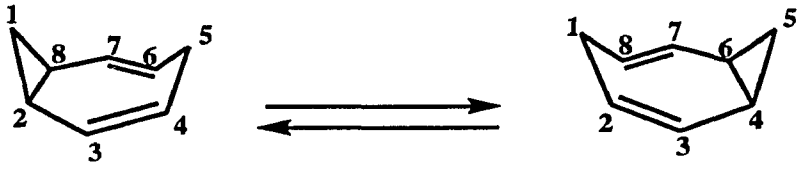


Homotropilidene

2.1 HOMOTROPILIDENE:

The Start Of Something Big

In 1963, W. von E. Doering and W. R. Roth reported that homotropilidene, C_8H_{10}, is surprising stable up to 305 °C without decomposition and undergoes rapid **degenerate Cope rearrangement** at 180 °C as shown in Figure 2–1:[1,2]



Homotropilidene **Homotropilidene**

Figure 2–1. Degenerate rearrangement of homotropilidene.

A **Cope rearrangement**, for Arthur Cope of MIT,[3] involves the breaking of a σ bond (C2—C8), formation of a new σ bond (C4—C6), and migration of π bonds. Again, the rearrangement is called **degenerate** to indicate that the two tautomers are structurally identical. A molecule, which rapidly (faster than 10^3 times per second) changes back and forth from one structure to an entirely equivalent structure is called **fluxional** and is said to exhibit **valence isomerization** or **valence tautomerism.**[4] The positions of the labeled nuclei are not the same in the two tautomeric structures. Interconversion of fluxional molecules must not be confused with conformational changes as, for example, in the interconversion of two equivalent chair forms of cyclohexane. In the formations of fluxional molecules, bonds are broken and made, that is, bonds change positions but the new molecule has the same structure as the original one; in conformational changes, no bonds are broken, no bonds are made.[5]

The existence of degenerate rearrangement can be detected with various spectroscopic and diffraction methods at variable temperatures. Cross-polarization (CP)

magic-angle-spinning (MAS) solid-state ^{13}C-NMR, along with ^{1}H-NMR, IR spectroscopy, and single-crystal X-ray diffraction have proved to be powerful tools in probing the nature of fluxional molecules. *Cross-polarization* and *magic-angle-spinning* are relatively recent advances in solid-state NMR for overcoming line-broadening, long relaxation times, and sensitivity problems associated with the NMR of solids.

The occurrence of a dynamic equilibrium for homotropilidene is evident from the solution ^{1}H NMR spectrum in Figure 2–2.

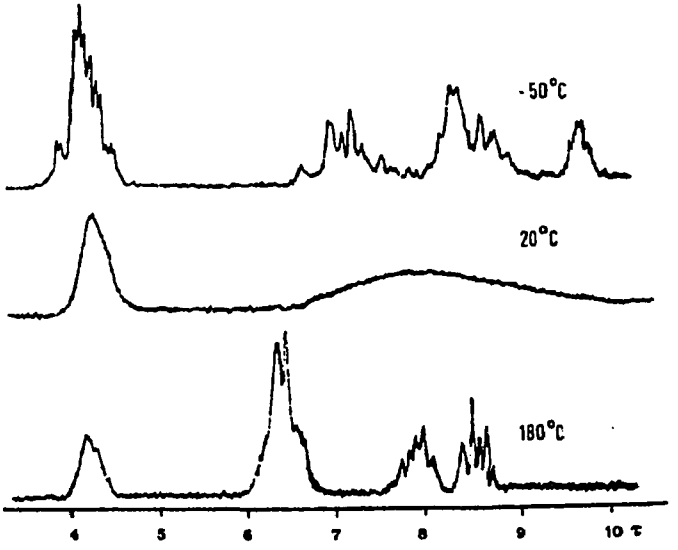
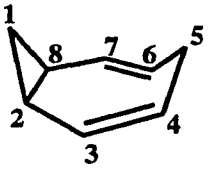


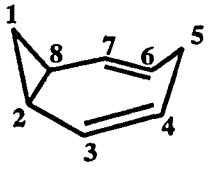
Figure 2–2. ^{1}H NMR spectrum of homotropilidene in carbon tetrachloride solution at –50, 20 and 180 °C with tetramethylsilane at τ=10.0. The τ scale is an old convention used to describe chemical shifts and is defined as $\tau = 10.00 - \delta$.[6]

At low temperature, –50 °C, the rate of equilibrium is slow enough that the rearrangement is frozen on the NMR time scale. The ^{1}H-NMR spectrum is well resolved and is consistent with the presence of four cyclopropyl ring protons (H1A, H1B, H2, H8), four olefinic protons (H3, H4, H6, H7), and two allylic protons (H5A, H5B).

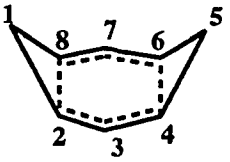


Homotropilidene

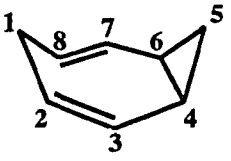
On heating, as room temperature is approached, the peaks of the spectrum become more and more diffuse until finally only the vinyl hydrogens are discernible. When the temperature is raised even more, a new spectrum gradually emerges and finally becomes well characterized at 180 °C. With increasing temperature, two of the cyclopropane ring protons (H2 H8) and two of the olefinic protons (H4, H6) coalesce with respect to their chemical shift while two of the olefinic protons (H3, H7) remain unchanged. Coalescence is also observed between the two of the cyclopropane ring protons (H1A, H1B) and two of the allylic protons (H5A, H5B). This means that the protons whose signals coalesce are undergoing a sufficiently rapid interchange with one another to result in an averaged signal on the NMR time scale.[7]



Homotropilidene



Homotropilidene
(averaged structure)



Homotropilidene

When the sample is cooled back to –50 °C, the low-temperature NMR spectrum reappears without modification.

To clarify the meaning of the phrase "NMR time scale" one should read the interesting article *The NMR Time Scale* by R. G. Bryant.[8]

The infrared spectrum of homotropilidene in Figure 2–3, however, remains unchanged over the same temperature range:

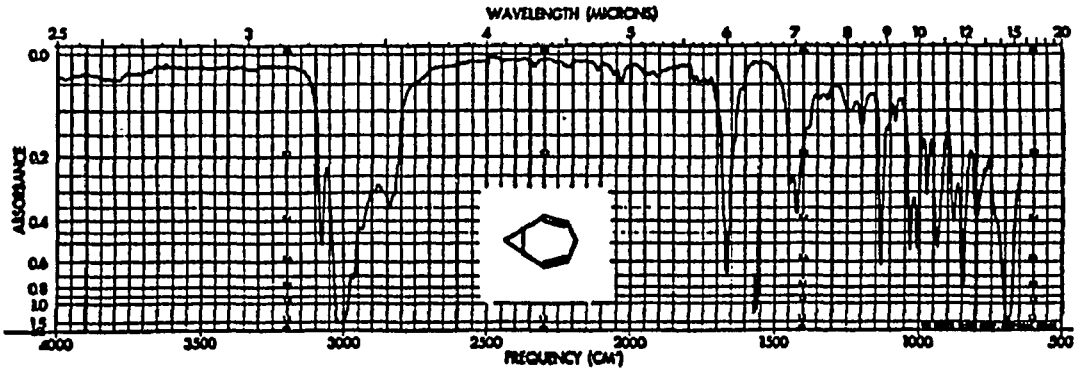


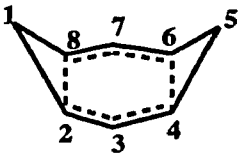
Figure 2–3. IR Spectrum of homotropilidene.

All this is consistent with the Heisenberg uncertainty principle,

$$\Delta E \, \Delta t \geq \tfrac{1}{2}\hbar$$

Since low energies are involved in NMR transitions, a long period of time is necessary for energy measurements. At 180 °C, the homotropilidene molecules are so rapidly interconverting that the NMR spectrum reports average band positions. In IR spectroscopy, the higher-energy transitions require less time for measurements, according with the uncertainty principle Even though the interconversion of homotropilidene at 180 °C is faster than at –50 °C, the rearrangement is nevertheless still slow on the IR time scale and the IR spectrum remains unchanged.

Since the temperature dependence of the NMR spectra may be consistently explained in terms of a Cope rearrangement, it is not unreasonable, then, to propose for the interconversion of homotropilidene to itself a state which is intermediate (transition state) between the two fluxional structures, that is,



Intermediate state or transition state of homotropilidene rearrangement

This symmetrical intermediate has a benzene-like structure and is thus referred to as **homobenzene** (Greek *homo-*, same, equal, like). To be more specific, since its π system is interrupted by two methylenes, the term **bishomobenzene** (Latin *bis-* two, twice, double) is preferred. Such compounds are also called **homoaromatic** and, in general, may be defined as compounds whose conjugated cyclic backbone contains one or more sp^3-hybridized carbon atoms. Saul Winstein introduced the concept of homoaromaticity in 1967.[9,10] The activation energy for the rearrangement of homotropilidene is 13.6 kcal/mole at –35° C. The same rearrangement may be shown again in Figure 2–4 to illustrate more clearly the conformations of homotropilidene and its transition state:

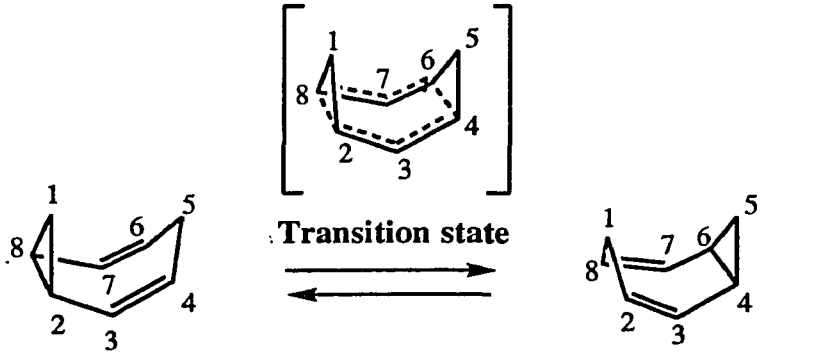
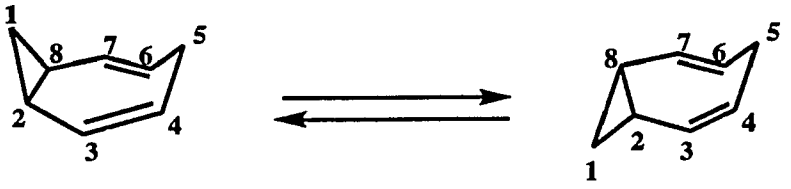


Figure 2–4. Degenerate rearrangement of homotropilidene.

2.2 MOLECULE IMPROVEMENT

Doering and Roth suggested that homotropilidene should have two conformations, one **chair-like** and the other **boat-like.**



Homotropilidene
(boat conformation)

Homotropilidene
(chair conformation)

Force field calculations have shown that the energy of the "boat" conformation is about 4 ± 2 kcal mole^{-1} higher in energy than the "chair" conformation as illustrated in Figure 2–5.[11]

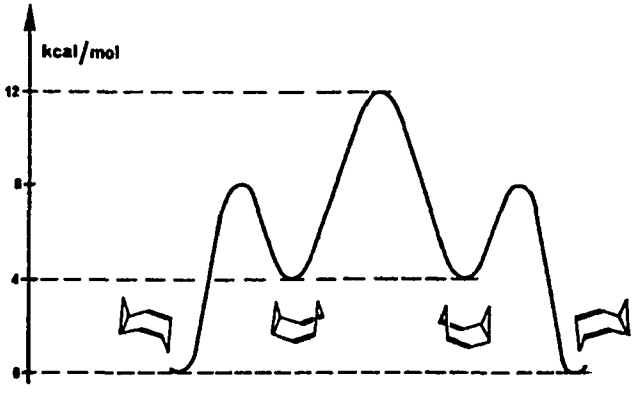
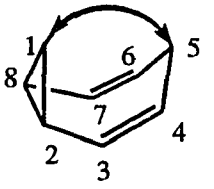


Figure 2–5. Energy profile of valence isomerization of homotropilidenes.

Doering and Roth pointed out that the **chair conformation**, being more stable, would not undergo rearrangement as readily as the **boat conformation**. By being less stable, the **boat conformation** then would be better suited for the **valency change**; and so, to preclude the unfavorable chair conformation, they predicted that the introduction of a C1—C5 *bridge* not only would preserve the favorable *boat-like conformation* of the

homotropilidene structure but also would introduce more *strain* in the molecule. The added strain destabilizes a tautomer by increasing the energy of the ground state. The bridge between C1 and C5, like a two-edged sword, would thus promote a more mobile tautomeric system by reducing the activation energy for the Cope rearrangement:



Bridged homotropilidene

This prediction of lowering the activation energy has been verified in many bridged analogs of homotropilidene, such as, **bullvalene, barbaralane, semibullvalene,** etc....

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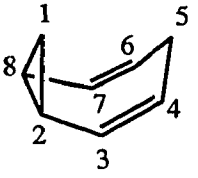
[11] H. Kessler, W. Ott, *J. Am. Chem. Soc.*, **98**, 5014 (1976).

CHAPTER 3

ALL THAT BULL AND MORE ...

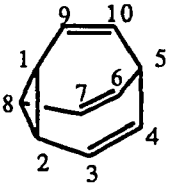
3.1 BULLVALENE

If in a homotropilidene molecule,



Homotropilidene

C1 and C5 are bridged with two double-bonded carbons, CH=CH, we obtain the structure **tricyclo[3.3.2.0^{4,6}]deca-3,6,9-triene** also called **bullvalene** ($C_{10}H_{10}$, m. p. 92 °C[1]).



Tricyclo[3.3.2.0^{4,6}]deca-3,6,9-triene
(Bullvalene)

Bullvalene decomposes to naphthalene above 400 °C.

The name **bullvalene** was coined in honor of W. von E. Doering, who was affectionately known at Yale as "The Bull." In 1963, W. von E. Doering and W. R. Roth proposed that bullvalene would be expected to undergo rapid degenerate Cope

rearrangement as in Figure 3–1 even faster than homotropilidene, since the freedom to change to the thermodynamically favored but kinetically prohibitive trans conformation would be permanently removed with the introduction of the CH=CH bridge between C1 and C5:[2,3]

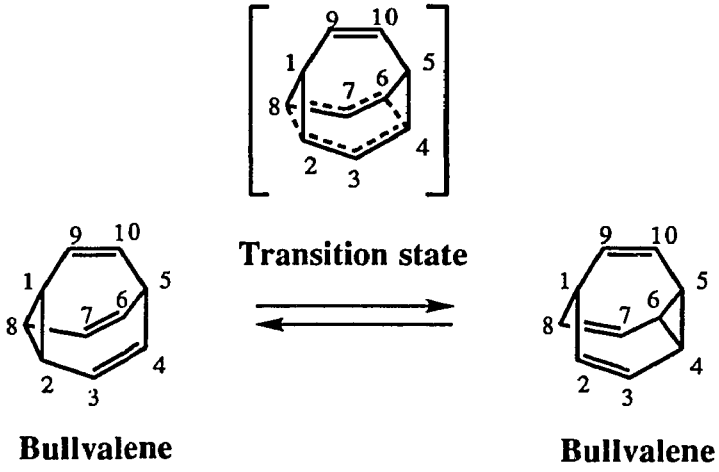


Figure 3–1. Degenerate Cope rearrangement of bullvalene

Due to the inherent symmetry of a bullvalene molecule, they suggested that any of the three cyclopropane bonds could be involved in the Cope rearrangement. The position of the cyclopropane ring of a Cope rearrangement shown above changes position from 1,2,8 to 4,5,6. This ring can also be at 1,2,9 or 4,5,10, or, etc., that is, the cyclopropane ring can be at any three adjacent carbon atoms. The total number of isomers from this dynamic process is 10!/3 (1209600), which is one third the permutations of 10 carbons. The factor 1/3 is needed because a bullvalene molecule has a three-fold rotation axis, making 2/3 of the isomers indistinguishable. They predicted furthermore that the ^{1}H NMR spectrum of bullvalene would consist of just one single sharp band. Later in the same year, Schröder synthesized bullvalene and confirmed that it undergoes rapid degenerate Cope rearrangement at temperatures above 100 °C as shown in the ^{1}H-NMR spectra in Figure 3–2.[4,5,6]

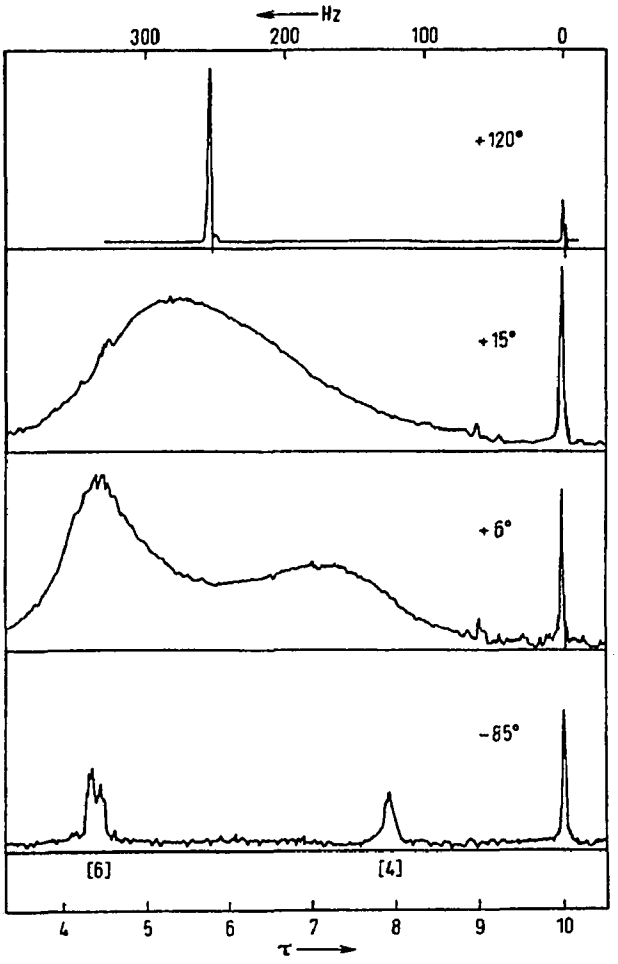


Figure 3–2. 60 MHz ^{1}H NMR spectra of bullvalene at four temperatures in CS_2. The scale of these spectra is expressed in terms of τ (tau) values. The τ scale is an old convention used to describe chemical shifts and is defined as $\tau = 10.00 - \delta$.[7]

The ^{1}H-NMR spectrum at 120 °C of bullvalene consists of a single sharp peak at 5.78 τ indicating Cope rearrangement at work. On cooling to –25 ° C, this peak broadens and divides into two bands with an area ratio of 6:4, corresponding to six vinyl protons and four allylic protons. This is consistent with a single nontautomeric structure at –25 °C. Further cooling to –85 °C does not alter the spectrum. At –85 °C, the spectrum consists of separate signals for six vinylic protons at 4.35 τ and three cyclopropane and methine protons at 7.92 τ. It is important to note that the chemical shift of the averaged spectrum at 120 °C, 5.78 τ, is equal to the arithmetic average (5.78 τ) obtained from the bands at –85 °C, that is,

$$\frac{(6\times 4.35)+(4\times 7.92)}{10} = 5.78\,\tau^{5}$$

Other NMR spectra[8] of bullvalene confirm the same dynamic properties of this molecule:

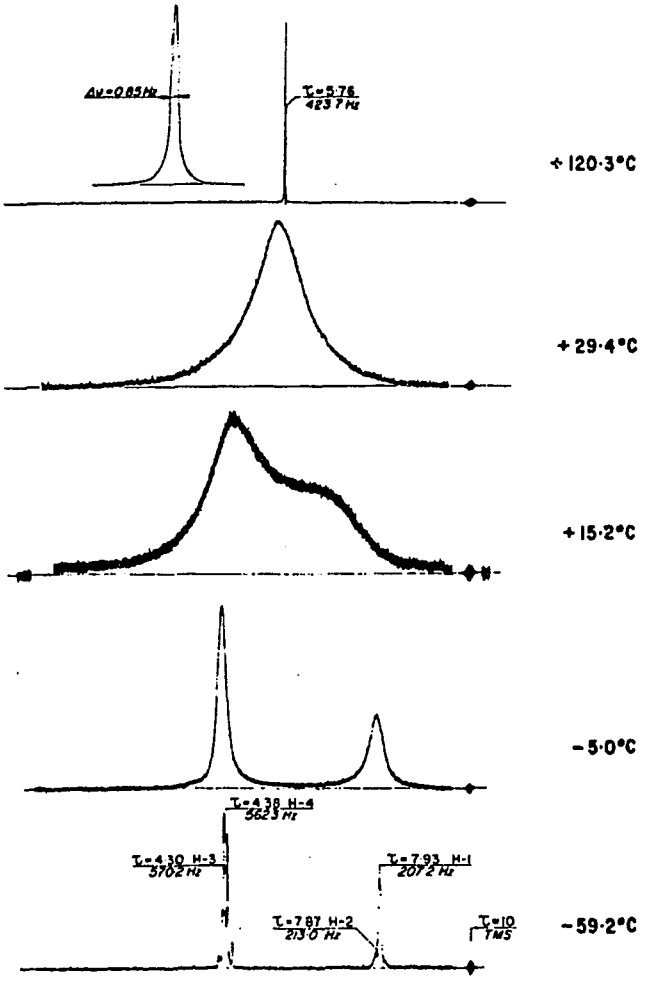


Figure 3–3. 100 MHz ^{1}H-NMR spectra of bullvalene in CS_2 at five temperatures (TMS as internal reference)

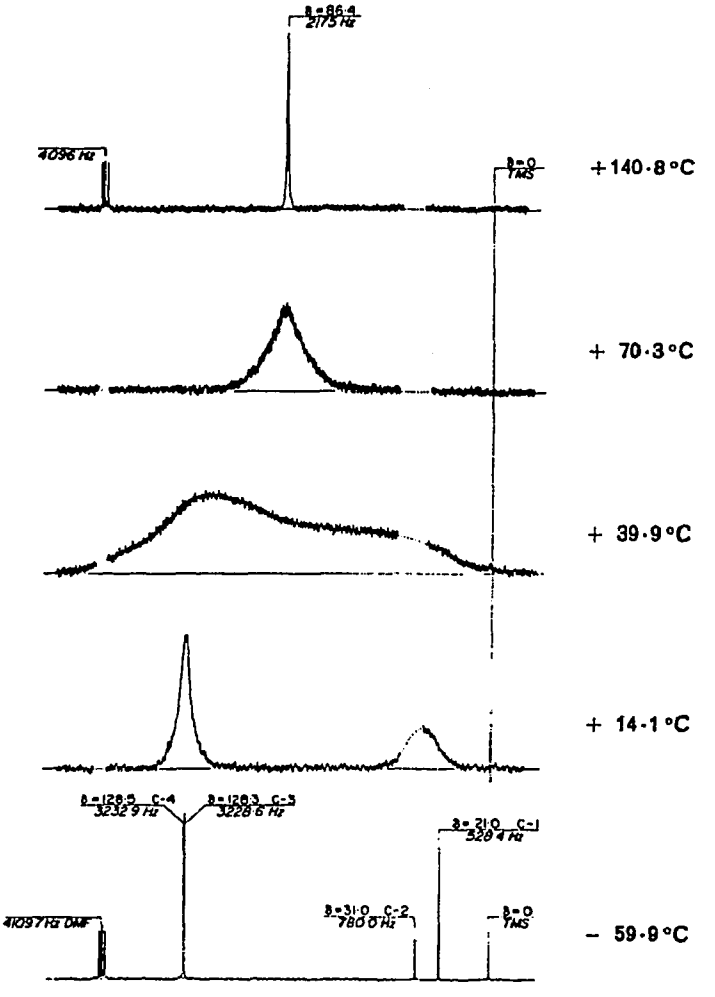


Figure 3–4. 25 MHz ^{13}C-NMR spectra of bullvalene at five temperatures in DMF-d_7 (FT mode, ^{1}H noise-decoupled. The signals of TMS or the carbonyl C of the solvent were uses as internal reference.). For clarity the methyl signals of the solvent are not represented.

Activation parameters for bullvalene in solution are listed in Table 3–1.

Table 3–1. Activation Parameters for Bullvalene from NMR[8]

Nucleus observed	E_a kcal mole^{-1}	A 10^{13}	k (0 °C) s^{-1}	$\Delta H^{\ddagger}$ kcal mole^{-1}	$\Delta S^{\ddagger}$ e.u.	$\Delta G^{\ddagger}$(0° C) kcal mole^{-1}
^{1}H (100 MHz)	13.10(8)	1.96(25)	649(15)	12.56(8)	0.48(25)	12.43(1)
^{13}C (25 MHz)	13.13(5)	2.31(15)	727(14)	12.58(5)	0.80(13)	12.36(1)
^{13}C+^{1}H	13.18(7)	2.37(7)	671(17)	12.64(7)	0.85(21)	12.41(1)

From Table 3–1, we see that $\Delta G^{\ddagger}$ is 12.4 kcal/mole at 0 °C. At other temperatures, the $\Delta G^{\ddagger}$for the interconversion of **bullvalene** has been determined by line-shape analysis to be 12.6 kcal/mole at 25 °C, and 12.8 kcal/mole at 100 °C.[9,10] These numbers, which are lower than the activation energy of homotropilidene (13.6 kcal/mole), provide support to the statement that the activation energies are weakly dependent on temperature.

The IR spectrum of bullvalene, shown in Figure 3–5, remains unchanged as the temperature is varied.

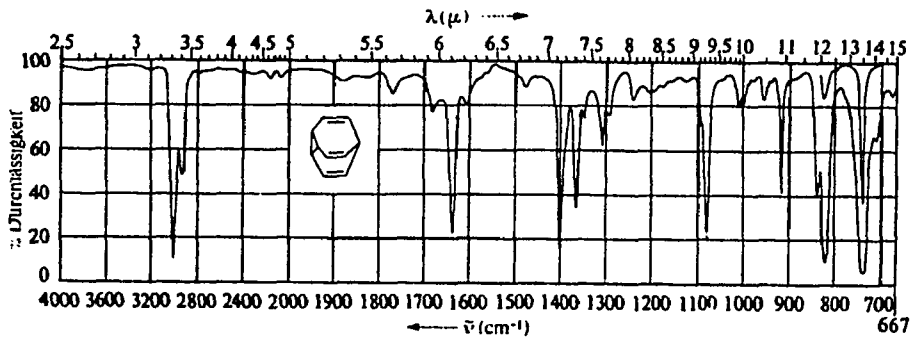


Figure 3–5. IR spectrum of bullvalene[5]

In the solid state, Meir and Earl pointed out that bullvalene still undergoes the Cope rearrangement as indicated by CP-MAS ^{13}C powder spectra at various temperatures in Figure 3–6.[11]

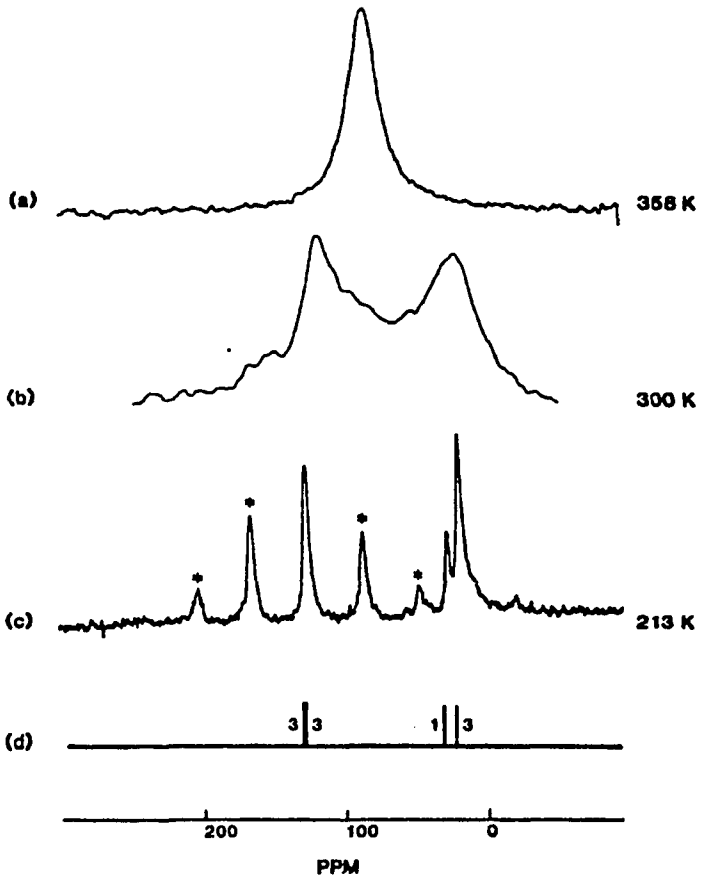


Figure 3–6. CP-MAS ^{13}C spectra of bullvalene powder at (a) 358 K, (b) 300 K, and (c) 213 K. The low-temperature spectrum (c) consists of three lines. the low-field one showing a sideband pattern. Spinning sidebands are marked with asterisks. The chemical shifts, observed in the low-temperature spectrum are very similar to those found for the dissolved molecule. Trace (d) of the figure shows the line positions for bullvalene in isotropic solution. The high temperature spectrum (a) consists of a single line at a resonance position equal to the weighted average of the low-temperature lines, indicating a fast Cope rearrangement (relative to the difference in chemical shifts taking place. Spectrum (b) shows an exchange-broadened spectrum.

According to their line-shape analysis, the Arrhenius activation energy, E_a, of bullvalene in the solid state is 14.3 kcal/mole. This value is very close to 13.1 kcal of the liquid phase in Table 3–1. The higher activation in the solid state may be an indication that crystal-packing forces of the solid phase, as one might suspect, may hinder the Cope rearrangement. Later in this chapter, we will encounter a replay of this dampening effect of the solid state on the Cope rearrangement in semibullvalene.

Single-crystal diffraction analyses of bullvalene seem to paint a totally different picture of its fluxional behavior in the solid state. Luger with the single-crystal neutron-diffraction analysis at 110 K[12] and Hoppe with a single-crystal X-ray diffraction analysis at 293 K[13] have claimed that **bullvalene** is highly ordered in the crystalline state and in contrast to its behavior in solution, this molecule exhibits no valence isomerization in the solid state. Another single-crystal X-ray analysis[14] of lesser quality also reported similar conclusions on the nonexistence of valence tautomerism by crystalline bullvalene. The following tables provide the diffraction data.

Table 3–2. Diffraction Data for Bullvalene at Two Temperatures from Neutron and X-ray Diffraction

	Neutron diffraction	X-ray diffraction
	110 K	**293 K**
Formula	$C_{10}H_{10}$	$C_{10}H_{10}$
Formula weight	130.19	130.19
Melting point (°C)	92[a]	92
Crystal system	monoclinic	monoclinic
Space group	$B2_1/c$[b]	$P2_1/c$
a (Å)	6.466(2)	6.207
b (Å)	20.559(4)	20.785
c (Å)	10.360(2)	10.518
β (°)	90.19(2)	148.57
V(Å^3)	1377.19	707.59
Z	8	4
d_x (g cm^{-3})	—	1.19
d_{calc} (g cm^{-3})	1.256	1.222
wavelength (Å)	1.0504	0.71073 (Mo $K\alpha$)
μ	2.417	0.6
R	0.066	0.098
R_w	0.065	—

[a] Under normal conditions, crystals of bullvalene sublime rapidly.

[b] The neutron analysis was carried out by using a transformed B-centered unit cell to avoid the obtuse β angle (a_p = 6.097, b_p = 20.559, c_p = 10.360 Å, β_p = 147.98°). The transformation from primitive cell (space group $P2_1/c$) is $\bar{a}_B \quad 2\,0\,1\,\bar{a}_P$, $\bar{b}_B \quad 0\,\bar{1}\,0\,\bar{b}_P$, $\bar{c}_B \quad 0\,0\,\bar{1}\,\bar{c}_P$.

Table 3–3. Atomic Coordinates for Bullvalene at **110 K** from Neutron diffraction and at **293 K** from X-ray Diffraction

Temperature	Atom	*x/a*	*y/b*	*z/c*
110 K (neutron)	C1	0.19683	-0.15708	-0.37155
	C2	0.02934	-0.19443	-0.44596
	C3	-0.13499	-0.16109	-0.51929
	C4	-0.23288	-0.10626	-0.48485
	C5	-0.18536	-0.06886	-0.36214
	C6	-0.22520	-0.10998	-0.24329
	C7	-0.12480	-0.16573	-0.21768
	C8	0.03377	-0.19679	-0.29837
	C9	0.20130	-0.08547	-0.36609
	C10	0.03733	-0.04557	-0.36154
	H1	0.34880	-0.17960	-0.37470
	H2	0.08510	-0.23900	-0.49040
	H3	-0.17720	-0.18360	-0.61080
	H4	-0.35180	-0.08700	-0.54900
	H5	-0.28640	-0.02610	-0.35910
	H6	-0.33850	-0.09280	-0.17320
	H7	-0.16060	-0.19070	-0.12810
	H8	0.09210	-0.24290	-0.26070
	H9	0.35440	-0.06350	-0.36520
	H10	0.06400	0.00650	-0.35740
293 K (X-ray)	C1	0.06860	-0.19383	-0.40894
	C2	0.06706	-0.19594	-0.26454
	C3	-0.24200	-0.16480	-0.34292
	C4	-0.43539	-0.11043	-0.46564
	C5	-0.36342	-0.07085	-0.54707
	C6	0.07612	-0.04732	-0.32448
	C7	0.39979	-0.08575	-0.16519
	C8	0.39565	-0.15569	-0.17300
	C9	-0.44280	-0.10839	-0.70730
	C10	-0.25250	-0.16175	-0.64286
	H1	0.16351	-0.23603	-0.40930
	H2	0.18480	-0.23855	-0.16225
	H3	-0.31437	-0.19101	-0.29465
	H4	-0.64297	-0.09108	-0.49778
	H5	-0.56074	-0.02573	-0.64330
	H6	0.14830	0.00402	-0.27990
	H7	0.66463	-0.06182	-0.02756
	H8	0.63299	-0.18295	-0.04943
	H9	-0.66262	-0.08367	-0.89652
	H10	-0.30651	-0.18712	-0.75652

Table 3–4. Isotropic Thermal Parameters-*B's* ($Å^2$) for Bullvalene at **110 K** from Neutron Diffraction and at **293 K** from X-ray Diffraction

	Neutron	X-ray
Atom	**110 K**	**293 K**
C1	1.25	4.33
C2	1.24	4.27
C3	1.26	3.96
C4	1.26	4.37
C5	1.18	3.99
C6	1.22	4.41
C7	1.20	4.28
C8	1.21	4.61
C9	1.22	4.18
C10	1.18	4.34
H1	2.76	
H2	2.61	
H3	3.00	
H4	3.00	
H5	2.53	
H6	2.92	
H7	2.84	
H8	2.61	
H9	2.92	
H10	2.84	

Table 3–5. Anisotropic Thermal Parameters for Bullvalene (U) at **110 K** from Neutron Diffraction and (β_{ij}) at **293 K** from X-ray Diffraction

	Atom	U
110 K	C1	0.0158
(neutron)	C2	0.0157
	C3	0.0159
	C4	0.0159
	C5	0.0150
	C6	0.0154
	C7	0.0152
	C8	0.0153
	C9	0.0154
	C10	0.0149
	H1	0.035
	H2	0.033
	H3	0.038
	H4	0.038
	H5	0.032
	H6	0.037
	H7	0.036
	H8	0.033
	H9	0.037
	H10	0.036

		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
293 K	C1	0.10930	0.00219	0.04526	0.00020	0.03111	-0.00032
(X-ray)	C2	0.10655	0.00220	0.03270	0.00052	0.02461	0.00050
	C3	0.10198	0.00268	0.03350	-0.00192	0.02620	-0.00078
	C4	0.08900	0.00313	0.03857	-0.00099	0.02597	-0.00103
	C5	0.07785	0.00194	0.03217	0.00036	0.01983	0.00015
	C6	0.11041	0.00201	0.03788	-0.00177	0.02700	-0.00100
	C7	0.07391	0.00318	0.02790	-0.00273	0.01842	-0.00143
	C8	0.07307	0.00326	0.02987	0.00176	0.01830	0.00069
	C9	0.11284	0.00277	0.03497	-0.00285	0.02825	-0.00169
	C10	0.08357	0.00310	0.02373	-0.00181	0.01769	-0.00019

The bond distances in Table 3–6 indicate almost normal single and double C—C bonds in the bullvalene molecule. The double bonds in bullvalene are somewhat longer than the value of an isolated C—C double bond (1.33 Å); while some single bonds are shorter than a normal C—C bond.

Table 3–6. Interatomic Distances (Å) in Bullvalene at **110 K** from Neutron Diffraction and at **293 K** from X-ray Diffraction

	110 K	**293 K**
C1—C2	1.533	1.528
C1—C8	1.536	1.527
C1—C9	1.474	1.457
C2—C3	1.473	1.444
C2—C8	1.530	1.563
C3—C4	1.342	1.322
C4—C5	1.516	1.504
C4—C6	2.504	2.441
C4—C10	2.480	2.503
C5—C6	1.516	1.513
C5—C10	1.517	1.509
C6—C7	1.343	1.323
C6—C10	2.480	2.463
C7—C8	1.471	1.455
C9—C10	1.341	1.312

Table 3–7. Bond Angles (°) in Bullvalene at **110 K** from Neutron diffraction and at **293 K** from X-ray diffraction

	110 K	**293 K**
C2—C1—C8	59.80	61.56
C2—C1—C9	122.23	122.34
C8—C1—C9	121.71	121.48
C1—C2—C8	60.17	59.20
C1—C2—C3	122.22	123.29
C3—C2—C8	122.76	120.96
C2—C3—C4	126.43	126.98
C3—C4—C5	123.68	124.12
C4—C5—C6	111.32	108.30
C4—C5—C10	110.68	112.35
C6—C5—C10	109.66	109.86
C5—C6—C7	123.56	123.96
C6—C7—C8	126.55	126.64
C1—C8—C2	60.02	59.24
C1—C8—C7	122.06	123.06
C7—C2—C8	122.92	121.37
C1—C9—C10	126.65	126.53
C5—C10—C9	123.85	124.43

Table 3–8. Root-Mean-Square Amplitudes (Å) of Thermal Vibrations for Bullvalene at **293 K** from X-ray Diffraction

	Atom	**Min.**	**Int'med.**	**Max.**
293 K	C1	0.208	0.224	0.265
	C2	0.206	0.234	0.254
	C3	0.187	0.212	0.264
	C4	0.189	0.226	0.280
	C5	0.198	0.211	0.259
	C6	0.192	0.253	0.258
	C7	0.174	0.231	0.280
	C8	0.187	0.252	0.277
	C9	0.185	0.209	0.283
	C10	0.190	0.209	0.291

From the drawings of bullvalene in Figures 3–7 to 9 we see that the vibrations of the carbon atoms are in the direction of the bonds.

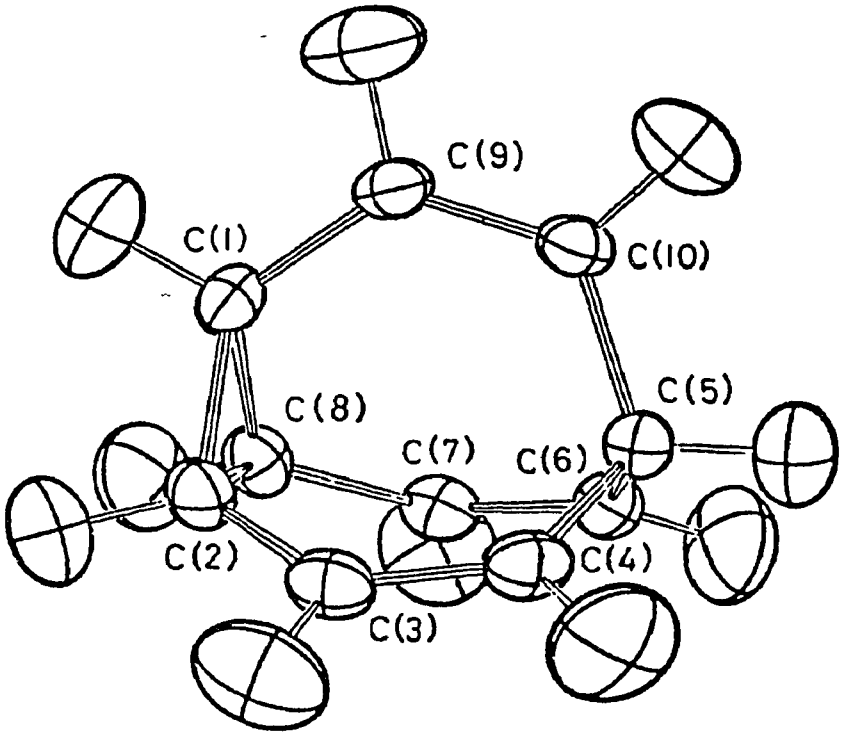


Figure 3–7. Bullvalene at **110 K** from neutron diffraction with 75% thermal ellipsoids.

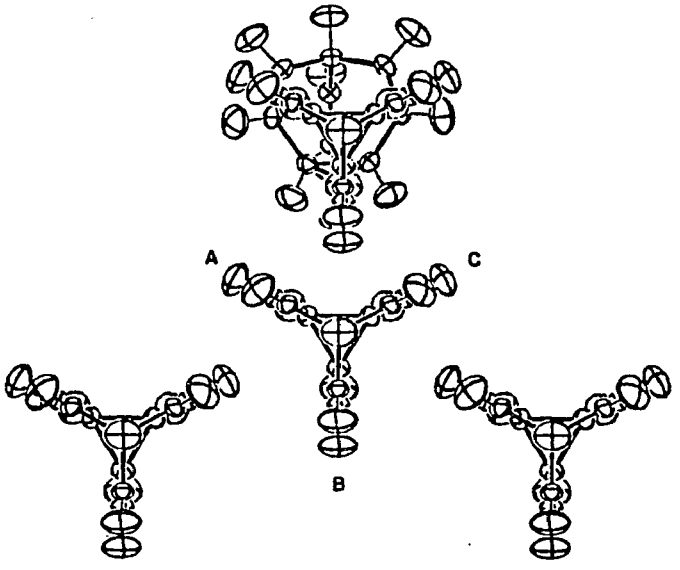


Figure 3–8. Bullvalene at **110 K** from neutron diffraction, illustrating the local environment of a bullvalene molecule viewed down the molecular three-fold axis.

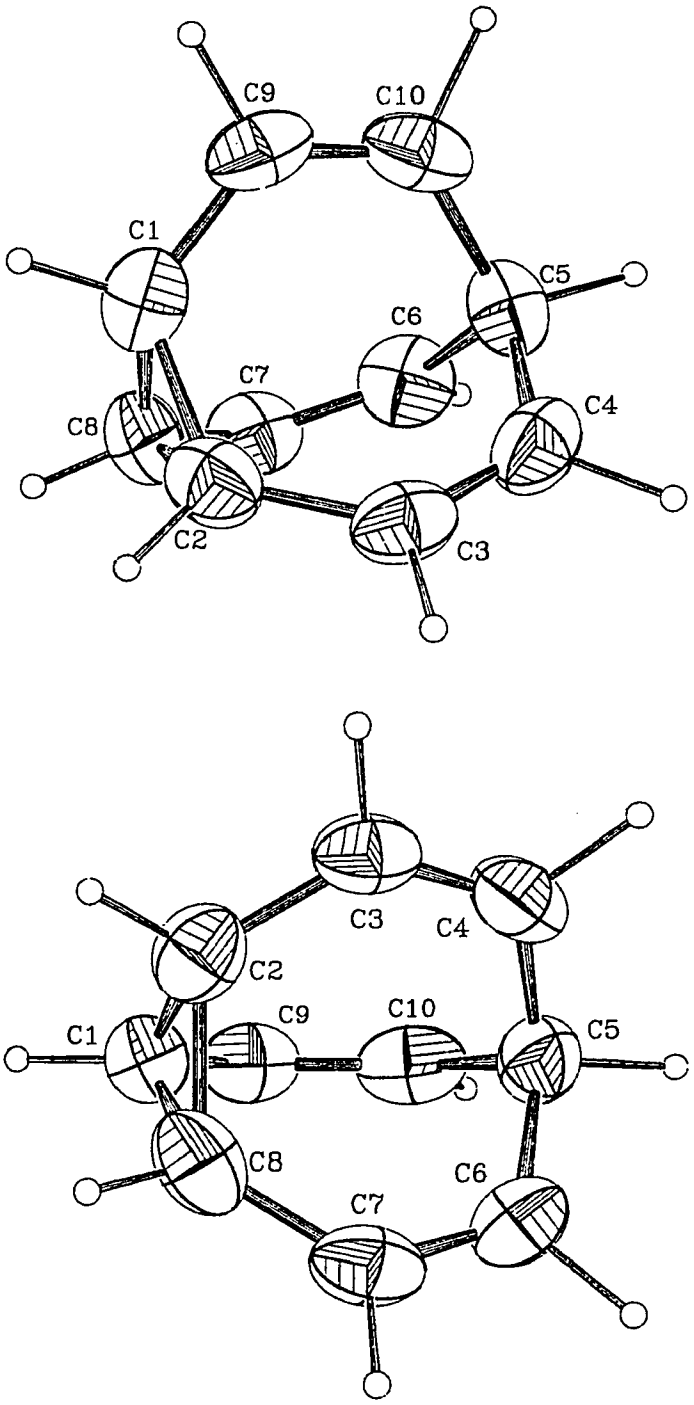


Figure 3–9. *ORTEP* drawings of bullvalene at **293 K** from X-ray diffraction.

A electron diffraction investigation of bullvalene[15] in the vapor phase has also confirmed the neutron and X-ray distances in this molecule.

With a deuterium NMR of single crystals of deuterated bullvalene in the temperature range from –13 to +80 °C, a recent paper[16] has rekindled the debate whether the Cope rearrangement is operational within a bullvalene molecule. According to the authors of this paper, the Cope rearrangement for bullvalene is, indeed, taking place in the solid state, after all! The next three figures are from this source.

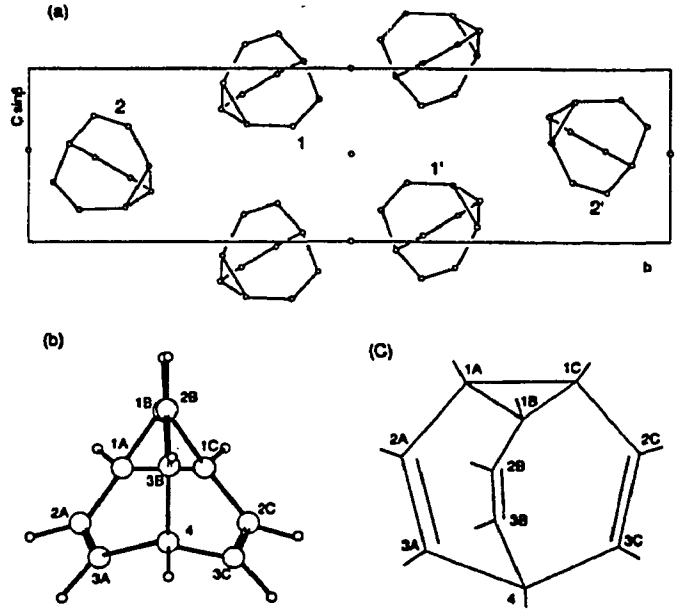


Figure 3–10. Projection of the crystal structure of bullvalene onto the crystallographic *bc*-plane of the monoclinic unit cell. (b) Projection of a single bullvalene molecule down the crystallographic *b*-axis on the *ac*-plane. (c) A line drawing of a bullvalene molecule showing the numbering system used in the single-crystal NMR.

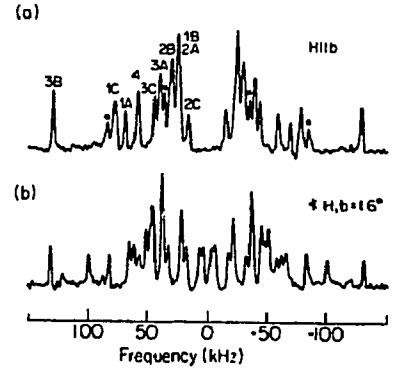


Figure 3–11. Deuterium NMR spectra at –13 °C of a single crystal of deuterated bullvalene. Trace (a) was taken with the *b*-axis parallel to the magnetic field, while the trace (b) was recorded after rotating the crystal by 1.6° about an axis perpendicular to the field direction. In trace (a) the peak assignments are in terms of the numbering system in Figure 3–10. The asterisk indicate unidentified peaks.

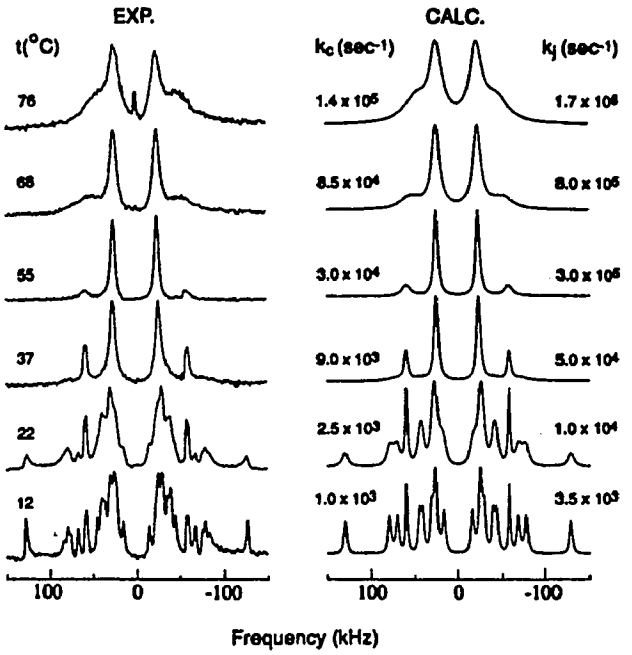
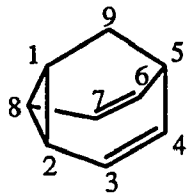


Figure 3–12. *Left*: Experimental deuterium NMR spectra from single crystals of deuterated bullvalene aligned with the *b*-axis parallel to the magnetic field at different temperatures. *Right*: Best-fit simulated spectra of the corresponding experimental set.

3.2 BARBARALANE

A more drastic reduction in activation energy may be achieved by replacing the CH=CH moiety in bullvalene with CH_2 to form **tricyclo[3.3.1.0^{2,8}]nona-3,6-diene** or **barbaralane**[17,18] (C_9H_{10}, m. p. 46 °C[19]). The name "barbaralane" was perhaps in honor of that special dream girl who provided the incentive and inspiration to make the research all worthwhile.



Tricyclo[3.3.1.0^{2,8}]nona-3,6-diene
(Barbaralane)

In solution, barbaralane undergoes the Cope rearrangement shown in Figure 3–13.

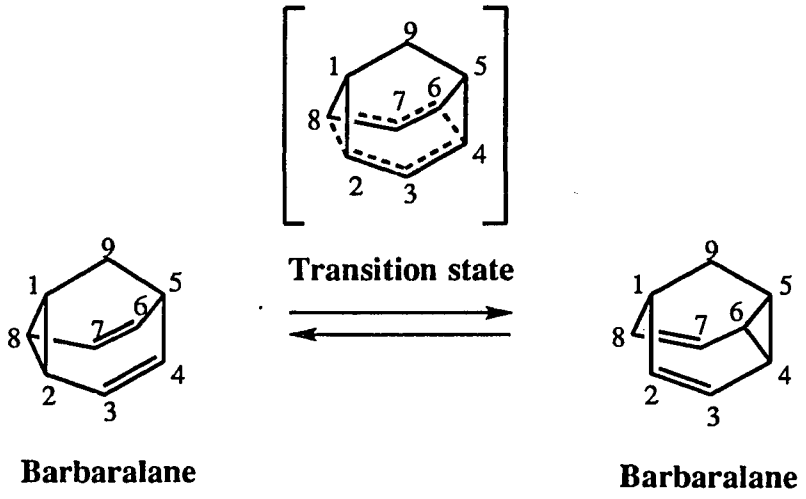


Figure 3–13. Degenerate Cope rearrangement of barbaralane.

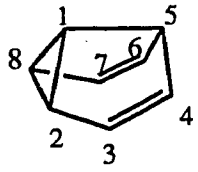
The energy of activation for the rearrangement of **barbaralane** is 7.6 kcal/mole at 25 °C and 7.8 kcal/mole at –77 °C.[20,10] The lower activation energy as compared to bullvalene has been attributed to an increase in the ground-state energy due to strain. At –100 °C, the interconversion has slowed to the point where the NMR spectrum is in accord with a single structure, that is, the rearrangement has been practically frozen out on the NMR time scale.

Henkel and Hane have reported, in their own words, "an efficient synthesis of barbaralane."[21]

3.3 SEMIBULLVALENE

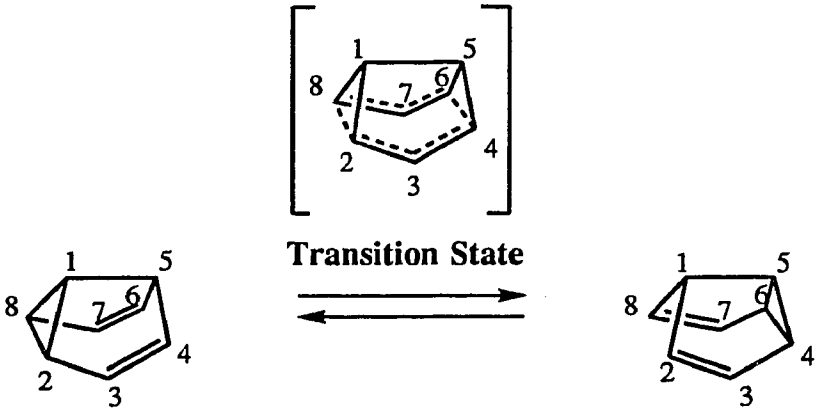
By removing the CH_2 from the **barbaralane** and forming a bond directly between C1 and C5, more strain is introduced in the new molecule **tricyclo[3.3.0.0^{2,8}]octa-3,6-diene** or with trivial name **semibullvalene** (C_8H_8,

approximate m. p. –85 °C). Semibullvalene was synthesized by Zimmermann and Grunewald in 1966.[22]



Tricyclo[3.3.0.0^{2,8}]octa-3,6-diene
(Semibullvalene)

The increase in strain in **semibullvalene** raises the energy of the ground state and thus produces a further reduction in the activation energy barrier for the Cope rearrangement in Figure 3–14.



Semibullvalene **Semibullvalene**

Figure 3–14. Degenerate Cope rearrangement of semibullvalene.

The proton spectra[5] in Figure 3–15 at high temperature indicate the dynamic properties of semibullvalene. At –167 °C, the peaks indicates the static structure of semibullvalene in solution.

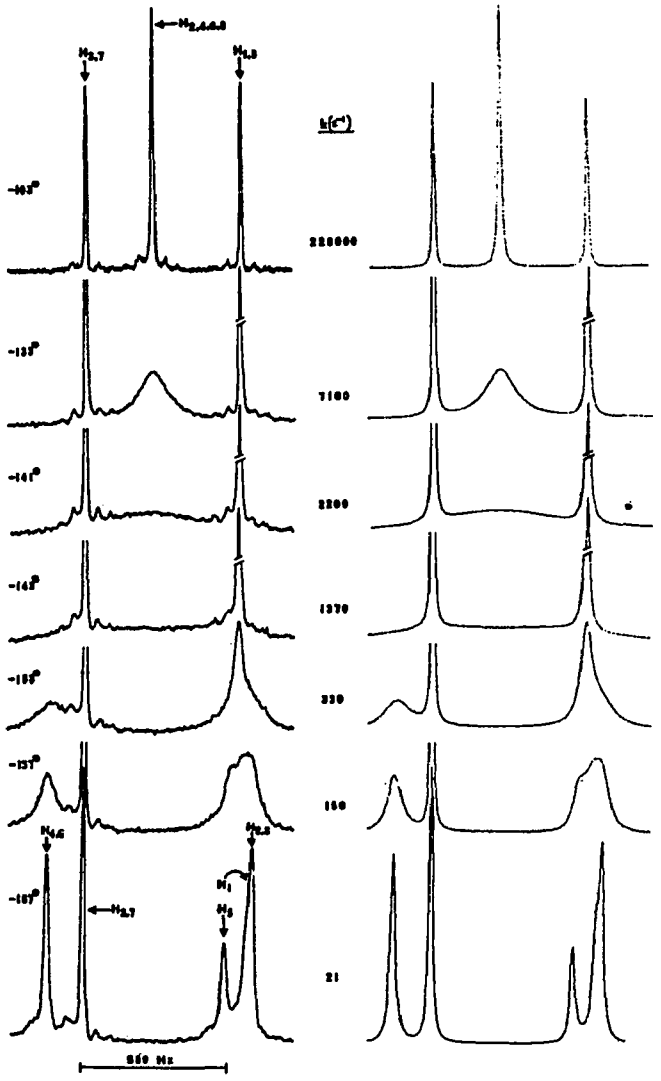


Figure 3–15. *Left*: 251 MHz ^{1}H-NMR spectra of semibullvalene in CCl_2F_2 at various temperatures. *Right*: calculated line shapes for various values of the rate constant for the degenerate Cope rearrangement in semibullvalene.

The Arrhenius activation energy E_a, obtained by a least-squares treatment of the data in Table 3-9 is 5.1(2) kcal/mole.

Table 3–9. Rate Data for the Cope Rearrangement in Semibullvalene

Temperature (°C)	**Rate constants** (sec^{-1})
-103	ca. 200,000
-133	7100
-141	2200
-143	1370
-153	330
-157	150
-167	ca. 20

The free energy of activation, $\Delta G^{\ddagger}$, is 5.5 ± 0.1 kcal/mole at –143 °C, while, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 4.8 ± 0.2 kcal/mole and –5.4 ± 3 eu, respectively. The free energy of activation, $\Delta G^{\ddagger}$, can be determined quite accurately from NMR data. The enthalpy of activation, $\Delta H^{\ddagger}$, and the entropy of activation, $\Delta S^{\ddagger}$, however, are obtained from the temperature dependence of $\Delta G^{\ddagger}$ and are frequently afflicted with large systematic errors.[5] Semibullvalene has a lower free energy of activation ($\Delta G^{\ddagger}$ = 5.5 kcal/mole at –143° C) than either bullvalene ($\Delta G^{\ddagger}$ = 12.8 kcal/mole at 100 °C) or barbaralane ($\Delta G^{\ddagger}$ = 7.8 kcal/mole at –77 °C).

The more recent high resolution ^{13}C-NMR spectra of semibullvalene by Günther, Quast, Grohmann, *et al.*, shown in Figure 3–16, also confirm that semibullvalene undergoes rapid Cope rearrangement at room temperature but is static at –155 °C.

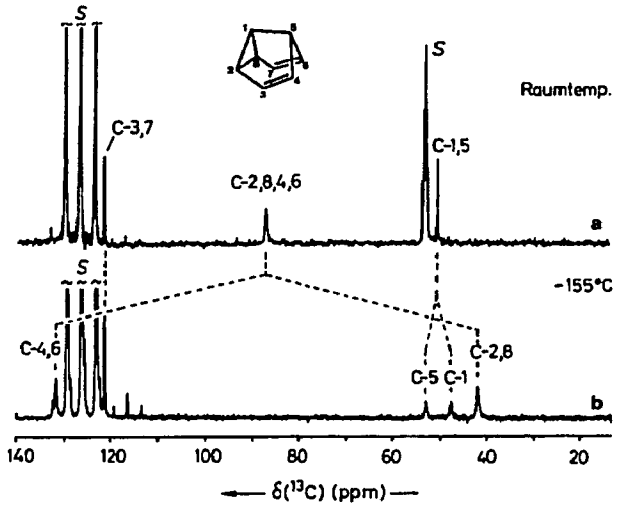


Figure 3–16. 100.6 MHz ^{13}C-NMR spectra of semibullvalene (a) fast exchange (b) slow exchange in CF_2Cl_2 and CD_2Cl_2.[23]

At room temperature the ^{13}C spectrum of semibullvalene in Figure 3–16 has three major peaks, approximately 51 ppm (corresponding to C1 and C5), 87 ppm (C2, C4, C6, and C8), and 121 ppm (C3 and C7). At –155 °C, the five major peaks are assignable to the carbon atoms of a "frozen" structure of semibullvalene.

Table 3–10. Summary of Activation Parameters for Semibullvalene

	Reference 10	Reference 23
Arrhenius method		
E_a (kcal mole^{-1})	5.55 ± 0.09	5.1 ± 0.2
ln A	12.24 ± 0.13	
Eyring method		
$\Delta H^{\ddagger}$ ((kcal mole^{-1})	5.24 ± 0.09	4.8 ± 0.2
$\Delta S^{\ddagger}$ (cal K^{-1} mole^{-1})	–3.24 ± 0.55	–5.4 ± 3
$\Delta G^{\ddagger}_{130K}$ ((kcal mole^{-1})	—	5.5 ± 0.2
$\Delta G^{\ddagger}_{173K}$ ((kcal mole^{-1})	5.80	5.7
$\Delta G^{\ddagger}_{298K}$ ((kcal mole^{-1})	6.20	—
r (correlation coeff.)	0.998	—

The degenerate Cope rearrangement of semibullvalene in solution becomes nondegenerate in the dynamic phase of the solid state. Macho, Miller, and Yannoni have not only observed the lifting of the degeneracy in the mirror-image rearrangement of semibullvalene caused by solid-state effect but also have conclusively demonstrated a dramatic solid-state suppression of the rate of rearrangement in semibullvalene from the ^{13}C NMR spectra shown in Figures 3–17 and 18.

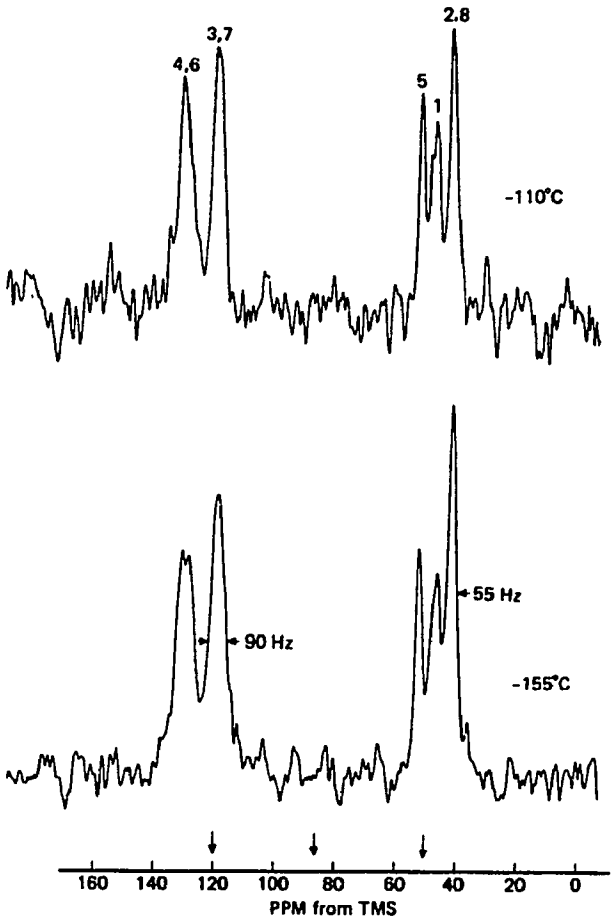


Figure 3–17. CP-MAS ^{13}C NMR Spectra of solid semibullvalene at –110 °C and at –155 °C, showing suppression of the degenerate Cope rearrangement. The arrows show the position of the averaged chemical shifts found in solution.[24]

At –155 °C, semibullvalene spectrum shows five clearly resolved carbon resonances. The chemical shifts and intensities are consistent with a static structure and correspond closely to the previous spectra of semibullvalene in solution at the low temperatures. From

Figure 3–18, the dynamics of semibullvalene seem to be characteristic of a glassy state. After annealing ("crystallization"), however, the crystalline semibullvalene exhibits a static behavior as shown in the variable-temperature, solid-state NMR spectra of Figure 3–18.

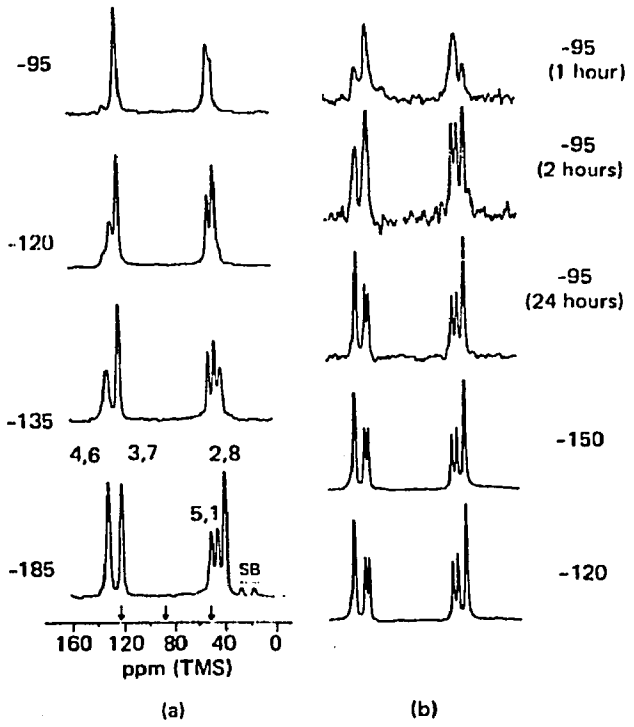


Figure 3–18. (a) CP-MAS ^{13}C NMR spectra of semibullvalene cooled into the solid state showing reversible dynamical behavior. The arrows mark the positions of the three resonances for the average spectrum obtained in solution. The peaks marked SB are the upfield spinning sidebands of the vinylic carbon resonances. (b) Spectra of the same sample during annealing at –95 °C. After annealing for several hours, the spectra no longer change with temperature cycling.[25]

They have calculated the rate constants, k_1 and k_2, for the nondegenerate Cope rearrangement at –132 °C to be 486 and 8514 s^{-1}, respectively (Figure 3–16). The $\Delta G^{\ddagger}$ for the slow process at this temperature is 6.3 kcal $mole^{-1}$. The free-energy profile is shown in Figure 3–19.

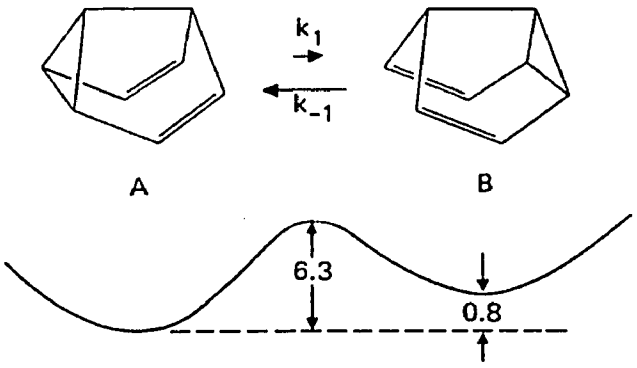


Figure 3–19. Free-energy profile (kcal/mole) for the nondegenerate Cope rearrangement of semibullvalene obtained from line-shape analysis of the previous CP-MAS ^{13}C spectra.

The corresponding rate constant for semibullvalene in solution at approximately the same temperature is 220,000 s^{-1}. The exchange rates corresponding to the higher energy barrier is about 10–20 times slower than those in solution.

In summary, Macho, Miller, and Yannoni have demonstrated that solid state-morphology can have significant influences on the Cope rearrangement of semibullvalene. This solid-state effect manifests itself as a perturbation of the equilibrium and as a rate retardation. The free energy of activation for the higher barrier, 6.3 kcal $mole^{-1}$ at –132 °C, for the rearrangement of semibullvalene in the solid state, however, is remarkably comparable to the solution value of 5.5 kcal $mole^{-1}$ at –143 °C.

Y. C. Wang and S. H. Bauer have determined the structure of semibullvalene in the gas phase by electron diffraction.[26] Bond distances and angles of the semibullvalene structure determined by the gas-phase electron diffraction are shown in Figure 3–20.

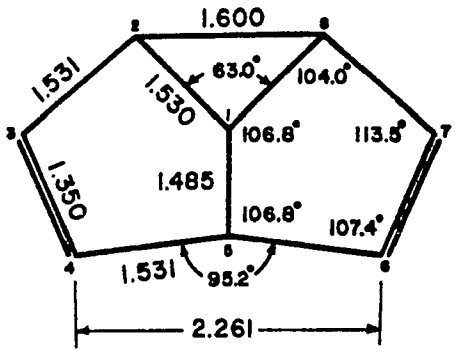


Figure 3–20. Structure of semibullvalene as determined by electron diffraction. The molecule is assumed to possess mirror symmetry so that the left portion of the molecule is the mirror image of the right. The mirror plane passes through the C1—C5 bond.[27]

Half of the semibullvalene molecule is assumed to be related to the other half by a mirror plane passing through the C1—C5 bond. Tables 3–11 and 3–12 list interatomic distances and angles in semibullvalene from the same electron-diffraction analysis.

Table 3–11. Interatomic Distances (Å) for Semibullvalene from Electron Diffraction

C1—C2	1.530
C1—C5	1.485
C2—C3	1.531
C2—C8	1.600
C3—C4	1.350
C4—C5	1.531
C4—C6	2.261

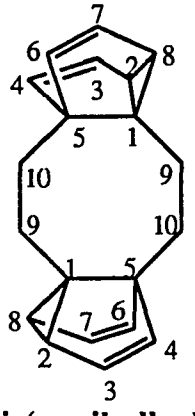
Table 3–12. Bond Angles (°) for Semibullvalene from Electron Diffraction

C2—C1—C8	63.0
C5—C1—C8	106.8
C1—C2—C3	104.0
C1—C2—C8	58.5
C2—C3—C4	113.5
C3—C4—C5	107.4
C1—C4—C5	106.8
C4—C5—C6	95.2

Wang and Bauer commented that the dynamics of rapid inversion are apparent in the thermally averaged structure of semibullvalene, as seen by electron diffraction. We must keep in mind, however, that the Wang and Bauer structure determination of semibullvalene has limited accuracy.

3.4 BIS(SEMIBULLVALENE)

If two semibullvalene molecules are linked at C1 and C5 with four methylenes, we obtain the interesting structure called bis(semibullvalene)[28]



Bis(semibullvalene)

The usual X-ray data of unit-cell parameters, fractional coordinates, interatomic distances, angles, and *ORTEP* drawing for bis(semibullvalene) follow. Thermal parameters are not included because they were not readily available. There are two half-molecules in the asymmetric unit. One half of a bis(semibullvalene) molecule is related to the other half a crystallographic inversion center. This type of intramolecular symmetry is reflected in the above numbering scheme. In examining the X-ray results, one must be aware that the numbering in the two independent moieties is not consistent and that the structure is subject to a static disorder!

Table 3–13. X-ray Crystal Diffraction Data for Bis(semibullvalene) at **123 K**

Formula	$C_{20}H_{20}$
Formula weight	260.38
Melting point (° C)	192-193
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	6.578(2)
b (Å)	9.969(4)
c (Å)	11.188(5)
α(°)	106.93(4)
β(°)	90.36(3)
γ(°)	94.84(3)
Volume (Å3)	699
Z	2[a]
d_{calc} (g cm^{-3})	1.237
R	0.094
R_w	—

[a] The asymmetric unit contains two independent half-molecules.

Table 3–14. Atomic Coordinates for Bis(semibullvalene) at **123 K**

Atom	*x/a*	*y/b*	*z/c*
C1	0.1530	0.3389	0.4113
C2	0.0570	0.2509	0.2890
C3	-0.1040	0.1640	0.3089
C4	-0.1369	0.1910	0.4379
C5	0.0040	0.3082	0.5120
C6	0.0740	0.1790	0.5365
C7	0.2660	0.1503	0.4743
C8	0.3150	0.2350	0.4057
C9	0.2310	0.4916	0.4233
C10	-0.0710	0.4251	0.6182
C11	-0.5059	0.3102	-0.1172
C12	-0.6610	0.1980	-0.1070
C13	-0.6250	0.1580	-0.0020
C14	-0.4530	0.2340	0.0630
C15	-0.3569	0.3330	-0.0052
C16	-0.2060	0.2220	-0.0520
C17	-0.2550	0.1442	-0.1703
C18	-0.4320	0.1860	-0.2178
C19	-0.5740	0.4325	-0.1586
C20	-0.2689	0.4797	0.0713
H1	0.107	0.242	0.177
H2	-0.164	0.072	0.254
H3	-0.244	0.153	0.452
H4	-0.016	0.151	0.614
H5	0.338	0.043	0.478
H6	0.484	0.295	0.383
H7	0.304	0.536	0.496
H8	0.347	0.486	0.348
H9	-0.102	0.397	0.697
H10	0.056	0.488	0.654
H11	-0.813	0.173	-0.153
H12	-0.697	0.065	0.026
H13	-0.404	0.255	0.173
H14	-0.061	0.227	-0.007
H15	-0.179	0.058	-0.228
H16	-0.481	0.204	-0.307
H17	-0.646	0.390	-0.256
H18	-0.457	0.498	-0.176
H19	-0.202	0.541	0.030
H20	-0.143	0.447	0.137

Table 3–15. Interatomic Distances (Å) for Bis(semibullvalene) at **123 K**

C1—C2	1.496	C11—C12	1.478
C1—C5	1.577	C11—C15	1.537
C1—C8	1.537	C11—C18	1.527
C1—C9	1.531	C11—C19	1.523
C2—C3	1.372	C12—C13	1.371
C2—C8	2.179	C12—C18	1.946
C3—C4	1.410	C13—C14	1.380
C3—C7	3.084	C13—C17	3.075
C4—C5	1.468	C14—C15	1.515
C4—C6	1.800	C14—C16	2.068
C5—C6	1.500	C15—C16	1.530
C5—C10	1.519	C15—C20	1.525
C6—C7	1.455	C16—C17	1.346
C7—C8	1.319	C17—C18	1.418
C9—C10	1.542	C19—C20	1.566

Table 3–16. Angles (°) or Bis(semibullvalene) at **123 K**

C2—C1—C5	104.3	C12—C11—C15	105.1
C2—C1—C8	91.8	C12—C11—C18	80.7
C2—C1—C9	118.0	C12—C11—C19	119.0
C5—C1—C8	102.6	C15—C11—C18	104.6
C5—C1—C9	119.0	C15—C11—C19	122.0
C8—C1—C9	116.9	C18—C11—C19	117.4
C1—C2—C3	110.0	C11—C12—C13	111.1
C2—C3—C4	110.7	C12—C13—C14	110.4
C3—C4—C5	111.1	C13—C14—C15	110.6
C1—C5—C4	103.1	C11—C15—C14	102.8
C1—C5—C6	104.8	C11—C15—C16	104.1
C1—C5—C10	122.3	C11—C15—C20	122.0
C4—C5—C6	74.7	C14—C15—C16	85.6
C4—C5—C10	121.2	C14—C15—C20	118.7
C6—C5—C10	120.4	C16—C15—C20	117.1
C5—C6—C7	107.8	C15—C16—C17	110.7
C6—C7—C8	112.5	C16—C17—C18	112.1
C1—C8—C7	111.4	C11—C18—C17	108.4
C1—C9—C10	113.4	C11—C19—C20	114.4
C5—C10—C9	113.9	C15—C20—C19	113.9

The interatomic distances of bis(semibullvalene), C2—C8 and C4—C6, in Table 3–15 are unusually long and short, respectively. The angle, C2—C1—C8, (Table 3–16) opens

up while the angle C4—C5—C6, closes when compared to the same angles from the semibullvalene structure of Wang and Bauer's electron diffraction analysis, reported earlier in this same chapter.

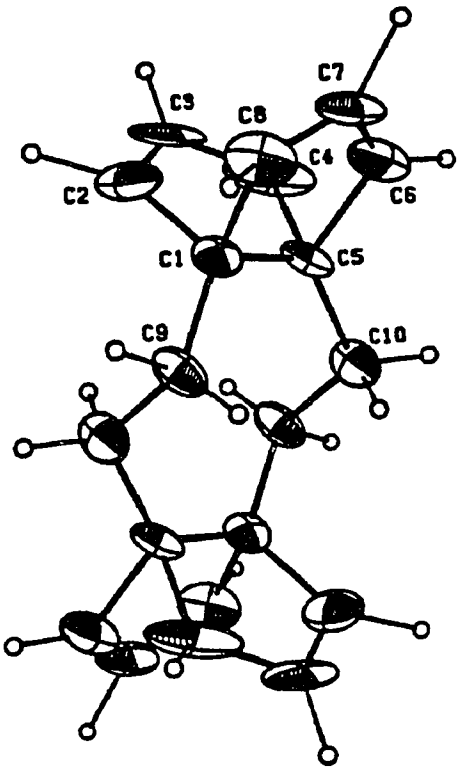


Figure 3–21. X-ray-structure of bis(semibullvalene) with 50% thermal ellipsoids. There are two independent halves of bis(semibullvalene) in the asymmetric unit, each of which resides around a crystallographic center of inversion.

The activation parameters of bis(semibullvalene) from NMR data are $E_a = 11.8$ kcal mole^{-1}, $\Delta H^{\ddagger}_{298K} = 11.2 \pm 0.2$ kcal mole^{-1}, $\Delta G^{\ddagger}_{298K} = 17.0 \pm 0.2$ kcal mole^{-1}, and $\Delta S^{\ddagger}_{298K} = -19.4 \pm 0.4$ eu. These values, however, are not necessarily activation energies for the Cope rearrangement of bis(semibullvalene) because they include the conformational changes of the eight-membered ring.

Conformational dynamics of seven- and eight-membered 1,5-cycloalkane-fused derivatives of semibullvalene have also been synthesized and analyzed.[29]

3.5 MORE MOLECULE IMPROVEMENT

In the continuing efforts to reduce the activation energy barrier, Hoffmann and Stohrer remarked that "no great philosophical insight is required for the recognition that a lower activation energy can be achieved by destabilizing the reactant or product, or by stabilizing the transition state, or by some combination of both."[30] To explore the possibilities in speeding up the Cope rearrangement of semibullvalene, let us take a closer look at its interconversion in Figure 3–22 to see how the molecule may be modified to reduce the activation energy.

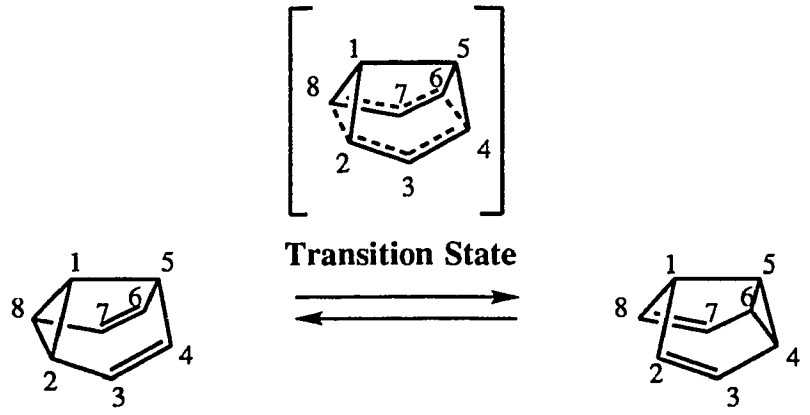
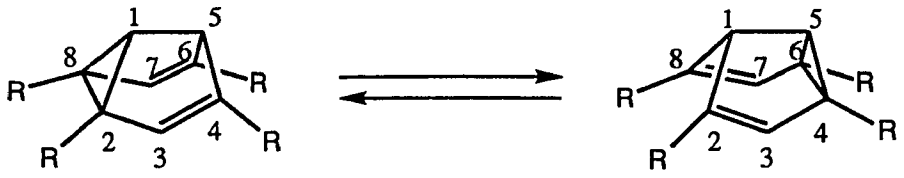


Figure 3–22. Degenerate Cope rearrangement of semibullvalene.

The conversion of one tautomer to the other involves the breaking of the C2—C8 bond for the tautomer on the left and the C4—C6 bond for the tautomer on the right. The breaking of this cyclopropane bond in each tautomer may be facilitated by weakening it, that is, by reducing the electron density within the bond. One way to promote this destabilization is to attach electron-withdrawing groups to C2, C4, C6, and C8.

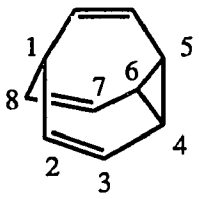


Sophisticated and elaborate arguments have demonstrated more specifically the role of appropriate substituents at strategic sites in the semibullvalene molecule for lowering the fluxional energy barrier. Quantum mechanical calculations by R. Hoffmann and W. Sthorer, using extended Hückel theory,[30] and by M. Dewar, using MINDO/2[31,32], predicted that *π-electron donors* at positions 1 and 5, and *π-electron acceptors* in positions 2,4,6, and 8 would lower the activation energy for the Cope rearrangement of semibullvalenes. Strong π-electron donors are NH_2, OH, OCH_3; weak π-electron donors are C_6H_5, CH_3. Strong π-electron acceptors are NO_2, CN, and $COOCH_3$; mild π-electron acceptors are Cl, Br, I. These are the same groups usually employed in basic aromatic chemistry to activate or deactivate the benzene ring.

These same arguments on the effects of electron donors and acceptors also apply directly to **bullvalene** and **barbaralane** derivatives. Early analogs of these two compounds gave support to the claims proposed by the donor-acceptor theory of Hoffmann and Dewar.

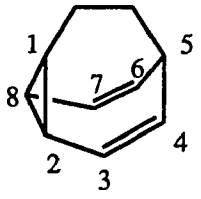
3.6 MORE BRIDGED DERIVATIVES OF HOMOTROPILIDENE

The activation energy for the interconversion of **dihydrobullvalene** (9.5 kcal/mole at –40 °C) is considerably less than that of **bullvalene** (12.8 kcal/mole), since the CH—CH bridge in the dihydro compound is a better electron donor than CH=CH in bullvalene:



Bullvalene

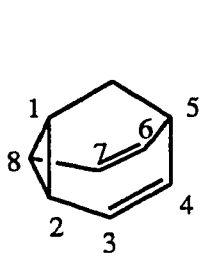
$\Delta G^{\ddagger} = 12.8$ kcal/mole



Dihydrobullvalene

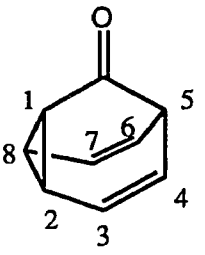
$\Delta G^{\ddagger} = 9.5$ kcal/mole

Conversely, replacement of the methylene bridge in barbaralane with the more electron-attracting carbonyl in **barbaralone** raises the activation energy from 7.8 to 9.6 kcal/mole; an even more drastic increase is observed in **protonated barbaralone** $\Delta G^{\ddagger}$ > 13.8 kcal/mole:



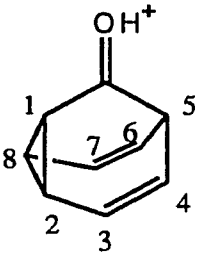
Barbaralane

$\Delta G^{\ddagger} = 7.6$ kcal/mole



Barbaralone

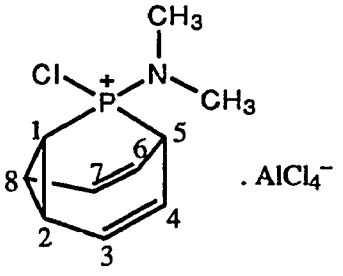
$\Delta G^{\ddagger} = 9.6$ kcal/mole



Protonated barbaralone

$\Delta G^{\ddagger} > 13.8$ kcal/mole

Even hetero atoms, such as phosphorous, have entered the arena of bishomoaromaticity. One such compound is 9-phosphabarbaralane:

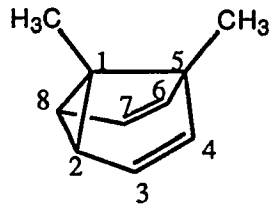


9-Phosphabarbaralane

The synthesis and characterization of this salt (m. p. dec. 262 °C) by NMR and single-crystal X-ray analyses have been reported in the literature.[33] This compound has bond distances for C2—C8 and C4—C6 of 1.949 and 2.054 Å, respectively. The angles, C2—C1—C8 and C4—C1—C5, are 81.5 and 88.7 °C. No activation parameters were reported.

3.7 1,5-DIMETHYLSEMIBULLVALENE

The compound 1,5-dimethylsemibullvalene



1,5-Dimethylsemibullvalene

whose ^{13}C NMR spectrum is shown in Figure 3–23, has the lowest activation energy measured so far by dynamic NMR. Its activation parameters from NMR data are $E_a = 12.6(2)$ kcal mole^{-1}, $\Delta H^{\ddagger} = 4.5(3)$ kcal mole^{-1}, $\Delta G^{\ddagger}_{298K} = 5.0(9)$ kcal mole^{-1}, and $\Delta S^{\ddagger}_{298K} = -1.6(8)$ cal K^{-1} mole^{-1}.[34]

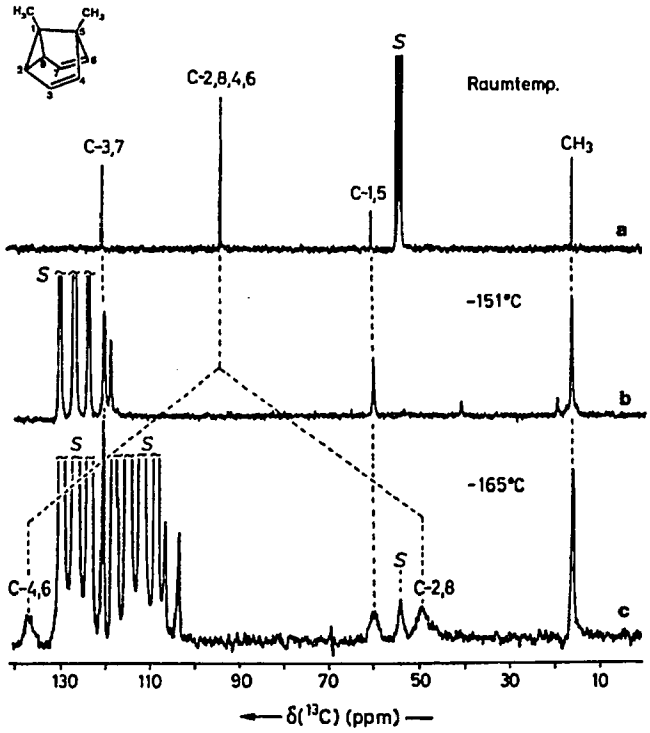


Figure 3–23. 100.6 MHz ^{13}C NMR spectrum of 1,5-dimethylsemibullvalene.

3.8 IN SUMMARY

The activation energies for the compounds mentioned above are summarized in Table 3—17.

Table 3-17. Summary of Free Energies of Activation for the Cope rearrangement

Compound	$\Delta G^{\ddagger}$ (kcal/mole)	Temperature (° C)
Homotropilidene	13.7	–35
Bullvalene	12.8	100
	12.6	25
	11.8	10
Dihydrobullvalene	9.5	–40
Barbaralane	7.8	–77
	7.6	25
Barbaralone	9.5	–40
Protonated Barbaralone	> 13.8	–5
Semibullvalene	6.2	25
	5.8	–100
	5.5	–143
1,5-Me_2semibullvalene	5.0	25
	4.8	–100

3.9 THE RESEARCH GOAL

The goal of this research, then, is directed toward the characterization of substituted semibullvalenes, which have a low energy of activation for the Cope rearrangement, approaching the bishomoaromatic state.

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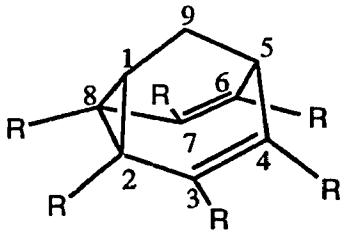
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CHAPTER 4

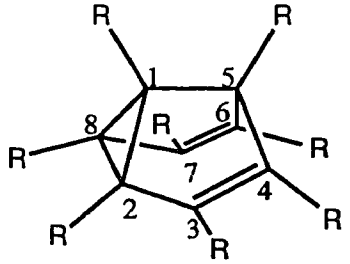
AN ACT OF BECOMING ...

In this chapter, we examine six compounds, referred to as the six *primary candidates* for the X-ray study, to examine how their **unit-cell parameters, density, interatomic distances** between ring atoms, **angles** of ring atoms, and ring-atoms' **root-mean-square displacements** of thermal vibrations from their equilibrium positions change with temperature. The changes must be viewed with reference to the Cope rearrangement in the solid state. The six primary candidates are:



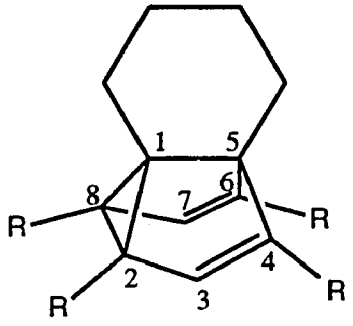
R = $COOCH_3$

2,4,6,8-Tetracarbomethoxybarbaralane
[Barbaralane-$(COOMe)_4$]



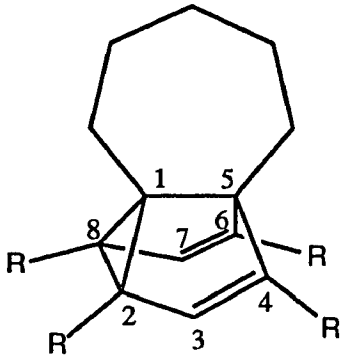
R = $COOCH_3$

Octacarbomethoxysemibullvalene
[Sb-$(COOMe)_8$]



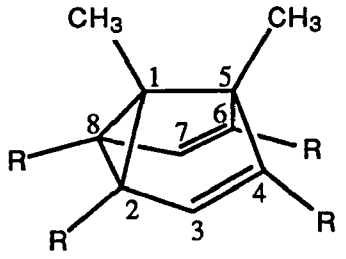
R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)



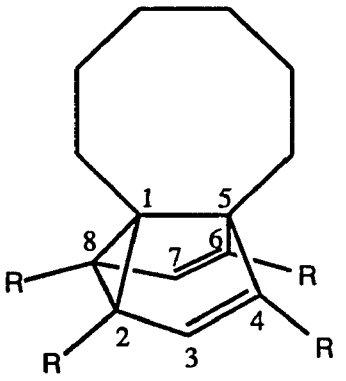
R = $COOCH_3$

1,5-Cycloheptano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-7)



R = $COOCH_3$

1,5-Dimethyl-2,4,6,8-tetra-carbomethoxysemibullvalene
(Sb-Me_2)

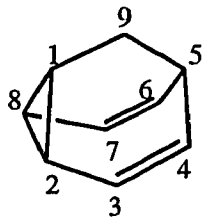


R = $COOCH_3$

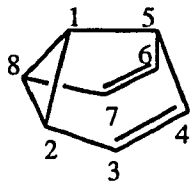
1,5-Cyclooctano-2,4,6,8-tetra-carbomethoxysemibullvalene
(Sb-8)

OVERVIEW

This chapter is descriptive in nature with explanations being few and far in between. Six of its sections describe separately these six candidates. A section is devoted entirely to give a detailed account of just one candidate. The basic style in each section has a monotonous, merciless, telegram appearance: **ChemDraw molecular drawing** of a candidate, table of **unit-cell parameters** at various temperatures followed by graphs of **unit-cell volume** and **density,** table of **interatomic ring distances** and associated **graphs**, table of **interatomic ring angles** and selected **graphs**, table of **root-mean-square displacements of thermal vibrations** for ring atoms and selected **graphs, *ORTEP* molecular drawings.** Generally, graphs of interatomic distances, which are *invariant* in the ring of a compound as the temperature is varied, are shown first, then those which exhibit *intermediate* modifications, and lastly those which display the *most dramatic* changes. For example, the interatomic distances, C1—C5 and C3—C7, remain stubbornly invariant to temperature in all of these six compounds; but the distances, C2—C8 and C4—C6, markedly elongate and contract, respectively, but to a varying degree in each candidate.



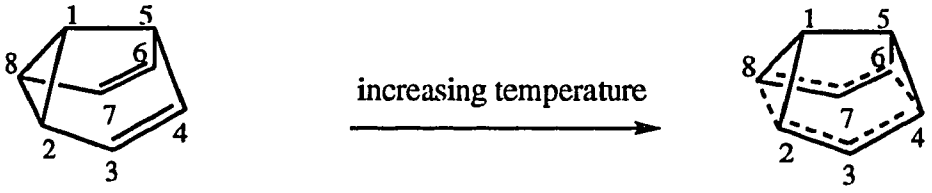
Barbaralane ring system



Semibullvalene ring system

We close the chapter by comparing corresponding key structural features of these six candidates, to bring out their different behavior as they respond and adjust to temperature changes. Available NMR and IR spectra of these six compounds are interjected to confirm or to complement the X-ray data.

As the temperature is raised, the structure of a candidate changes toward the bishomoaromatic state. The single bonds in the semibullvalene ring system, C2—C3 and C7—C8, tend to become shorter, while the double bonds, C3—C4 and C6—C7, compensate by becoming longer, with both sets of single and double bonds striving to achieve a common end, that is, benzene's bond length of 1.40 Å. At the same time, the bond distance, C2—C8, elongates, while the interatomic distance, C4—C6 compensates by contracting, with both aiming toward equality, as illustrated in Figure 4–1.

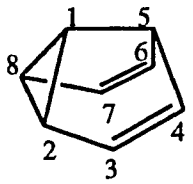


Semibullvalene ring system → **Bishomobenzene structure**

Figure 4–1. The changing semibullvalene ring as the temperature is increased.

The six candidates undergo Cope rearrangement in solution. In the solid state, however, no significant structural alterations take place in barbaralane-$(COOMe)_4$ with temperature; gradual changes creep in Sb-$(COOMe)_8$; and spectacular transformations

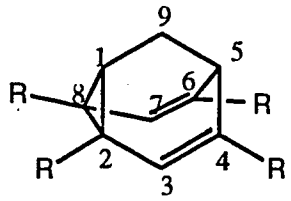
occur in Sb-8. The six compounds are, then, arranged in order of increasing dynamic behavior in the solid state: barbaralane-$(COOMe)_4$ being the least dynamic or nearly static while Sb-8 is the most dynamic. The rest fall between these two extremes. Stepping over one candidate to the next, we see that the trend toward the bishomoaromatic state intensifies. The climax is reached when Sb-8 achieves at room temperature the long-sought bishomobenzene structure, where the single bonds in the semibullvalene ring system, C2—C3 and C7—C8, and double bonds, C3—C4 and C6—C7 are all equal, along with the interatomic distances, C2—C8 and C4—C6.



Semibullvalene ring system

4.1 2,4,6,8-TETRACARBOMETHOXYBARBARALANE

The compound **2,4,6,8-tetracarbomethoxybarbaralane** or just referred to as **barbaralane-$(COOMe)_4$**



R = $COOCH_3$

2,4,6,8-Tetracarbomethoxybarbaralane
[Barbaralane-(COOMe)4]

is endowed with structural features that practically do not change with temperature in the solid state. The purpose for introducing this barbaralane derivative is to provide a base line needed to compare the five derivatives of semibullvalene, which do, indeed,

exhibit changes as the temperature is varied. Some pertinent X-ray crystal data barbaralane-$(COOMe)_4$ are listed in Table 4–1

Table 4–1. X-ray Crystal Data for Barbaralane-$(COOMe)_4$ at Two Temperatures

	115 K	**295 K**[a]
Formula	$C_{17}H_{18}O_8$	$C_{17}H_{18}O_8$
Formula weight	350.33	350.33
Melting point (°C)	99–100	99–100
Crystal size (mm)	0.10 x 0.36 x 0.50	0.10 x 0.36 x 0.50
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	7.757(1)	7.854(1)
b (Å)	16.101(5)	16.206(2)
c (Å)	12.866(3)	12.982(2)
β (°)	90.08(1)	90.64(1)
Cell volume ($Å^3$)	1606.9(1.0)	1652.3(7)
Z	4	4
d_{calc} ($g\ cm^{-3}$)	1.448	1.408
μ(Cu $K\alpha$) (cm^{-1})	9.4	9.2
R	0.044	0.046
R_w	0.059	0.059

[a] **295 K** denotes room temperature

Figure 4–2 shows quantitatively the expansion of barbaralane-$(COOMe)_4$ unit-cell volume as the temperature is increased from 115 to 295 K (room temperature).

V = b + mT	
b	1577.9
m	0.25222
R	1

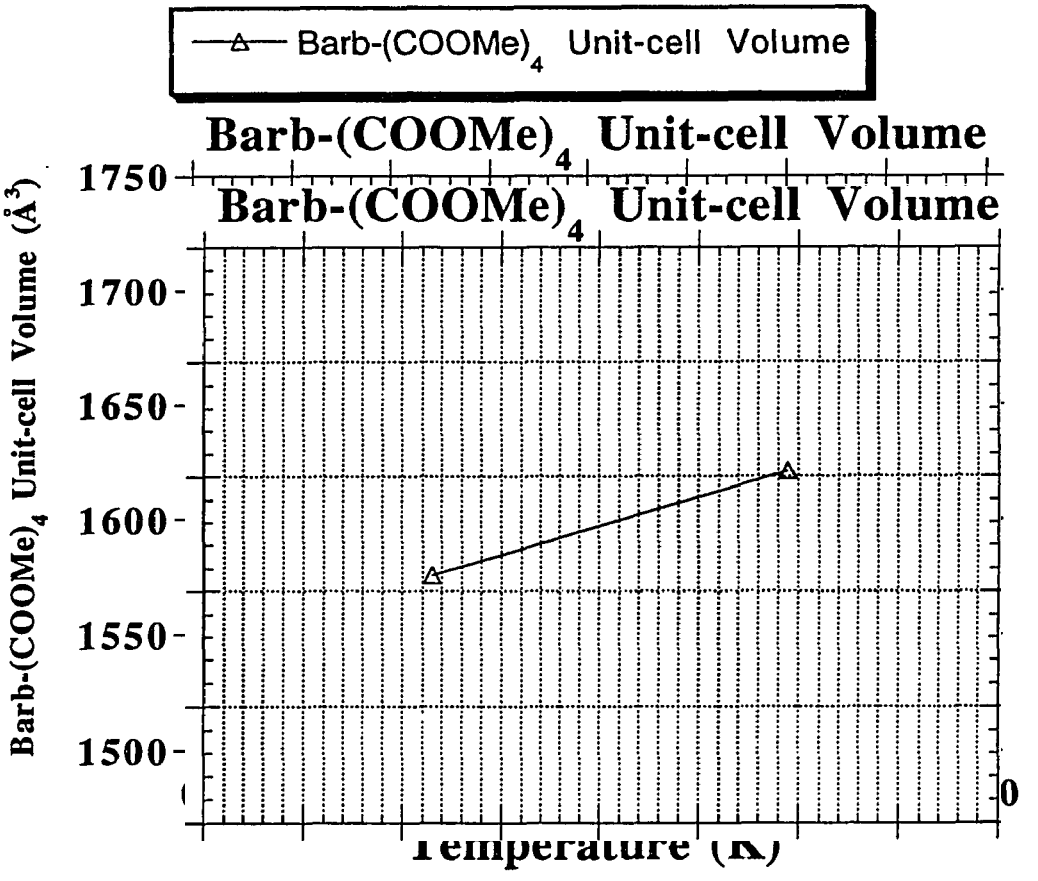


Figure 4–2. A plot of unit-cell volume versus temperature for barbaralane-$(COOMe)_4$.

According to the slope in Figure 4–2, the unit-cell volume of barbaralane-$(COOMe)_4$ expands at the rate of 2.5 $Å^3$ for every 10 °C rise in temperature for four molecules (100 non-H-s and 72 H's) in the unit cell. The density, as expected, plays a counter melody to the volume and thus diminishes, as seen in Figure 4–3.

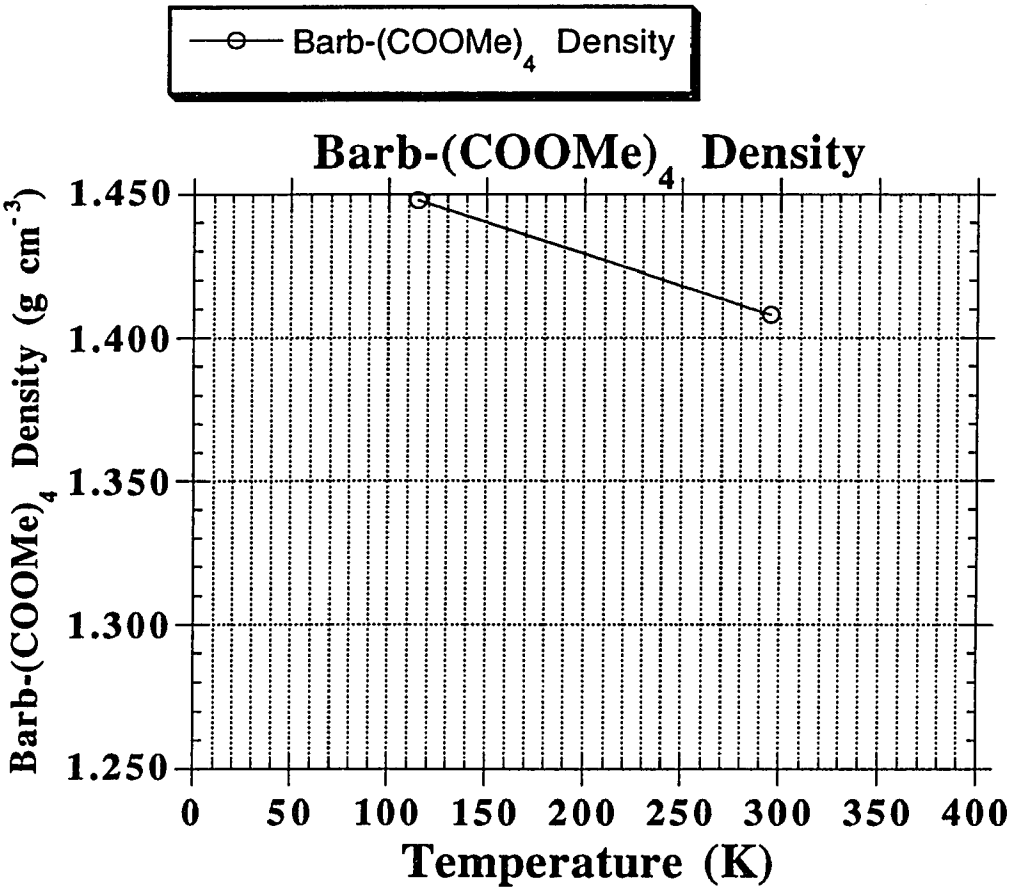


Figure 4–3. A plot of density versus temperature for barbaralane-$(COOMe)_4$.

The interatomic ring distances and angles in tables 4–2 and 4–3 and in the accompanying plots clearly indicate that the structure of barbaralane-$(COOMe)_4$ does not change appreciably with temperature and, in fact, may be considered nearly static in the solid state at both 115 and 295 K (room temperature). The X-ray structure of this compound remains virtually unchanged between 115 and 295 K with the molecule exhibiting a somewhat "normal" bond length for the C2—C8 (1.61 Å) and a long C4—C6 interatomic distance of 2.40 Å (Table 4–2). The single and the double ring in the ring are essentially localized. The double bonds, C3—C4 and C6—C7 are 1.34 Å, a length which is characteristic of isolated double bonds.

Table 4–2. Selected Interatomic Distances (Å) in the Ring of Barbaralane-$(COOMe)_4$ at Two Temperatures.

	115 K	**295 K**
C1—C2	1.494(2)	1.490(2)
C1—C5	2.513(2)	2.509(2)
C1—C8	1.520(2)	1.518(2)
C1—C9	1.505(2)	1.509(2)
C2—C3	1.473(2)	1.473(2)
C2—C8	1.608(2)	1.611(2)
C3—C4	1.342(2)	1.337(2)
C3—C7	3.046(2)	3.042(2)
C4—C5	1.519(2)	1.515(2)
C4—C6	2.400(2)	2.396(2)
C5—C6	1.512(2)	1.511(2)
C5—C9	1.545(2)	1.539(2)
C6—C7	1.340(2)	1.339(2)
C7—C8	1.466(2)	1.464(2)
C2—C3 + C3—C4	2.815	2.810
C6—C7 + C7—C8	2.806	2.803
C2—C8 + C4—C6	4.008	4.007

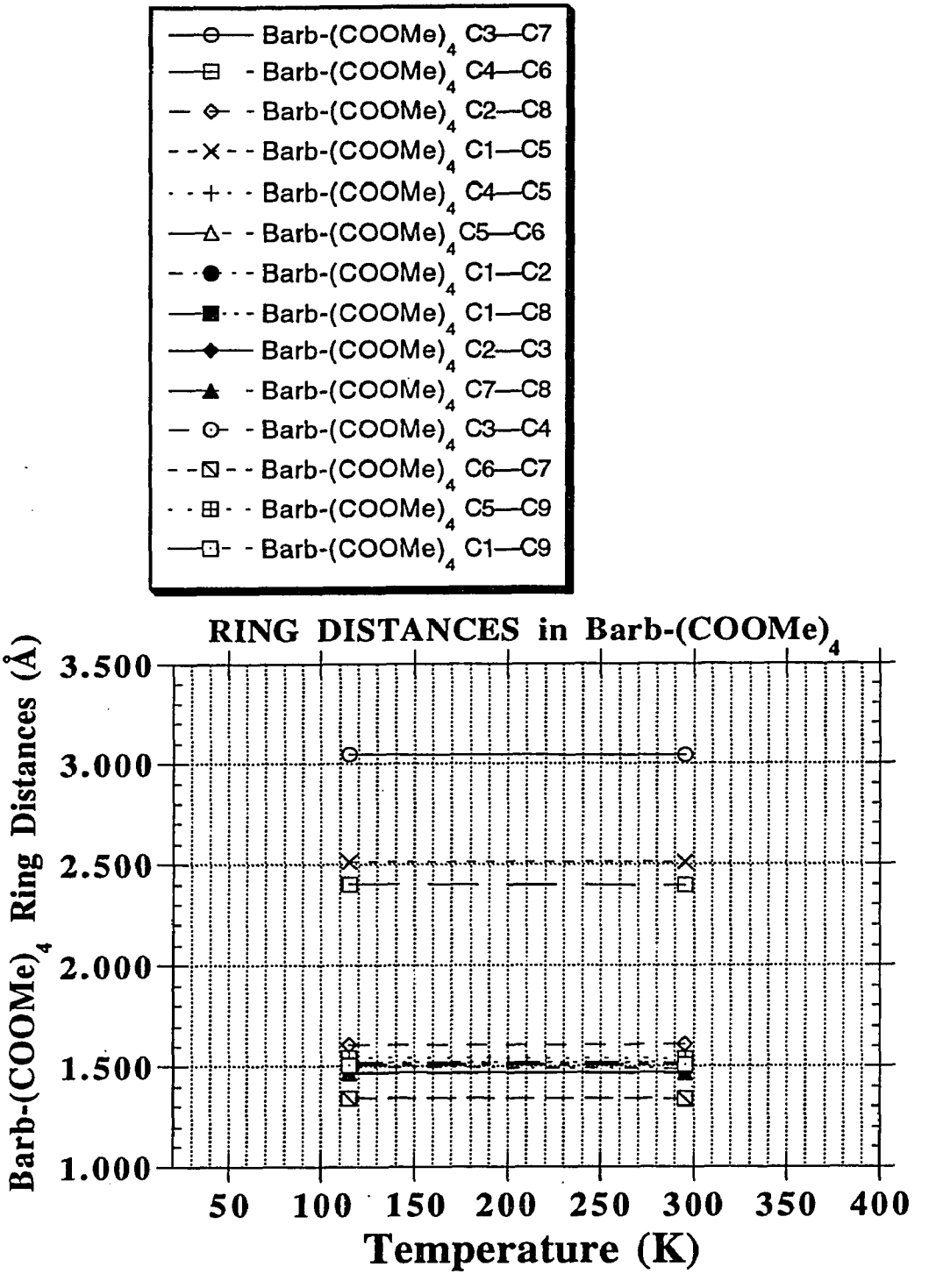


Figure 4–4. Plots of selected interatomic distances in the ring of barbaralane-$(COOMe)_4$ versus temperature.

Ring angles in Table 4–3 tell the same story as the distances, that is, no changes in the barbaralane ring system occur in the solid state as the temperature is varied.

Table 4–3. Selected Interatomic Angles (°) in the Ring of Bararbaralane-(COOMe)$_4$ at Two Temperatures

	115 K	**295 K**[a]
C2—C1—C8	64.5(1)	64.8(1)
C2—C1—C9	116.1(1)	116.1(1)
C8—C1—C9	115.3(1)	115.1(1)
C1—C2—C3	118.3(1)	118.4(1)
C1—C2—C8	58.5(1)	58.5(1)
C3—C2—C8	119.0(1)	118.8(1)
C2—C3—C4	121.3(1)	121.3(1)
C3—C4—C5	119.0(1)	119.1(1)
C4—C5—C6	104.7(1)	104.7(1)
C4—C5—C9	109.1(1)	109.5(1)
C6—C5—C9	109.1(1)	109.1(1)
C5—C6—C7	119.5(1)	119.2(1)
C6—C7—C8	121.4(1)	121.6(1)
C1—C8—C2	57.0(1)	56.8(1)
C1—C8—C7	118.1(1)	118.1(1)
C2—C8—C7	119.6(1)	119.4(1)
C1—C9—C5	110.9(1)	110.8(1)
$(\alpha+\beta)/2$[b]	84.6	84.8
C3—M[c]—C7	89.0	89.0

[a] **295 K** denotes room temperature.
[b] α = C2—C1—C8, β = C4—C5—C6.
[c] M = midpoint between C1 and C5 bond.

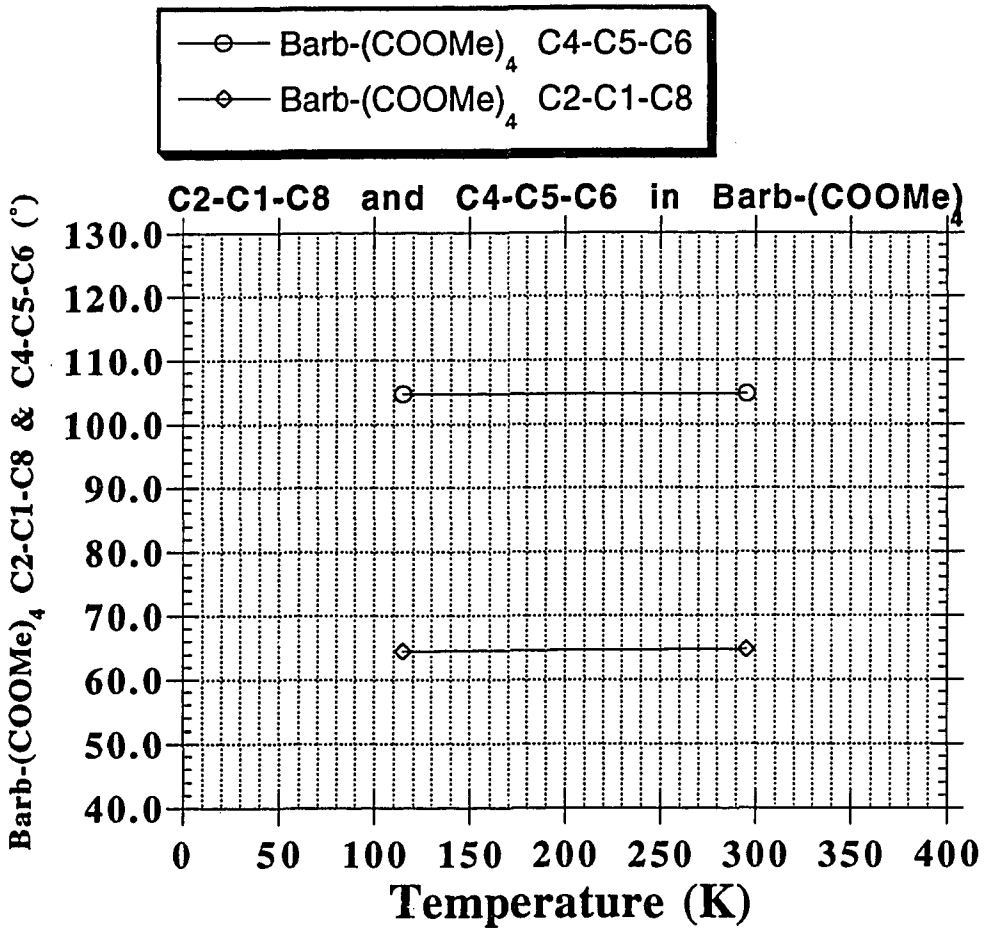


Figure 4–5. Plots of the angles C2—C1—C8 and C4—C5—C6 in barbaralane-$(COOMe)_4$ versus temperature.

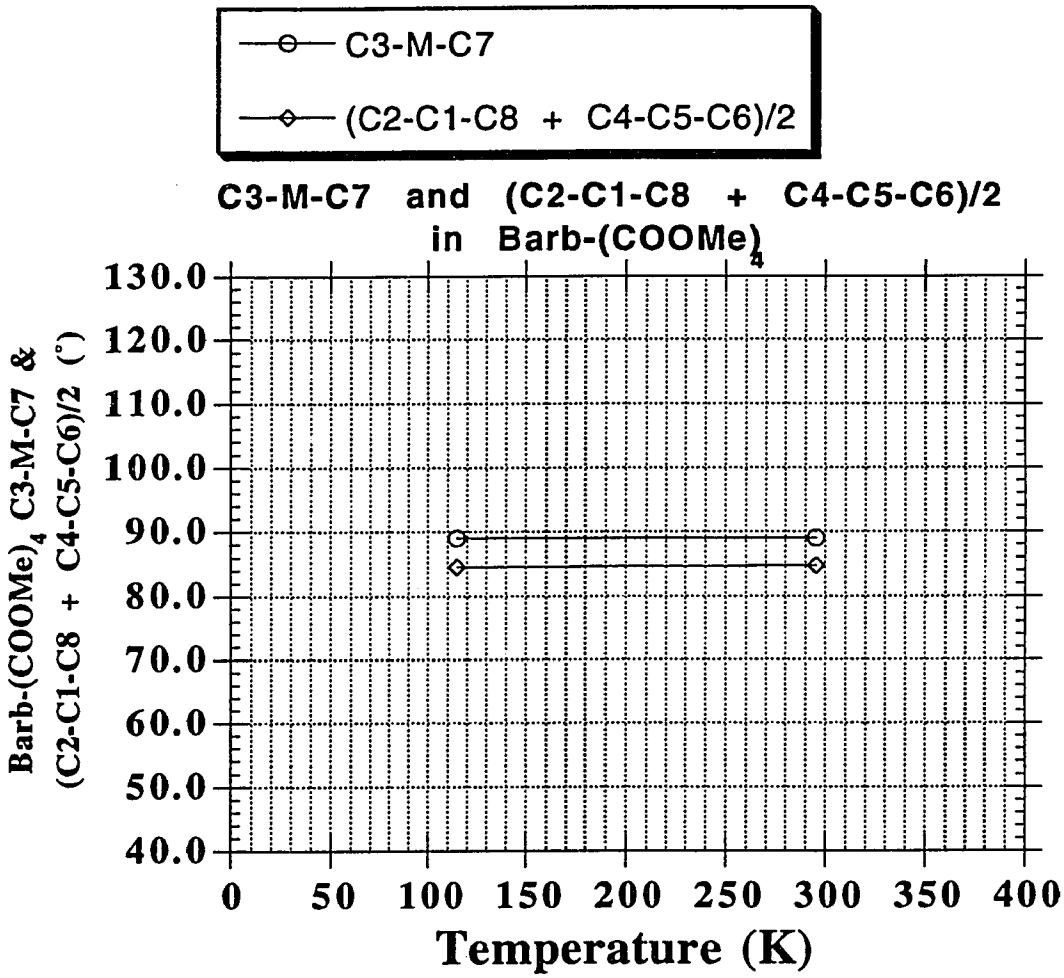


Figure 4–6. Plots of the angle C3—M—C7 (M = midpoint between C1 and C5) and the average angle of C2—C1—C8 and C4—C5—C6 in barbaralane-$(COOMe)_4$ versus temperature.

The root-mean-square amplitudes of thermal vibrations of the ring atoms barbaralane-$(COOMe)_4$ in Table 4–4 show normal thermal changes with increasing temperature.

Table 4–4. Selected Root-Mean-Square Amplitudes (Å) of Thermal Vibrations (Å) in the Ring of Bararbaralane-$(COOMe)_4$ at Two Temperatures.

		Min.	Int'med	Max.
115 K	C1	0.095	0.122	0.129
	C2	0.094	0.120	0.134
	C3	0.093	0.128	0.136
	C4	0.089	0.123	0.138
	C5	0.097	0.120	0.134
	C6	0.100	0.121	0.129
	C7	0.098	0.126	0.128
	C8	0.091	0.119	0.134
	C9	0.101	0.127	0.129
295 K	C1	0.164	0.182	0.192
	C2	0.161	0.176	0.195
	C3	0.160	0.190	0.196
	C4	0.158	0.184	0.198
	C5	0.164	0.175	0.195
	C6	0.162	0.177	0.181
	C7	0.159	0.180	0.192
	C8	0.162	0.169	0.191
	C9	0.166	0.187	0.195

The maximum root-mean-square displacements of just C2, C4, C6, and C8 in barbaralane-$(COOMe)_4$ are plotted against temperature in Figure 4–7 and 8.

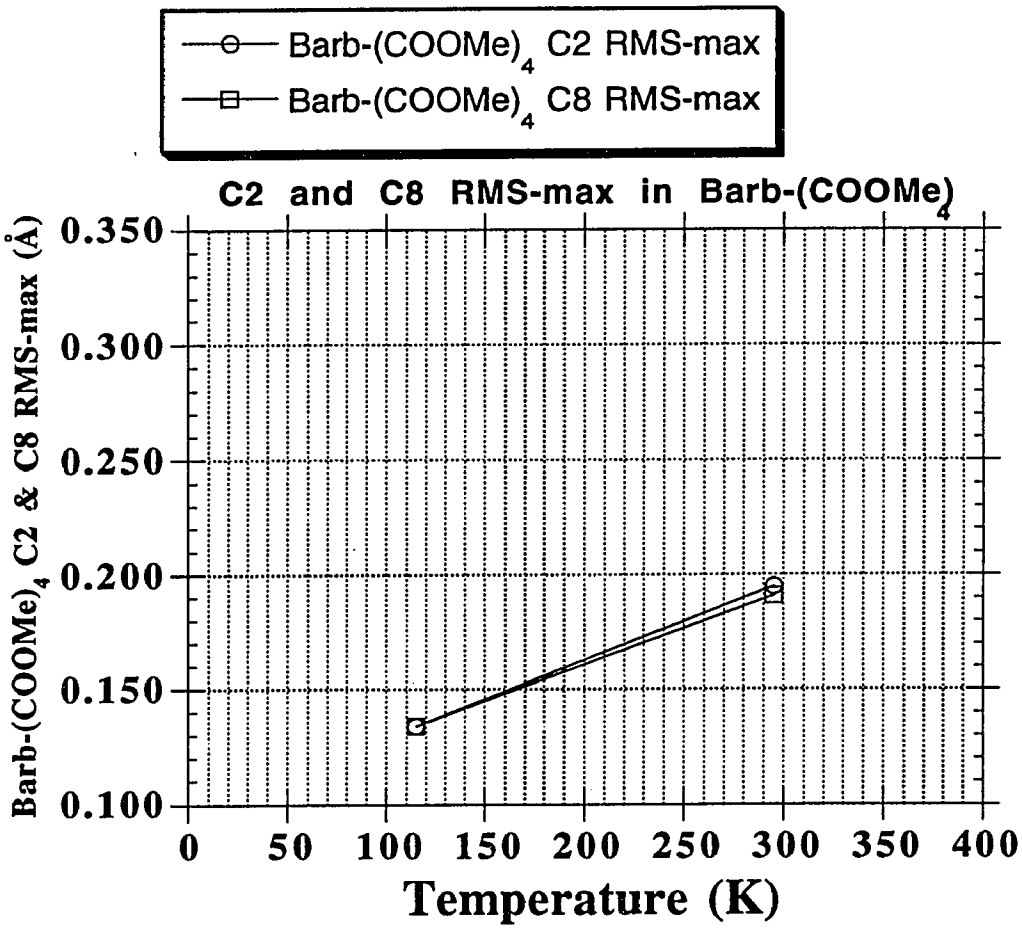


Figure 4–7. Plots of C2 RMS-max and C8 RMS-max in barbaralane-$(COOMe)_4$ versus temperature.

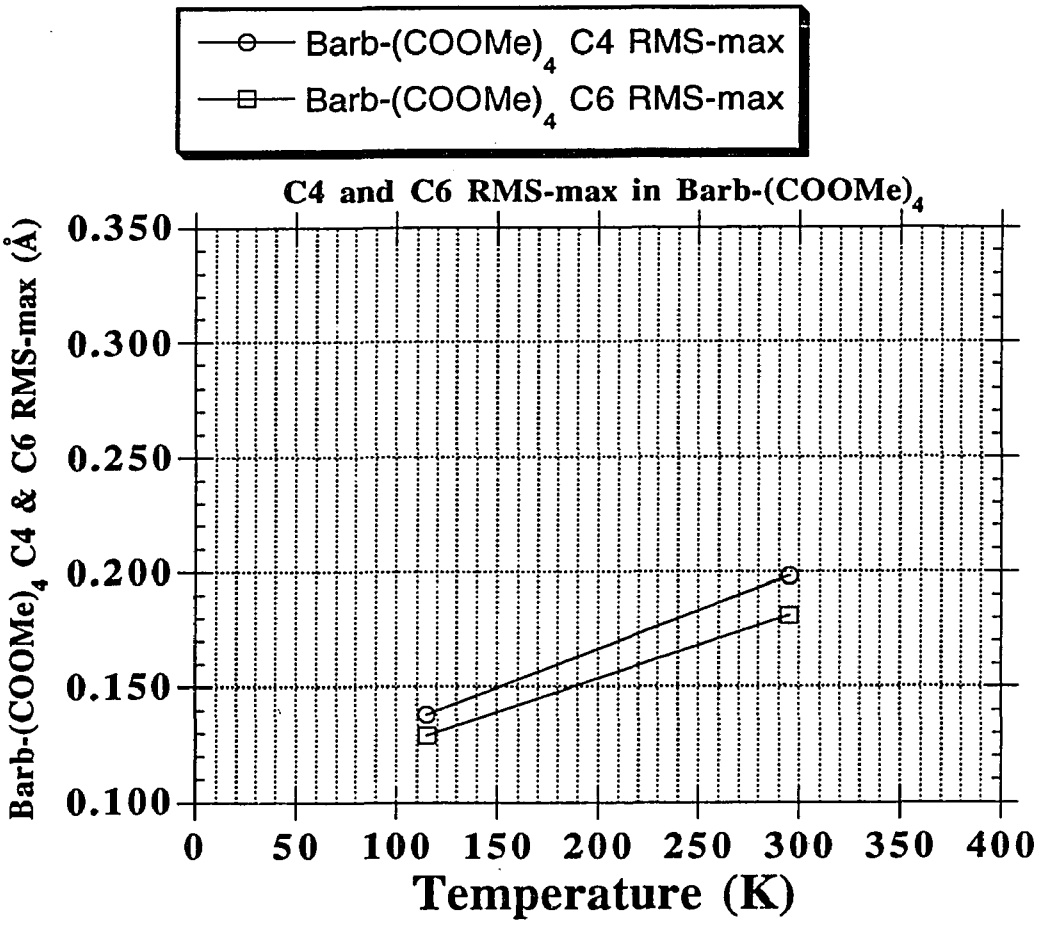


Figure 4–8. Plots of C4 RMS-max and C6 RMS-max in barbaralane-(COOMe)$_4$ versus temperature.

ORTEP drawings of barbaralane-(COOMe)$_4$ are shown in Figures 4–9 and 10.

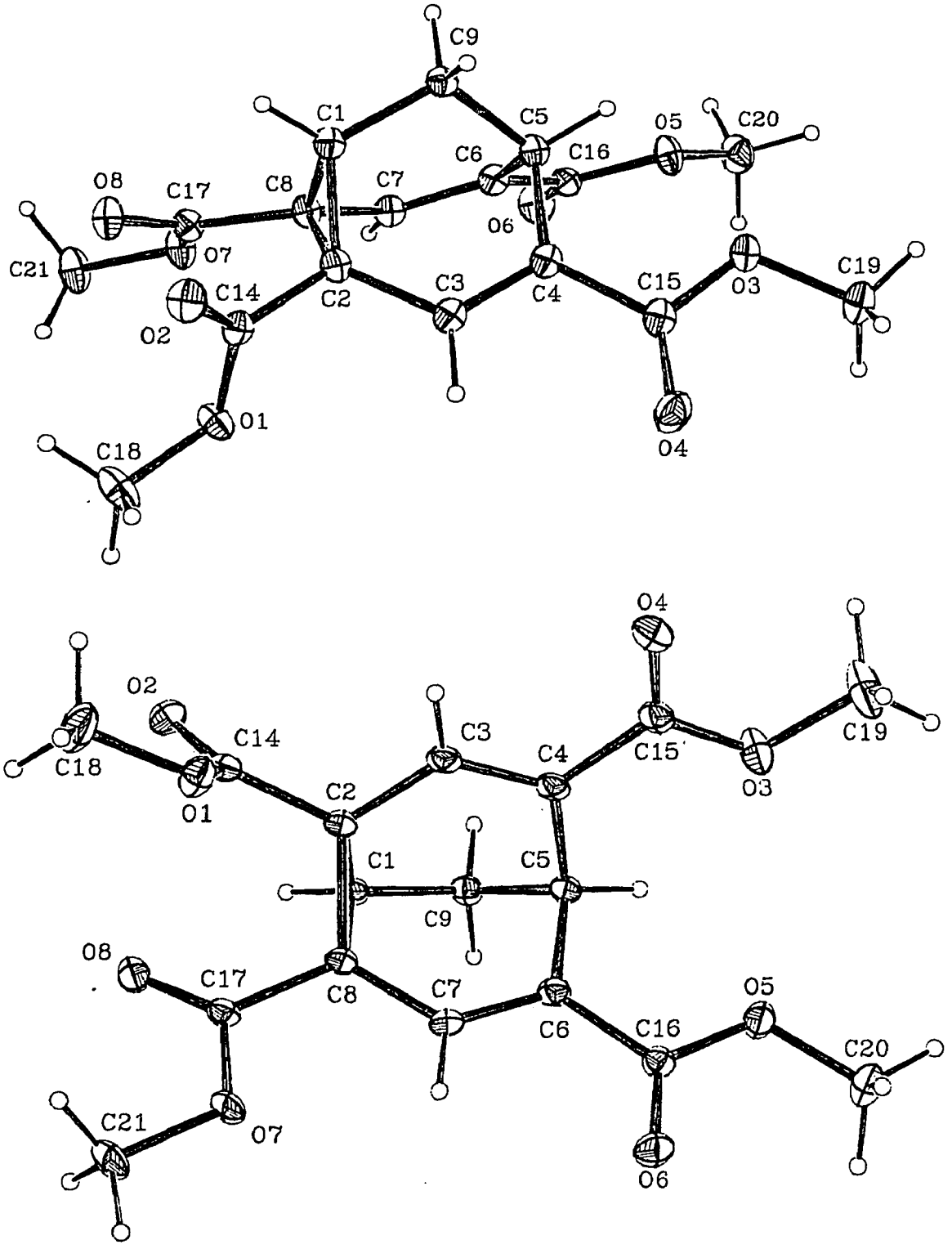


Figure 4–9. *ORTEP* drawings of barbaralane-$(COOMe)_4$ at **115 K** with 50% thermal ellipsoids.

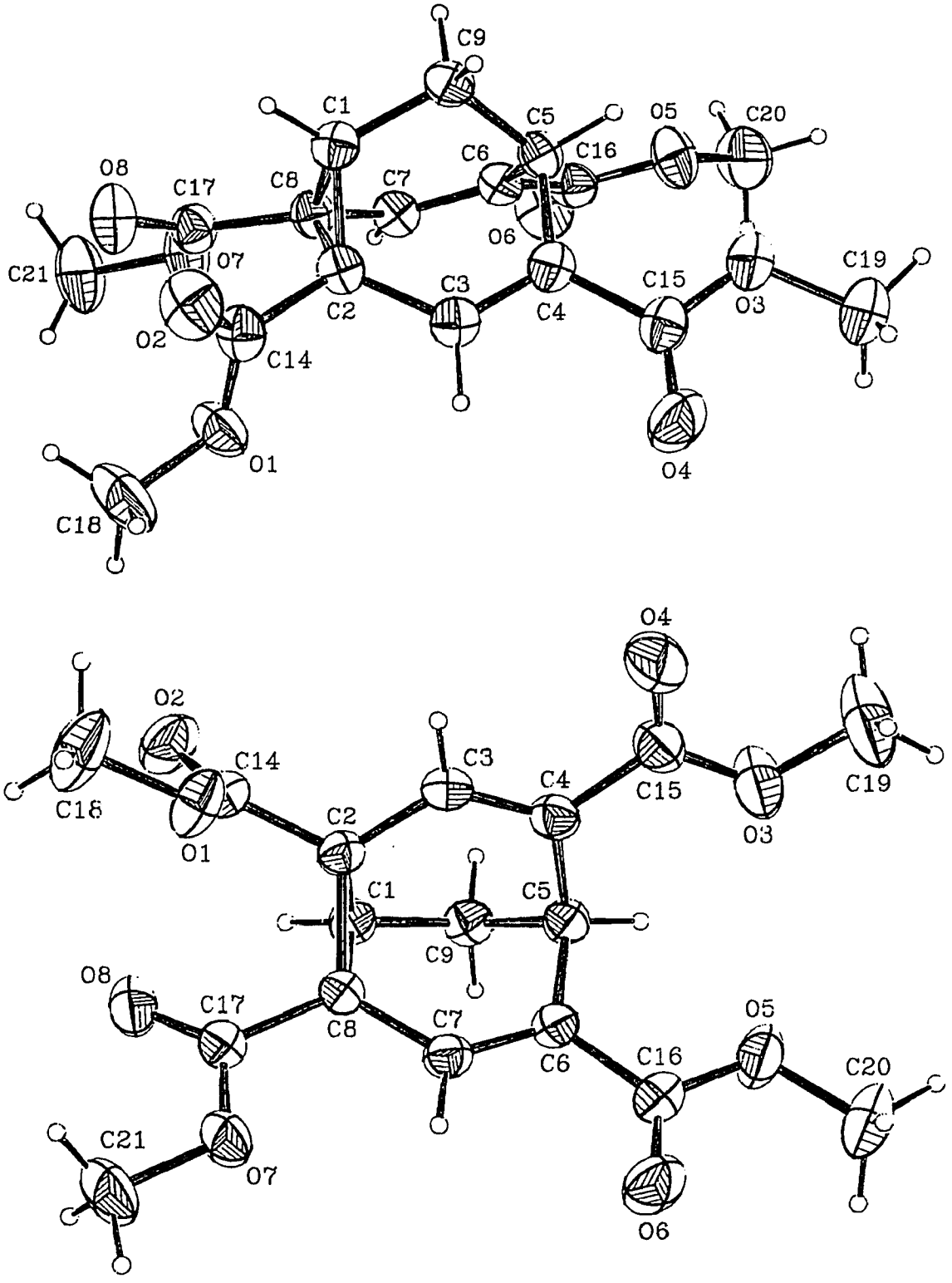
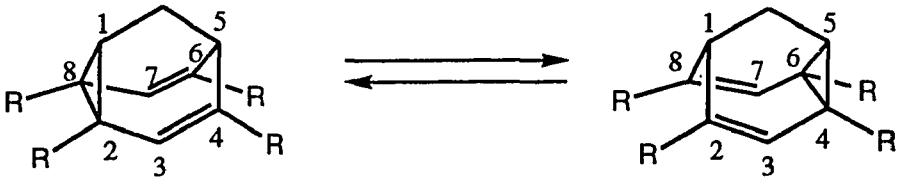


Figure 4–10. *ORTEP* drawings of barbaralane-$(COOMe)_4$ at **295 K** with 50% thermal ellipsoids.

Up to now, derivatives of barbaralane have not been fruitful in the search for neutral homoaromatic compounds in the solid state. In solution, however, the proton and ^{13}C NMR spectra (Figure 4–11) of 2,4,6,8-tetracarbomethoxybarbaralane at room temperature are consistent with a rapidly equilibrating system:



R = $COOCH_3$
2,4,6,8-Tetracarbo-methoxybarbaralane

R = $COOCH_3$
2,4,6,8-Tetracarbo-methoxybarbaralane

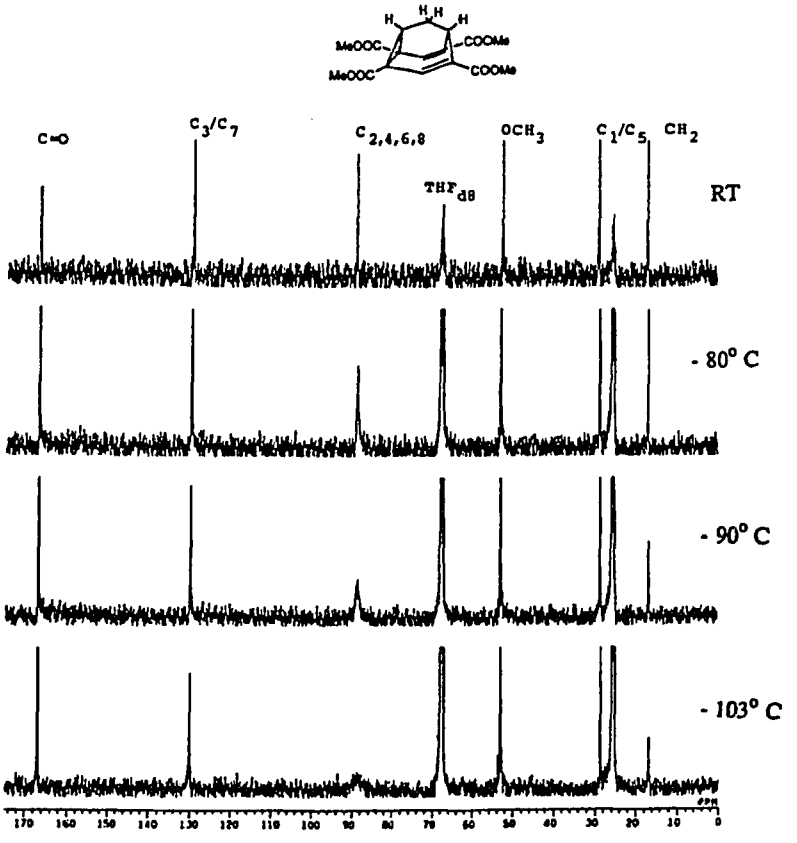


Figure 4–11. Variable temperature solution ^{13}C NMR spectra of 2,4,6,8-tetra-carbomethoxybarbaralane.

The activation energy of barbaralane-$(COOMe)_4$ in solution is 6.2 kcal/mole, which is 1.6 kcal smaller than its parent compound, barbaralane.

The solid-state CP-MAS ^{13}C NMR spectra in Figures 4–12 and 13 clearly show that barbaralane-$(COOMe)_4$ has a static structure with separate cyclopropyl and olefinic carbons.

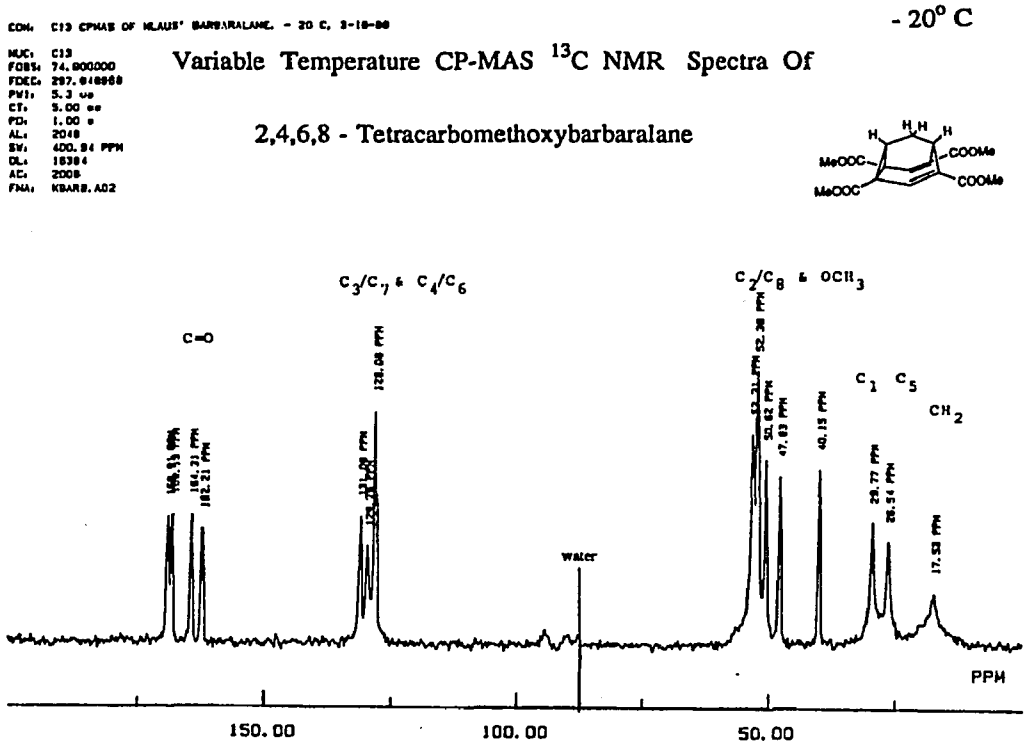


Figure 4–12. CP-MAS ^{13}C NMR spectrum of 2,4,6,8-tetracarbomethoxybarbaralane at –20 °C.

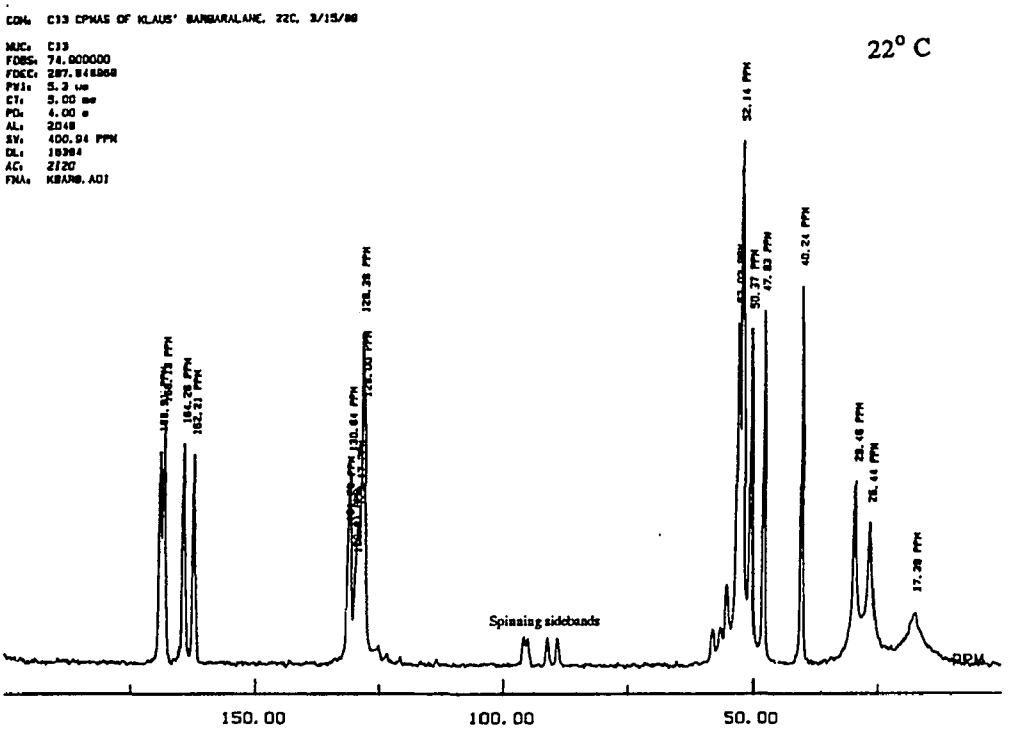


Figure 4–13. CP-MAS ^{13}C NMR spectrum of 2,4,6,8-tetracarbomethoxybarbaralane at 22 °C.

In solution, barbaralane-$(COOMe)_4$ undergoes Cope rearrangement so rapidly that an averaged carbonyl stretching frequency appears at 1725 cm^{-1} in Figure 4–14.

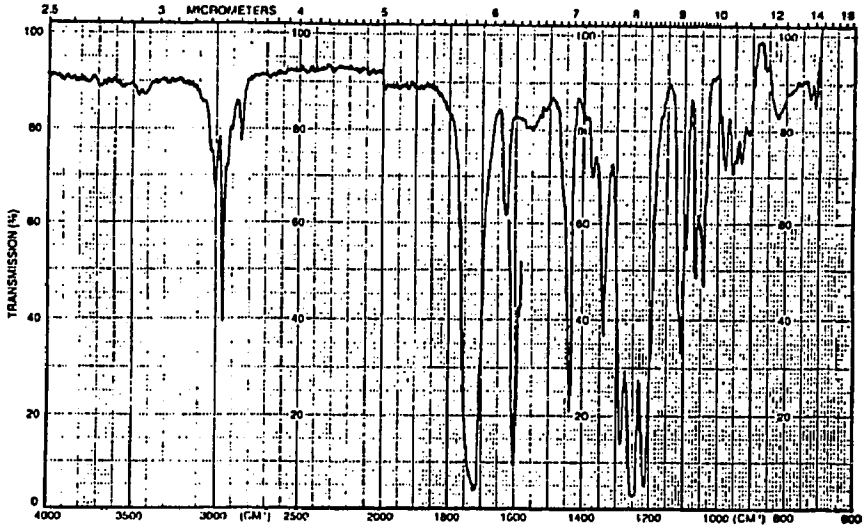


Figure 4–14. IR spectrum of 2,4,6,8-tetracarbomethoxybarbaralane in CCl_4 at room temperature

The solid-state IR spectra of barbaralane-$(COOMe)_4$ are shown in Figures 4–15, 16, and 17. The two carbonyl bands in Figure 4–15 indicate the presence of two types of ester groups, namely, cyclopropane and olefinic esters. In the high resolution IR spectrum in Figure 4–16, three carbonyl IR bands appear, corresponding to the three different orientations of the ester groups as seen in the *ORTEP* drawings of Figures 4–9 and 10.

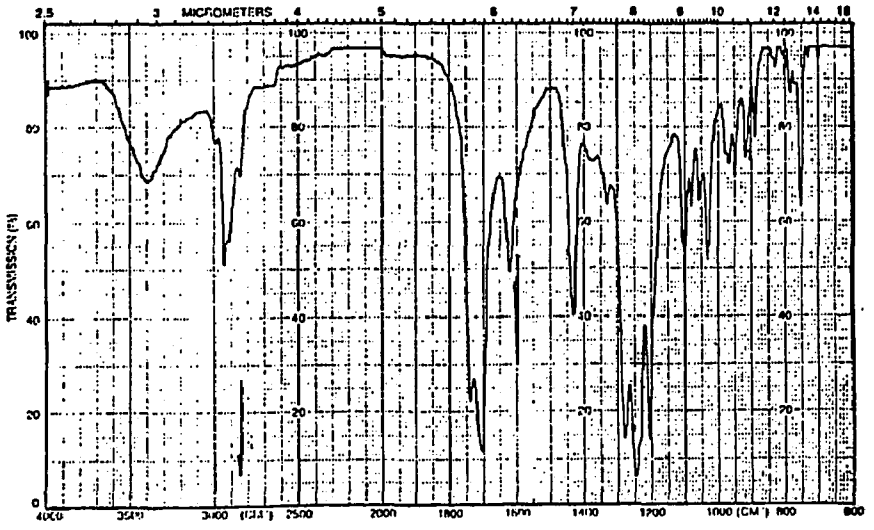


Figure 4–15. Solid-state (KBr pellets) IR spectrum of 2,4,6,8-tetracarbomethoxy-barbaralane at room temperature (Perkin Elmer 1310 spectrophotometer).

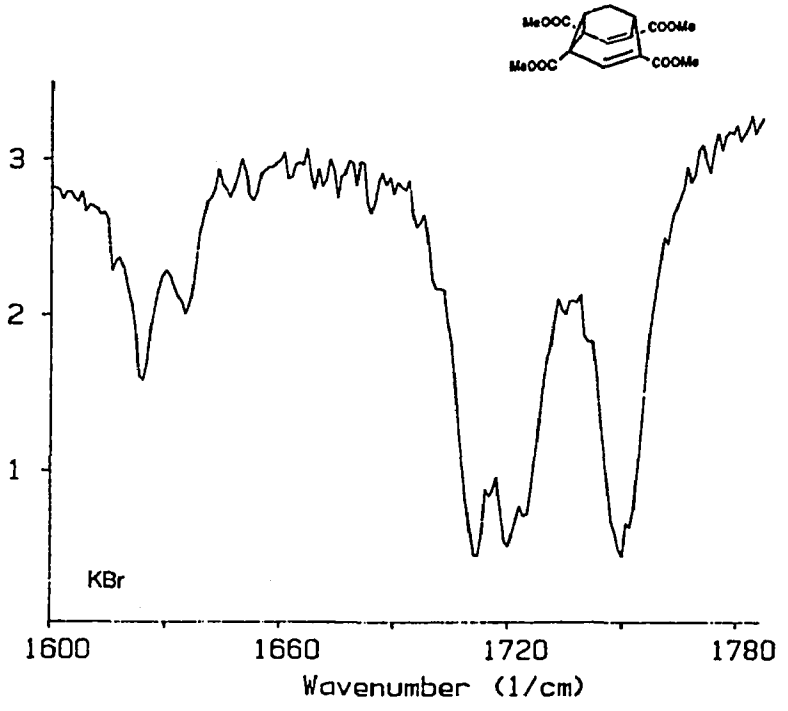
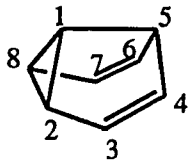


Figure 4–16. High resolution solid-state FT-IR spectrum of 2,4,6,8-tetracarbomethoxy-barbaralane at room temperature (Beckman 4240 spectrophotometer).

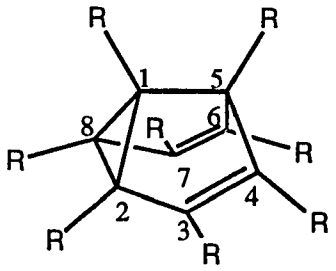
4.2 OCTACARBOMETHOXYSEMIBULLVALENE

If all the eight hydrogen atoms in semibullvalene



Tricyclo[3.3.0.0^{2,8}]octa-3,6-diene
(Semibullvalene)

are replaced with eight methylester groups, we have the compound **octacarbomethoxysemibullvalene** or simply Sb-(COOMe)$_8$.[1]



R = $COOCH_3$
Octacarbomethoxysemibullvalene
[Sb-(COOMe)$_8$]

This compound crystallized in the monoclinic crystal system and centric space group $P2_1/n$ with four molecules in the unit cell or one molecule in the asymmetric unit. Relevant X-ray crystal data information are listed in Table 4–5.

Table 4–5. X-ray Crystal Data for Sb-(COOMe)$_8$ at Five Temperatures

	115 K	**153 K**	**181 K**
Formula	$C_{24}H_{24}O_{16}$	$C_{24}H_{24}O_{16}$	$C_{24}H_{24}O_{16}$
Formula weight	568.45	568.45	568.45
Melting point (°C)	162–163.2	162–163.2	162–163.2
Crystal size (mm)	0.10 x 0.29 x 0.35	0.10 x 0.29 x 0.35	0.10 x 0.29 x 0.35
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	10.442(3)	10.450(3)	10.455(2)
b (Å)	30.412(4)	30.469(3)	30.518(3)
c (Å)	9.407(1)	9.413(1)	9.416(1)
β (°)	116.53(1)	116.38(1)	116.26(1)
Cell volume (Å^3)	2672.5(17.8)	2685.0(18.2)	2694.4(12.2)
Z	4	4	4
d_{calc} (g cm^{-3})	1.413	1.406	1.401
μ(Cu $K\alpha$) (cm^{-1})	10.07	10.02	9.98
R	0.035	0.036	0.037
R_w	0.043	0.045	0.045

Table 4–5 (cont'd). X-ray Crystal Data for Sb-(COOMe)$_8$ at Five Temperatures

	236 K	**294 K**
Formula	$C_{24}H_{24}O_{16}$	$C_{24}H_{24}O_{16}$
Formula weight	568.45	568.45
Melting point (°C)	162–163.2	162–163.2
Crystal size (mm)	0.10 x 0.29 x 0.35	0.10 x 0.29 x 0.35
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	10.475(1)	10.498(1)
b (Å)	30.616(2)	30.719(1)
c (Å)	9.426(1)	9.440(1)
β (°)	116.05(1)	115.885(1)
Cell volume (Å^3)	2716.0(7.7)	2738.8(6.5)
Z	4	4
d_{calc} (g cm^{-3})	1.390	1.379
μ(Cu $K\alpha$) (cm^{-1})	9.90	9.82
R	0.040	0.042
R_w	0.048	0.050

The unit-cell volume changes linearly with temperature as illustrated in Figure 4–17.

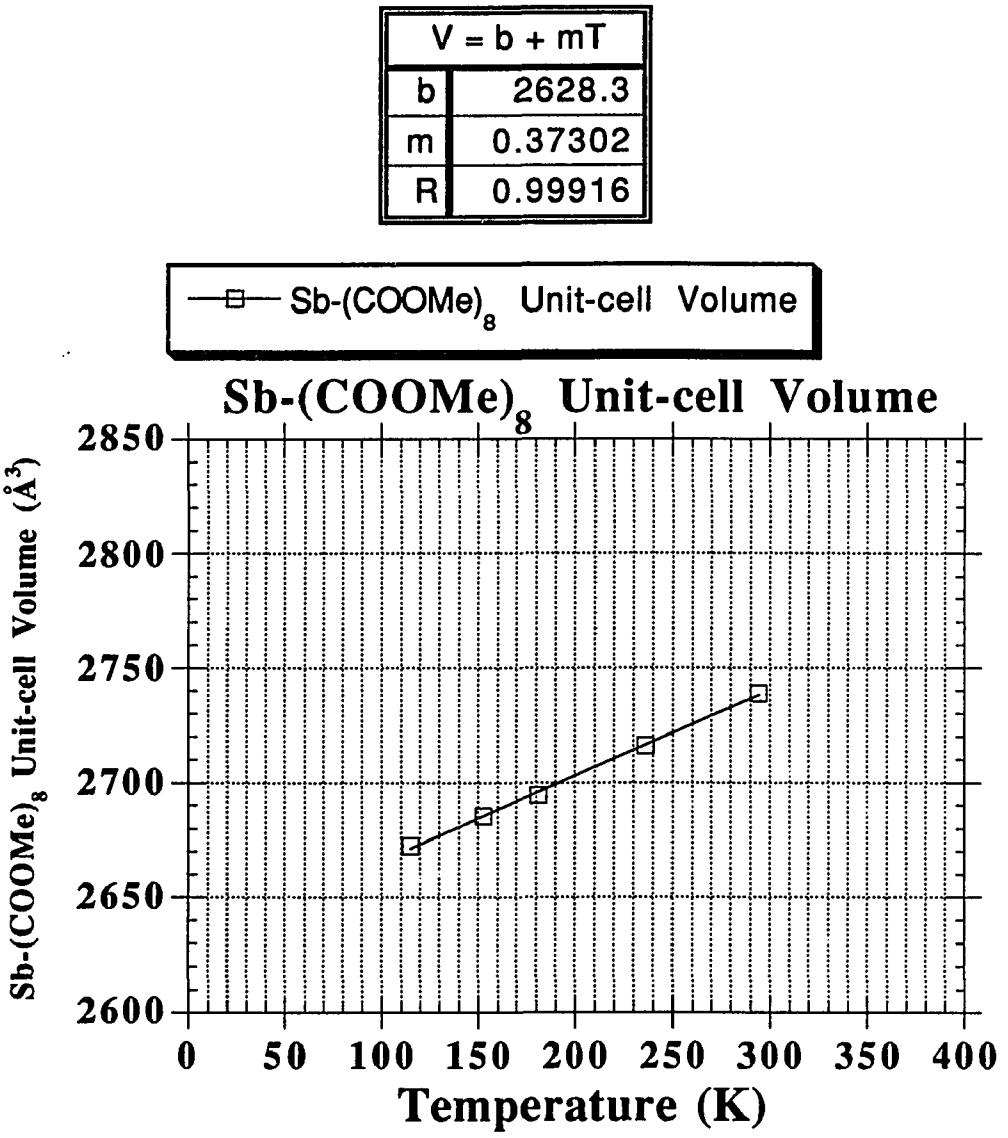


Figure 4–17. A plot of Sb-(COOMe)8 unit-cell volume versus temperature.

According to the slope in Figure 4–17, the unit-cell volume of Sb-(COOMe)8 expands at the rate of 3.7 $Å^3$ for every 10 °C rise in temperature for four molecules (160 non-H's and 96 H's) in the unit cell. As the volume of the unit cell expands, the density in Figure 4–18 decreases.

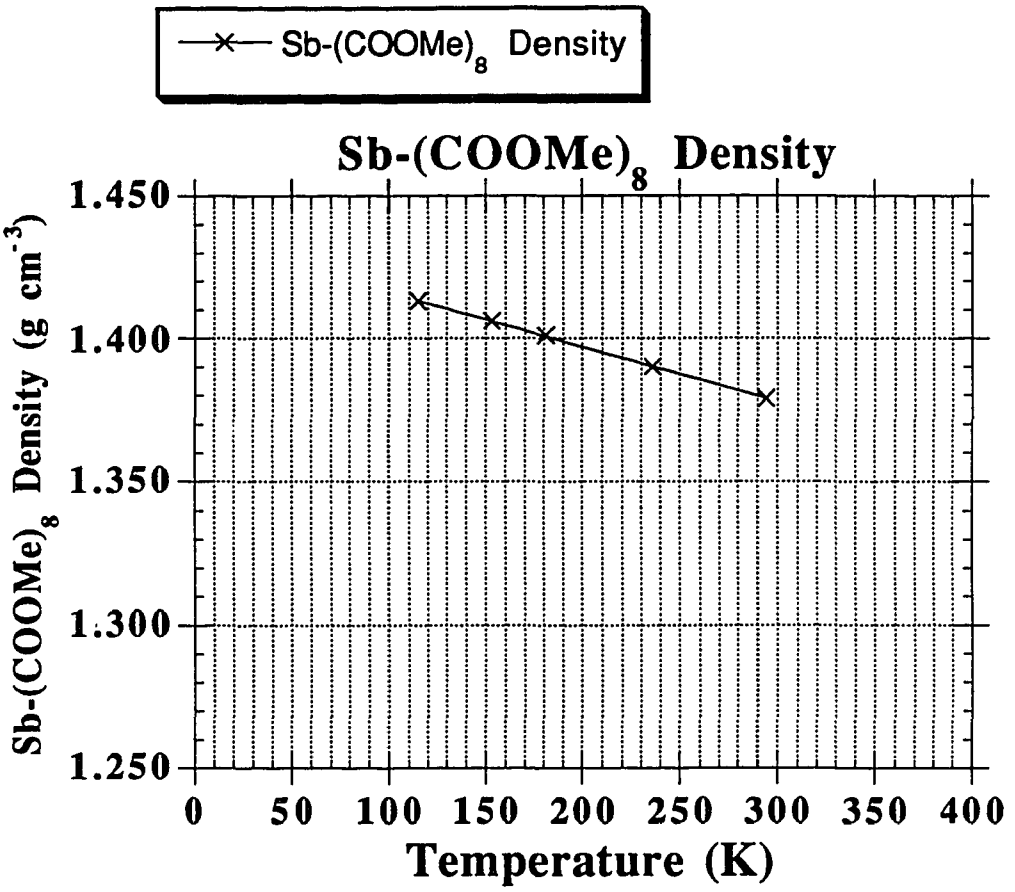


Figure 4–18. A plot of Sb-(COOMe)$_8$ density versus temperature.

The structure of Sb-(COOMe)$_8$, like barbaralane-(COOMe)$_4$, also changes very little from 115 K to room temperature. Some minute changes in the structure of Sb-(COOMe)$_8$, begin to emerge in this temperature range. From Table 4–6, the cyclopropyl bond distance C2—C8 elongates from 1.602 Å at 115 K to 1.614 Å at 294 K, while the interatomic distance C4—C6 becomes shorter (from 2.385 to 2.374 Å) as the temperature increases. The single bonds C2—C3 and C7—C8 become shorter as the temperature increases to compensate for the lengthening of the double bonds C3—C4 and C6—C7.

Table 4–6. Selected Interatomic Distances (Å) in Sb-$(COOMe)_8$ at Five Temperatures.

	115 K	153 K	181 K	236 K	294 K
C1—C2	1.503(3)	1.504(3)	1.507(3)	1.507(3)	1.504(4)
C1—C5	1.562(2)	1.559(2)	1.560(2)	1.559(3)	1.557(3)
C1—C8	1.504(3)	1.507(4)	1.504(4)	1.505(4)	1.505(4)
C2—C3	1.481(2)	1.486(2)	1.482(2)	1.482(3)	1.478(3)
C2—C8	1.602(3)	1.602(3)	1.600(3)	1.607(3)	1.614(4)
C3—C4	1.341(3)	1.340(3)	1.336(3)	1.340(3)	1.344(4)
C3—C7	3.079(3)	3.080(3)	3.080(3)	3.080(3)	3.078(4)
C4—C5	1.529(3)	1.531(3)	1.532(3)	1.530(3)	1.527(3)
C4—C6	2.385(3)	2.388(3)	2.385(3)	2.382(3)	2.374(4)
C5—C6	1.539(3)	1.539(3)	1.538(3)	1.544(4)	1.541(4)
C6—C7	1.338(3)	1.337(3)	1.336(3)	1.342(3)	1.344(4)
C7—C8	1.484(3)	1.483(3)	1.485(3)	1.484(3)	1.482(3)
C2—C3 + C3—C4	2.822	2.826	2.818	2.822	2.822
C6—C7 + C7—C8	2.822	2.820	2.821	2.826	2.826
C2—C8 + C4—C6	3.987	3.990	3.985	3.989	3.988

To compare distinguishing features of interatomic distances of ring atoms in Sb-$(COOMe)_8$, they are plotted together against temperature in Figure 4–19, but congestion results. To clear up this congestion in the plots of interatomic distances, we will also display them in separate sets to bring out more clearly the changes which take place in the semibullvalene ring system as the temperature is varied; often, we will even resort to a change of scale to emphasize or to show more clearly those changes which accompany or occur with temperature variation.

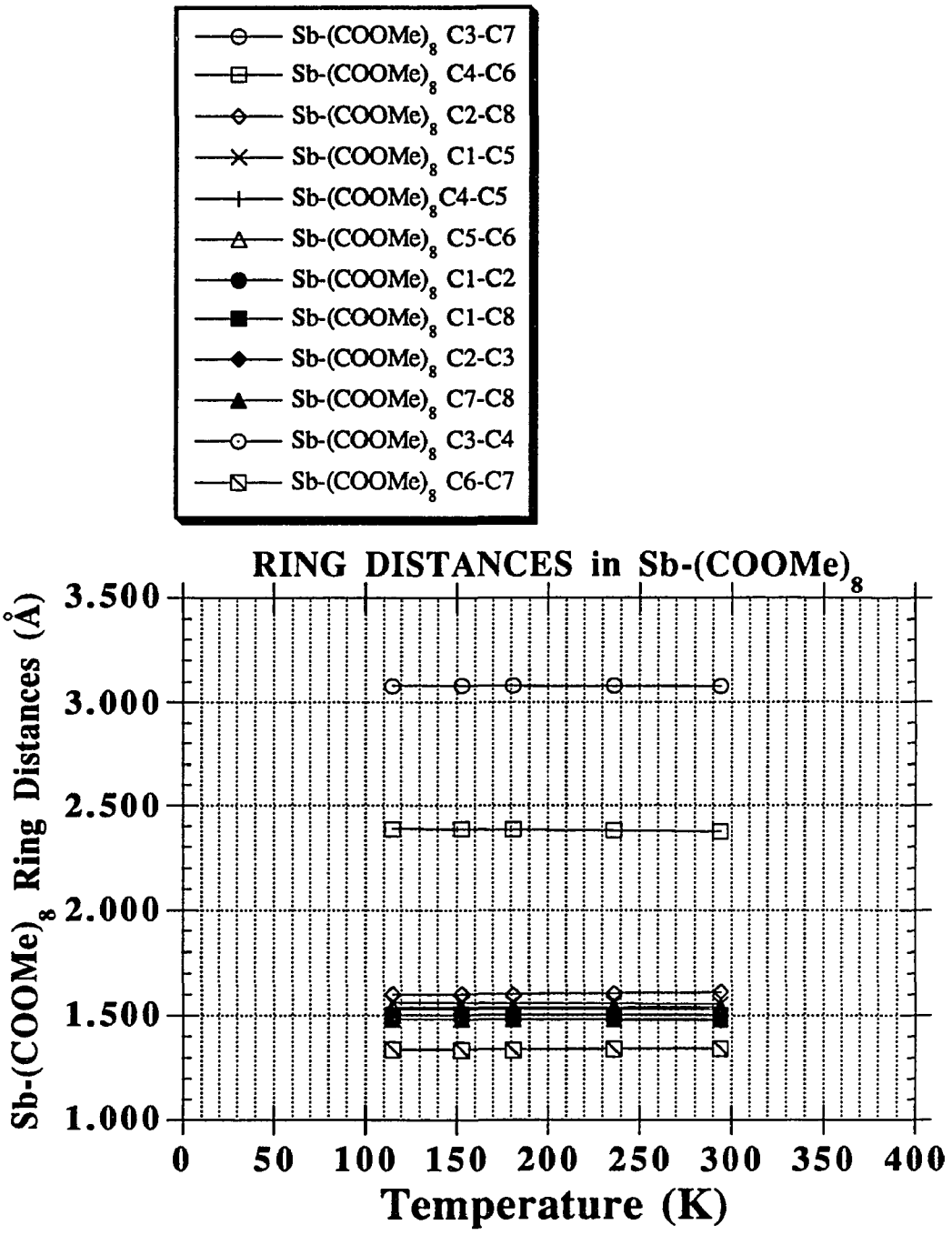


Figure 4–19. Plots of selected interatomic distances in the ring of Sb-(COOMe)$_8$ versus temperature.

To clear up the congestion in Figure 4–19, we will display separately plots of interatomic distances. In all these six compounds, the interatomic distances, C1—C5 and C3—C7, do not change at all as the temperature is varied, as shown in Figure 4–20.

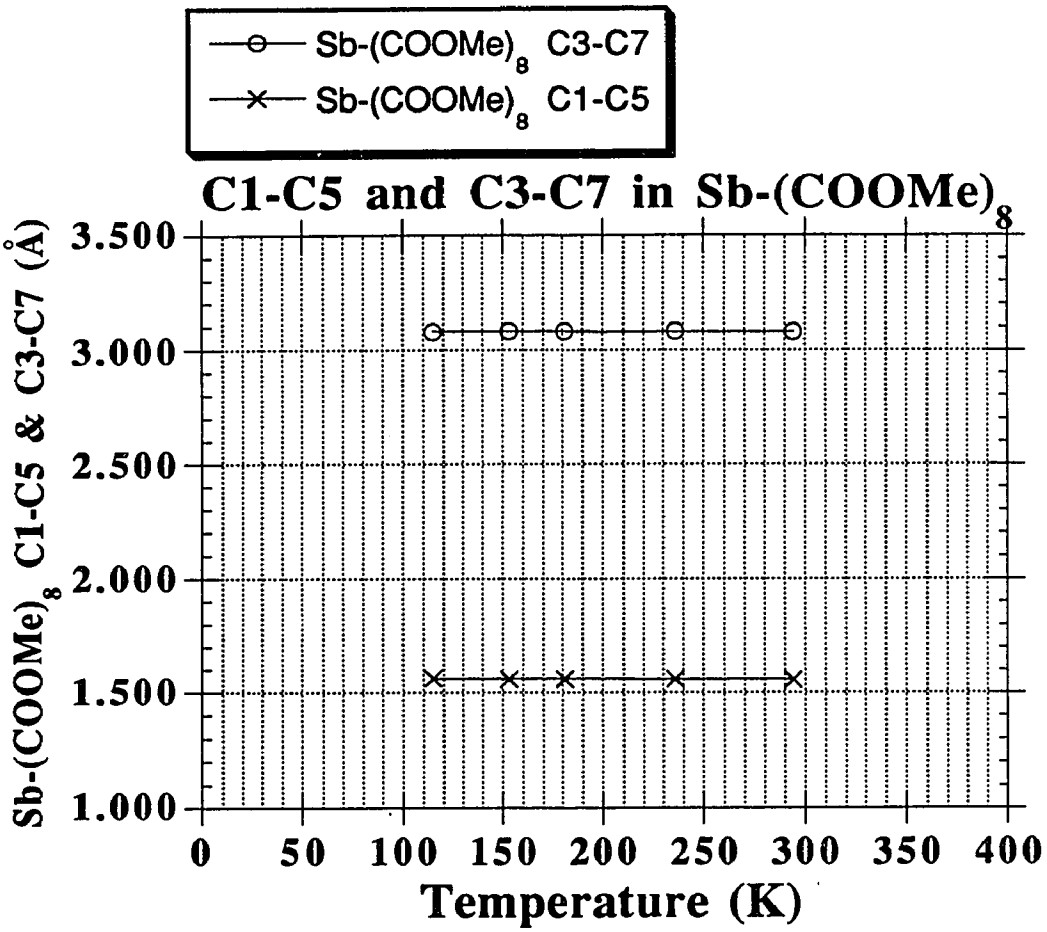


Figure 4–20. Plots of C1—C5 and C3—C7 distances in Sb-(COOMe)$_8$ versus temperature.

Figures 4–21 and 23 illustrate the shortening of the C2—C3 and C7—C8 bonds and concomitant lengthening of the C3—C4 and C6—C7 bonds.

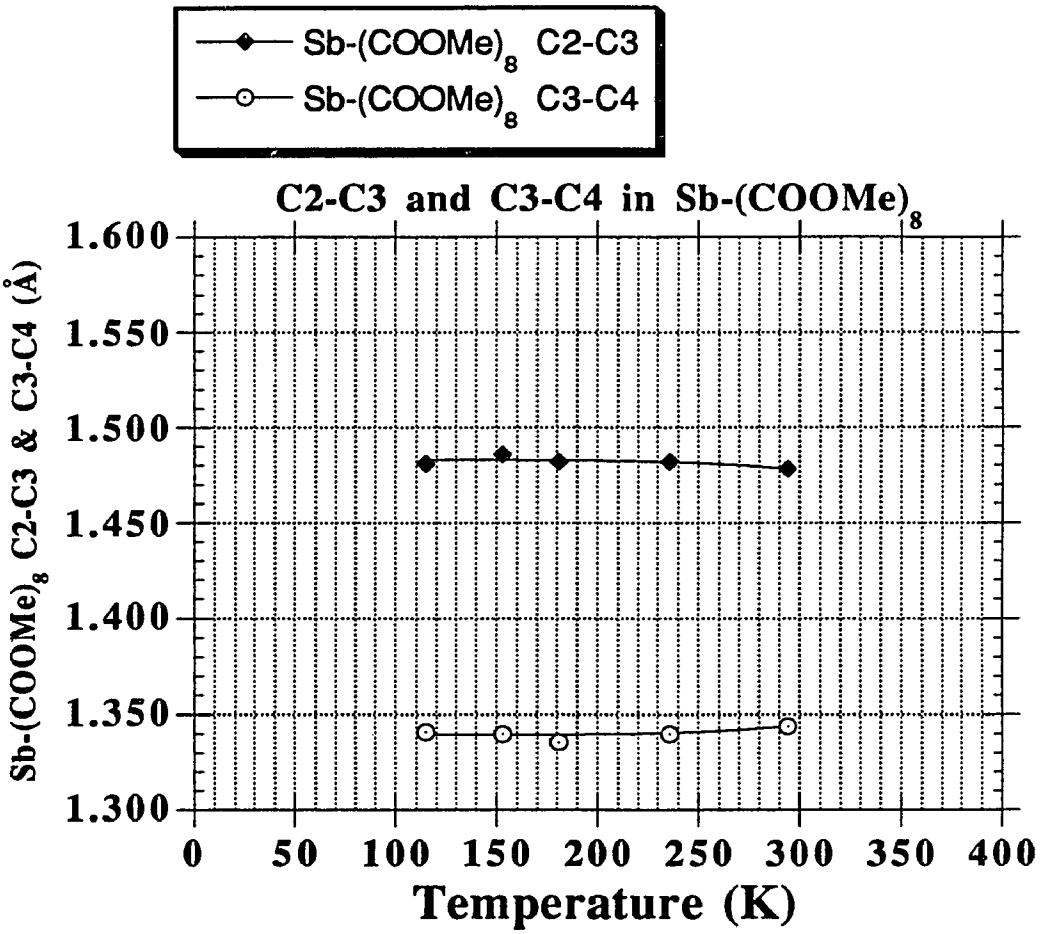


Figure 4–21. Plots of C2—C3 and C3—C4 distances in Sb-(COOMe)8 versus temperature.

Even though the bond distance C2—C3 lengthens and C3—C4 becomes shorter as the temperature increases the sum of these distances remains a constant throughout the temperature range as evident in Figure 4–22.

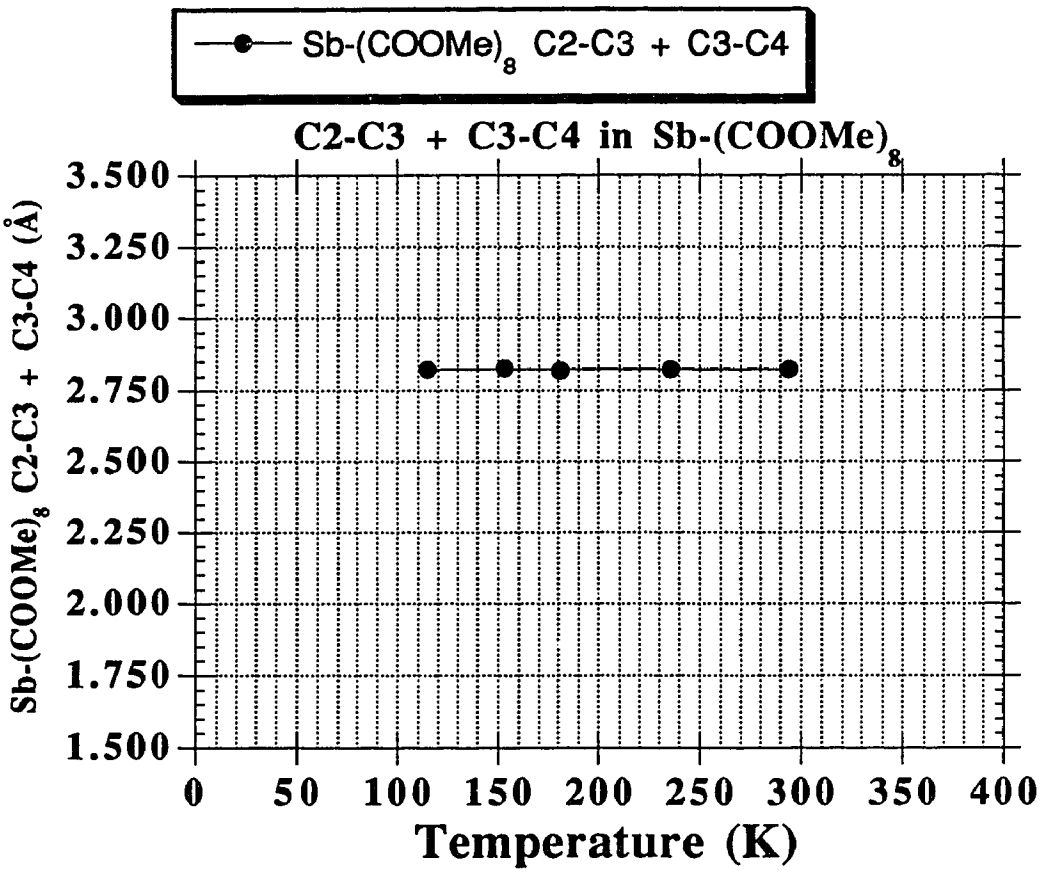


Figure 4–22. A plot of the sum of the distances C2—C3 and C3—C4 in Sb-(COOMe)$_8$ versus temperature.

An analogous argument also holds for the behavior of C6—C7 and C7—C8. As C6—C7 becomes longer, C7—C8 becomes shorter with increasing temperature (Figure 4–23.

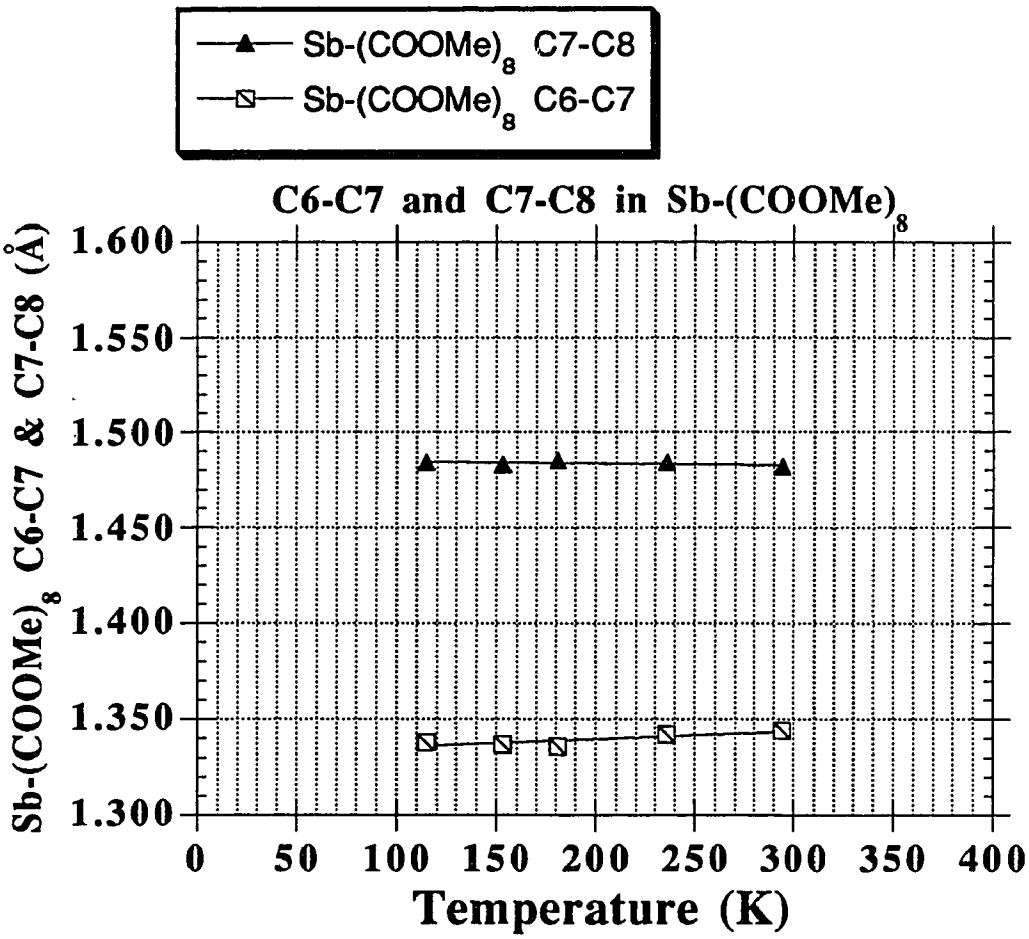


Figure 4–23. Plots of C6—C7 and C7—C8 distances in Sb-(COOMe)$_8$ versus temperature.

Again, the sum of C6—C7 and C7—C8 distances stays constant in the same temperature range (Figure 4–24).

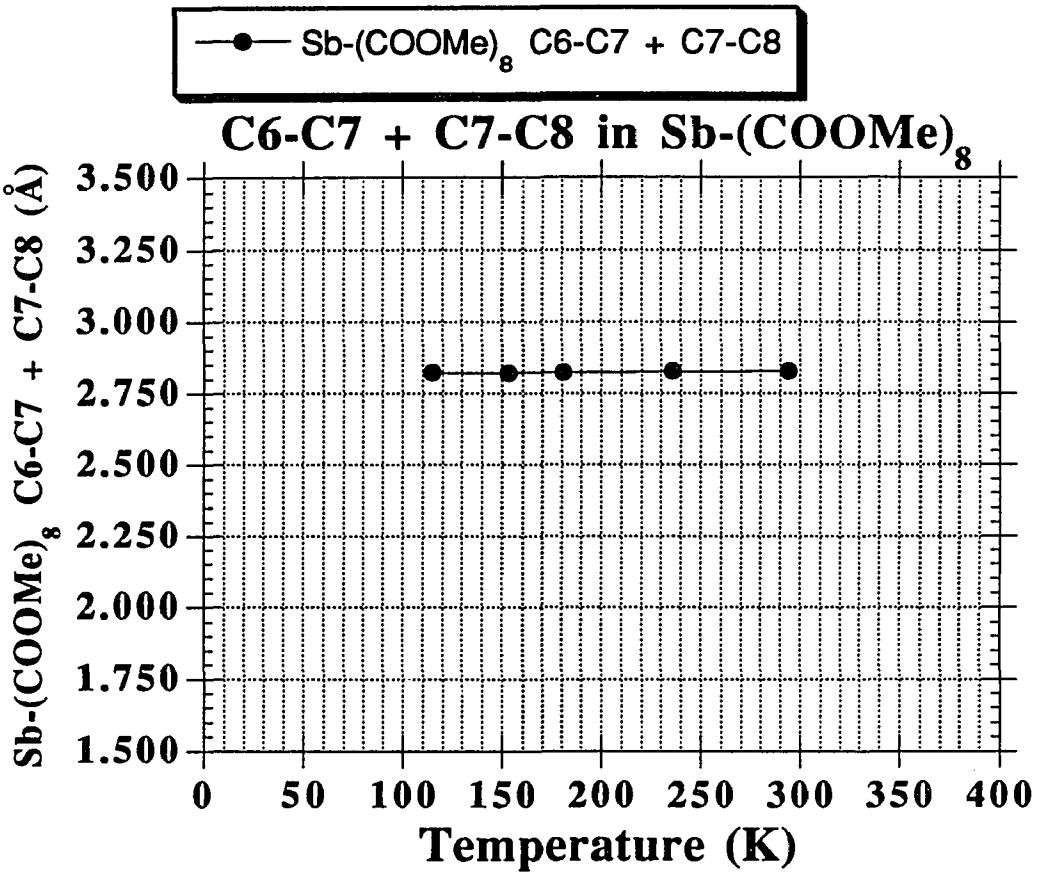


Figure 4–24. A plot of the sum of the distances C6—C7 and C7—C8 in Sb-(COOMe)$_8$ versus temperature.

The interatomic distances C2—C8 and C4—C6 (Figure 4–25) also follow a trend of lengthening and shortening, similar to C2—C3 and C3—C4.

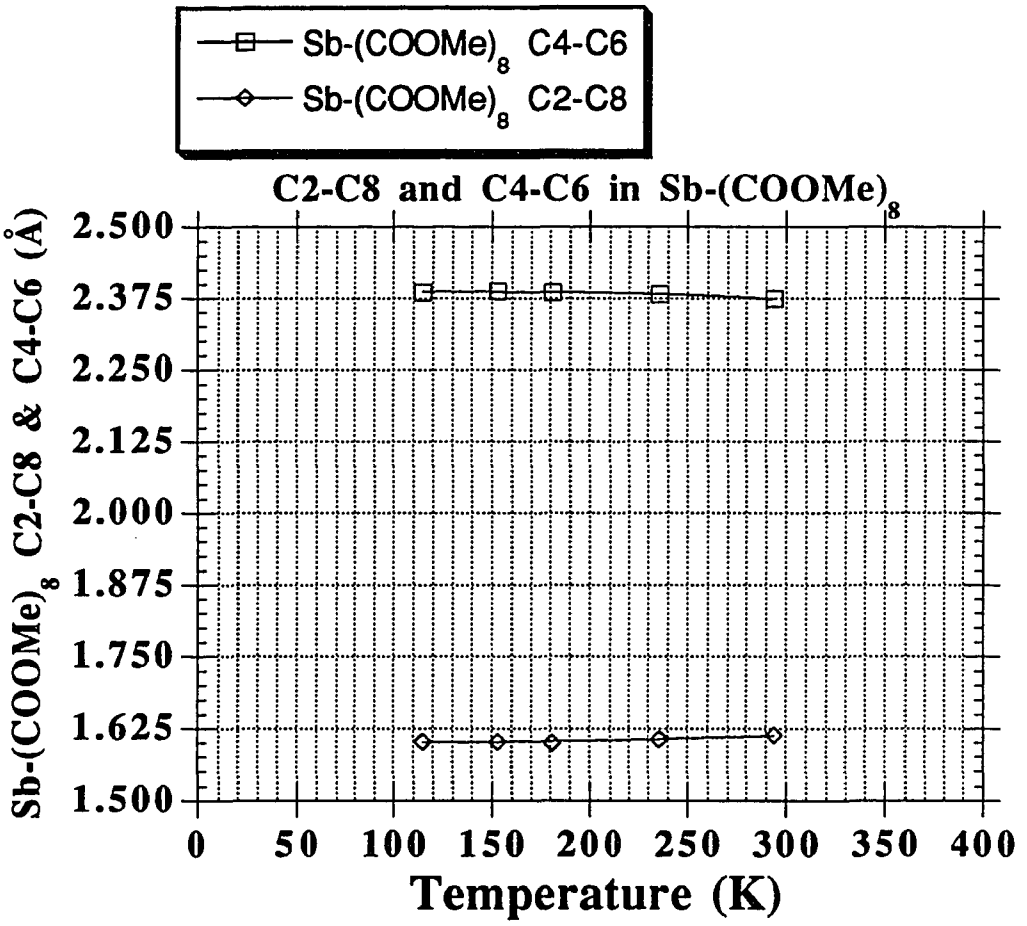


Figure 4–25. Plots of C2—C8 and C4—C6 distances in Sb-(COOMe)$_8$ versus temperature.

Again, the sum of C2—C8 and C4—C6 distances is constant in the same temperature range (Figure 4–26).

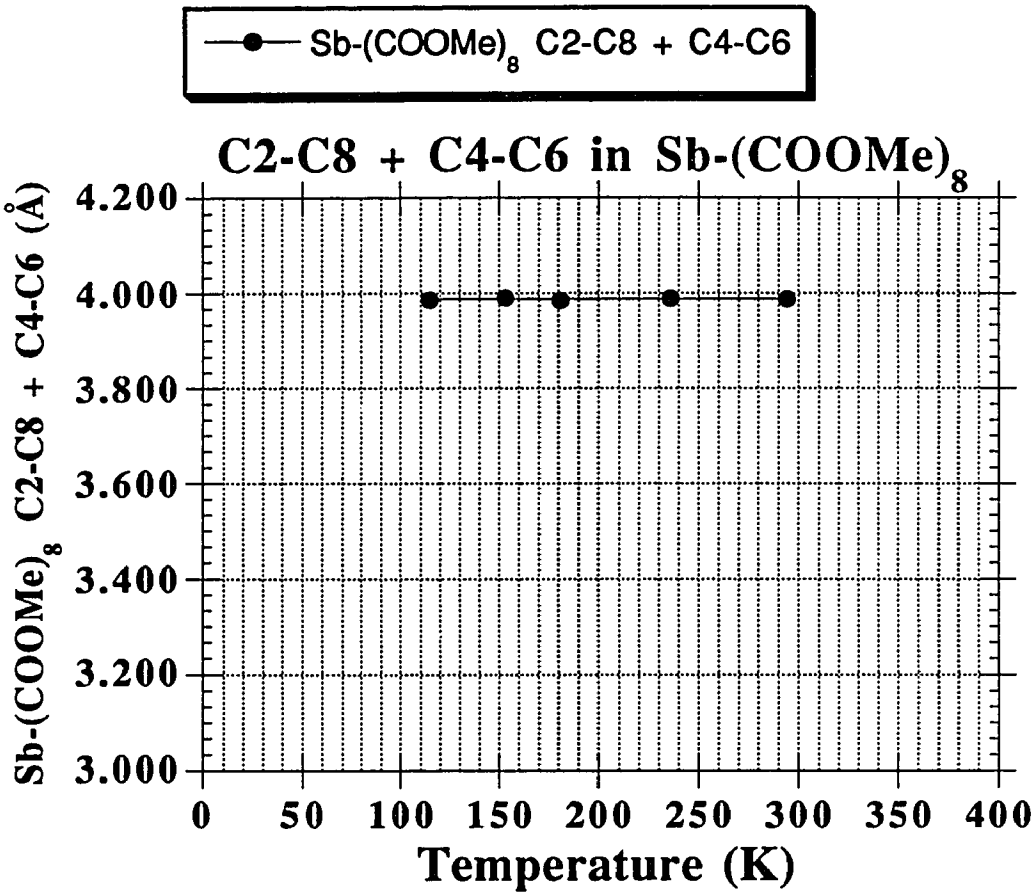


Figure 4–26. A plot of the sum of the distances C2—C8 and C4—C6 in Sb-(COOMe)$_8$ versus temperature.

Selected angles in the semibullvalene ring of Sb-$(COOMe)_8$ are listed in Table 4–7.

Table 4–7. Selected Interatomic Angles (°) in the Ring of Sb-$(COOMe)_8$ at Five Temperatures.

	115 K	153 K	181 K	236 K	294 K
C2—C1—C5	104.5(1)	104.4(1)	104.4(1)	104.5(2)	104.7(2)
C2—C1—C8	64.4(1)	64.3(2)	64.2(2)	64.5(2)	64.9(2)
C5—C1—C8	105.2(2)	105.1(2)	105.3(2)	105.3(2)	105.4(2)
C1—C2—C3	106.8(2)	106.7(2)	106.6(2)	106.7(2)	106.6(2)
C1—C2—C8	57.9(1)	58.0(1)	57.8(1)	57.7(2)	57.6(2)
C3—C2—C8	119.8(2)	120.0(2)	120.1(2)	119.8(2)	119.6(2)
C2—C3—C4	111.7(2)	111.7(2)	111.9(2)	111.8(2)	111.8(2)
C3—C4—C5	110.0(1)	109.9(2)	110.0(2)	110.0(2)	109.9(2)
C5—C4—C6	39.1(1)	39.1(1)	39.1(1)	39.4(1)	39.5(1)
C1—C5—C4	103.0(1)	103.3(2)	103.1(2)	103.3(2)	103.2(2)
C1—C5—C6	102.4(2)	102.5(2)	102.3(2)	102.6(2)	102.6(2)
C4—C5—C6	102.0(2)	102.1(2)	101.9(2)	101.6(2)	101.4(2)
C4—C6—C5	38.8(1)	38.8(1)	39.0(1)	39.0(1)	39.1(1)
C5—C6—C7	110.5(2)	110.3(2)	110.5(2)	110.0(2)	110.1(2)
C6—C7—C8	111.9(2)	112.1(2)	112.0(2)	112.1(2)	112.1(3)
C1—C8—C2	57.8(1)	57.8(1)	58.0(1)	57.8(2)	57.5(2)
C1—C8—C7	106.1(2)	106.1(2)	106.0(2)	106.1(2)	106.1(2)
C2—C8—C7	119.9(1)	119.7(1)	119.7(1)	119.8(2)	119.6(2)
$(\alpha+\beta)/2$[a]	83.2	83.2	83.1	83.1	83.2
C3—M[b]—C7	86.6	86.6	86.7	86.6	86.6

[a] α = C2—C1—C8, β = C4—C5—C6.
[b] M = midpoint between C1 and C5 bond.

The angles, C2—C1—C8 and C4—C5—C6, in Figure 4–27 change approximately by 0.5 ° as C2—C8 and C4—C6 vary.

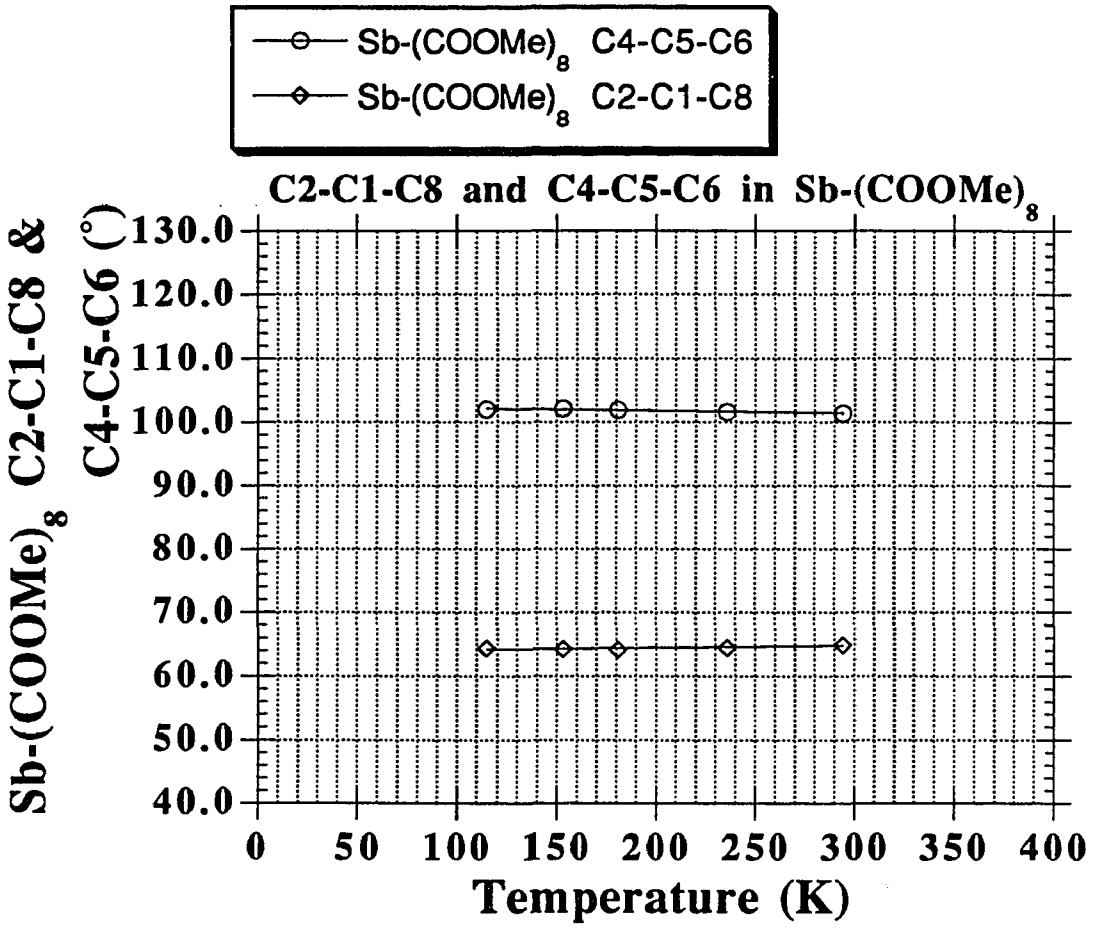


Figure 4–27. Plots of the angles C2—C1—C8 and C4—C5—C6 in Sb-(COOMe)$_8$ versus temperature.

Another angle, C3—M—C7, where M is the midpoint between C1 and C5, is of interest because it remains invariant in spite of the changes in the interatomic distances C2—C8 and C4—C6. The angle from the average of C2—C1—C8 and C4—C5—C6 also remains constant with temperature (Figure 28). The fact that both angles are nearly the same means that the two five-membered rings are almost planar.

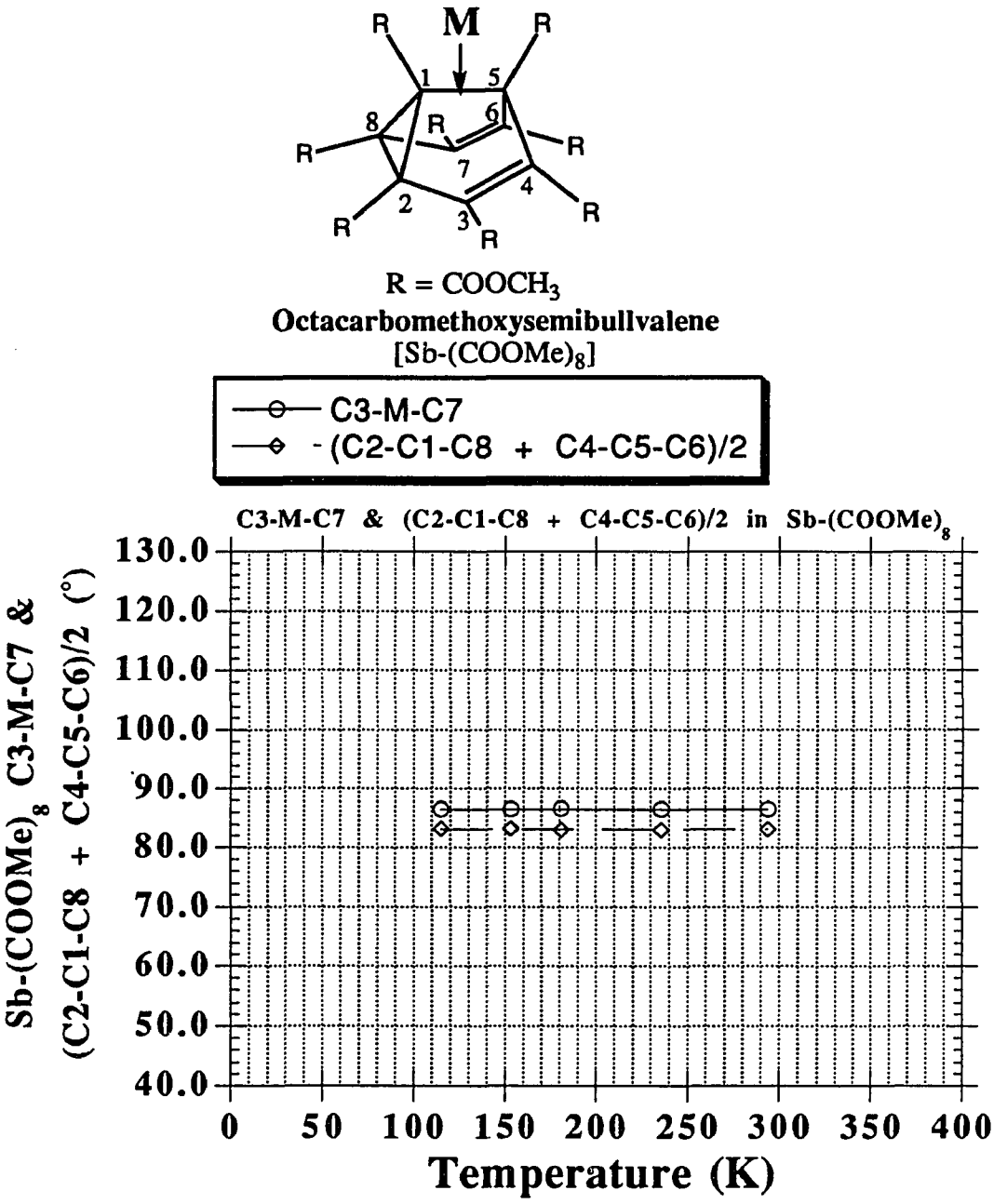


Figure 4–28. Plots of the angle C3—M—C7 (M = midpoint between C1 and C5) and the average angle of C2—C1—C8 and C4—C5—C6 in Sb-(COOMe)$_8$ versus temperature.

The root-mean-square amplitudes of thermal vibrations for the ring atoms in Table 4–8, Figure 4–29, and Figure 4–30 are of no help to assess the small changes which occur in the distances and angles.

Table 4–8. Selected Root-Mean-Square Amplitudes of Thermal Vibrations (Å) in the Ring of Sb-$(COOMe)_8$ at Five Temperatures.

		Min.	Int'med	Max.
115 K	C1	0.091	0.111	0.125
	C2	0.101	0.105	0.129
	C3	0.085	0.111	0.130
	C4	0.082	0.116	0.133
	C5	0.096	0.109	0.122
	C6	0.092	0.111	0.133
	C7	0.083	0.102	0.126
	C8	0.100	0.105	0.125
153 K	C1	0.108	0.128	0.136
	C2	0.116	0.125	0.152
	C3	0.110	0.126	0.144
	C4	0.104	0.127	0.145
	C5	0.115	0.128	0.137
	C6	0.112	0.126	0.147
	C7	0.105	0.125	0.139
	C8	0.111	0.127	0.142
181 K	C1	0.116	0.133	0.146
	C2	0.122	0.130	0.150
	C3	0.115	0.130	0.157
	C4	0.112	0.140	0.152
	C5	0.121	0.133	0.145
	C6	0.121	0.127	0.151
	C7	0.117	0.126	0.147
	C8	0.116	0.135	0.148
236 K	C1	0.131	0.156	0.159
	C2	0.143	0.148	0.175
	C3	0.137	0.149	0.170
	C4	0.137	0.161	0.166
	C5	0.134	0.152	0.166
	C6	0.139	0.150	0.173
	C7	0.134	0.145	0.168
	C8	0.135	0.156	0.161
294 K	C1	0.153	0.169	0.178
	C2	0.159	0.171	0.189
	C3	0.154	0.165	0.191
	C4	0.159	0.179	0.189
	C5	0.154	0.163	0.190
	C6	0.160	0.164	0.198
	C7	0.151	0.165	0.188
	C8	0.152	0.176	0.184

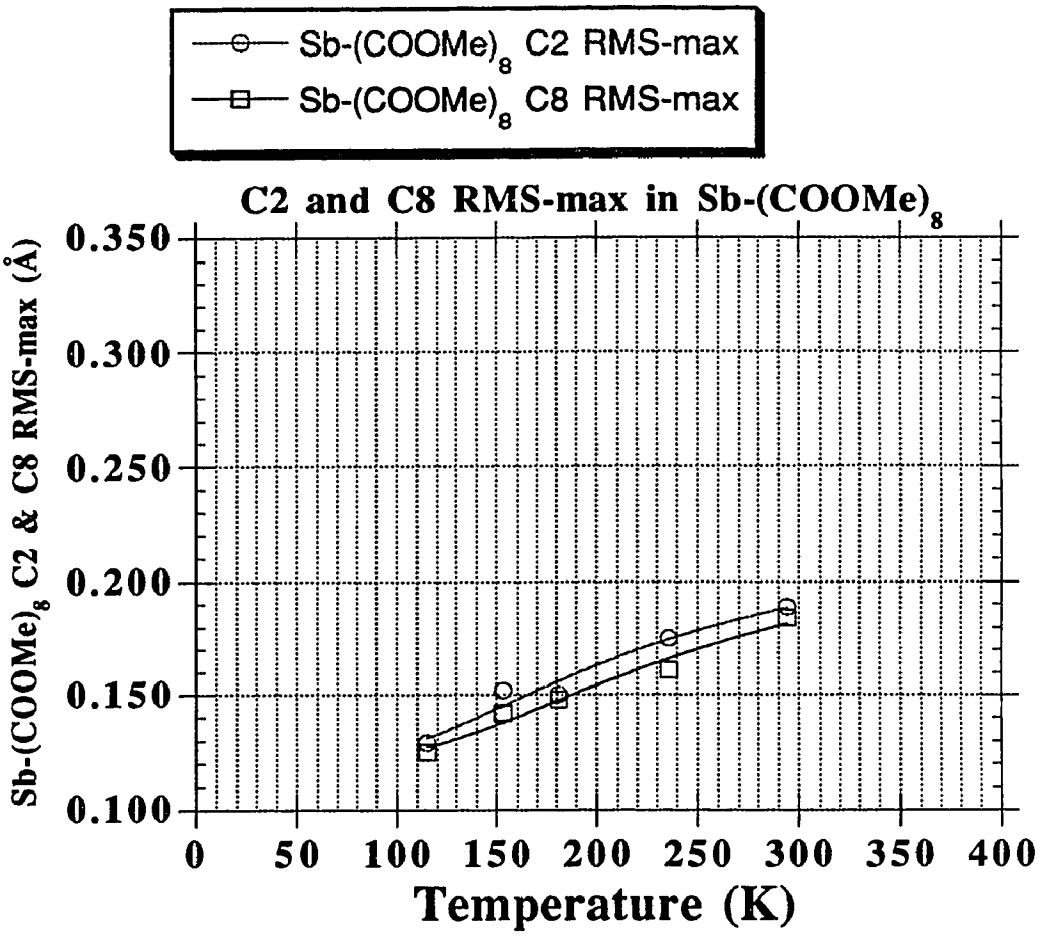


Figure 4–29. Plots of C2 RMS-max and C8 RMS-max in Sb-(COOMe)$_8$ versus temperature.

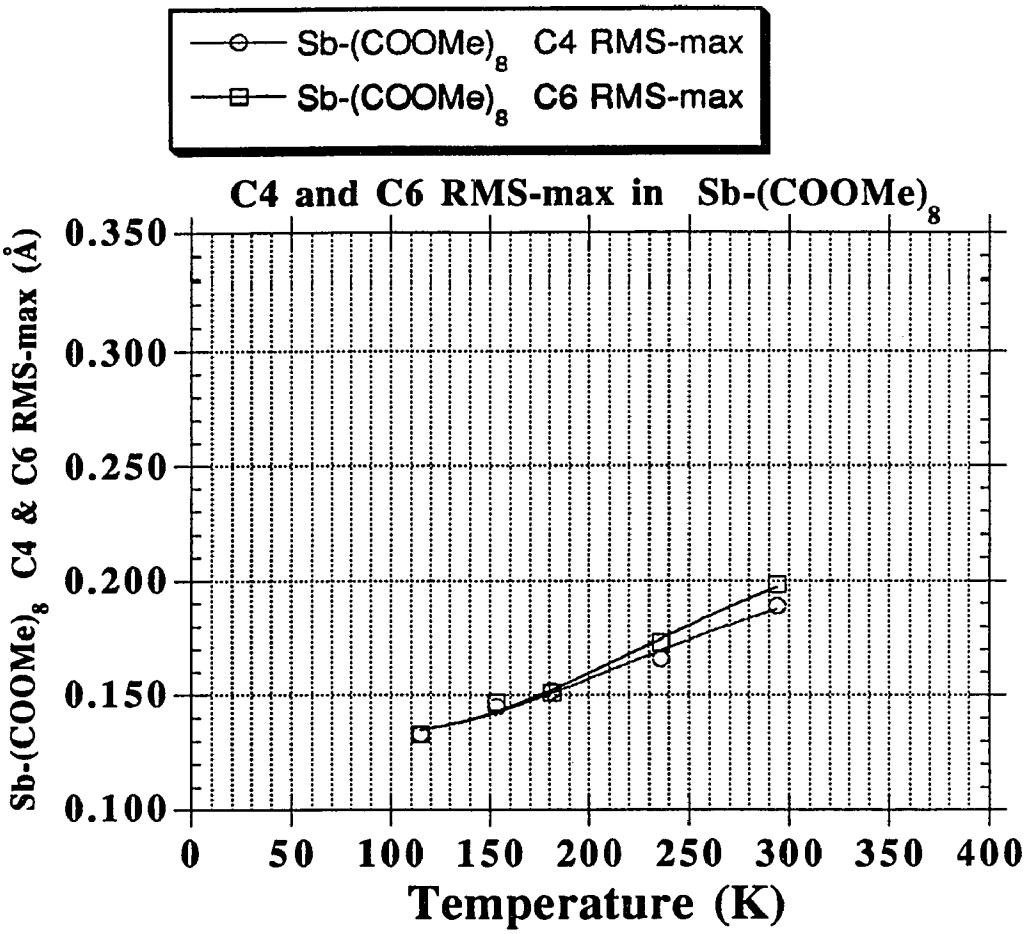


Figure 4–30. Plots of C4 RMS-max and C6 RMS-max in Sb-(COOMe)$_8$ versus temperature.

ORTEP drawings of Sb-$(COOMe)_8$ at the five temperatures are shown in the following figures:

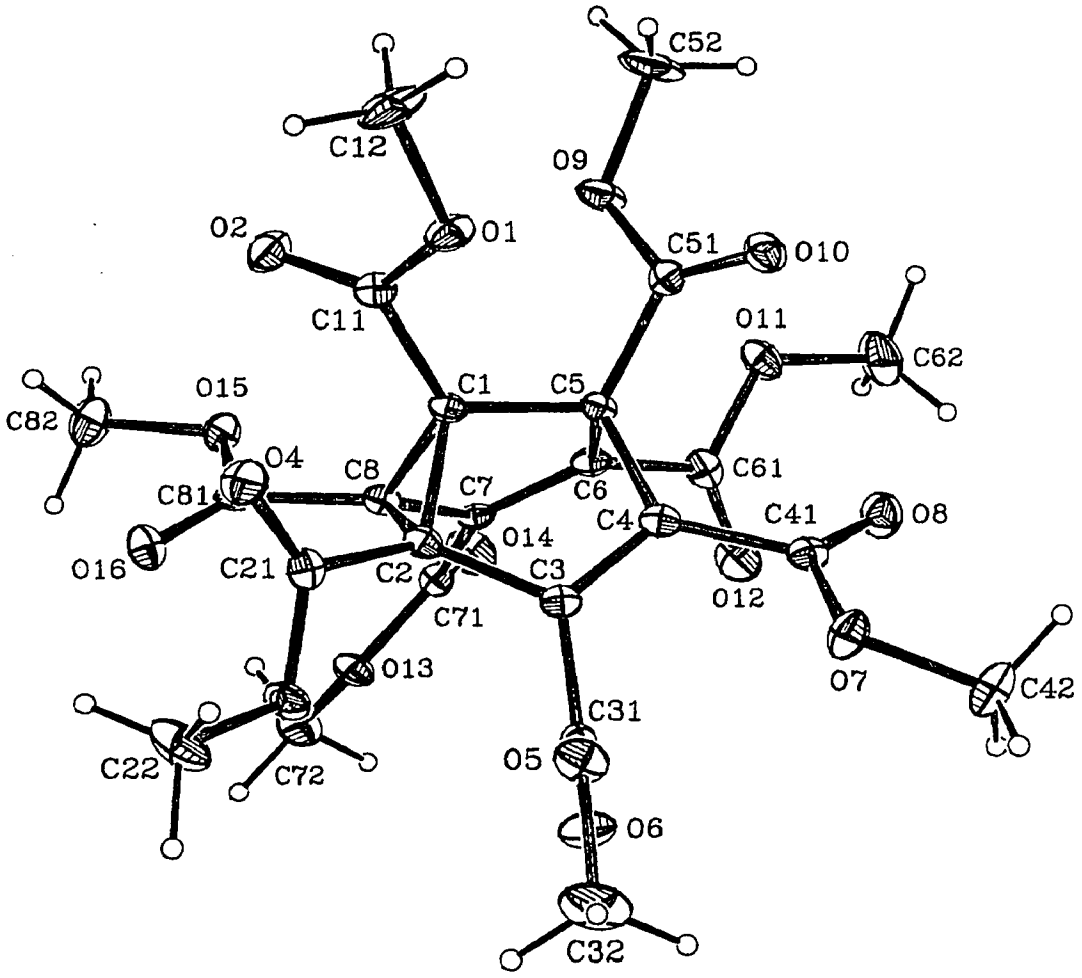


Figure 4–31. *ORTEP* drawing of octacarbomethoxysemibullvalene at **115 K** with 50% thermal ellipsoids.

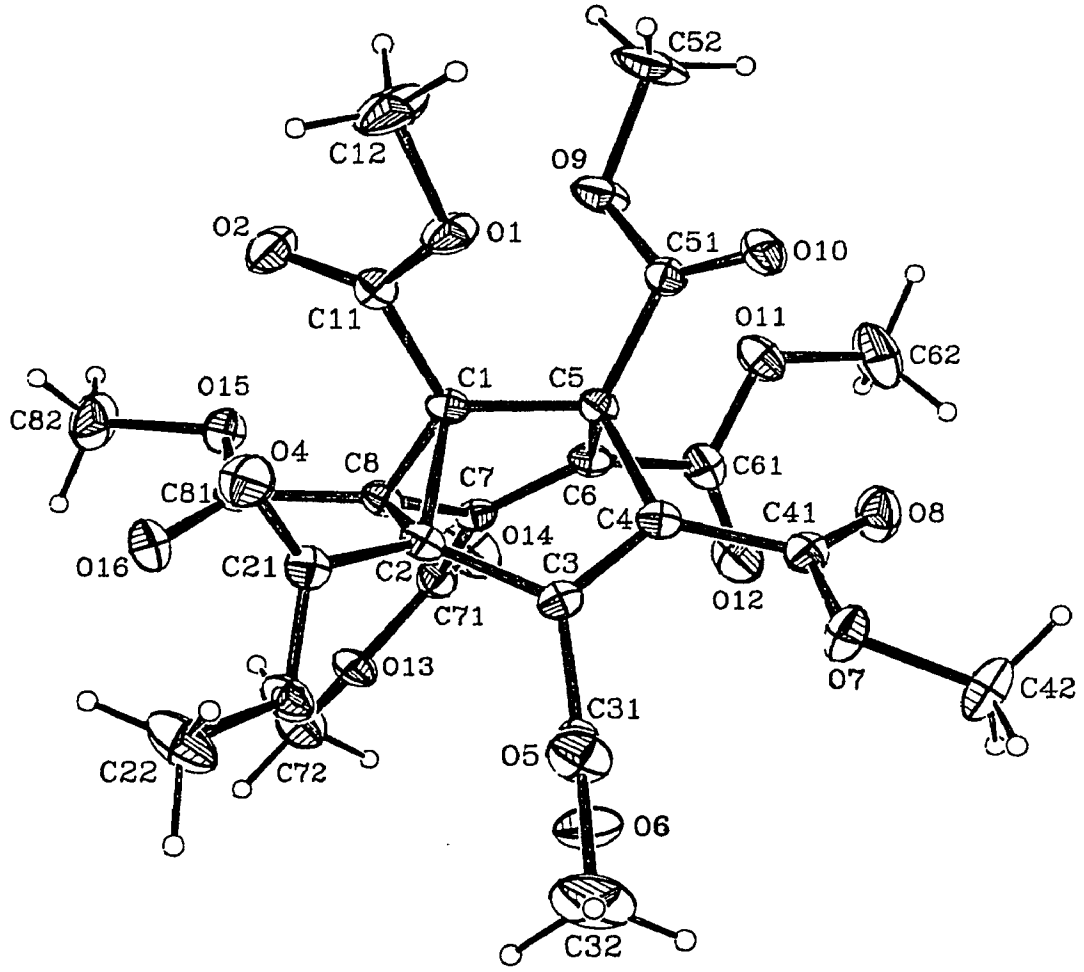


Figure 4–32. *ORTEP* drawing of octacarbomethoxysemibullvalene at **153 K** with 50% thermal ellipsoids.

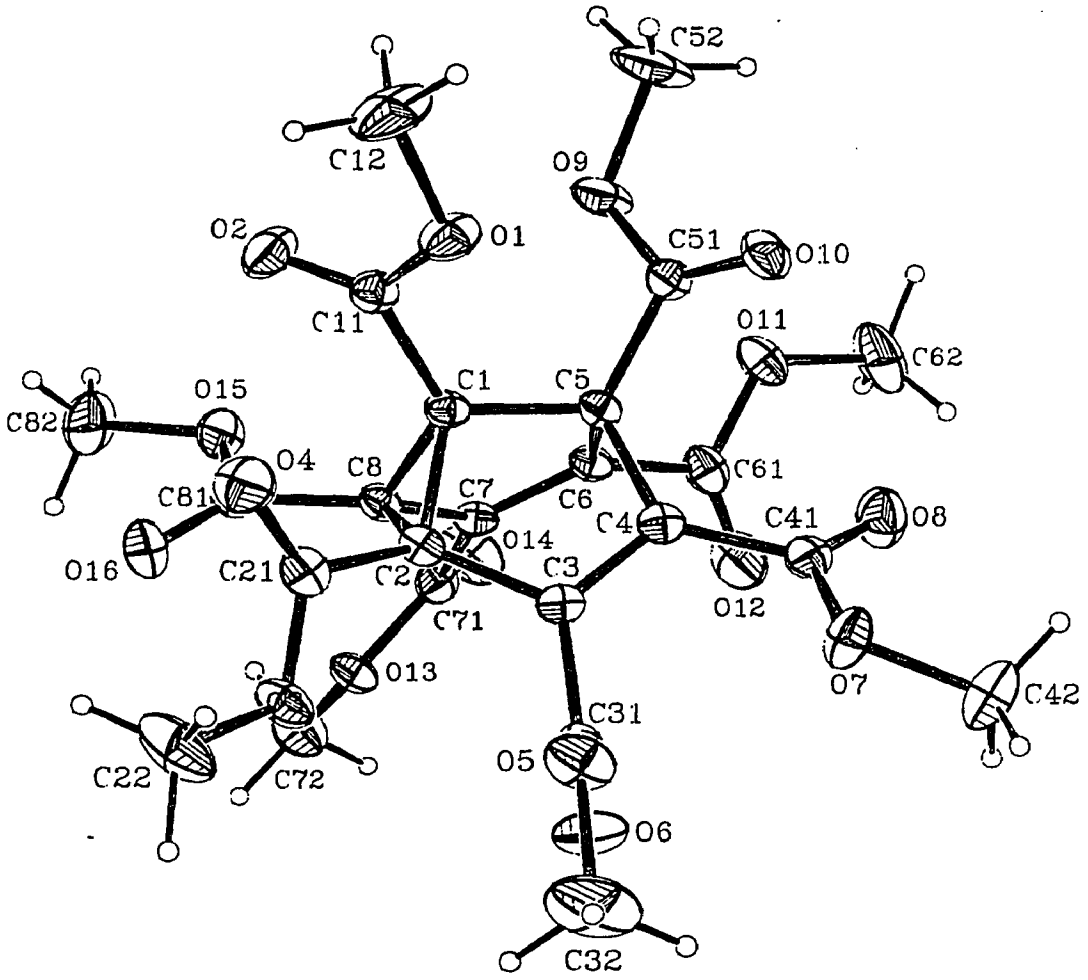


Figure 4–33. *ORTEP* drawing of octacarbomethoxysemibullvalene at **181 K** with 50% thermal ellipsoids.

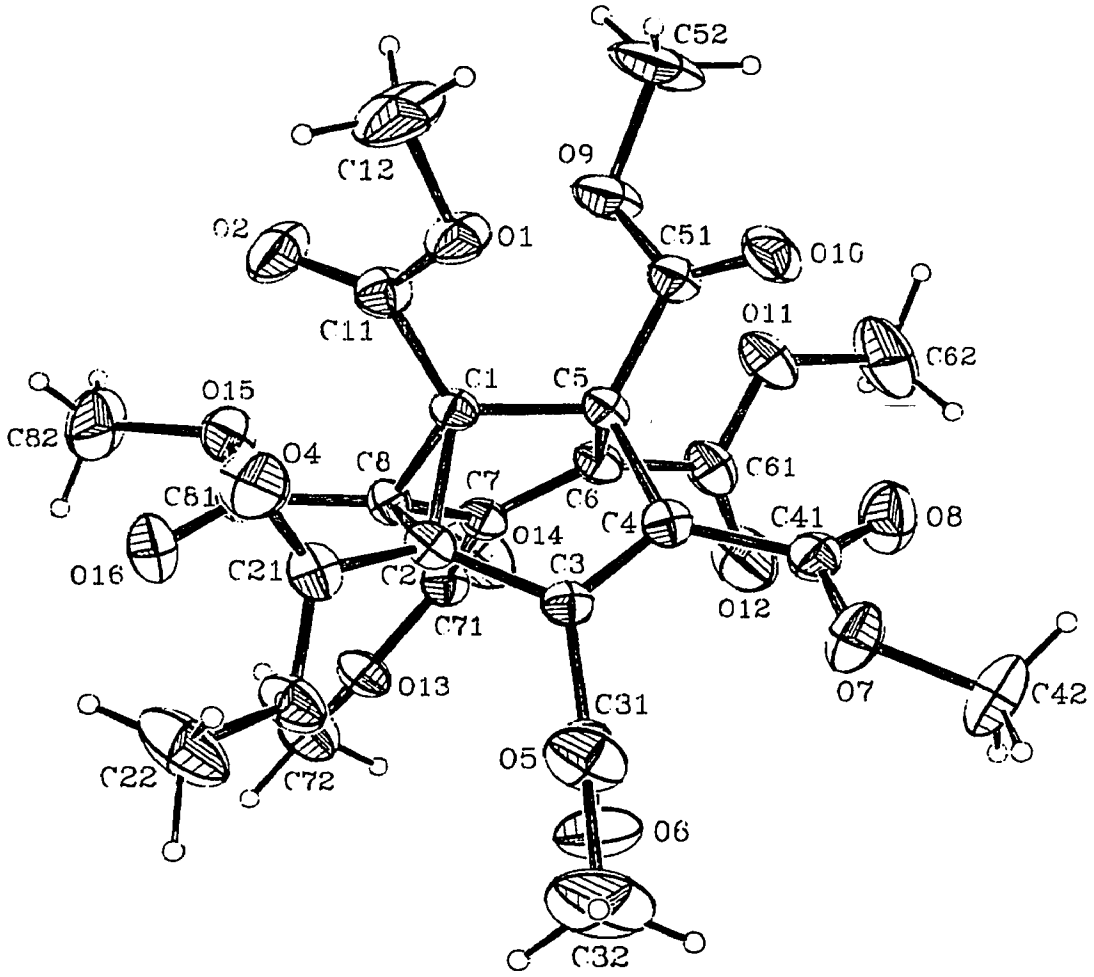


Figure 4–34. *ORTEP* drawing of octacarbomethoxysemibullvalene at **236 K** with 50% thermal ellipsoids.

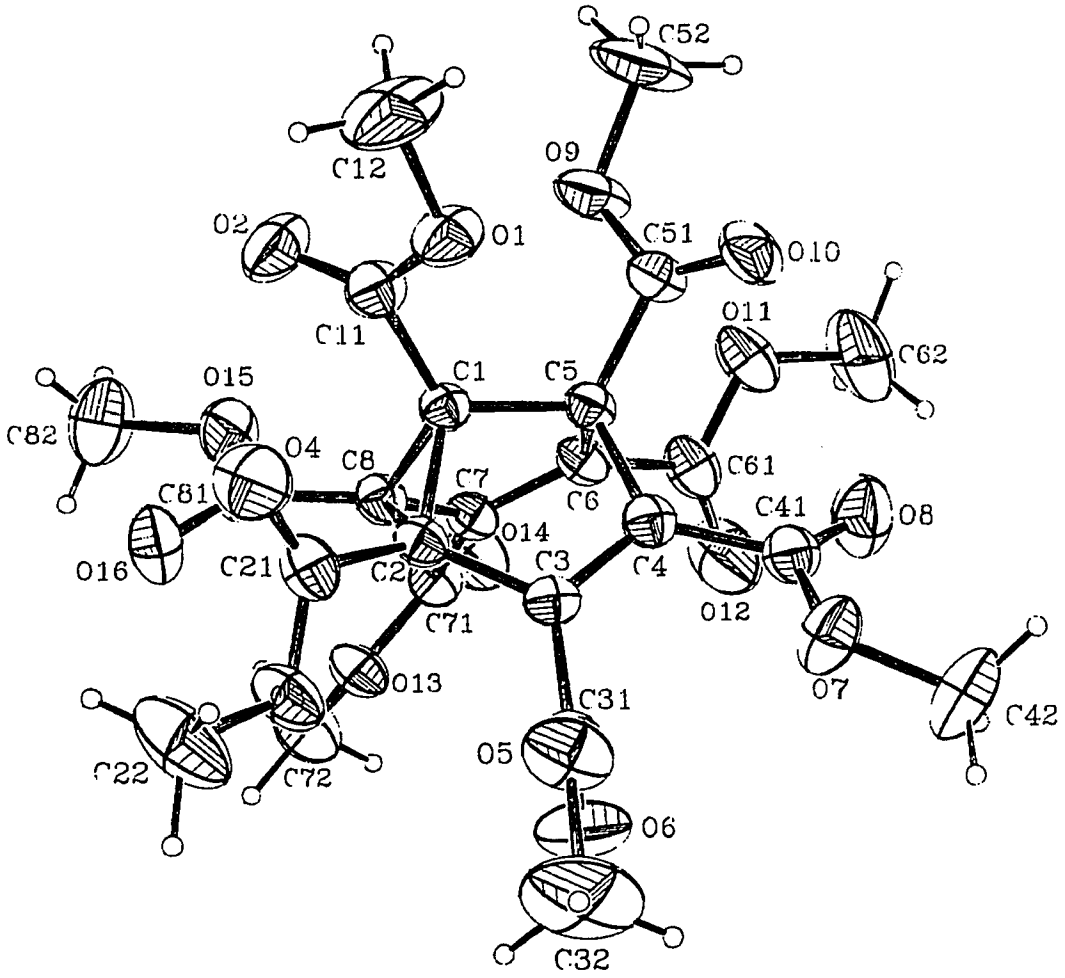


Figure 4–35. *ORTEP* drawing of octacarbomethoxysemibullvalene at **294 K** with 50% thermal ellipsoids.

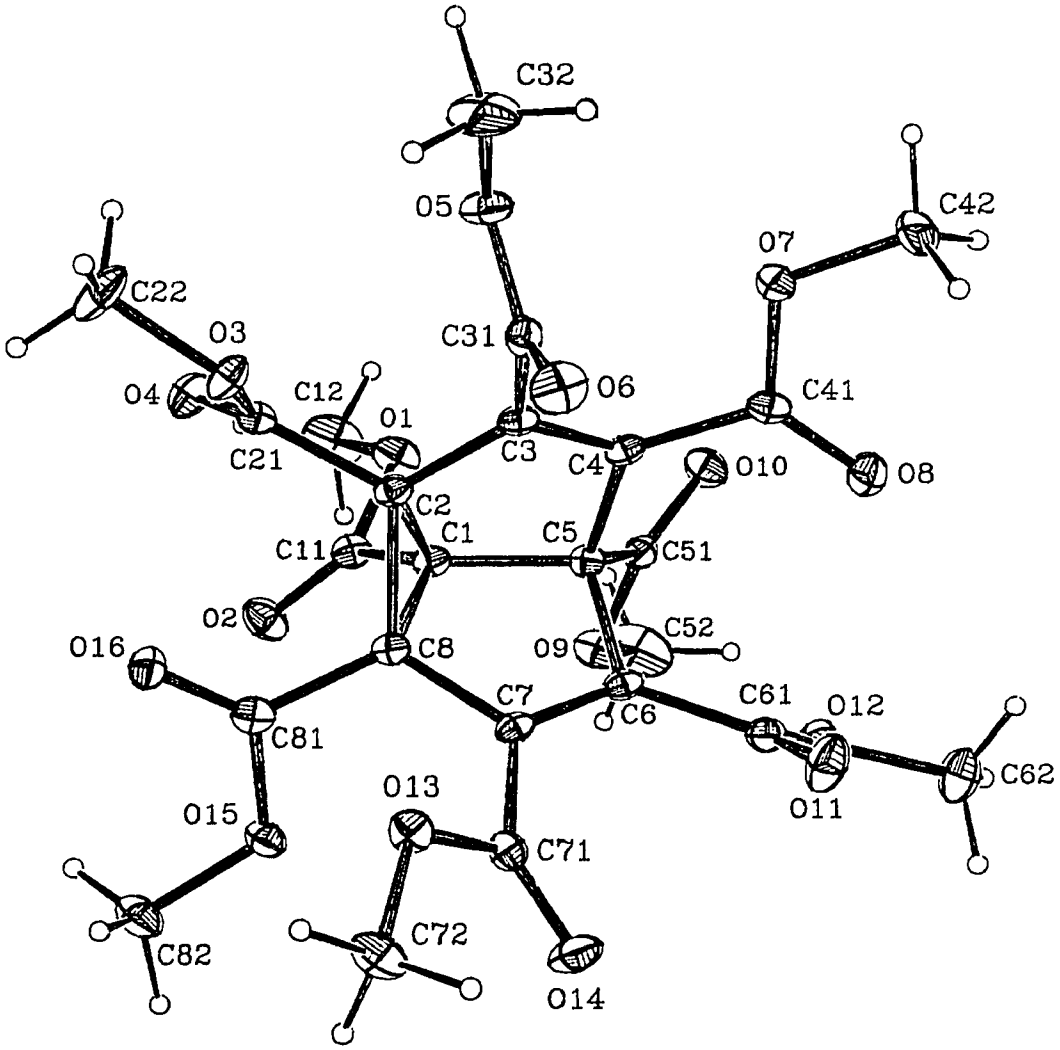


Figure 4–36. *ORTEP* drawing of octacarbomethoxysemibullvalene at **115 K** with 50% thermal ellipsoids.

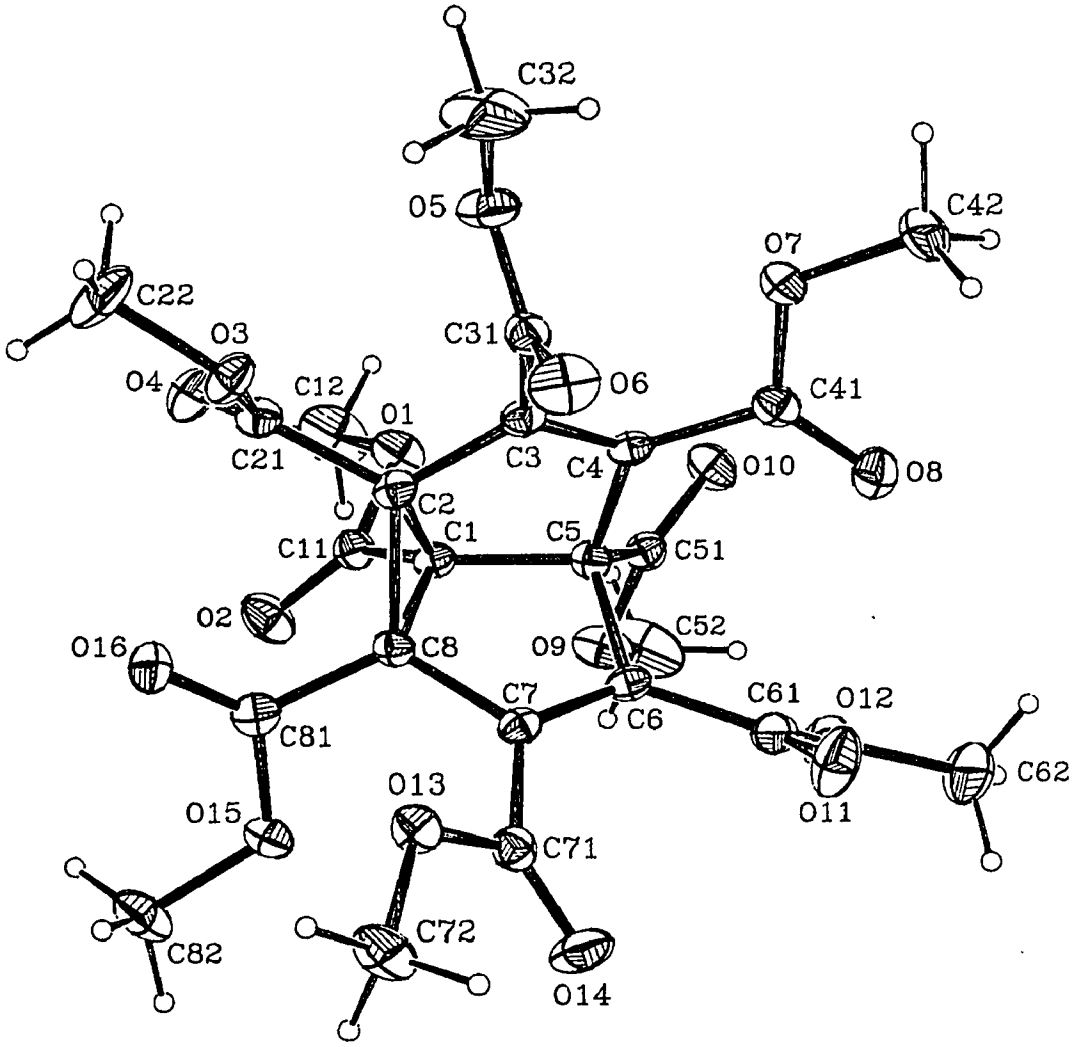


Figure 4–37. *ORTEP* drawing of octacarbomethoxysemibullvalene at **153 K** with 50% thermal ellipsoids.

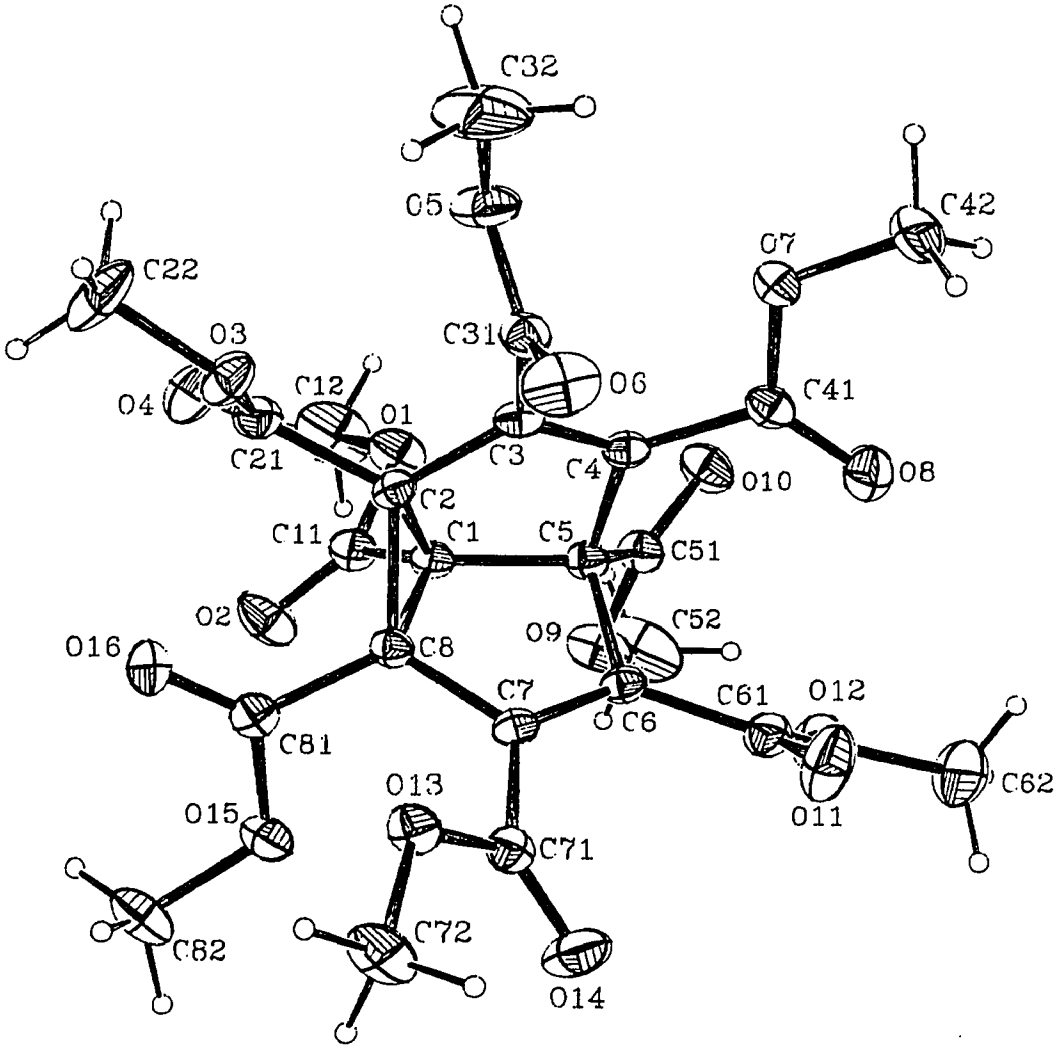


Figure 4–38. *ORTEP* drawing of octacarbomethoxysemibullvalene at **181 K** with 50% thermal ellipsoids.

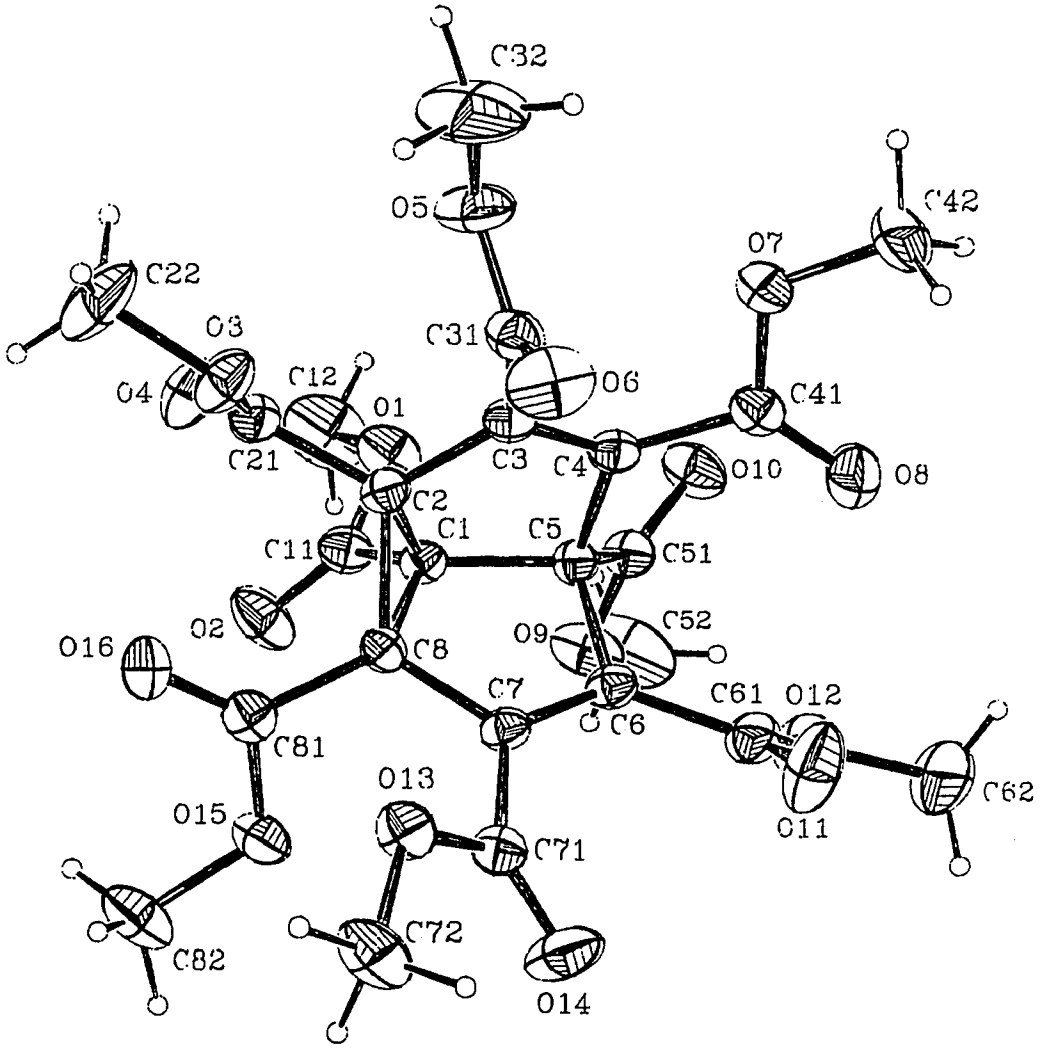


Figure 4–39. *ORTEP* drawing of octacarbomethoxysemibullvalene at **236 K** with 50% thermal ellipsoids.

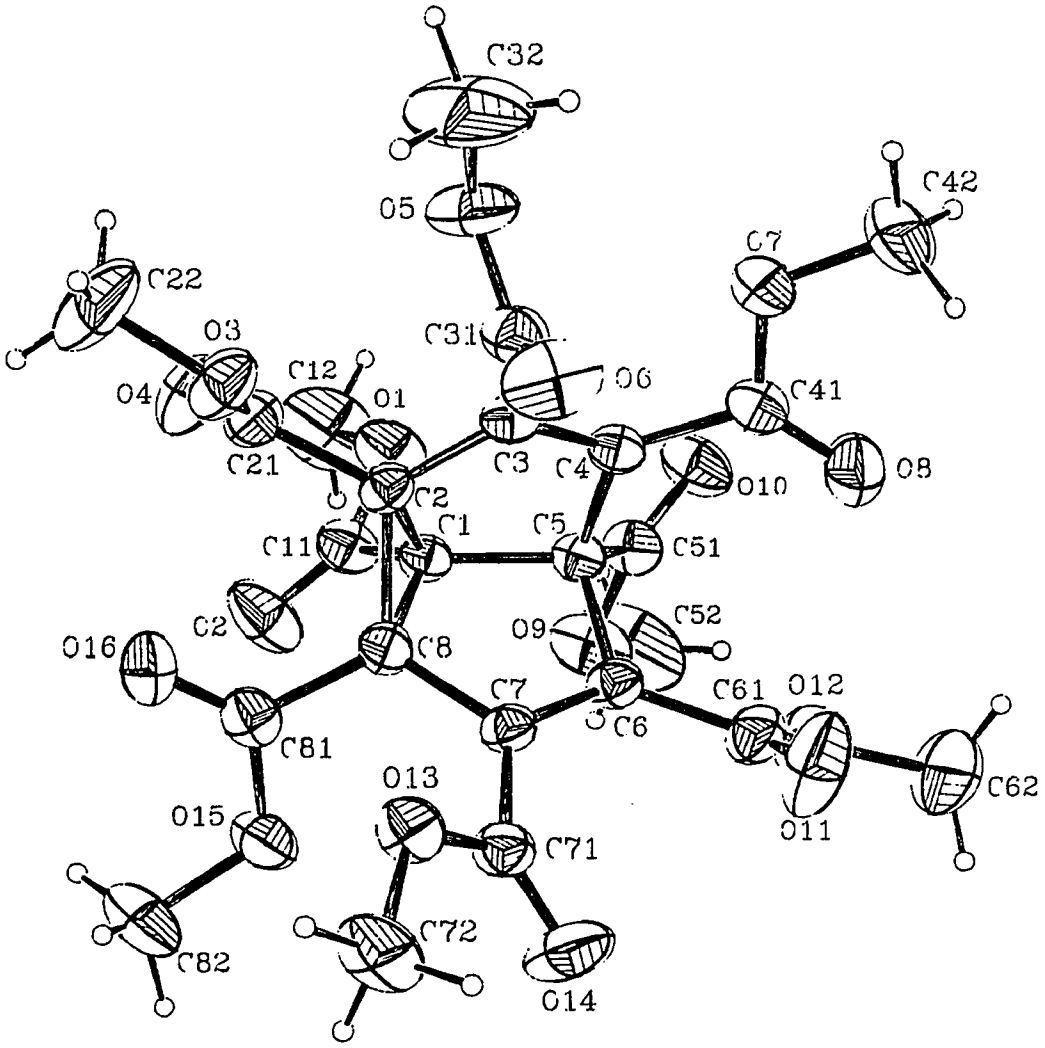
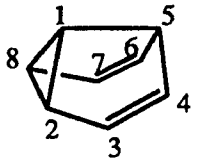


Figure 4–40. *ORTEP* drawing of octacarbomethoxysemibullvalene at **294 K** with 50% thermal ellipsoids.

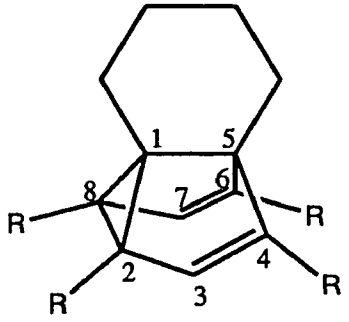
4.3 SB-6

If the hydrogens on the carbons, C1 and C5, in semibullvalene



Tricyclo[3.3.0.0^{2,8}]octa-3,6-diene
(Semibullvalene)

are replaced with a chain of four methylenes to form a six-membered ring on top of semibullvalene and four ester groups replace the four hydrogens at C2, C4, C6, and C8, we obtain the annulated compound **1,5-cyclohexano-2,4,6,8-tetracarbomethoxy-semibullvalene** or simply Sb-6



R = $COOCH_3$

1,5-cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Selected X-ray crystal data for Sb-6 is displayed in Table 4–9. The data shows that an Sb-6 crystal contains two independent molecules (designated as unprimed and primed), that is, two molecules not related by crystallographic symmetry.

Table 4–9. X-ray Crystal Data for Sb-6 at Various Temperatures

	115 K	**153 K**	**181 K**
Formula	$C_{20}H_{22}O_8$	$C_{20}H_{22}O_8$	$C_{20}H_{22}O_8$
Formula weight	390.39	390.39	390.39
Melting point (°C)	117–118	117–118	117–118
Crystal size (mm)	0.21 x 0.25 x 0.33	0.21 x 0.25 x 0.33	0.32 x 0.50 x 0.64
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P2/n*	*P2/n*	*P2/n*
a (Å)	41.319(3)	41.364(2)	41.388(2)
b (Å)	7.317(1)	7.341(1)	7.358(3)
c (Å)	12.104(1)	12.140(1)	12.163(2)
β (°)	98.00(1)	98.07(1)	98.11(1)
Cell volume (Å^3)	3623.74(2.87)	3649.91(2.74)	3666.90(4.90)
Z	8	8	8
d_{calc} (g cm^{-3})	1.431	1.421	1.414
μ(Cu $K\alpha$) (cm^{-1})	8.92	8.86	8.82
R	0.046	0.047	0.046
R_w	0.054	0.055	0.060

Table 4–9 (cont'd). X-ray Crystal Data for Sb-6 at Various Temperatures

	181 K	**208 K**	**208 K**
Formula	$C_{20}H_{22}O_8$	$C_{20}H_{22}O_8$	$C_{20}H_{22}O_8$
Formula weight	390.39	390.39	390.39
Melting point (°C)	117–118	117–118	117–118
Crystal size (mm)	0.21 x 0.25 x 0.33	0.32 x 0.50 x 0.64	0.21 x 0.25 x 0.33
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P2/n*	*P2/n*	*P2/n*
a (Å)	41.319(2)	41.423(2)	41.421(2)
b (Å)	7.361(1)	7.379(4)	7.382(1)
c (Å)	12.163(1)	12.188(2)	12.186(1)
β (°)	98.10(1)	98.14(1)	98.14(1)
Cell volume (Å^3)	3668.68(2.61)	3687.99(5.57)	3688.69(2.32)
Z	8	8	8
d_{calc} (g cm^{-3})	1.414	1.406	1.406
μ(Cu $K\alpha$) (cm^{-1})	8.81	8.77	8.77
R	0.047	0.045	0.049
R_w	0.053	0.060	0.056

Table 4–9 (cont'd). X-ray Crystal Data for Sb-6 at Various Temperatures

	236 K	**236 K**	**265 K**
Formula	$C_{20}H_{22}O_8$	$C_{20}H_{22}O_8$	$C_{20}H_{22}O_8$
Formula weight	390.39	390.39	390.39
Melting point (°C)	117–118	117–118	117–118
Crystal size (mm)	0.32 x 0.50 x 0.64	0.21 x 0.25 x 0.33	0.32 x 0.50 x 0.64
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P2/n*	*P2/n*	*P2/n*
a (Å)	41.455(2)	41.451(2)	41.483(2)
b (Å)	7.405(4)	7.407(1)	7.437(1)
c (Å)	12.210(3)	12.209(1)	12.231(1)
β (°)	98.10(2)	98.17(1)	98.21(1)
Cell volume (Å^3)	3710.03(8.46)	3710.32(2.38)	3734.82(2.73)
Z	8	8	8
d_{calc} (g cm^{-3})	1.398	1.398	1.388
μ(Cu $K\alpha$) (cm^{-1})	8.72	8.72	8.66
R	0.046	0.051	0.048
R_w	0.060	0.059	0.061

Table 4–9 (cont'd). X-ray Crystal Data for Sb-6 at Various Temperatures

	294 K	**294 K**	**295 K**
Formula	$C_{20}H_{22}O_8$	$C_{20}H_{22}O_8$	$C_{20}H_{22}O_8$
Formula weight	390.39	390.39	390.39
Melting point (°C)	117–118	117–118	117–118
Crystal size (mm)	0.32 x 0.50 x 0.64	0.21 x 0.25 x 0.33	0.32 x 0.50 x 0.64
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P2/n*	*P2/n*	*P2/n*
a (Å)	41.518(2)	41.518(2)	41.522(2)
b (Å)	7.463(1)	7.462(1)	7.467(1)
c (Å)	12.253(1)	12.254(1)	12.255(1)
β (°)	98.22(1)	98.21(1)	98.24(1)
Cell volume (Å^3)	3757.82(2.00)	3757.56(1.95)	3760.49(3.87)
Z	8	8	8
d_{calc} (g cm^{-3})	1.380	1.380	1.379
μ(Cu $K\alpha$) (cm^{-1})	8.61	8.61	8.60
R	0.049	0.048	0.055
R_w	0.062	0.056	0.080

Table 4–9 (cont'd). X-ray Crystal Data for Sb-6 at Various Temperatures

	322 K	**335 K**
Formula	$C_{20}H_{22}O_8$	$C_{20}H_{22}O_8$
Formula weight	390.39	390.39
Melting point (°C)	117–118	117–118
Crystal size (mm)	0.21 x 0.25 x 0.33	0.21 x 0.25 x 0.33
Crystal system	monoclinic	monoclinic
Space group	*P2/n*	*P2/n*
a (Å)	41.558(1)	41.574(2)
b (Å)	7.493(1)	7.509(1)
c (Å)	12.276(1)	12.285(1)
β (°)	98.22(1)	98.22(1)
Cell volume (Å^3)	3783.39(1.91)	3796.08(1.87)
Z	8	8
d_{calc} (g cm^{-3})	1.371	1.366
μ(Cu $K\alpha$) (cm^{-1})	8.55	8.52
R	0.048	0.053
R_w	0.056	0.061

Figure 4–41 illustrates that the unit-cell volume, as expected, expands with increasing temperature.

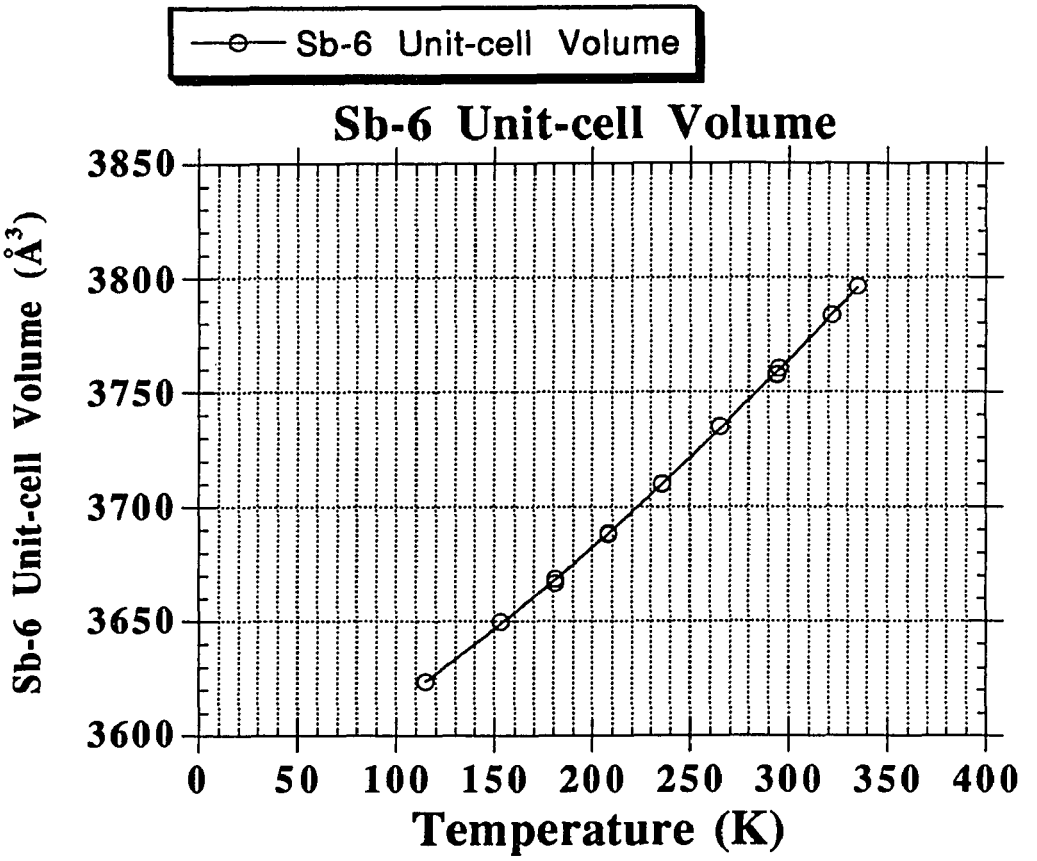


Figure 4–41. A plot of Sb-6 unit-cell volume versus temperature.

The slightly curved plot in Figure 4–41 is nearly a straight line. In fact, for the purpose of comparing Sb-6 with the other five compounds, we fit the volume-temperature data points of Sb-6 with a straight line as in Figure 4–42.

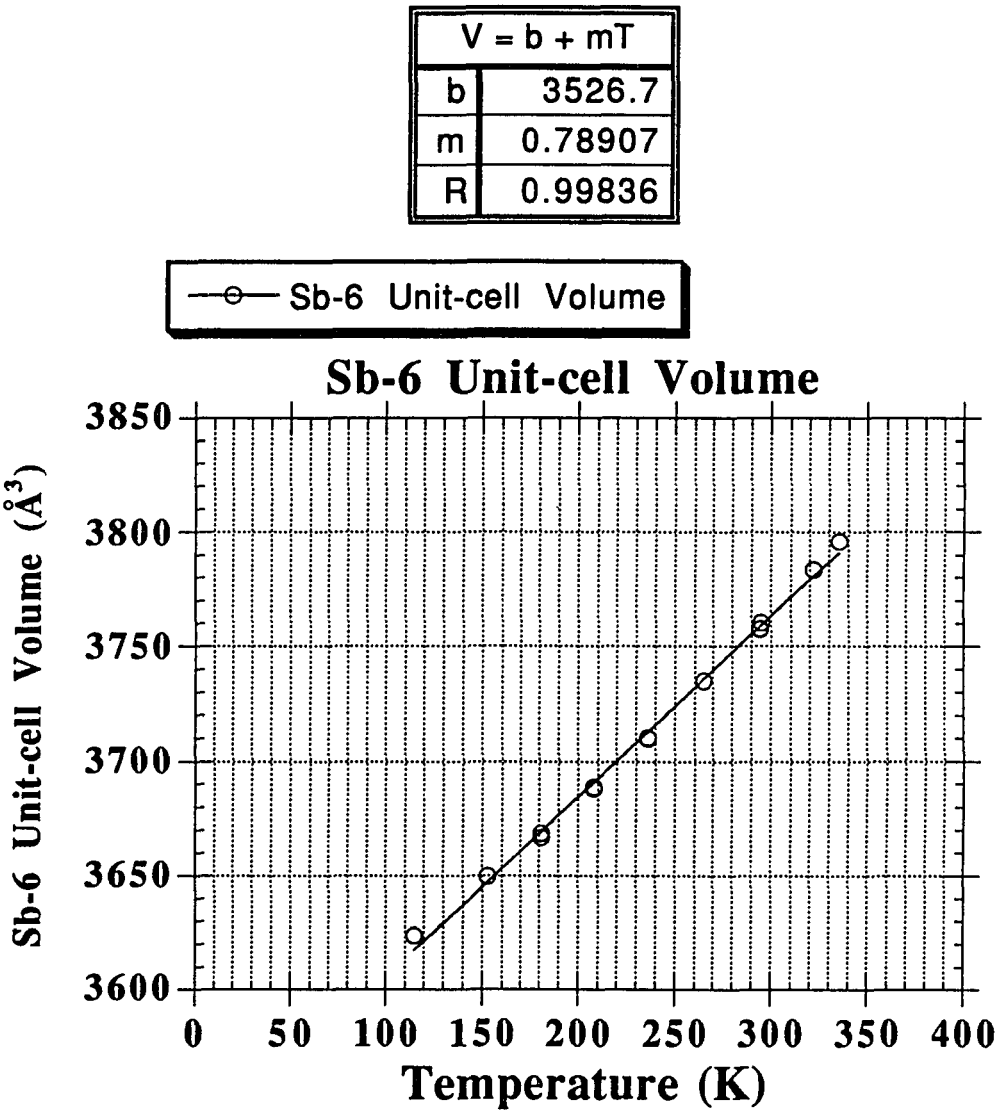


Figure 4–42. A plot of Sb-6 unit-cell volume versus temperature.

According to the slope in Figure 4–42, the unit-cell volume of Sb-6 expands at the rate of 7.9 $Å^3$ for every 10 °C rise in temperature for eight molecules in the unit cell or 3.95 $Å^3$ for four molecules in one half of the unit cell (112 non-H's and 88 H's).

The density of Sb-6 in Figure 4–43 decreases as the volume of the unit cell expands with increasing temperature.

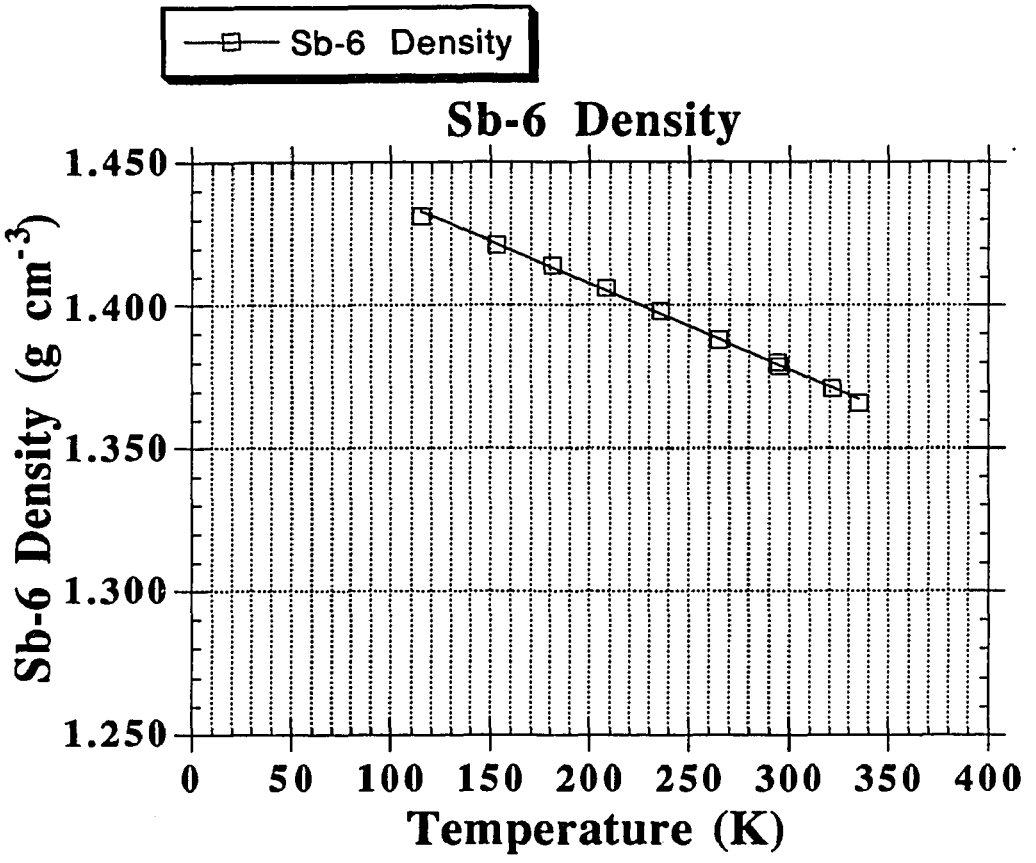


Figure 4–43. A plot of Sb-6 density versus temperature.

Table 4–10 lists selected interatomic distances in the ring of Sb-6.

Table 4–10. Selected Interatomic Distances (Å) in the Ring of Sb-6 at Various Temperatures.

	115 K		153 K		181 K	
	unprimed	primed	unprimed	primed	unprimed	primed
C1—C2	1.491(5)	1.490(5)	1.496(5)	1.485(5)	1.486(4)	1.489(4)
C1—C5	1.559(4)	1.561(4)	1.560(4)	1.556(4)	1.569(3)	1.566(3)
C1—C8	1.525(5)	1.517(4)	1.529(5)	1.513(5)	1.518(3)	1.512(3)
C2—C3	1.476(5)	1.468(4)	1.468(5)	1.463(5)	1.470(3)	1.460(3)
C2—C8	1.638(4)	1.652(4)	1.644(5)	1.667(5)	1.639(3)	1.685(3)
C3—C4	1.340(5)	1.335(5)	1.331(5)	1.334(5)	1.336(3)	1.341(3)
C3—C7	3.060(5)	3.066(4)	3.067(5)	3.059(5)	3.066(3)	3.058(3)
C4—C5	1.528(5)	1.526(5)	1.536(5)	1.532(5)	1.537(4)	1.525(3)
C4—C6	2.360(5)	2.356(5)	2.369(5)	2.340(5)	2.364(3)	2.325(3)
C5—C6	1.532(4)	1.532(5)	1.536(4)	1.530(5)	1.531(3)	1.526(3)
C6—C7	1.341(5)	1.333(4)	1.340(5)	1.330(5)	1.339(4)	1.343(3)
C7—C8	1.467(4)	1.472(5)	1.463(4)	1.461(5)	1.469(3)	1.455(3)
C2—C3 + C3—C4	2.816	2.803	2.799	2.797	2.806	2.801
C6—C7 + C7—C8	2.808	2.805	2.803	2.791	2.808	2.798
C2—C8 + C4—C6	3.998	4.008	4.013	4.007	4.003	4.010

Table 4–10 (cont'd). Selected Interatomic Distances (Å) in the Ring of Sb-6 at Various Temperatures.

	181 K		208 K		208 K	
	unprimed	primed	unprimed	primed	unprimed	primed
C1—C2	1.495(5)	1.486(5)	1.491(4)	1.489(4)	1.488(5)	1.483(6)
C1—C5	1.563(4)	1.567(4)	1.568(3)	1.566(3)	1.571(5)	1.567(5)
C1—C8	1.524(5)	1.517(5)	1.516(4)	1.514(3)	1.525(5)	1.510(5)
C2—C3	1.481(5)	1.455(5)	1.470(3)	1.460(3)	1.474(5)	1.458(5)
C2—C8	1.640(5)	1.683(5)	1.641(3)	1.697(4)	1.644(5)	1.698(5)
C3—C4	1.336(5)	1.345(5)	1.337(3)	1.348(3)	1.335(5)	1.347(5)
C3—C7	3.069(5)	3.057(5)	3.068(4)	3.061(3)	3.065(5)	3.055(5)
C4—C5	1.532(5)	1.530(5)	1.529(4)	1.522(4)	1.537(6)	1.516(5)
C4—C6	2.354(5)	2.328(5)	2.355(3)	2.307(4)	2.357(5)	2.302(5)
C5—C6	1.531(4)	1.527(5)	1.531(3)	1.518(4)	1.525(5)	1.525(5)
C6—C7	1.341(5)	1.332(4)	1.340(4)	1.347(3)	1.349(5)	1.338(5)
C7—C8	1.466(4)	1.461(5)	1.476(3)	1.454(4)	1.458(5)	1.450(5)
C2—C3 + C3—C4	2.817	2.800	2.807	2.808	2.809	2.805
C6—C7 + C7—C8	2.807	2.793	2.816	2.801	2.807	2.788
C2—C8 + C4—C6	3.994	4.011	3.996	4.004	4.001	4.000

Table 4–10 (cont'd). Selected Interatomic Distances (Å) in the Ring of Sb-6 at Various Temperatures.

	236 K		**236 K**		**265 K**	
	unprimed	primed	unprimed	primed	unprimed	primed
C1—C2	1.488(4)	1.487(4)	1.498(6)	1.477(6)	1.491(4)	1.487(4)
C1—C5	1.568(3)	1.565(3)	1.567(5)	1.571(5)	1.567(3)	1.561(3)
C1—C8	1.516(4)	1.514(3)	1.528(6)	1.511(5)	1.516(4)	1.508(4)
C2—C3	1.469(3)	1.455(3)	1.473(6)	1.457(5)	1.466(4)	1.448(4)
C2—C8	1.641(4)	1.714(4)	1.646(6)	1.721(6)	1.653(4)	1.735(4)
C3—C4	1.337(3)	1.349(4)	1.340(6)	1.347(6)	1.338(4)	1.354(4)
C3—C7	3.062(4)	3.061(3)	3.076(6)	3.052(5)	3.062(4)	3.060(4)
C4—C5	1.529(4)	1.522(4)	1.537(6)	1.512(6)	1.527(4)	1.522(4)
C4—C6	2.351(4)	2.290(4)	2.355(6)	2.280(6)	2.348(4)	2.275(4)
C5—C6	1.524(3)	1.519(4)	1.527(5)	1.518(6)	1.530(4)	1.517(4)
C6—C7	1.342(4)	1.348(3)	1.352(6)	1.346(5)	1.342(4)	1.355(4)
C7—C8	1.471(3)	1.446(4)	1.463(5)	1.444(6)	1.471(3)	1.437(4)
C2—C3 + C3—C4	2.806	2.804	2.813	2.804	2.804	2.802
C6—C7 + C7—C8	2.813	2.794	2.815	2.790	2.813	2.792
C2—C8 + C4—C6	3.992	4.004	4.001	4.001	4.001	4.010

Table 4–10 (cont'd). Selected Interatomic Distances (Å) in the Ring of Sb-6 at Various Temperatures.

	294 K		294 K		295 K	
	unprimed	primed	unprimed	primed	unprimed	primed
C1—C2	1.487(4)	1.482(4)	1.489(5)	1.479(5)	1.488(4)	1.488(4)
C1—C5	1.566(3)	1.566(3)	1.566(4)	1.569(4)	1.564(3)	1.561(3)
C1—C8	1.515(4)	1.507(4)	1.520(5)	1.509(5)	1.518(4)	1.514(4)
C2—C3	1.464(4)	1.448(4)	1.467(5)	1.441(5)	1.460(4)	1.440(3)
C2—C8	1.658(4)	1.749(4)	1.663(5)	1.759(5)	1.665(4)	1.754(4)
C3—C4	1.337(4)	1.352(4)	1.337(5)	1.352(5)	1.341(4)	1.353(4)
C3—C7	3.064(4)	3.058(4)	3.062(5)	3.062(5)	3.058(4)	3.057(4)
C4—C5	1.528(4)	1.522(4)	1.531(5)	1.519(5)	1.540(4)	1.515(4)
C4—C6	2.335(4)	2.262(4)	2.338(5)	2.252(5)	2.346(4)	2.250(4)
C5—C6	1.523(4)	1.519(4)	1.526(5)	1.522(5)	1.527(4)	1.524(4)
C6—C7	1.340(4)	1.352(4)	1.346(5)	1.351(5)	1.338(4)	1.346(3)
C7—C8	1.467(4)	1.440(4)	1.462(4)	1.432(5)	1.459(3)	1.438(4)
C2—C3 + C3—C4	2.801	2.800	2.804	2.793	2.801	2.793
C6—C7 + C7—C8	2.807	2.792	2.808	2.783	2.797	2.784
C2—C8 + C4—C6	3.993	4.011	4.001	4.011	4.011	4.004

Table 4–10 (cont'd). Selected Interatomic Distances (Å) in the Ring of Sb-6 at Various Temperatures.

	322 K		335 K	
	unprimed	primed	unprimed	primed
C1—C2	1.488(5)	1.477(5)	1.489(5)	1.476(6)
C1—C5	1.564(4)	1.568(4)	1.560(5)	1.559(5)
C1—C8	1.519(5)	1.506(4)	1.516(6)	1.509(5)
C2—C3	1.467(4)	1.436(4)	1.457(6)	1.440(5)
C2—C8	1.670(5)	1.769(5)	1.685(6)	1.793(6)
C3—C4	1.335(4)	1.352(4)	1.334(5)	1.359(6)
C3—C7	3.063(5)	3.058(4)	3.054(6)	3.059(6)
C4—C5	1.534(5)	1.516(5)	1.530(6)	1.524(6)
C4—C6	2.329(5)	2.235(5)	2.324(6)	2.237(6)
C5—C6	1.525(4)	1.514(5)	1.528(5)	1.519(6)
C6—C7	1.341(5)	1.355(4)	1.346(6)	1.352(5)
C7—C8	1.453(4)	1.431(4)	1.449(5)	1.432(6)
C2—C3 + C3—C4	2.802	2.788	2.791	2.799
C6—C7 + C7—C8	2.794	2.786	2.795	2.784
C2—C8 + C4—C6	3.999	4.004	4.009	4.030

As before, we plot all the interatomic distances of the previous table against temperature in Figure 4–44 for the unprimed molecule and in Figure 4–45 for the primed molecule.

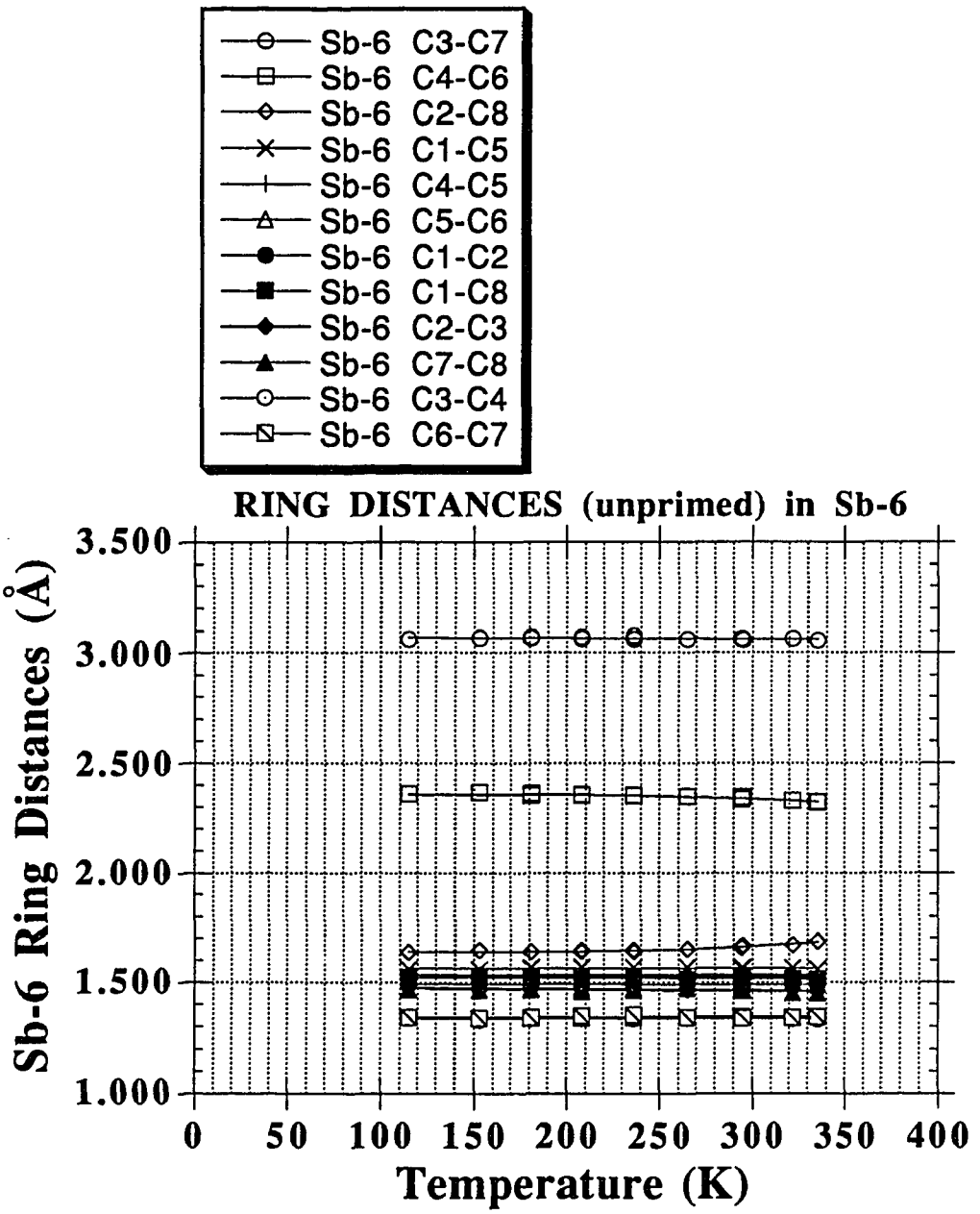


Figure 4–44. Plots of selected interatomic distances (unprimed) in the ring of Sb-6 versus temperature.

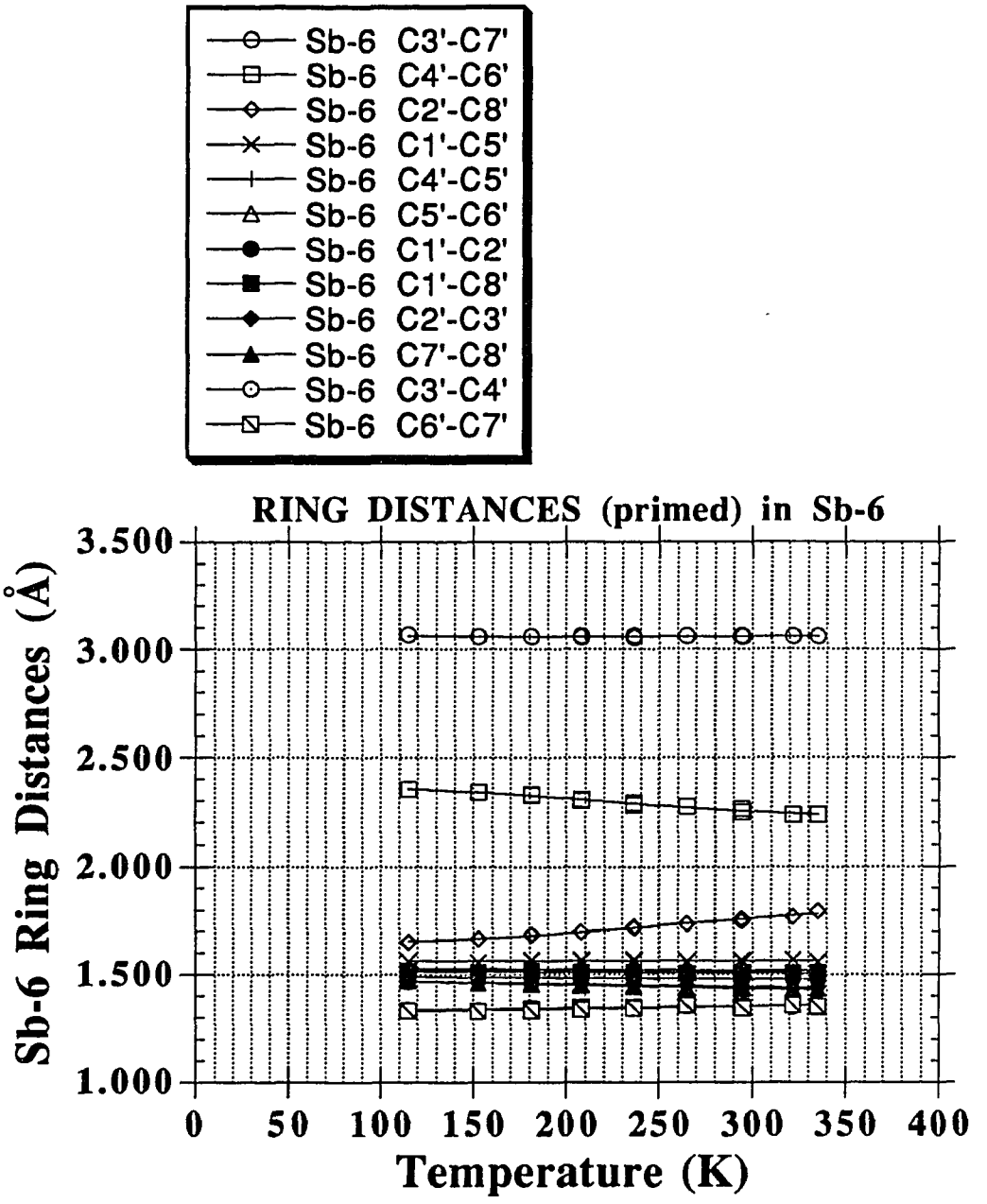


Figure 4–45. Plots of selected interatomic distances (primed) in the ring of Sb-6 versus temperature.

These graphs bring out structural differences in the two independent molecules. These two molecules have different interatomic measurements. By and large, more dramatic changes with temperature occur in the primed molecule of Sb-6 than in the unprimed molecule. From these distances, we can see that the structure of the primed molecule is

closer to the bishomoaromatic state than that of the unprimed. Again to relieve the congestion, we plot certain sets of these distances separately as shown in the following figures.

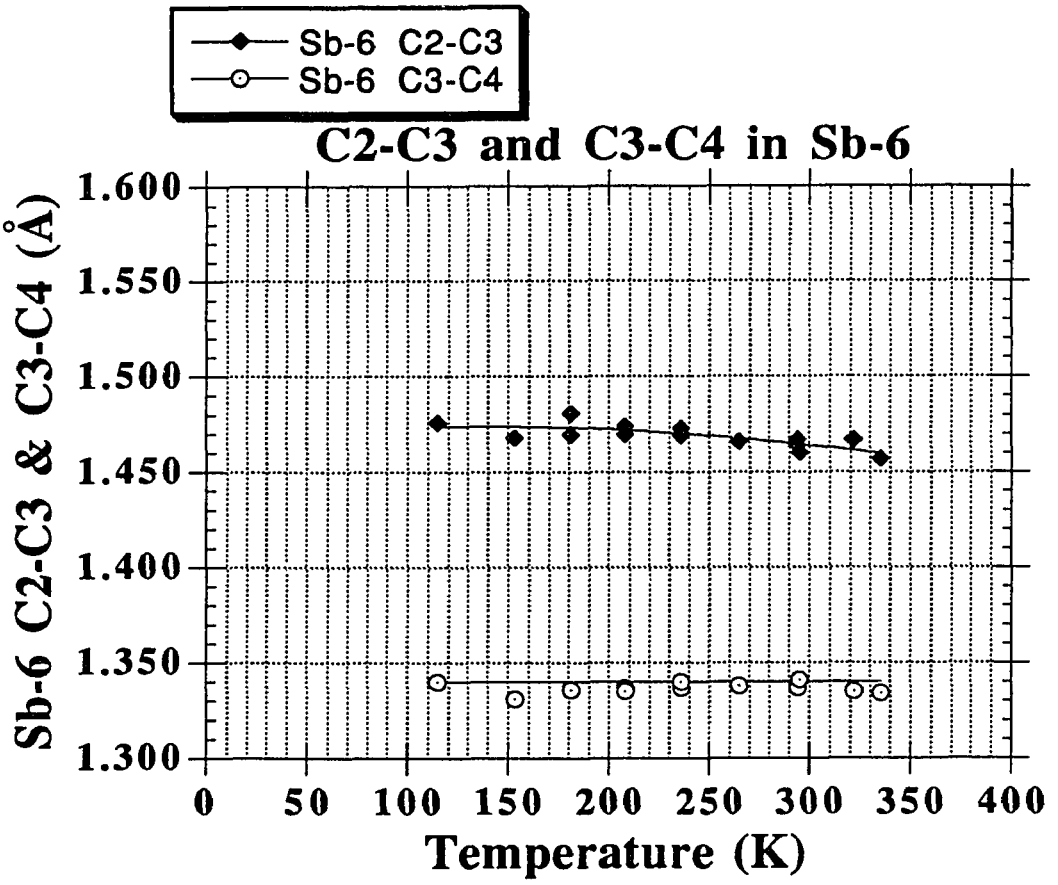


Figure 4–46. Plots of C2—C3 and C3—C4 distances (unprimed) in Sb-6 versus temperature.

The sum of the distances C2—C3 and C3—C4 in Sb-6 remains nearly constant as the temperature is varied (Figure 4–47).

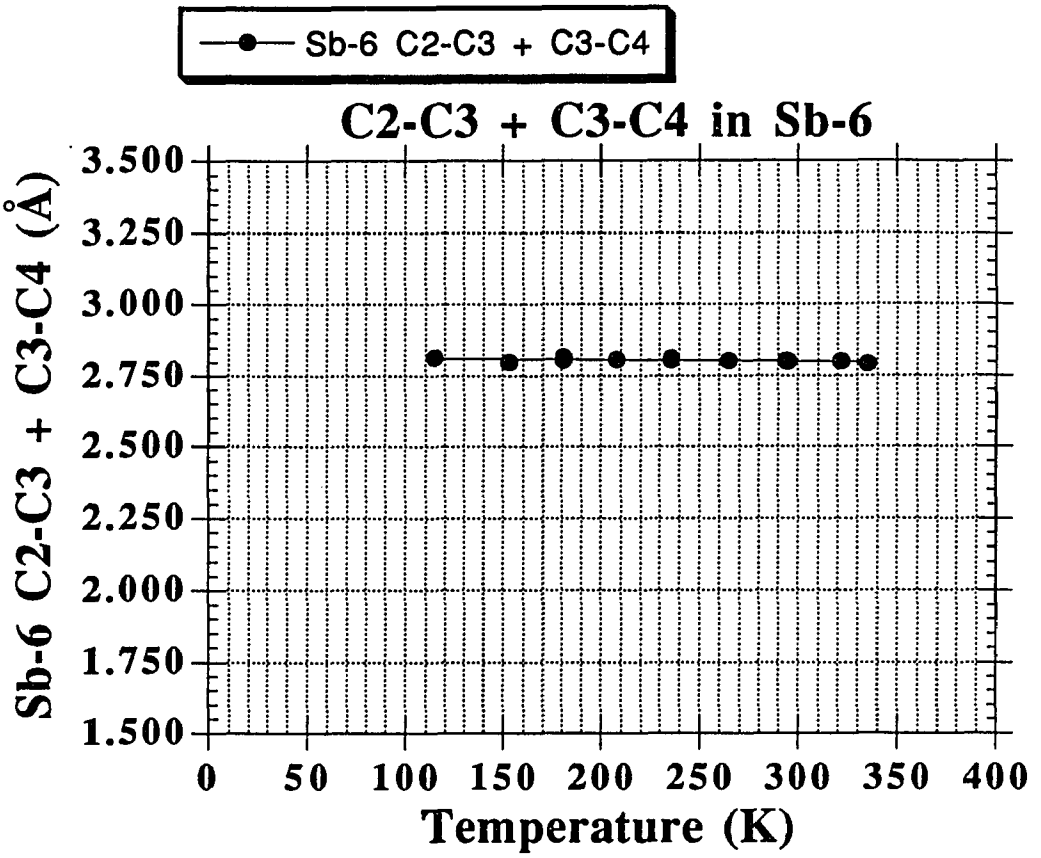


Figure 4–47. A plot of the sum of the distances C2—C3 and C3—C4 (unprimed) in Sb-6 versus temperature.

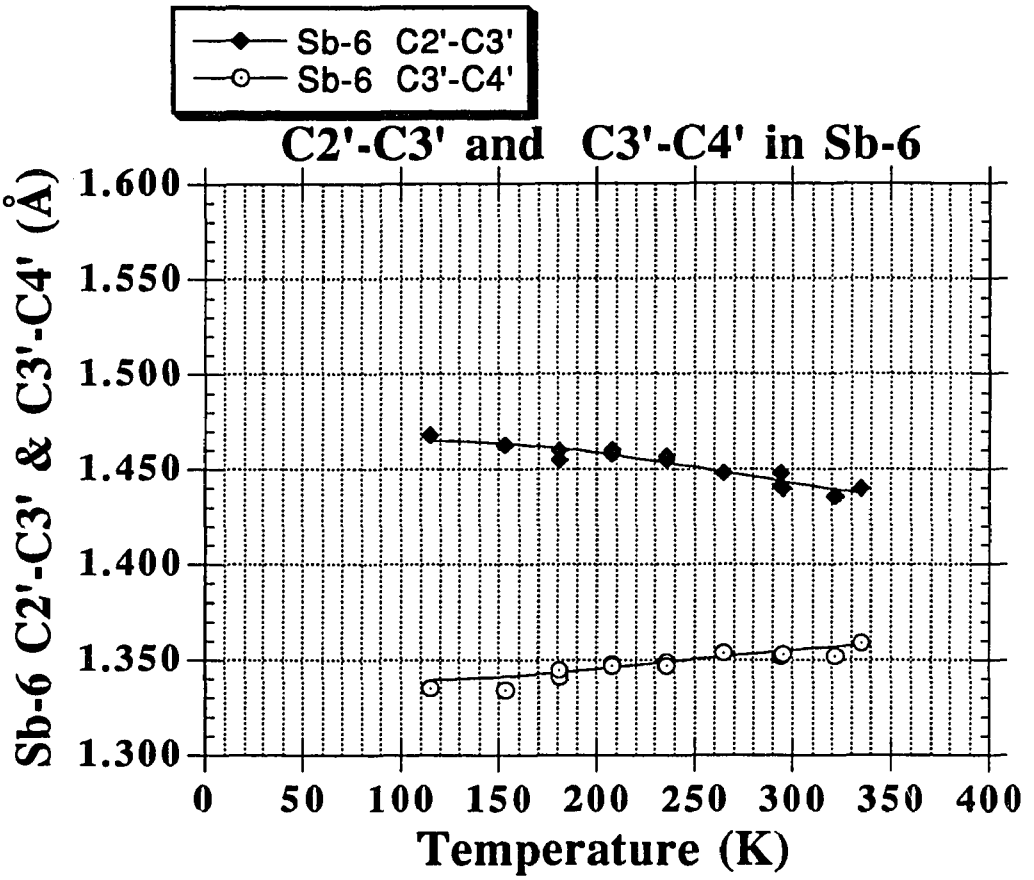


Figure 4–48. Plots of C2'—C3' and C3'—C4' distances (primed) in Sb-6 versus temperature.

The sum of the distances C2'—C3' and C3'—C4' in Sb-6 remains constant as the temperature is varied (Figure 4–49).

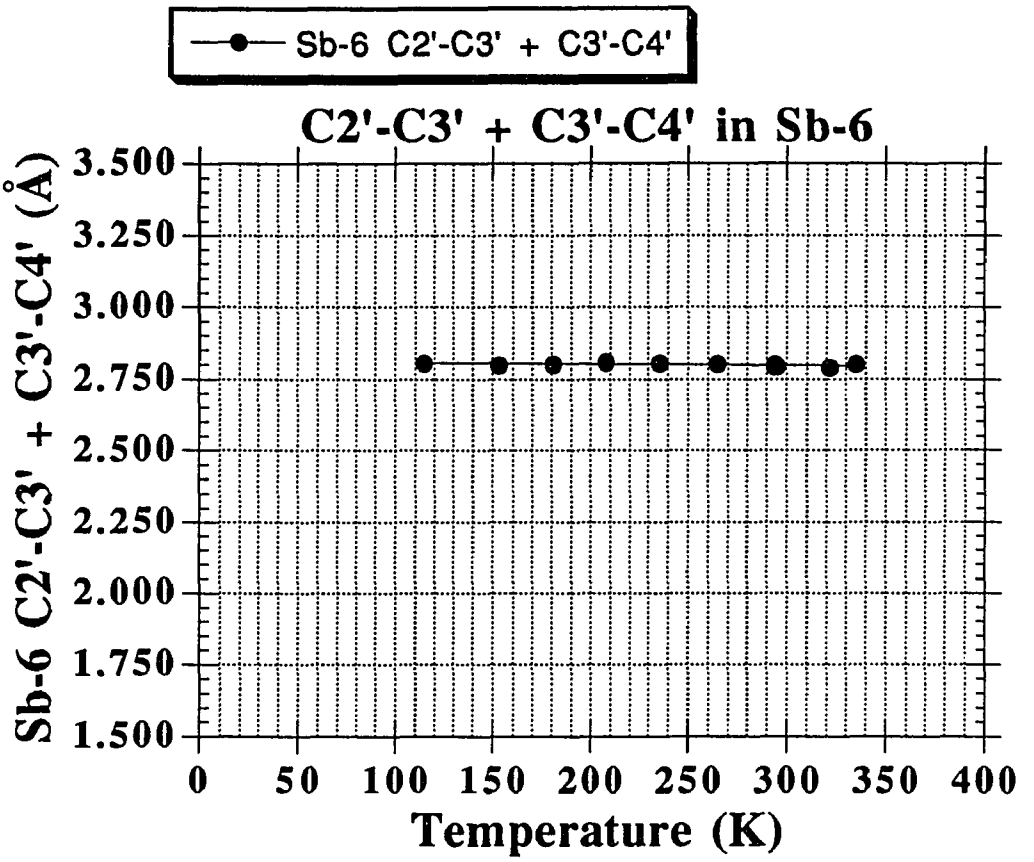


Figure 4–49. A plot of the sum of the distances C2'—C3' and C3'—C4' (primed) in Sb-6 versus temperature.

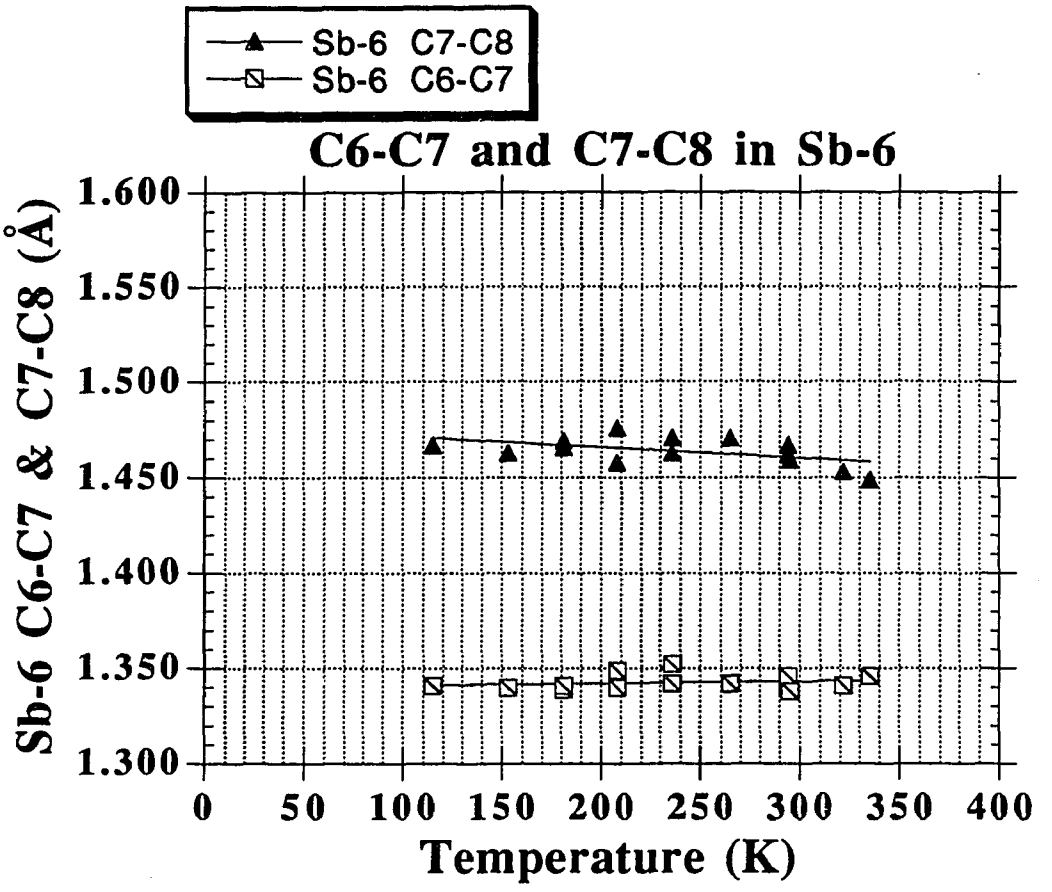


Figure 4–50. Pots of C6—C7 and C7—C8 distances (unprimed) in Sb-6 versus temperature.

The sum of the distances C6—C7 and C7—C8 in Sb-6 remains nearly constant as the temperature is varied (Figure 4–51).

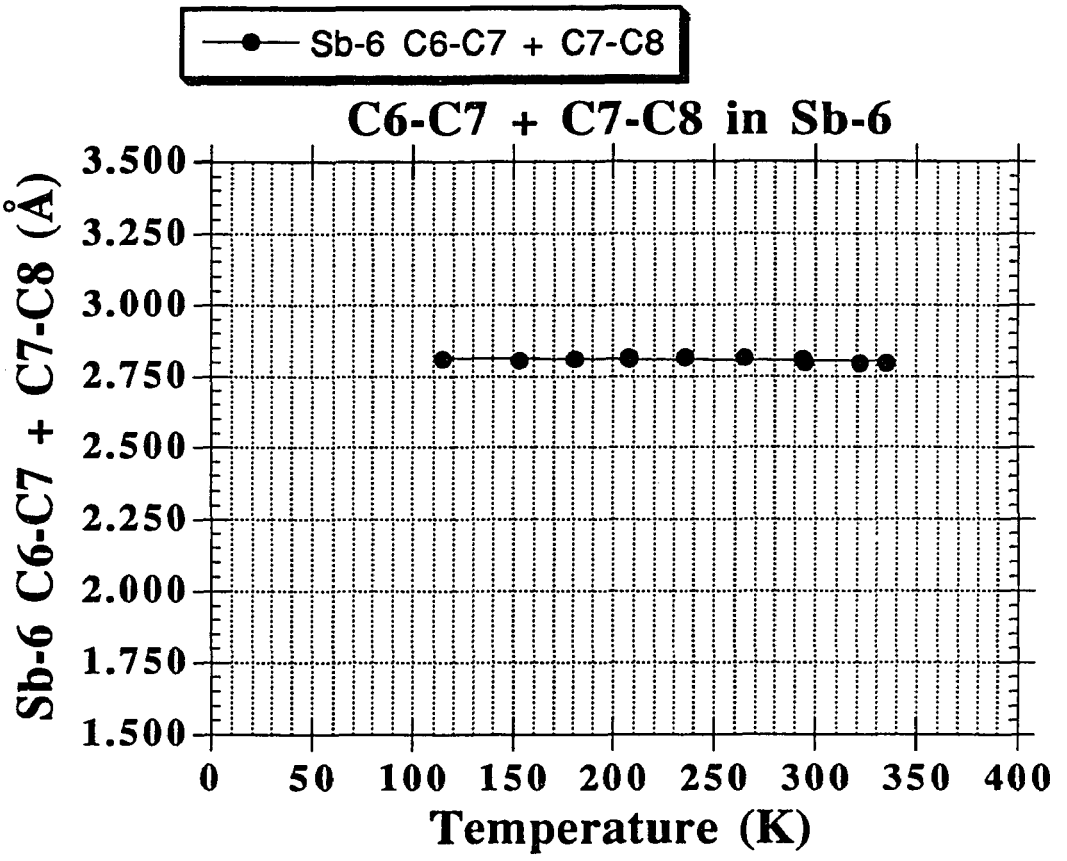


Figure 4–51. A plot of the sum of the distances C6—C7 and C7—C8 (unprimed) in Sb-6 versus temperature.

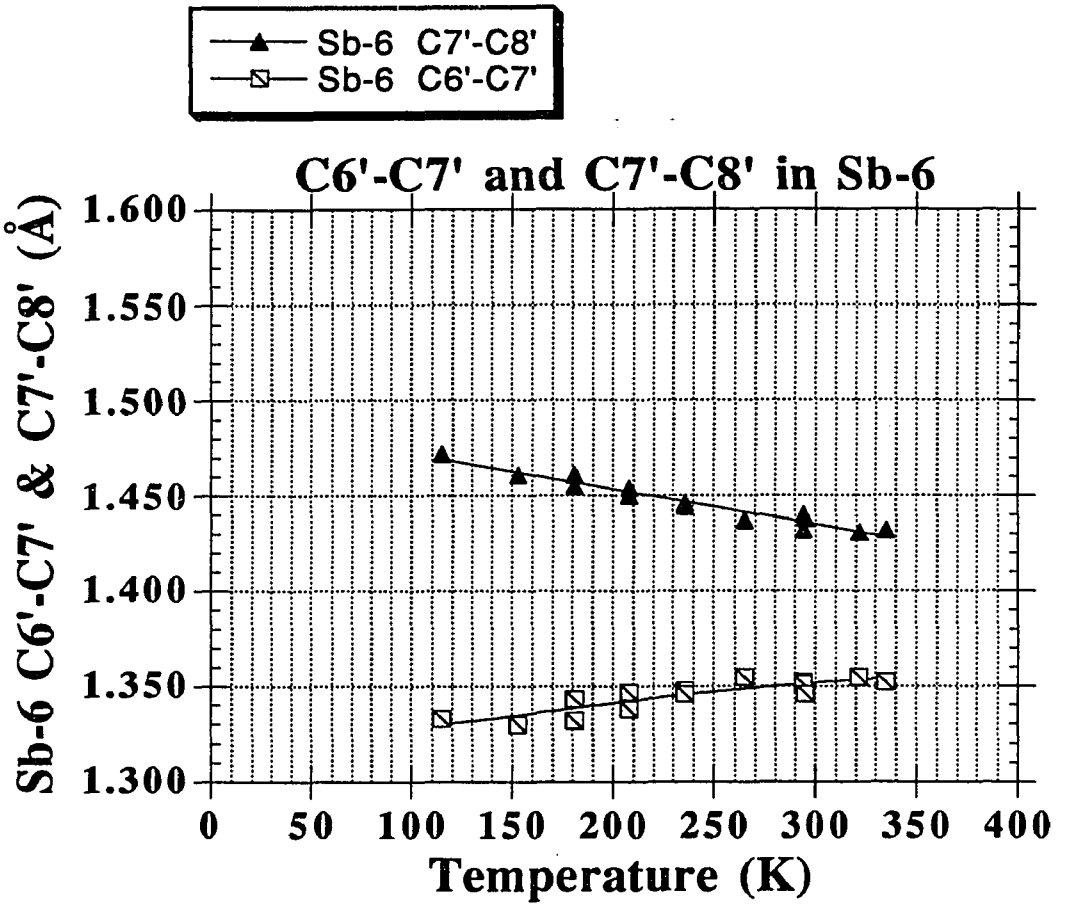


Figure 4–52. Plots of C6'—C7' and C7'—C8' distances (primed) in Sb-6 versus temperature.

The sum of the distances C6'—C7' and C7'—C8' in Sb-6 remains nearly constant as the temperature is varied (Figure 4–53).

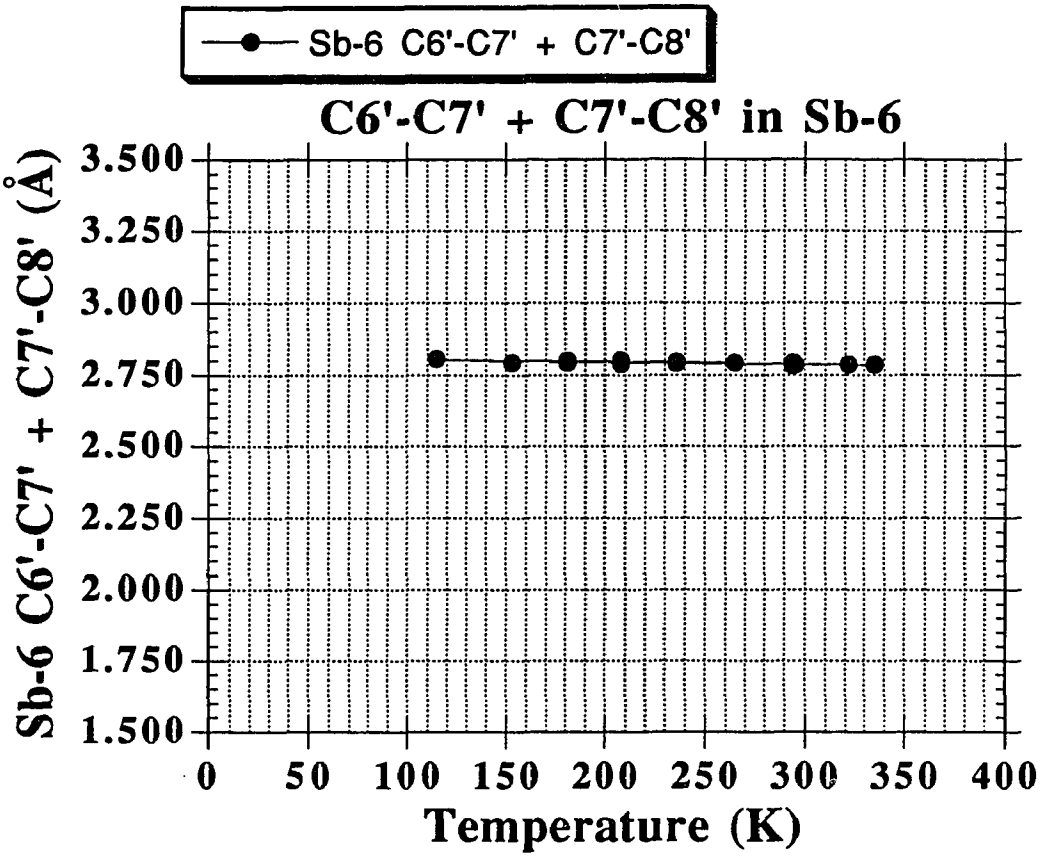


Figure 4–53. A plot of the sum of the distances C6'—C7' and C7'—C8' (primed) in Sb-6 versus temperature.

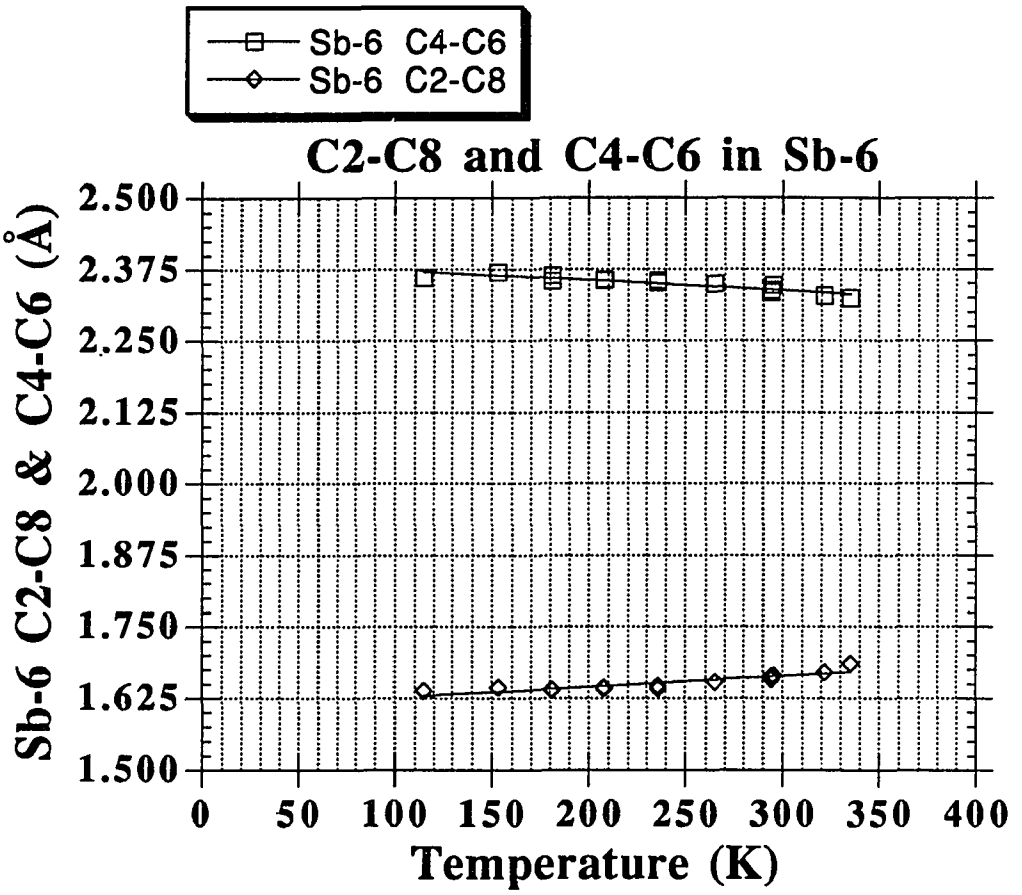


Figure 4–54. Plots of the distances C2—C8 and C4—C6 (unprimed) in Sb-6 versus temperature.

The sum of the distances C2—C8 and C4—C6 in Sb-6 remains constant with increasing temperature (Figure 4–55).

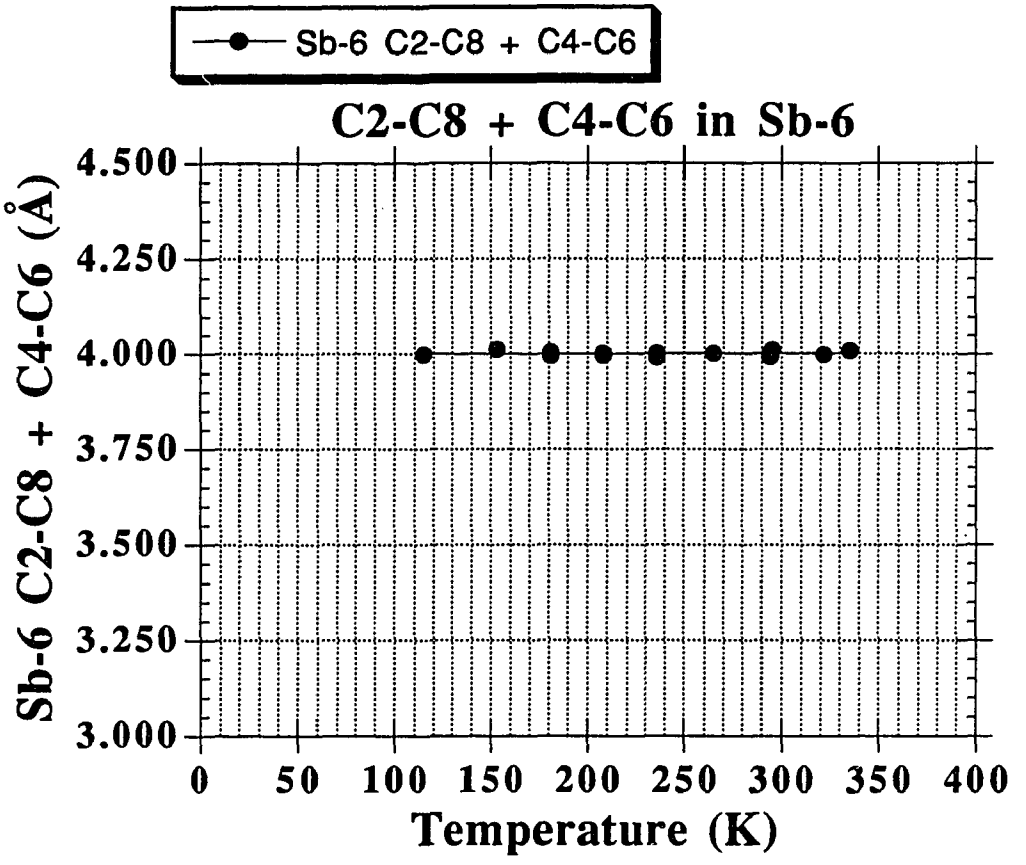


Figure 4–55. A plot of the sum of the distances C2—C8 and C4—C6 (unprimed) in Sb-6 versus temperature.

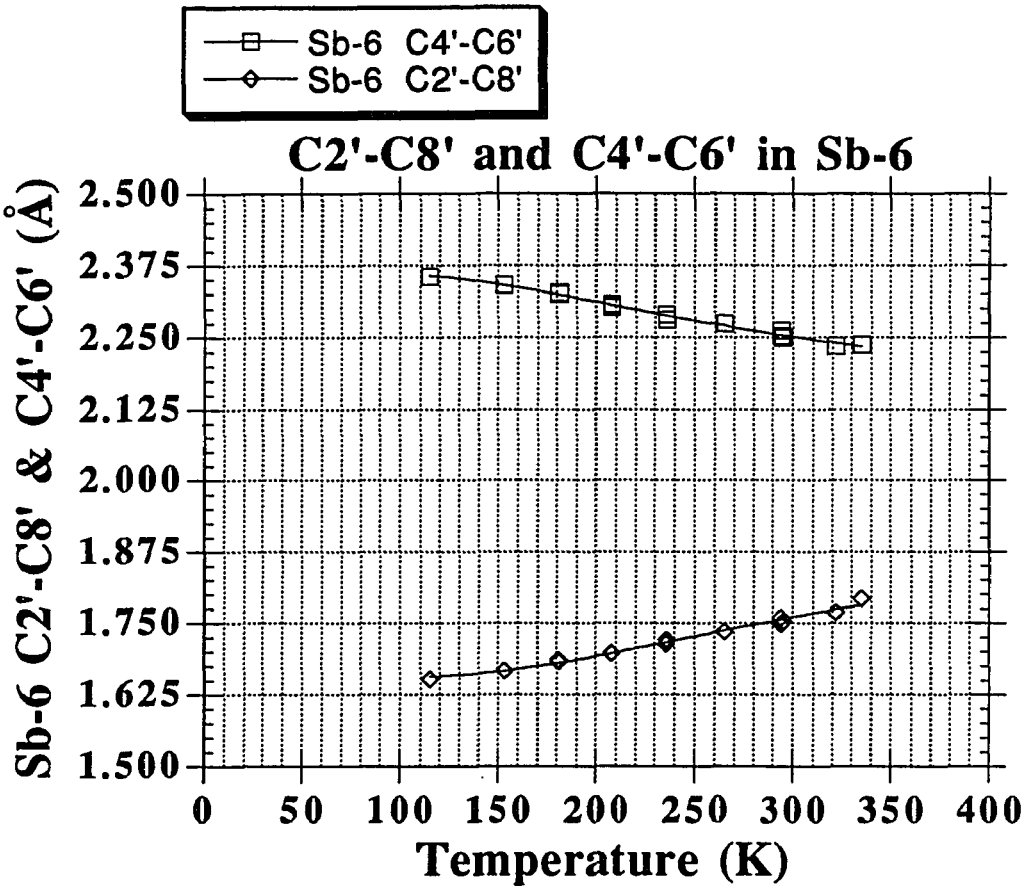


Figure 4–56. Plots of the distances C2'—C8' and C4'—C6' (primed) in Sb-6 versus temperature.

The sum of the distances C2'—C8' and C4'—C6' in Sb-6 remains constant as the temperature is varied (Figure 4–57).

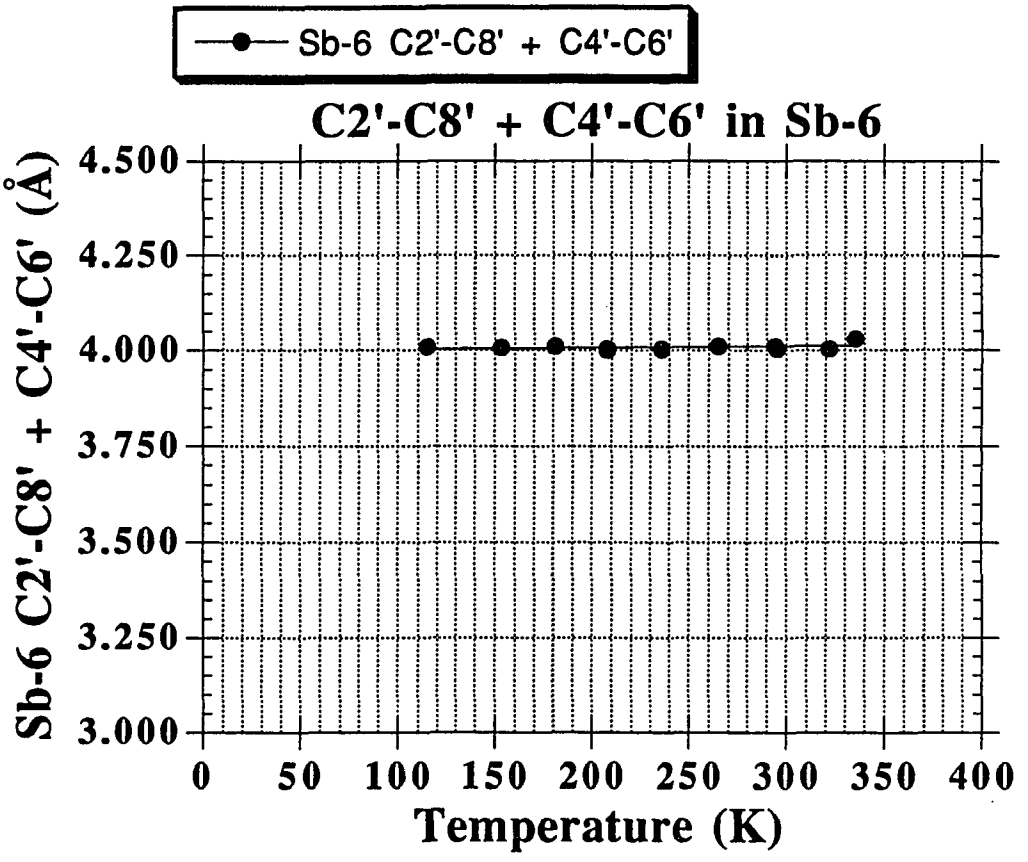


Figure 4–57. A plot of the sum of the distances C2'—C8' and C4'—C6' (primed) in Sb-6 versus temperature.

Table 4–11 lists angles in the ring of Sb-6 for both independent molecules.

Table 4–11. Selected Angles (°) in the Ring of Sb-6 at Various Temperatures

	115 K		153 K		181 K	
	unprimed	primed	unprimed	primed	unprimed	primed
C2—C1—C5	104.5(3)	104.5(3)	104.6(3)	104.8(3)	105.0(2)	104.4(2)
C2—C1—C8	65.8(2)	66.7(2)	65.8(2)	67.5(2)	66.1(2)	68.3(2)
C5—C1—C8	104.0(2)	104.1(3)	104.3(2)	104.1(3)	104.4(2)	104.0(2)
C1—C2—C3	107.7(3)	107.8(3)	107.5(3)	108.2(3)	107.8(2)	108.5(2)
C1—C2—C8	58.1(2)	57.5(2)	58.1(2)	57.0(2)	57.9(2)	56.5(1)
C3—C2—C8	117.5(2)	117.7(3)	117.9(3)	117.2(3)	118.1(2)	117.4(2)
C2—C3—C4	111.0(3)	111.2(3)	111.6(3)	110.9(3)	111.1(2)	110.8(2)
C3—C4—C5	110.3(3)	110.5(3)	110.3(3)	110.7(3)	110.8(2)	110.9(2)
C5—C4—C6	39.6(2)	39.7(2)	39.6(2)	40.1(2)	39.5(1)	40.3(1)
C1—C5—C4	103.0(3)	102.8(3)	102.5(3)	102.5(3)	101.8(2)	102.7(2)
C1—C5—C6	102.6(3)	102.6(2)	102.3(3)	102.7(2)	102.4(2)	102.9(2)
C4—C5—C6	100.9(3)	100.8(3)	100.9(3)	99.7(3)	100.8(2)	99.3(2)
C4—C6—C7	39.5(2)	39.5(2)	39.5(2)	40.2(2)	39.7(1)	40.3(1)
C5—C6—C5	111.5(3)	111.5(3)	111.5(3)	111.3(3)	111.4(2)	111.1(2)
C6—C7—C8	110.8(3)	110.9(3)	111.2(3)	111.2(3)	111.5(2)	111.2(2)
C1—C8—C2	56.1(2)	55.9(2)	56.1(2)	55.4(2)	56.0(1)	55.2(1)
C1—C8—C7	107.4(3)	107.5(3)	107.1(3)	107.6(3)	107.0(2)	108.1(2)
C2—C8—C7	120.3(3)	119.8(3)	120.1(3)	119.6(3)	120.0(2)	118.8(2)
$(\alpha+\beta)/2$[a]	83.7	83.8	83.8	83.6	83.8	83.8
C3—M[b]—C7	85.5	85.9	85.8	85.8	85.9	85.7

[a] α = C2—C1—C8, β = C4—C5—C6.
[b] M = midpoint between C1 and C5 bond.

Table 4–11 (cont'd). Selected Angles (°) in the Ring of Sb-6 at Various Temperatures

	181 K		208 K		208 K	
	unprimed	primed	unprimed	primed	unprimed	primed
C2—C1—C5	104.4(3)	104.2(3)	104.7(2)	104.4(2)	104.7(3)	104.7(3)
C2—C1—C8	65.8(2)	68.1(2)	66.2(2)	68.8(2)	66.1(3)	69.1(3)
C5—C1—C8	104.1(2)	103.9(3)	104.5(2)	103.9(2)	104.0(3)	104.0(3)
C1—C2—C3	107.8(3)	108.7(3)	107.8(2)	108.5(2)	108.0(3)	108.3(3)
C1—C2—C8	57.9(2)	56.8(2)	57.6(2)	56.3(2)	58.0(2)	56.2(2)
C3—C2—C8	117.9(2)	117.5(3)	118.2(2)	117.3(2)	117.9(3)	117.2(3)
C2—C3—C4	110.9(3)	111.1(3)	110.9(2)	110.7(2)	110.9(3)	110.7(3)
C3—C4—C5	110.7(3)	110.2(3)	111.0(2)	110.8(2)	110.9(3)	111.0(3)
C5—C4—C6	39.8(2)	40.4(2)	39.7(1)	40.6(1)	39.5(2)	40.9(2)
C1—C5—C4	103.0(3)	102.9(3)	102.3(2)	102.9(2)	102.0(3)	102.6(3)
C1—C5—C6	102.6(3)	102.6(2)	102.3(2)	103.1(2)	102.6(3)	102.8(3)
C4—C5—C6	100.5(3)	99.2(3)	100.6(2)	98.8(2)	100.7(3)	98.4(3)
C4—C6—C5	39.8(2)	40.5(2)	39.6(1)	40.7(1)	39.8(2)	40.7(2)
C5—C6—C7	111.3(3)	111.8(3)	111.7(2)	111.4(2)	111.4(3)	111.4(3)
C6—C7—C8	111.2(3)	110.9(3)	110.9(2)	110.8(2)	111.2(3)	111.2(3)
C1—C8—C2	56.3(2)	55.0(2)	56.2(2)	54.9(1)	55.9(2)	54.7(2)
C1—C8—C7	107.2(3)	108.0(3)	107.2(2)	108.2(2)	107.5(3)	108.3(3)
C2—C8—C7	120.1(3)	118.7(3)	119.7(2)	118.5(2)	120.0(3)	118.4(3)
$(\alpha+\beta)/2$[a]	83.2	83.7	83.4	83.8	83.4	83.8
C3—M[b]—C7	85.8	85.6	85.8	85.7	85.7	85.7

[a] α = C2—C1—C8, β = C4—C5—C6.
[b] M = midpoint between C1 and C5 bond.

Table 4–11 (cont'd). Selected Angles (°) in the Ring of Sb-6 at Various Temperatures

	236 K		236 K		265 K	
	unprimed	primed	unprimed	primed	unprimed	primed
C2—C1—C5	104.6(2)	104.6(2)	104.4(3)	104.6(3)	104.6(2)	104.7(2)
C2—C1—C8	66.2(2)	69.6(2)	65.9(3)	70.4(3)	66.7(2)	70.8(2)
C5—C1—C8	104.3(2)	103.9(2)	104.0(3)	104.0(3)	104.5(2)	103.9(2)
C1—C2—C3	107.8(2)	108.7(2)	108.0(3)	108.6(3)	107.9(2)	108.9(2)
C1—C2—C8	57.7(2)	55.9(2)	57.9(3)	55.7(2)	57.4(2)	55.2(2)
C3—C2—C8	118.1(2)	116.8(2)	118.1(3)	116.7(3)	117.9(2)	116.5(2)
C2—C3—C4	111.1(2)	110.6(2)	110.9(4)	110.8(4)	111.1(2)	110.7(2)
C3—C4—C5	110.7(2)	111.0(2)	110.7(3)	110.9(3)	110.8(2)	110.7(2)
C5—C4—C6	39.6(1)	41.1(1)	39.6(2)	41.3(2)	39.9(1)	41.4(1)
C1—C5—C4	102.4(2)	102.8(2)	102.6(3)	102.9(3)	102.5(2)	103.0(2)
C1—C5—C6	102.5(2)	103.0(2)	102.7(3)	103.0(3)	102.4(2)	103.1(2)
C4—C5—C6	100.7(2)	97.8(2)	100.5(3)	97.6(3)	100.4(2)	97.0(2)
C4—C6—C7	39.7(1)	41.2(1)	39.9(2)	41.1(2)	39.8(1)	41.6(1)
C5—C6—C5	111.5(2)	111.5(2)	111.4(3)	111.2(4)	111.4(2)	111.3(2)
C6—C7—C8	111.0(2)	110.8(2)	111.0(3)	111.4(4)	111.1(2)	110.6(2)
C1—C8—C2	56.0(2)	54.5(2)	56.2(2)	53.9(2)	55.9(2)	54.0(2)
C1—C8—C7	107.2(2)	108.6(2)	107.4(3)	108.3(3)	107.3(2)	109.1(2)
C2—C8—C7	119.7(2)	118.5(2)	120.2(3)	117.9(3)	119.4(2)	118.2(2)
$(\alpha+\beta)/2$[a]	83.5	83.7	83.2	84.0	83.6	83.9
C3—M[b]—C7	85.8	85.7	85.8	85.8	85.7	85.7

[a] α = C2—C1—C8, β = C4—C5—C6.
[b] M = midpoint between C1 and C5 bond.

Table 4–11 (cont'd). Selected Angles (°) in the Ring of Sb-6 at Various Temperatures.

	294 K		294 K		295 K	
	unprimed	primed	unprimed	primed	unprimed	primed
C2—C1—C5	104.6(2)	104.8(2)	104.3(3)	104.6(3)	104.8(2)	104.7(2)
C2—C1—C8	67.0(2)	71.6(2)	67.1(3)	72.1(3)	67.3(2)	71.5(2)
C5—C1—C8	104.3(2)	103.9(2)	104.1(3)	104.1(3)	104.5(2)	104.1(2)
C1—C2—C3	108.2(2)	109.0(2)	108.2(3)	109.3(3)	108.2(2)	108.8(2)
C1—C2—C8	57.3(2)	54.9(2)	57.4(2)	54.7(2)	57.2(2)	54.9(2)
C3—C2—C8	118.1(2)	116.1(2)	117.9(3)	116.5(3)	117.8(2)	116.4(2)
C2—C3—C4	110.8(3)	110.7(3)	111.2(3)	110.8(3)	111.3(2)	111.0(2)
C3—C4—C5	111.0(2)	110.9(2)	110.5(3)	110.9(3)	110.3(2)	110.9(2)
C5—C4—C6	40.0(1)	41.9(1)	40.0(2)	42.2(2)	39.9(1)	42.4(1)
C1—C5—C4	102.3(2)	102.8(2)	102.8(3)	102.8(3)	102.4(2)	103.1(2)
C1—C5—C6	102.6(2)	103.0(2)	102.8(3)	102.7(2)	102.5(2)	103.1(2)
C4—C5—C6	99.9(2)	96.2(2)	99.8(3)	95.6(3)	99.8(2)	95.5(2)
C4—C6—C7	40.1(1)	42.0(1)	40.2(2)	42.2(2)	40.3(1)	42.1(1)
C5—C6—C5	111.7(2)	111.7(2)	111.3(3)	111.6(3)	111.3(2)	111.3(2)
C6—C7—C8	110.9(2)	110.4(2)	111.1(3)	110.9(3)	111.6(2)	111.1(2)
C1—C8—C2	55.7(2)	53.5(2)	55.6(2)	53.1(2)	55.5(2)	53.6(2)
C1—C8—C7	107.4(2)	109.3(2)	107.6(3)	109.1(3)	107.1(2)	108.7(2)
C2—C8—C7	119.2(2)	117.8(2)	119.2(3)	117.4(3)	119.1(2)	117.4(2)
$(\alpha+\beta)/2$[a]	83.5	83.9	83.4	83.9	83.6	83.5
C3—M[b]—C7	85.8	85.5	85.7	85.9	85.7	85.7

[a] α = C2—C1—C8, β = C4—C5—C6.
[b] M = midpoint between C1 and C5 bond.

Table 4–11 (cont'd). Selected Angles (°) in the Ring of Sb-6 at Various Temperatures

	322 K		335 K	
	unprimed	primed	unprimed	primed
C2—C1—C5	104.5(3)	104.5(2)	104.9(3)	105.1(3)
C2—C1—C8	67.4(2)	72.7(2)	68.2(3)	73.9(3)
C5—C1—C8	104.1(2)	103.9(2)	104.6(3)	104.3(3)
C1—C2—C3	108.3(3)	109.4(3)	107.9(3)	109.4(3)
C1—C2—C8	57.2(2)	54.4(2)	56.7(2)	53.9(2)
C3—C2—C8	117.8(2)	116.1(3)	117.6(3)	115.8(3)
C2—C3—C4	111.0(3)	110.9(3)	111.3(4)	110.6(3)
C3—C4—C5	110.8(3)	110.8(3)	110.8(3)	110.5(3)
C5—C4—C6	40.3(2)	42.4(2)	40.5(2)	42.6(2)
C1—C5—C4	102.6(2)	103.0(2)	102.4(3)	103.0(3)
C1—C5—C6	102.7(2)	103.0(2)	102.6(3)	103.0(3)
C4—C5—C6	99.2(3)	95.1(3)	98.9(3)	94.7(3)
C4—C6—C7	40.5(2)	42.5(2)	40.6(2)	42.8(2)
C5—C6—C5	111.3(3)	111.6(3)	111.0(3)	111.8(4)
C6—C7—C8	111.4(3)	110.6(3)	111.5(4)	110.5(4)
C1—C8—C2	55.4(2)	52.9(2)	55.1(2)	52.2(2)
C1—C8—C7	107.6(3)	109.3(2)	107.6(3)	109.2(3)
C2—C8—C7	119.2(3)	117.3(2)	118.6(3)	116.5(3)
$(\alpha+\beta)/2$[a]	83.3	83.9	83.6	84.3
C3—M[b]—C7	85.8	85.9	85.7	85.6

[a] α = C2—C1—C8, β = C4—C5—C6.
[b] M = midpoint between C1 and C5 bond.

The following graphs better illustrate the data of the previous table.

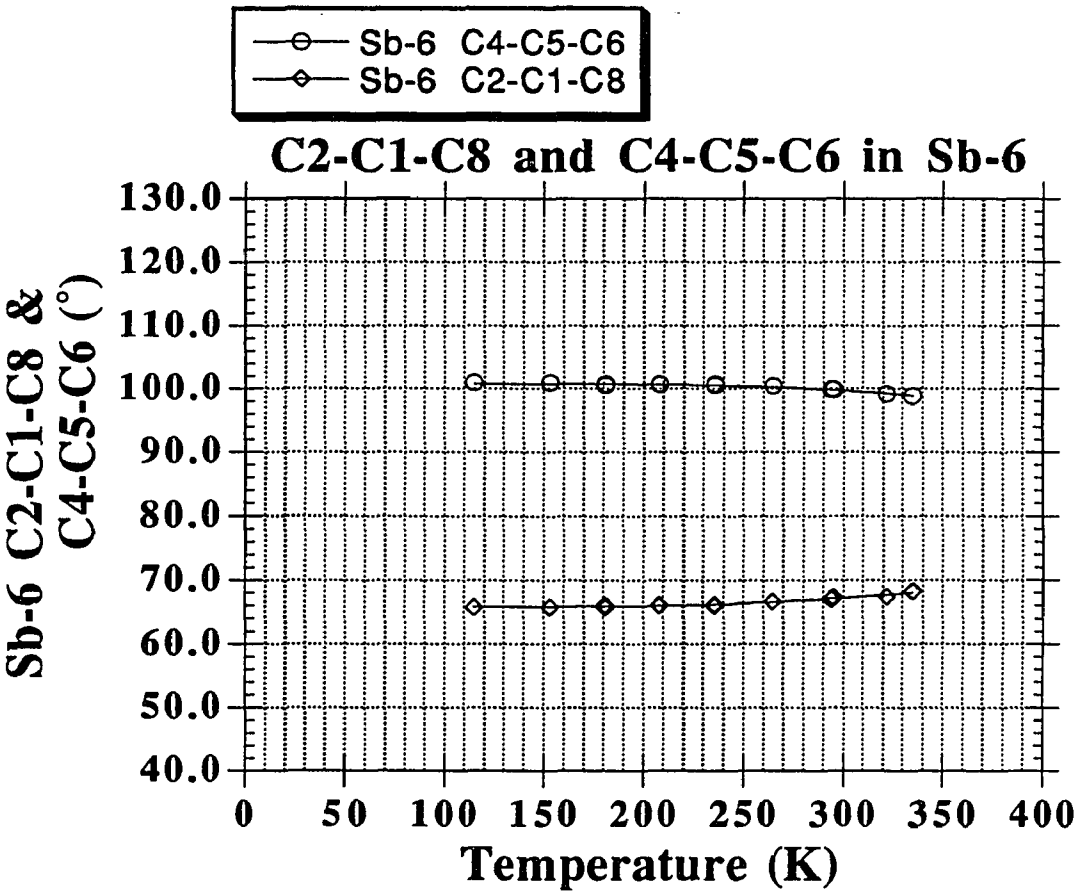


Figure 4–58. Plots of the angles C2—C1—C8 and C4—C5—C6 (unprimed) in Sb-6 versus temperature.

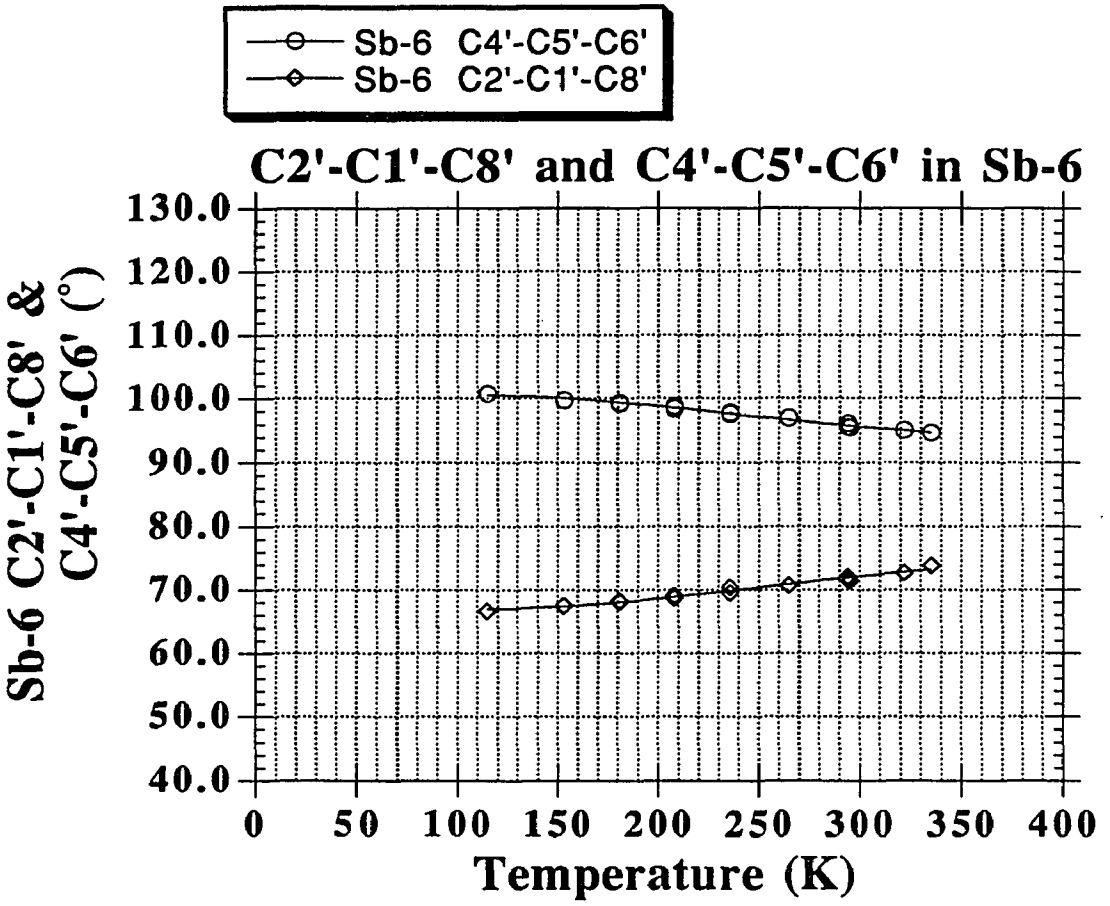


Figure 4–59. Plots of the angles C2'—C1'—C8' and C4'—C5'—C6' (primed) in Sb-6 versus temperature.

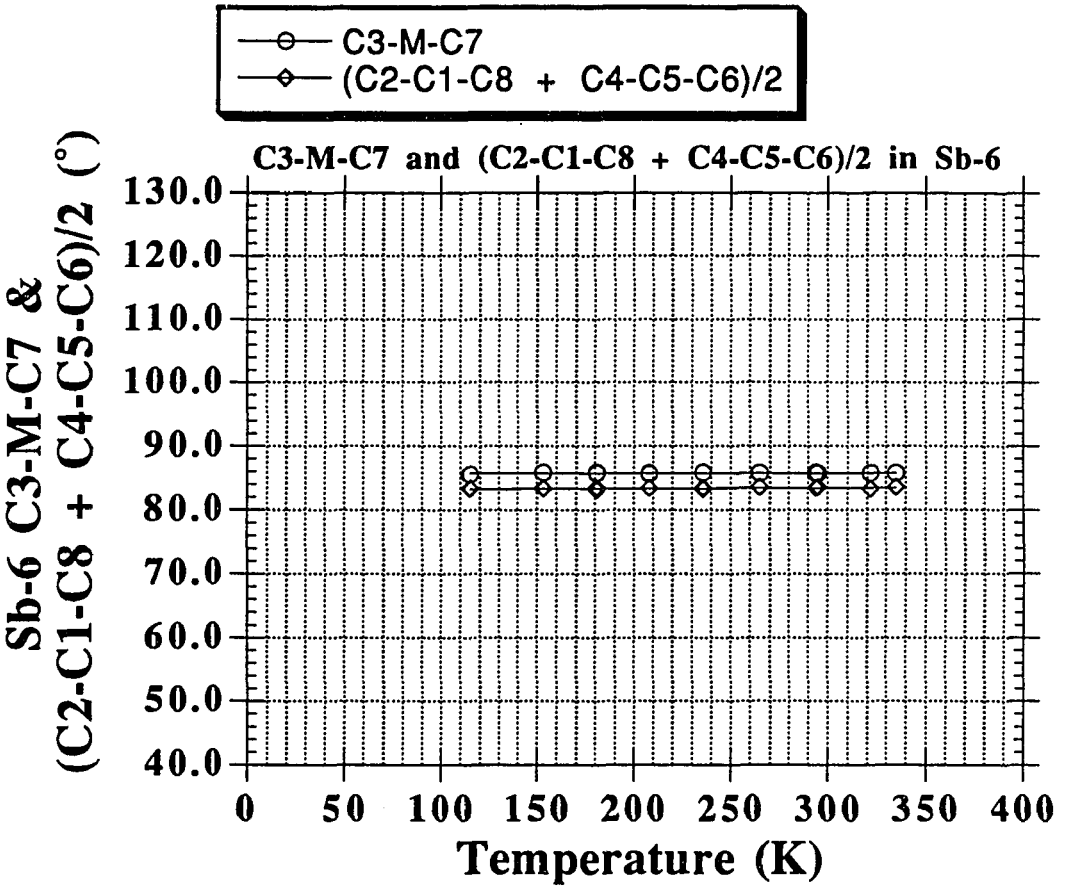


Figure 4–60. Plots of the angle C3—M—C7 (M = midpoint between C1 and C5) and the average angle of C2—C1—C8 and C4—C5—C6 in Sb-6 versus temperature.

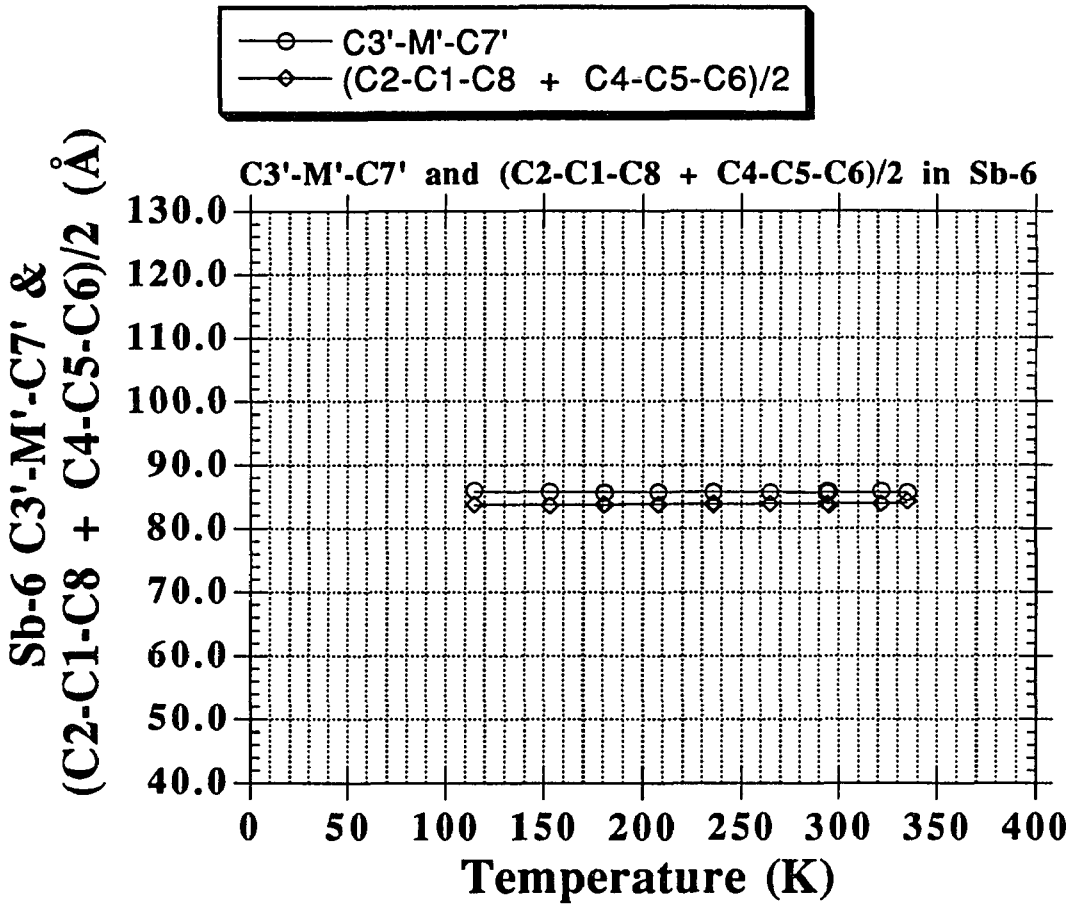


Figure 4–61. Plots of the angle C3'—M'—C7 (M' = midpoint between C1' and C5') and the average angle of C2'—C1'—C8' and C4'—C5'—C6' in Sb-6 versus temperature.

The root-mean-square displacements in Table 4–12 indicated that the maximum amplitudes of C2, C4, C6, C8 in the primed molecule of Sb-6 are generally bigger than those corresponding ones in the unprimed molecule.

Table 4–12. Selected Root-Mean-Square Amplitudes (Å) of Thermal Vibrations in the Ring of Sb-6 at Various Temperatures

		unprimed			primed		
		Min.	Int'med	Max.	Min.	Int'med	Max.
115 K	C1	0.089	0.109	0.118	0.084	0.112	0.117
	C2	0.080	0.117	0.126	0.096	0.101	0.129
	C3	0.101	0.117	0.132	0.084	0.114	0.129
	C4	0.085	0.123	0.130	0.101	0.118	0.122
	C5	0.093	0.109	0.128	0.085	0.113	0.125
	C6	0.091	0.124	0.136	0.108	0.126	0.131
	C7	0.108	0.122	0.137	0.100	0.119	0.139
	C8	0.091	0.116	0.135	0.088	0.120	0.135
153 K	C1	0.114	0.117	0.141	0.093	0.120	0.142
	C2	0.111	0.134	0.140	0.117	0.131	0.154
	C3	0.124	0.133	0.147	0.125	0.130	0.144
	C4	0.122	0.139	0.142	0.124	0.141	0.148
	C5	0.108	0.120	0.146	0.101	0.129	0.132
	C6	0.123	0.141	0.151	0.126	0.142	0.153
	C7	0.116	0.136	0.161	0.124	0.131	0.152
	C8	0.101	0.140	0.147	0.107	0.144	0.162
181 K	C1	0.129	0.144	0.154	0.122	0.144	0.155
	C2	0.127	0.148	0.164	0.123	0.159	0.179
	C3	0.129	0.155	0.170	0.130	0.148	0.168
	C4	0.130	0.155	0.164	0.131	0.159	0.165
	C5	0.123	0.146	0.159	0.119	0.141	0.153
	C6	0.142	0.152	0.174	0.139	0.168	0.191
	C7	0.137	0.155	0.180	0.133	0.146	0.180
	C8	0.129	0.163	0.168	0.132	0.157	0.183
181 K	C1	0.110	0.140	0.150	0.116	0.138	0.146
	C2	0.121	0.130	0.149	0.121	0.145	0.173
	C3	0.121	0.139	0.165	0.124	0.140	0.151
	C4	0.123	0.150	0.157	0.130	0.151	0.155
	C5	0.123	0.136	0.139	0.103	0.140	0.150
	C6	0.124	0.147	0.158	0.124	0.156	0.179
	C7	0.129	0.144	0.181	0.130	0.135	0.167
	C8	0.117	0.154	0.161	0.115	0.148	0.176

Table 4–12 (cont'd). Selected Root-Mean-Square Amplitudes (Å) of Thermal Vibrations in the Ring of Sb-6 at Various Temperatures.

		unprimed			primed		
		Min.	Int'med	Max.	Min.	Int'med	Max.
208 K	C1	0.138	0.149	0.158	0.127	0.147	0.163
	C2	0.133	0.154	0.171	0.128	0.157	0.194
	C3	0.139	0.155	0.178	0.143	0.159	0.161
	C4	0.138	0.161	0.166	0.138	0.165	0.175
	C5	0.134	0.156	0.162	0.121	0.147	0.164
	C6	0.153	0.159	0.166	0.149	0.173	0.203
	C7	0.149	0.160	0.186	0.147	0.152	0.184
	C8	0.144	0.166	0.173	0.140	0.161	0.195
208 K	C1	0.118	0.143	0.162	0.106	0.151	0.155
	C2	0.133	0.145	0.162	0.126	0.149	0.189
	C3	0.142	0.147	0.173	0.142	0.152	0.155
	C4	0.144	0.148	0.157	0.136	0.158	0.179
	C5	0.134	0.144	0.157	0.120	0.134	0.148
	C6	0.146	0.156	0.159	0.147	0.169	0.194
	C7	0.142	0.151	0.180	0.138	0.146	0.174
	C8	0.132	0.153	0.177	0.124	0.160	0.192
236 K	C1	0.146	0.161	0.172	0.139	0.158	0.171
	C2	0.141	0.163	0.183	0.142	0.166	0.211
	C3	0.143	0.163	0.191	0.155	0.170	0.174
	C4	0.143	0.174	0.178	0.146	0.175	0.192
	C5	0.148	0.160	0.174	0.130	0.158	0.171
	C6	0.162	0.171	0.184	0.157	0.178	0.225
	C7	0.155	0.170	0.197	0.152	0.164	0.194
	C8	0.150	0.176	0.191	0.144	0.175	0.214
236 K	C1	0.134	0.151	0.174	0.131	0.153	0.173
	C2	0.135	0.145	0.183	0.132	0.160	0.205
	C3	0.137	0.157	0.192	0.139	0.158	0.172
	C4	0.138	0.156	0.182	0.137	0.172	0.192
	C5	0.124	0.155	0.161	0.132	0.145	0.166
	C6	0.143	0.161	0.181	0.150	0.187	0.205
	C7	0.153	0.165	0.193	0.143	0.151	0.185
	C8	0.132	0.174	0.181	0.138	0.165	0.208
265 K	C1	0.154	0.171	0.183	0.149	0.161	0.182
	C2	0.152	0.172	0.195	0.154	0.175	0.227
	C3	0.156	0.176	0.202	0.166	0.176	0.185
	C4	0.149	0.190	0.190	0.152	0.185	0.205
	C5	0.155	0.175	0.187	0.139	0.173	0.181
	C6	0.176	0.180	0.200	0.163	0.191	0.239
	C7	0.167	0.184	0.208	0.166	0.173	0.207
	C8	0.159	0.187	0.207	0.155	0.188	0.223

Table 4–12 (cont'd). Selected Root-Mean-Square Amplitudes (Å) of Thermal Vibrations in the Ring of Sb-6 at Various Temperatures

		unprimed			primed		
		Min.	Int'med	Max.	Min.	Int'med	Max.
294 K	C1	0.162	0.181	0.196	0.158	0.175	0.196
	C2	0.163	0.181	0.212	0.164	0.186	0.247
	C3	0.169	0.188	0.212	0.175	0.192	0.199
	C4	0.161	0.198	0.208	0.157	0.196	0.222
	C5	0.164	0.186	0.191	0.151	0.177	0.195
	C6	0.186	0.191	0.213	0.169	0.204	0.262
	C7	0.178	0.190	0.221	0.169	0.182	0.223
	C8	0.167	0.203	0.224	0.163	0.194	0.242
294 K	C1	0.158	0.184	0.196	0.158	0.175	0.192
	C2	0.161	0.194	0.206	0.159	0.195	0.239
	C3	0.168	0.193	0.212	0.170	0.180	0.203
	C4	0.167	0.189	0.208	0.162	0.202	0.213
	C5	0.166	0.182	0.197	0.154	0.170	0.192
	C6	0.179	0.190	0.223	0.177	0.200	0.263
	C7	0.174	0.190	0.222	0.173	0.173	0.224
	C8	0.165	0.186	0.226	0.151	0.196	0.244
295 K	C1	0.177	0.190	0.198	0.175	0.181	0.193
	C2	0.172	0.194	0.221	0.164	0.192	0.254
	C3	0.183	0.195	0.216	0.177	0.198	0.207
	C4	0.184	0.202	0.213	0.169	0.207	0.232
	C5	0.185	0.188	0.200	0.167	0.182	0.207
	C6	0.193	0.205	0.222	0.176	0.208	0.266
	C7	0.192	0.202	0.229	0.188	0.190	0.228
	C8	0.183	0.204	0.227	0.167	0.204	0.251
322 K	C1	0.173	0.193	0.205	0.167	0.191	0.203
	C2	0.175	0.202	0.224	0.166	0.204	0.264
	C3	0.181	0.196	0.225	0.187	0.195	0.210
	C4	0.180	0.206	0.216	0.172	0.215	0.237
	C5	0.181	0.190	0.196	0.167	0.183	0.202
	C6	0.195	0.201	0.233	0.180	0.208	0.278
	C7	0.199	0.199	0.237	0.179	0.194	0.237
	C8	0.176	0.201	0.246	0.168	0.210	0.251
335 K	C1	0.179	0.204	0.213	0.175	0.189	0.210
	C2	0.170	0.205	0.224	0.168	0.219	0.262
	C3	0.184	0.205	0.231	0.194	0.203	0.211
	C4	0.178	0.217	0.236	0.172	0.223	0.240
	C5	0.187	0.191	0.213	0.166	0.186	0.214
	C6	0.199	0.202	0.244	0.187	0.197	0.291
	C7	0.191	0.212	0.254	0.189	0.200	0.248
	C8	0.173	0.212	0.257	0.157	0.212	0.274

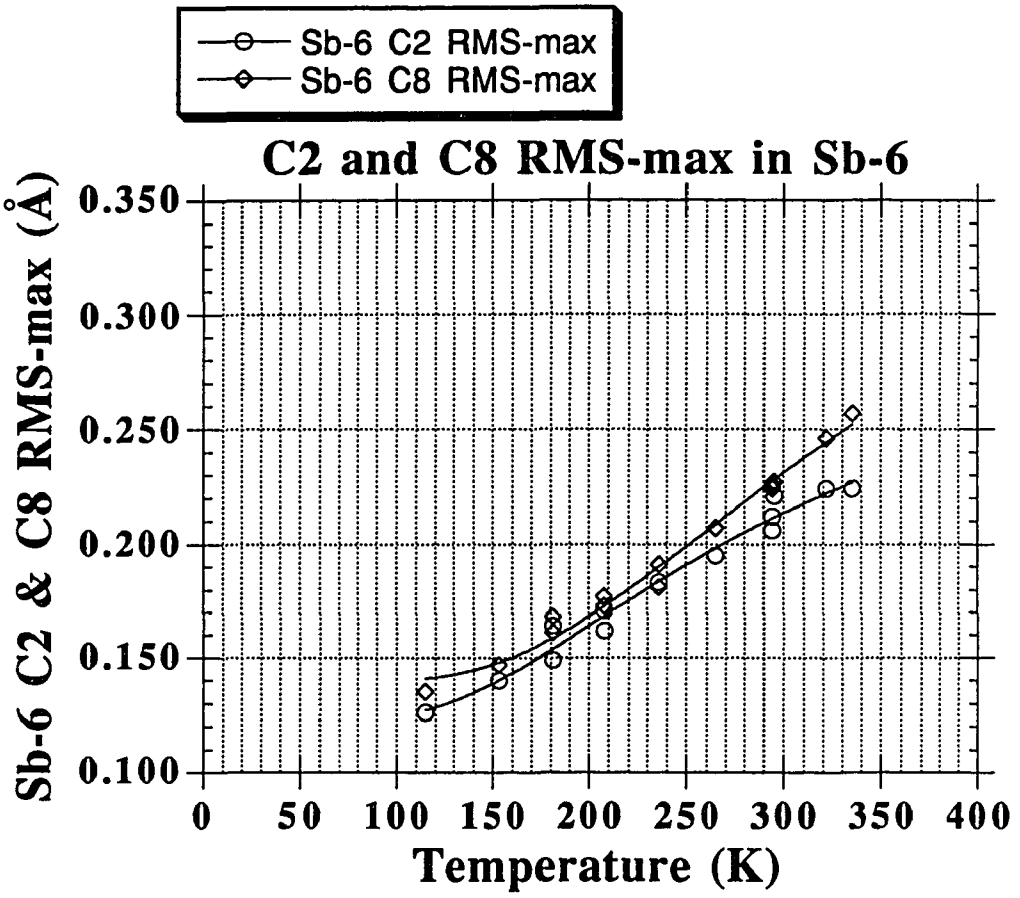


Figure 4–62. Plots of C2 RMS-max and C8 RMS-max in Sb-6 versus temperature.

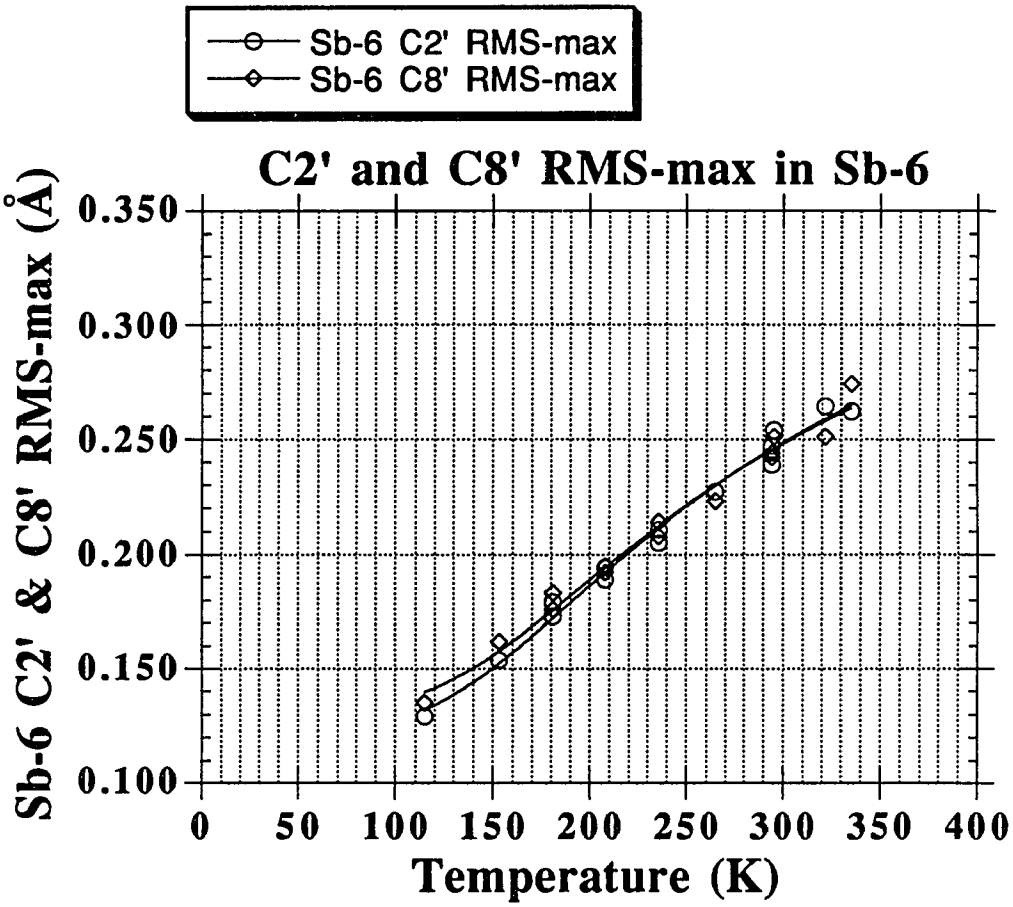


Figure 4–63. Plots of C2' RMS-max and C8' RMS-max in Sb-6 versus temperature.

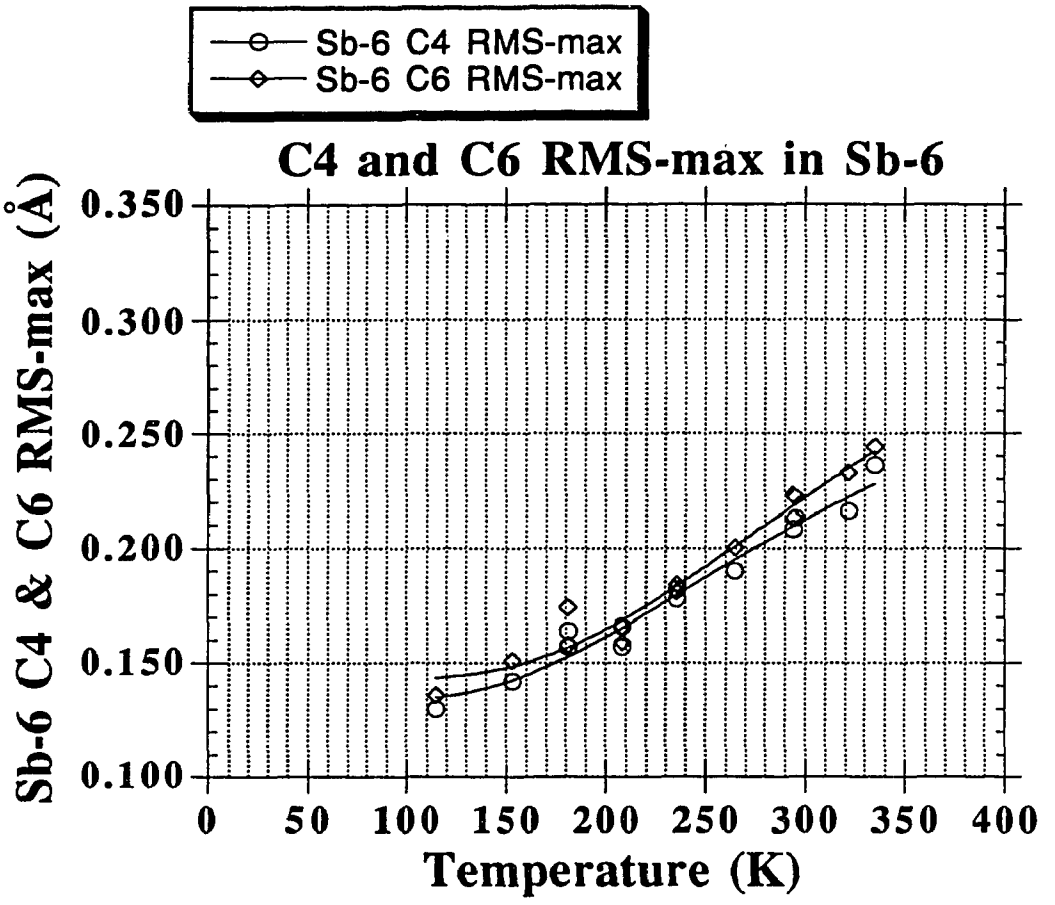


Figure 4–64. Plots of C4 RMS-max and C6 RMS-max in Sb-6 versus temperature.

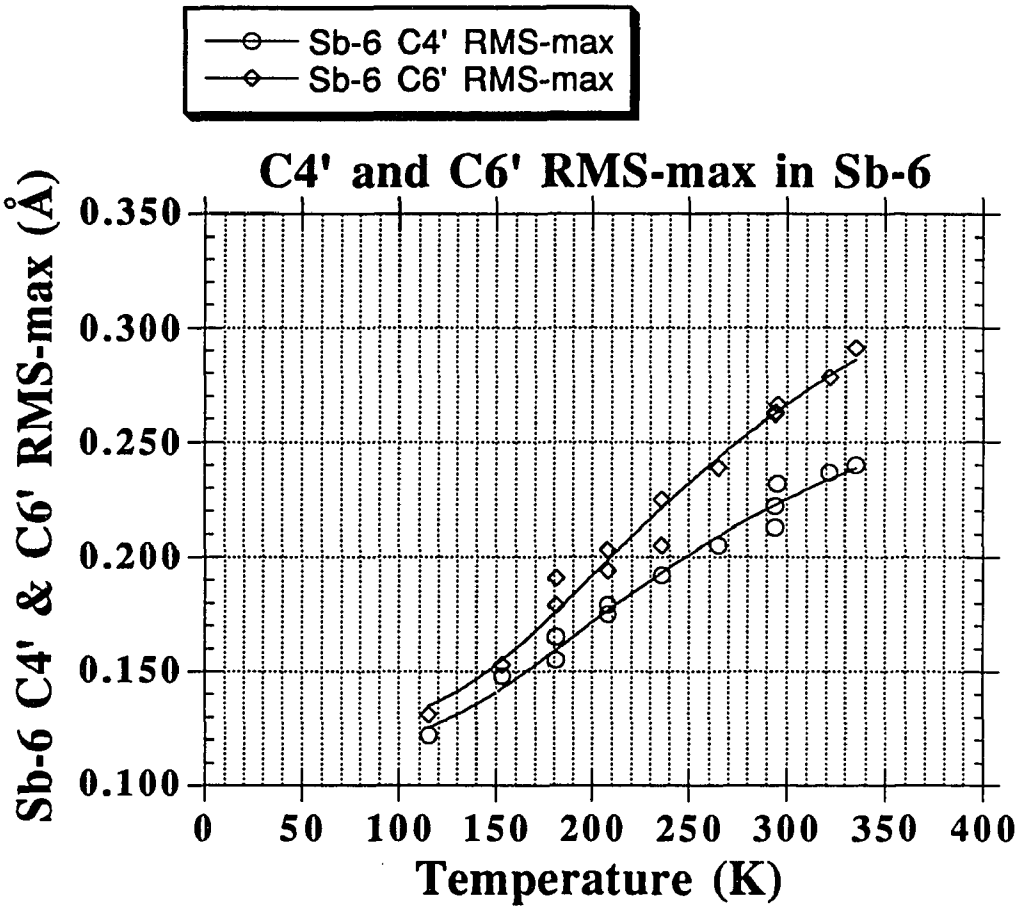


Figure 4–65. Plots of C4' RMS-max and C6' RMS-max in Sb-6 versus temperature.

ORTEP drawings of two independent molecules of Sb-6 are found at the end of this section.

A single-crystal X-ray analysis has also been carried out on a polymorph of Sb-6. Some relevant X-ray data is listed in Table 4–13.

Table 4–13. X-ray Crystal Data for Polymorph of Sb-6 at **295 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	123-124
Crystal size (mm)	0.13 x 0.55 x 0.84
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.798(1)
b (Å)	7.681(1)
c (Å)	22.872(1)
β (°)	95.86(1)
Cell volume (Å^3)	1887.03
Z	4
d_{calc} (g cm^{-3})	1.374
μ(Cu Kα) (cm^{-1})	8.57
R	0.054
R_w	0.082

This polymorph of Sb-6 crystallizes in the same monoclinic crystal system as the earlier sample of Sb-6 but in a different space group. The asymmetric unit has just one independent molecule instead of two. Judging from the interatomic distances C2—C8 and C4—C6 in Table 4–14, which are 1.829 and 2.197 Å, respectively, we see that this polymorph is closer to the bishomoaromatic state than the primed molecule of Sb-6 reported earlier.

Table 4–14. Selected Interatomic Distances (Å) in the Ring of Sb-6 Polymorph at **295 K**

C1—C2	1.485(2)
C1—C5	1.566(2)
C1—C8	1.510(2)
C2—C3	1.414(2)
C2—C8	1.829(3)
C3—C4	1.362(2)
C3—C7	3.056(3)
C4—C5	1.520(3)
C4—C6	2.197(3)
C5—C6	1.519(2)
C6—C7	1.362(2)
C7—C8	1.425(2)
C2—C3 + C3—C4	2.776
C6—C7 + C7—C8	2.787
C2—C8 + C4—C6	4.026

Table 4–15. Selected Interatomic Angles (°) in the Ring of Sb-6 Polymorph at 295 K.

C2—C1—C5	104.2(1)
C2—C1—C8	75.3(1)
C5—C1—C8	104.4(1)
C1—C2—C3	110.8(1)
C1—C2—C8	53.0(1)
C3—C2—C8	113.6(1)
C2—C3—C4	110.2(2)
C3—C4—C5	111.3(1)
C5—C4—C6	43.7(1)
C1—C5—C4	102.9(1)
C1—C5—C6	102.9(1)
C4—C5—C6	92.6(1)
C4—C6—C5	43.7(1)
C5—C6—C7	111.2(2)
C6—C7—C8	111.2(2)
C1—C8—C2	51.7(1)
C1—C8—C7	108.8(1)
C2—C8—C7	117.5(1)
$(\alpha+\beta)/2$[a]	84.0
C3—M[b]—C7	85.5

[a] α = C2—C1—C8, β = C4—C5—C6.
[b] M = midpoint between C1 and C5 bond.

Table 4–16. Selected Root-Mean-Square Amplitudes (Å) of Thermal Vibrations in the Ring of Sb-6 Polymorph at **295 K.**

		Min.	Int'med	Max.
295 K	C1	0.181	0.181	0.184
	C2	0.175	0.186	0.246
	C3	0.180	0.190	0.190
	C4	0.178	0.199	0.260
	C5	0.178	0.190	0.199
	C6	0.180	0.203	0.249
	C7	0.181	0.198	0.217
	C8	0.181	0.189	0.295

The structure of Sb-6 polymorph is plagued with disorder in the four ester groups. Each group was resolved into three moieties as illustrated in the *ORTEP* drawings of rotamers A, B, C in Figures 4–102 through 107. The occupancies of these rotamers are approximately 50%, 25%, and 25%, respectively. The esters moieties in the minor rotamers, B and C, could possibly be interchanged.

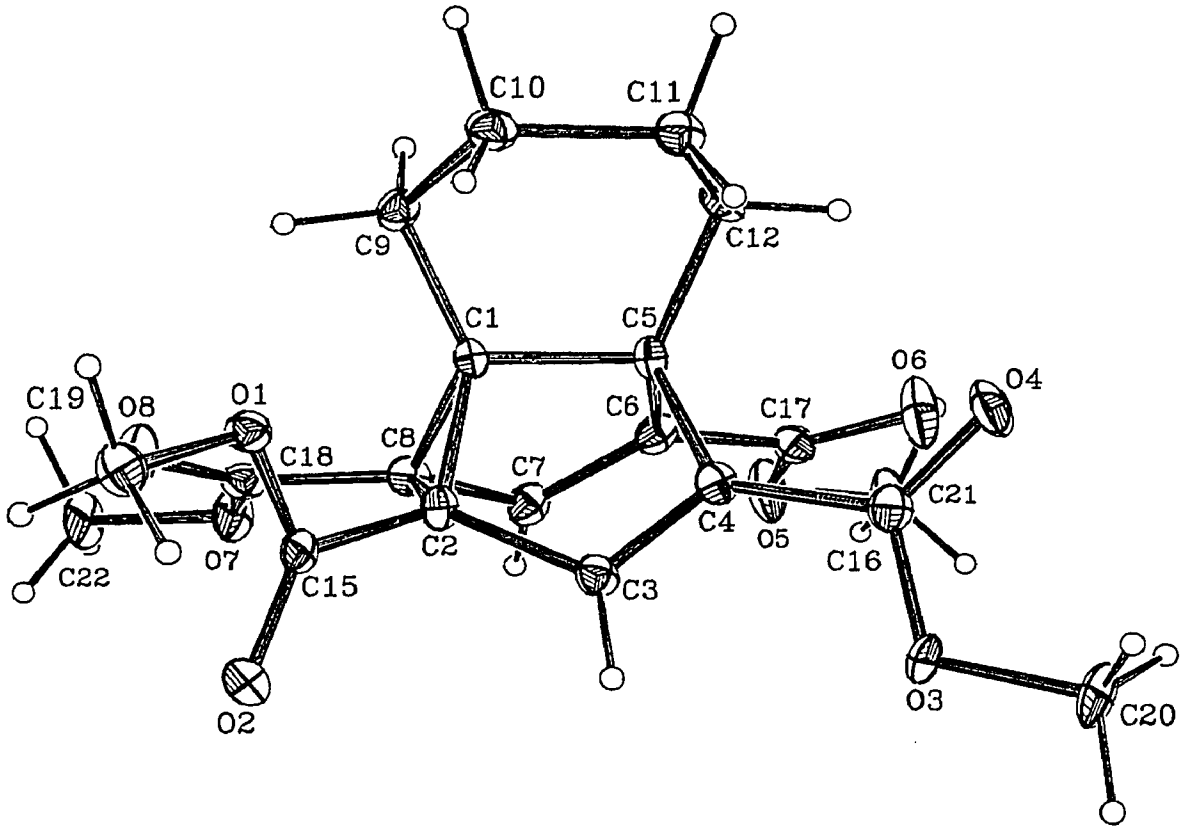


Figure 4–66. *ORTEP* drawing of Sb-6 (unprimed) at **115 K** with 50% thermal ellipsoids.

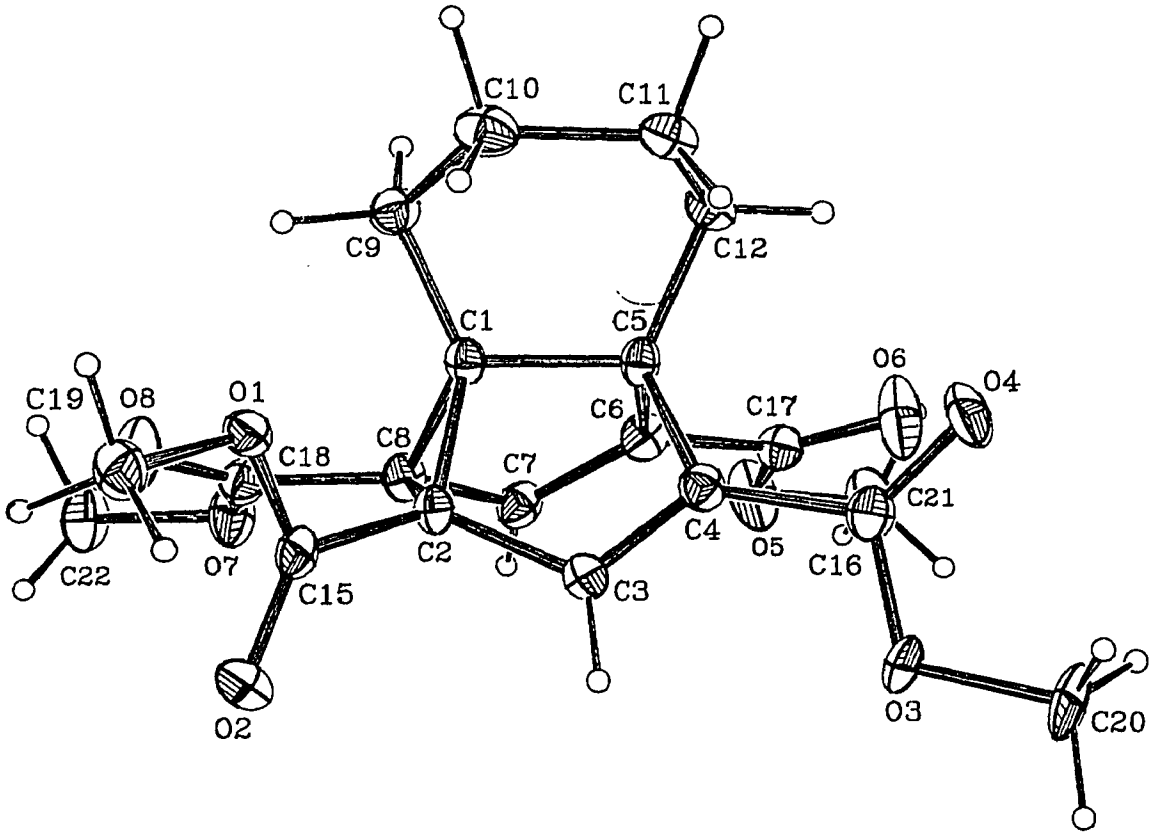


Figure 4–67. *ORTEP* drawing of Sb-6 (unprimed) at **153 K** with 50% thermal ellipsoids.

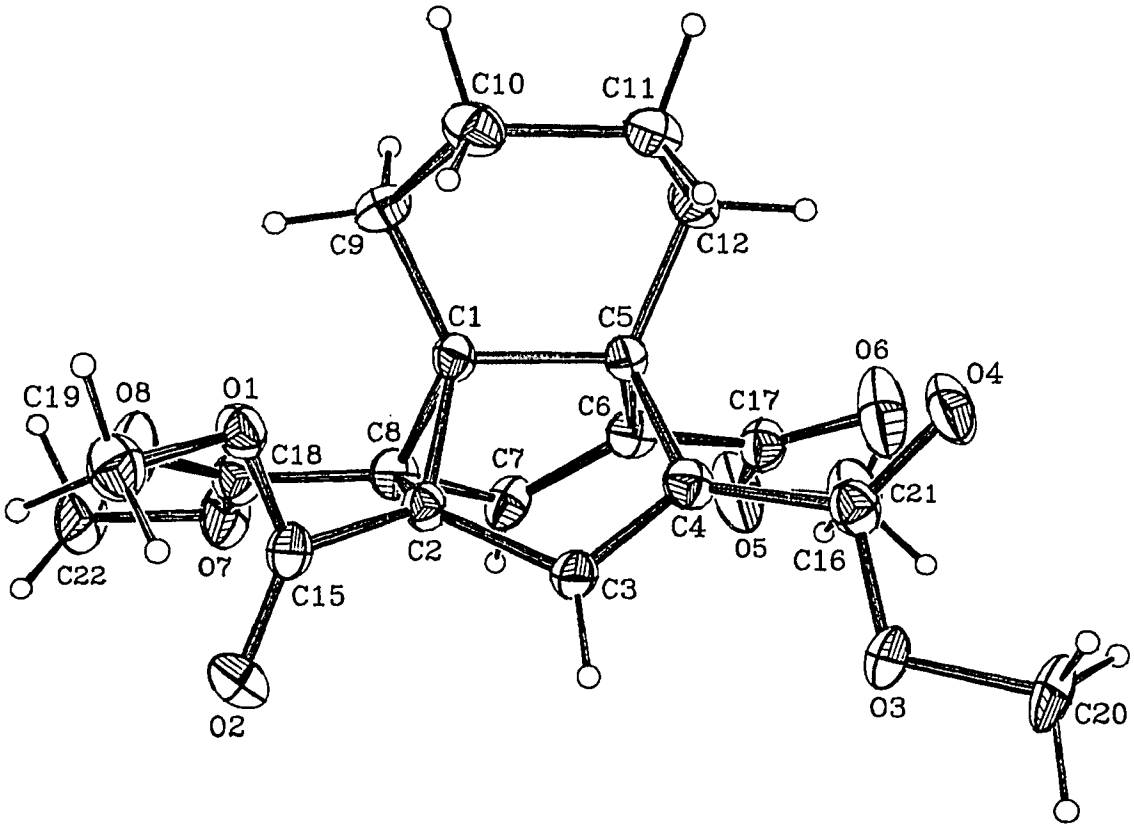


Figure 4–68. *ORTEP* drawing of Sb-6 (unprimed) at **181 K** with 50% thermal ellipsoids.

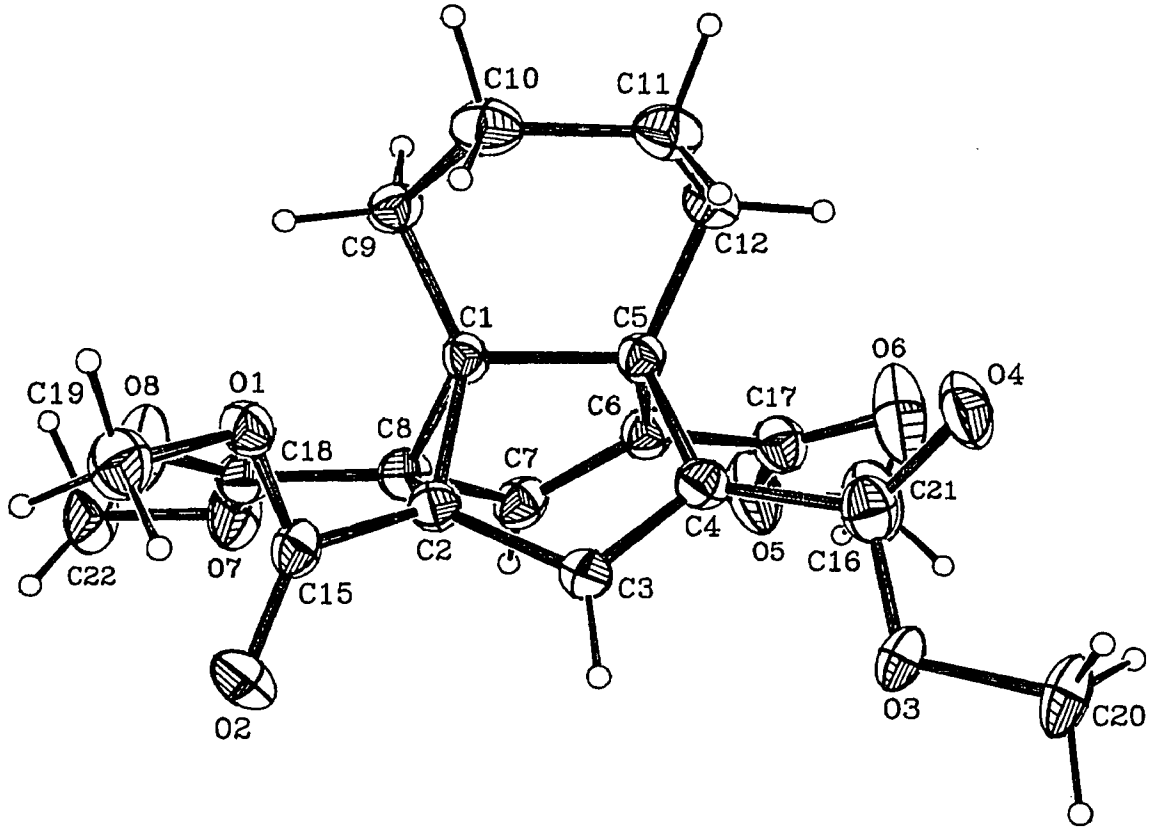


Figure 4–69. *ORTEP* drawing of Sb-6 (unprimed) at **208 K** with 50% thermal ellipsoids.

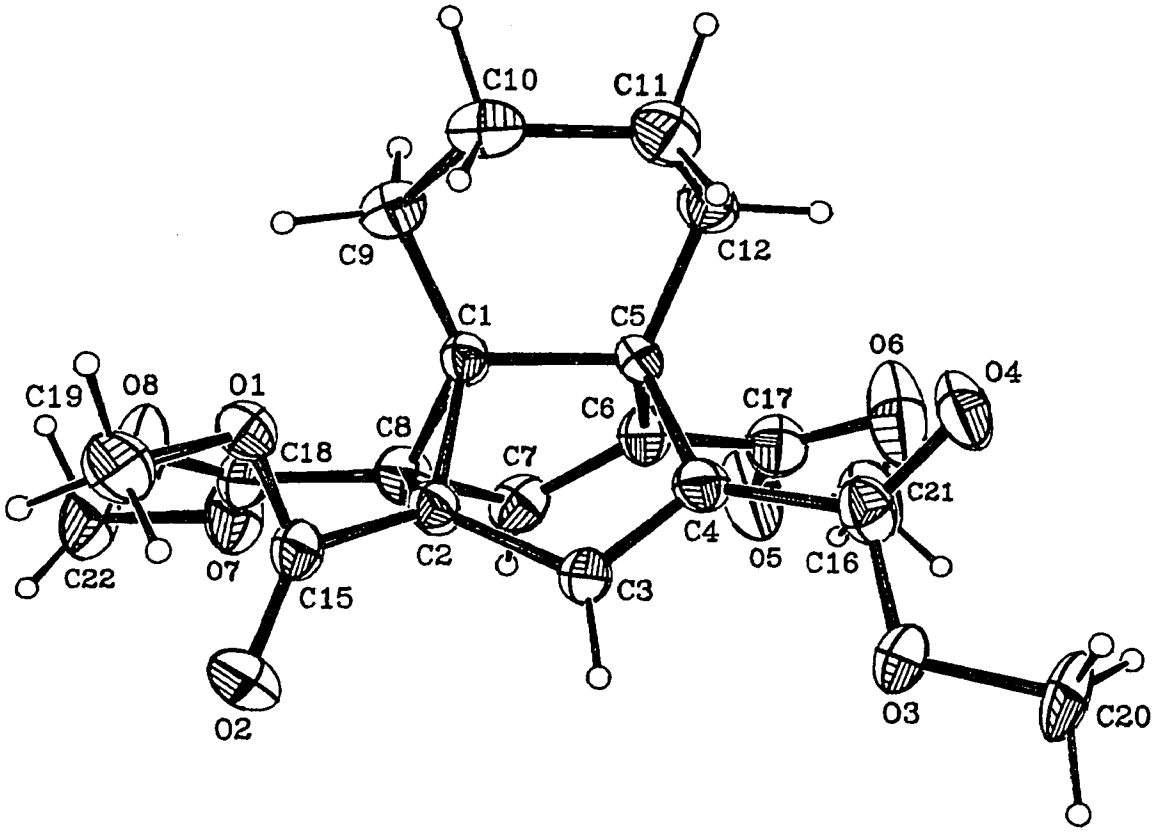


Figure 4–70. *ORTEP* drawing of Sb-6 (unprimed) at **236 K** with 50% thermal ellipsoids.

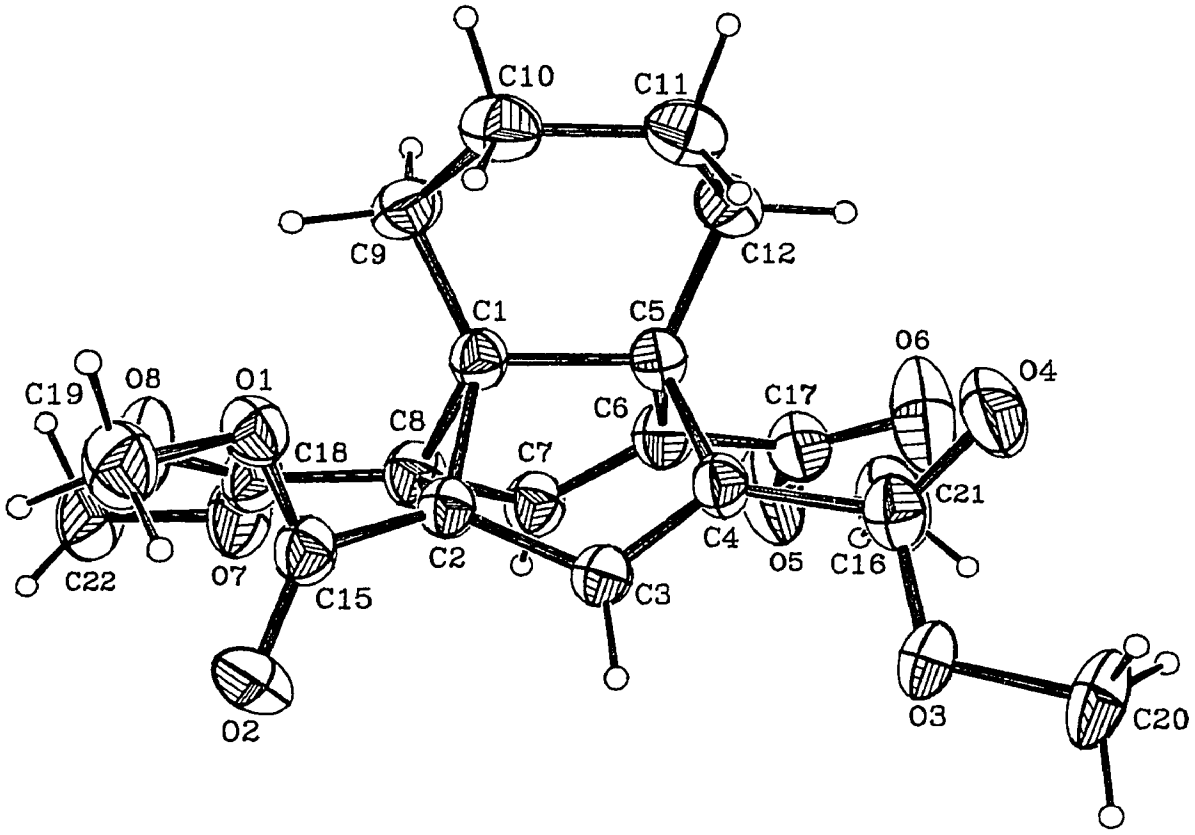


Figure 4–71. *ORTEP* drawing of Sb-6 (unprimed) at **265 K** with 50% thermal ellipsoids.

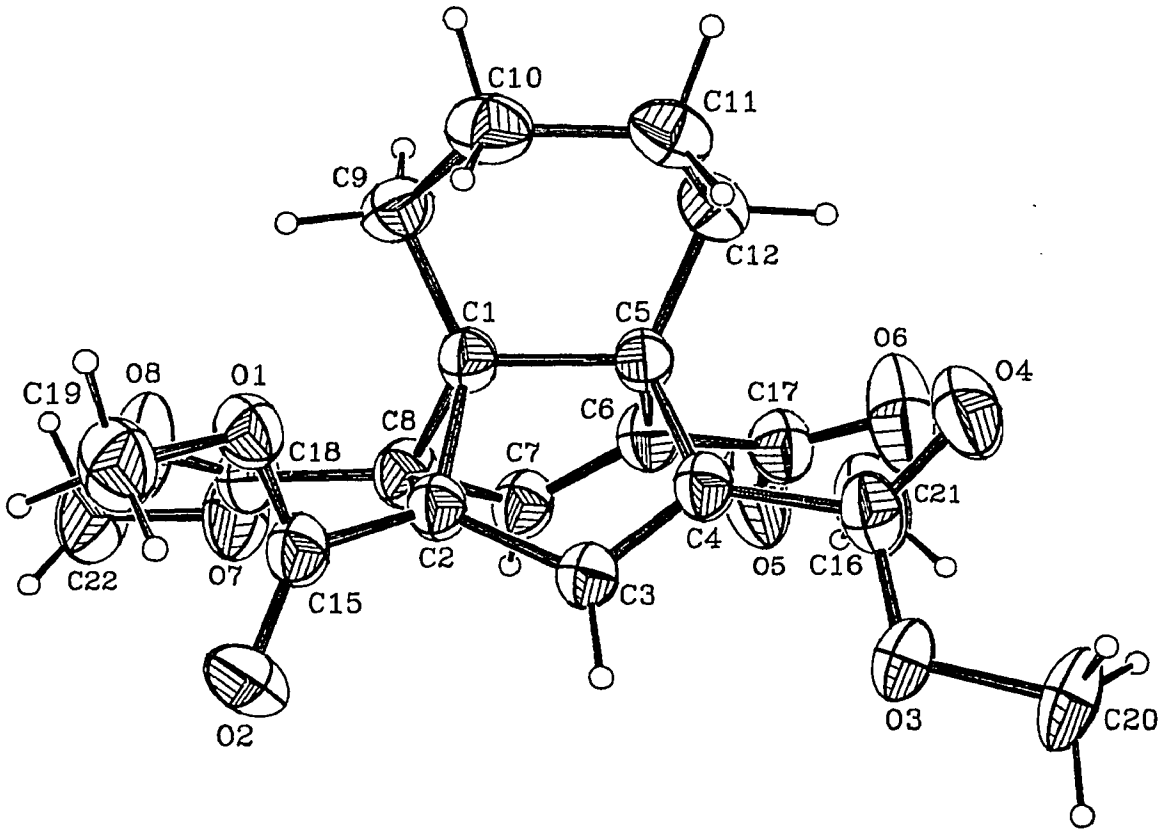


Figure 4–72. *ORTEP* drawing of Sb-6 (unprimed) at **294 K** with 50% thermal ellipsoids.

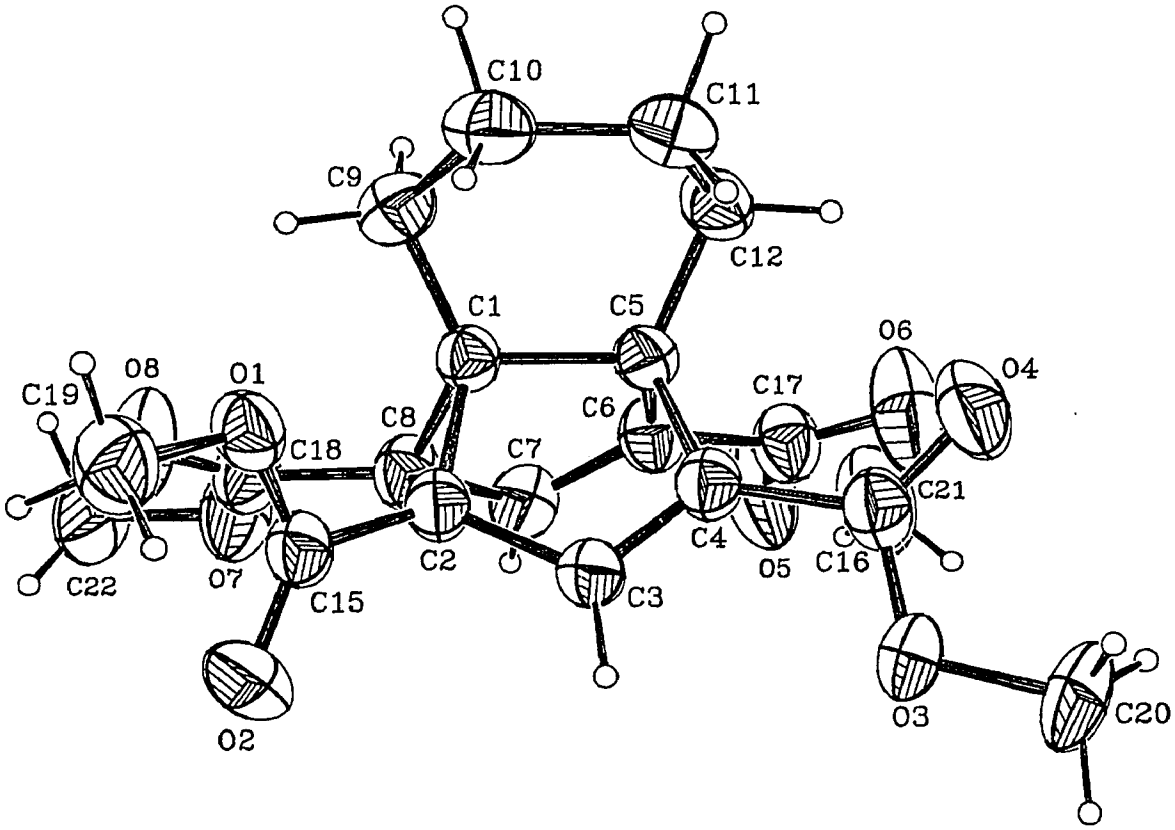


Figure 4–73. *ORTEP* drawing of Sb-6 (unprimed) at **322 K** with 50% thermal ellipsoids.

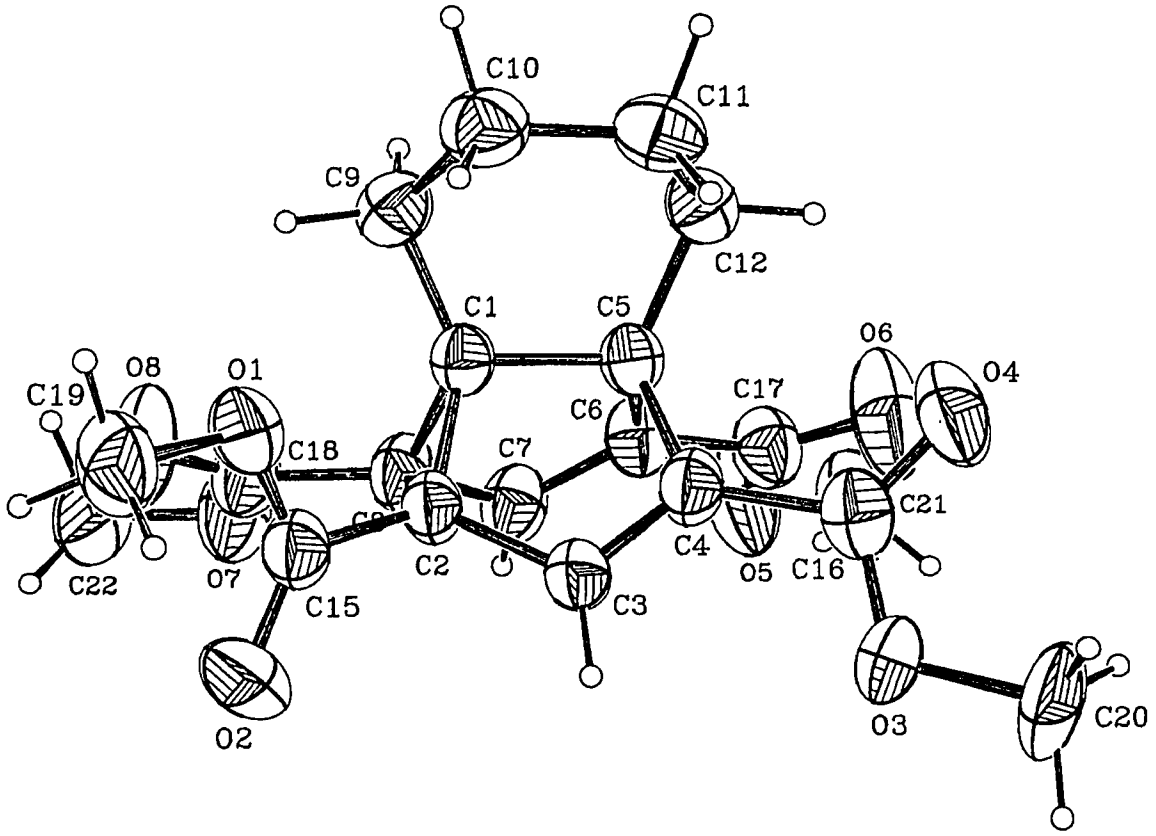


Figure 4–74. *ORTEP* drawing of Sb-6 (unprimed) at **335 K** with 50% thermal ellipsoids.

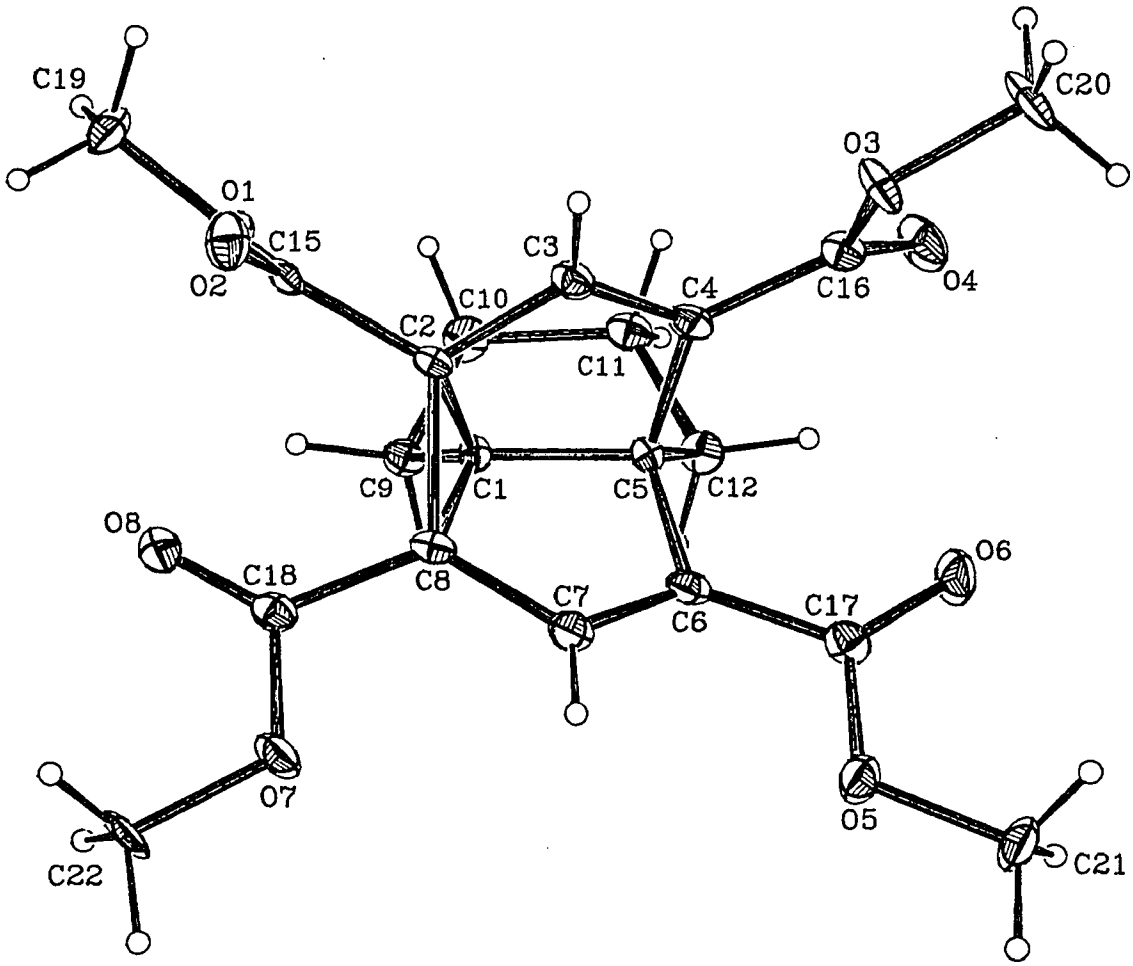


Figure 4–75. *ORTEP* drawing of Sb-6 (unprimed) at **115 K** with 50% thermal ellipsoids.

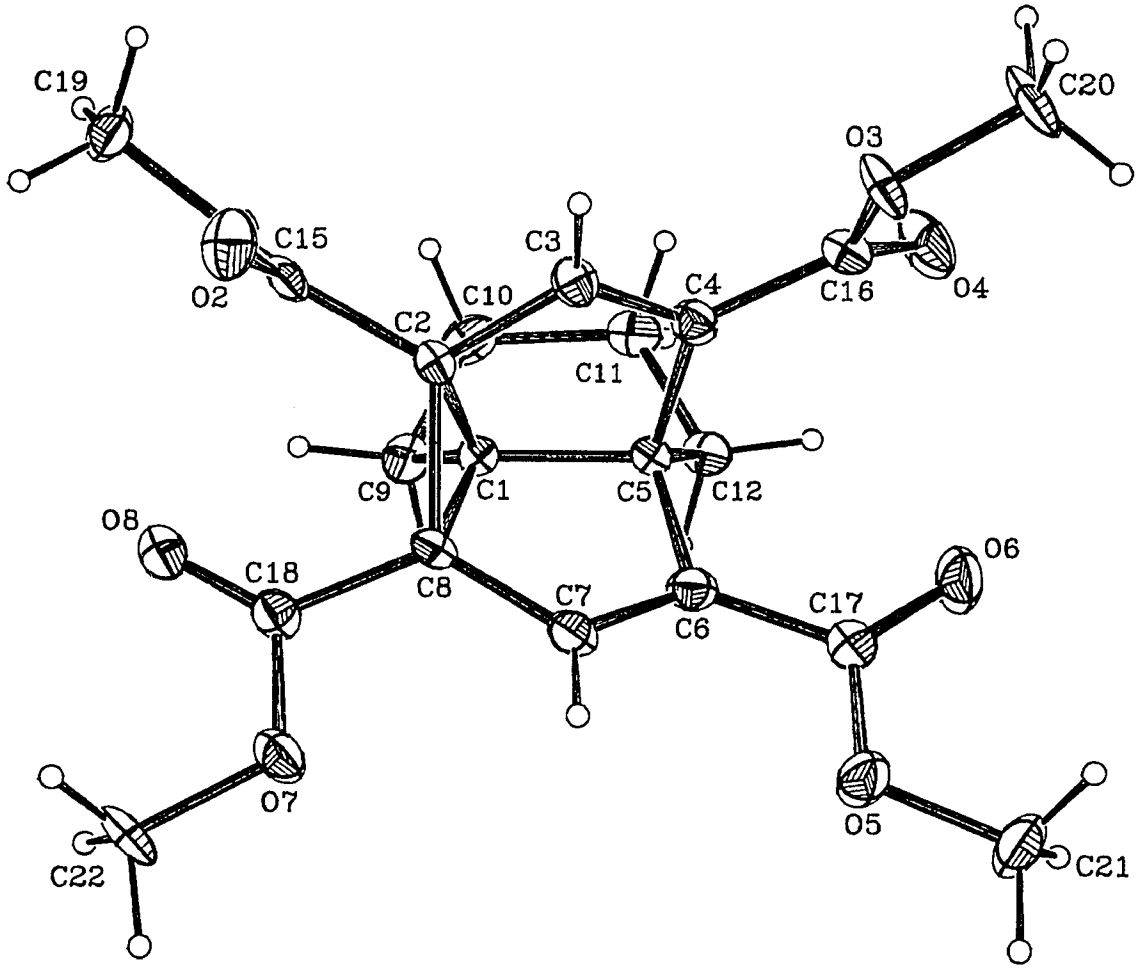


Figure 4–76. *ORTEP* drawing of Sb-6 (unprimed) at **153 K** with 50% thermal ellipsoids.

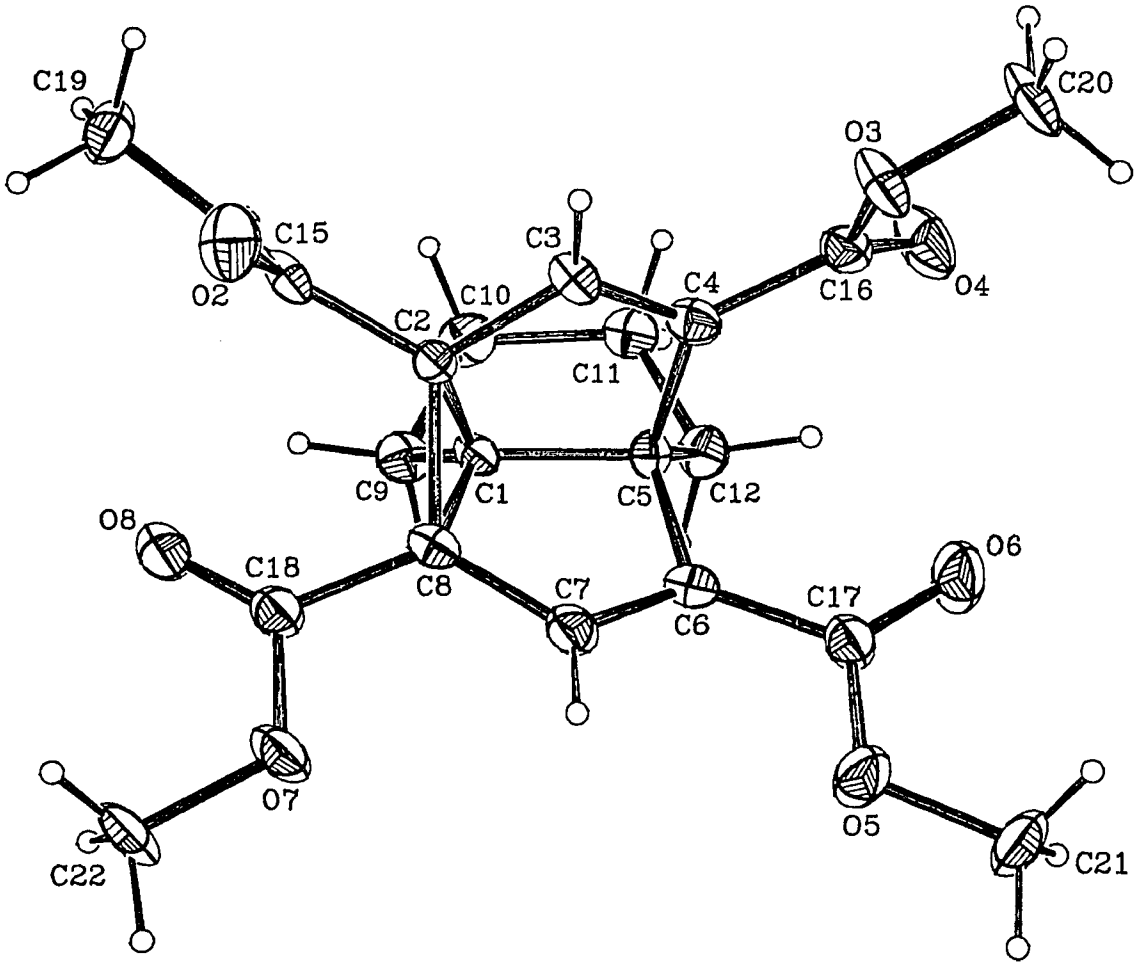


Figure 4–77. *ORTEP* drawing of Sb-6 (unprimed) at **181 K** with 50% thermal ellipsoids.

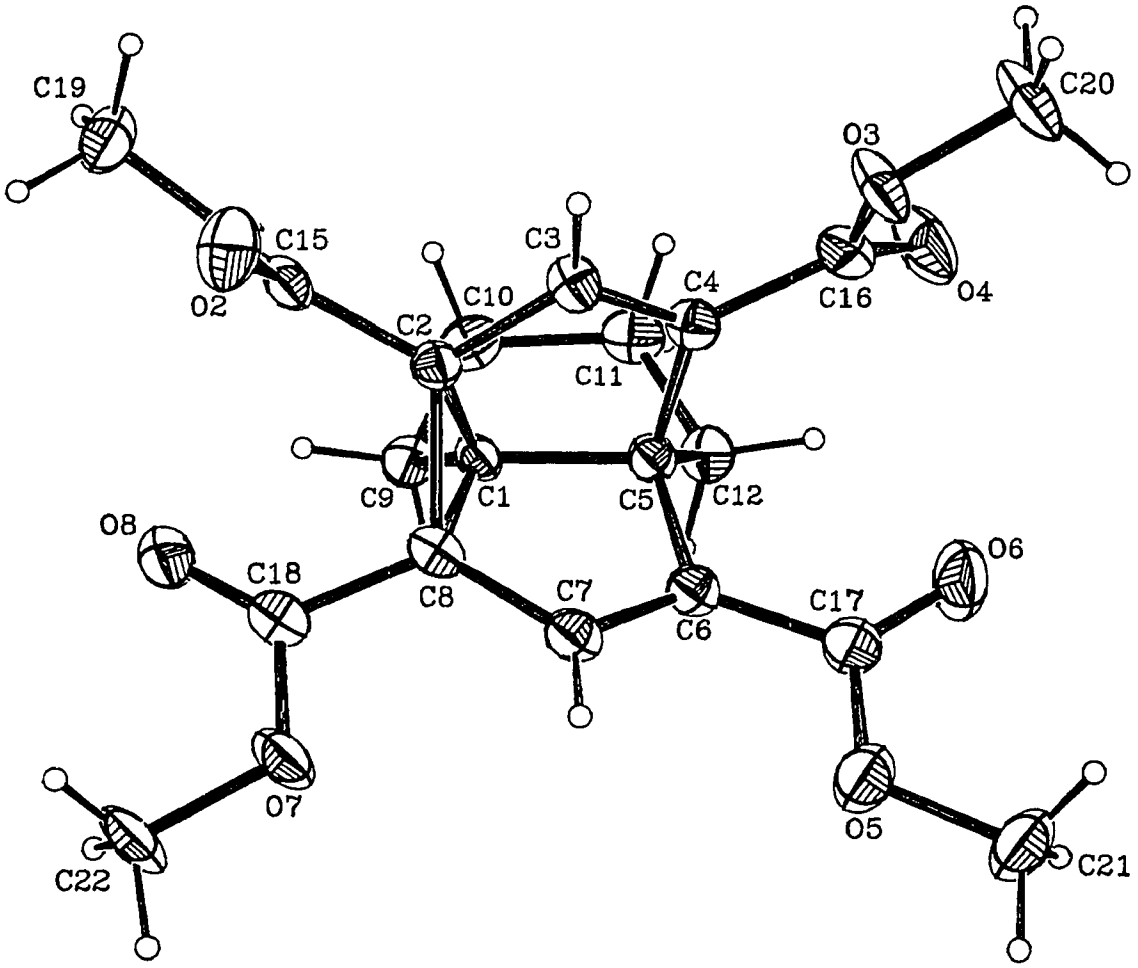


Figure 4–78. *ORTEP* drawing of Sb-6 (unprimed) at **208 K** with 50% thermal ellipsoids.

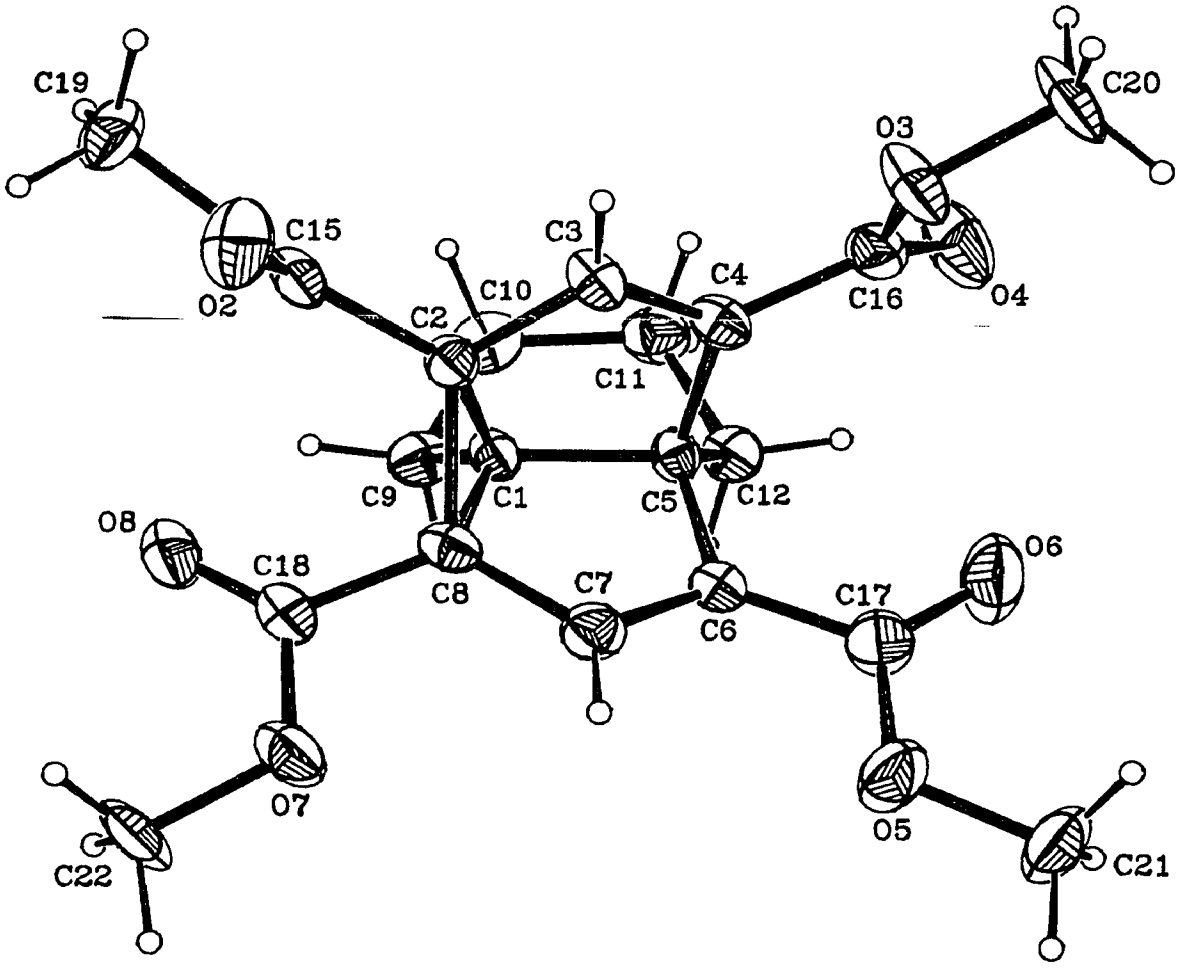


Figure 4–79. *ORTEP* drawing of Sb-6 (unprimed) at **236 K** with 50% thermal ellipsoids.

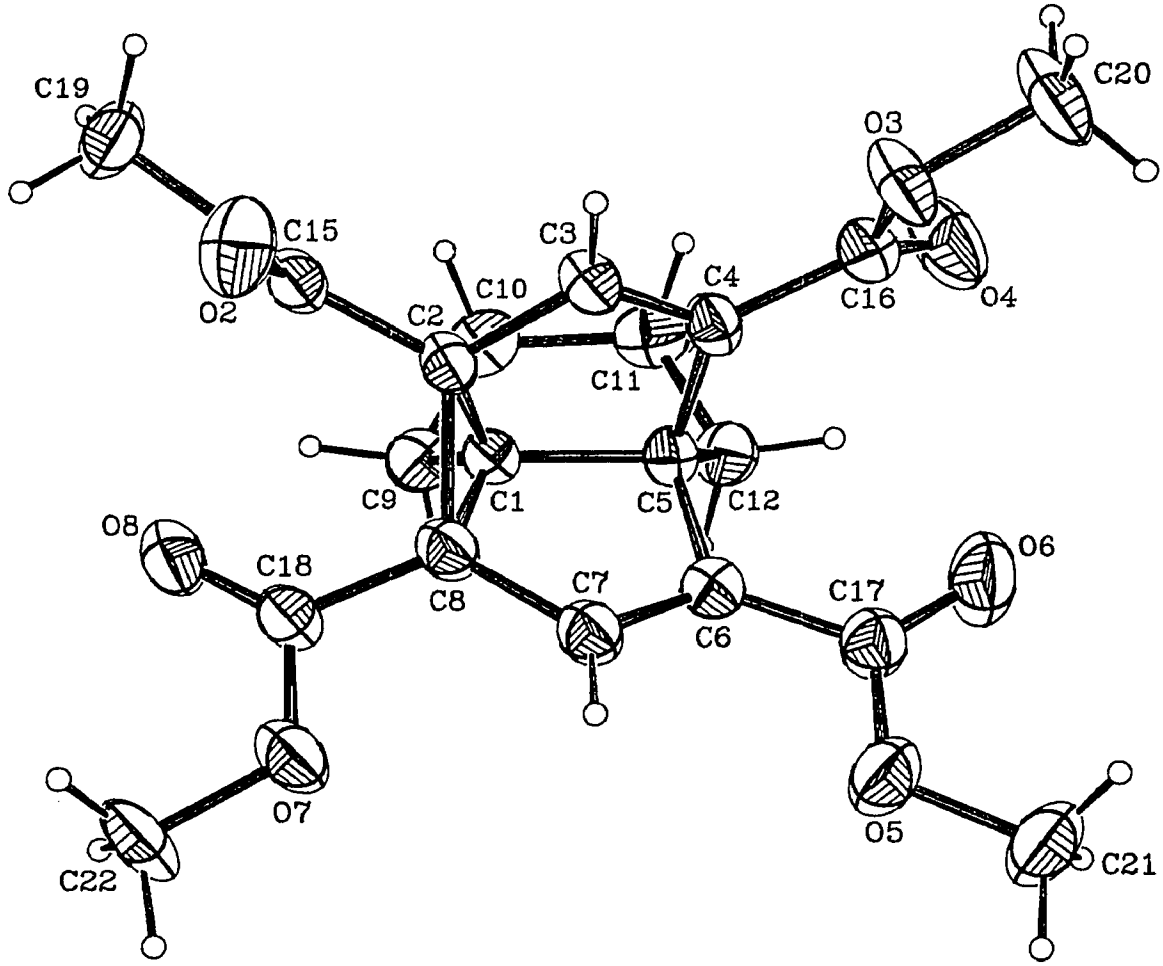


Figure 4–80. *ORTEP* drawing of Sb-6 (unprimed) at **265 K** with 50% thermal ellipsoids.

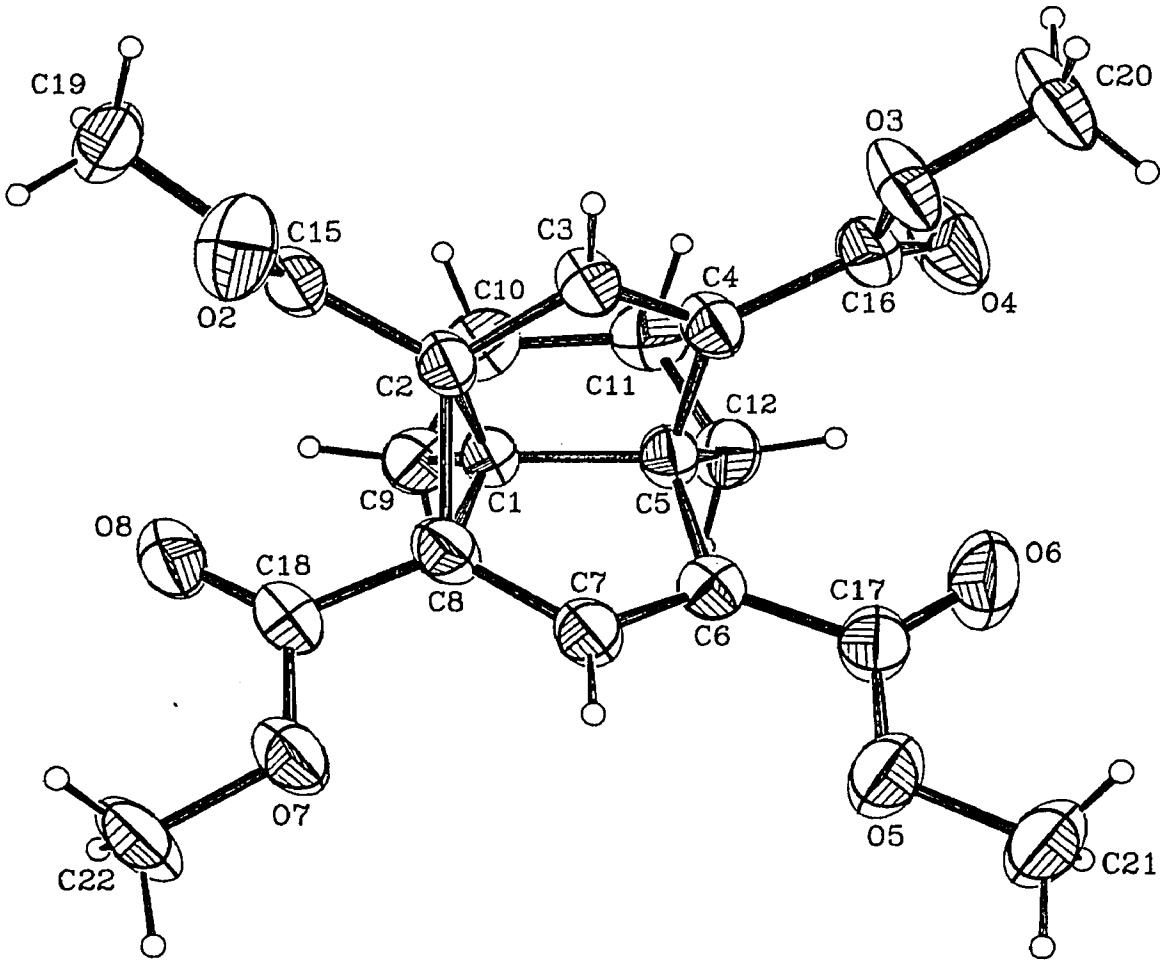


Figure 4–81. *ORTEP* drawing of Sb-6 (unprimed) at **294 K** with 50% thermal ellipsoids.

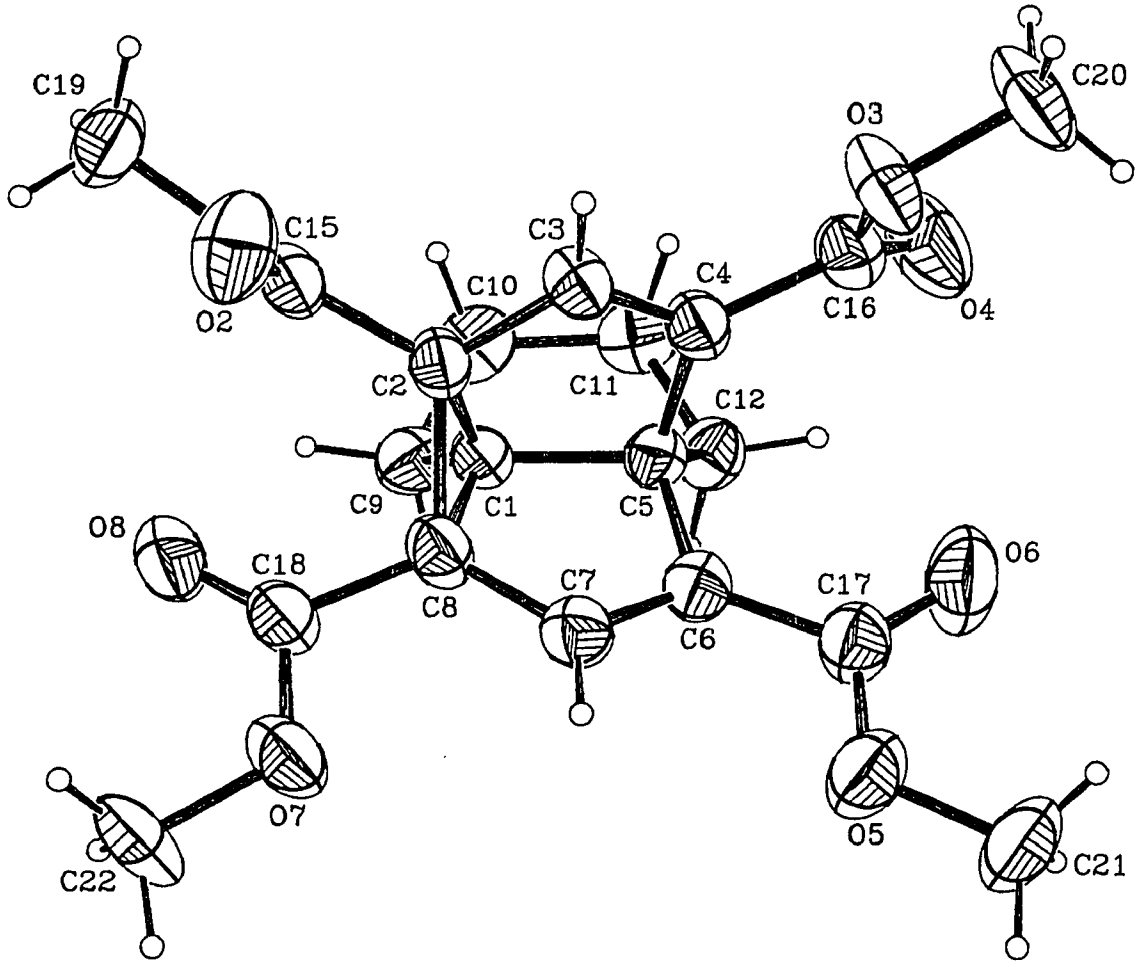


Figure 4–82. *ORTEP* drawing of Sb-6 (unprimed) at **322 K** with 50% thermal ellipsoids.

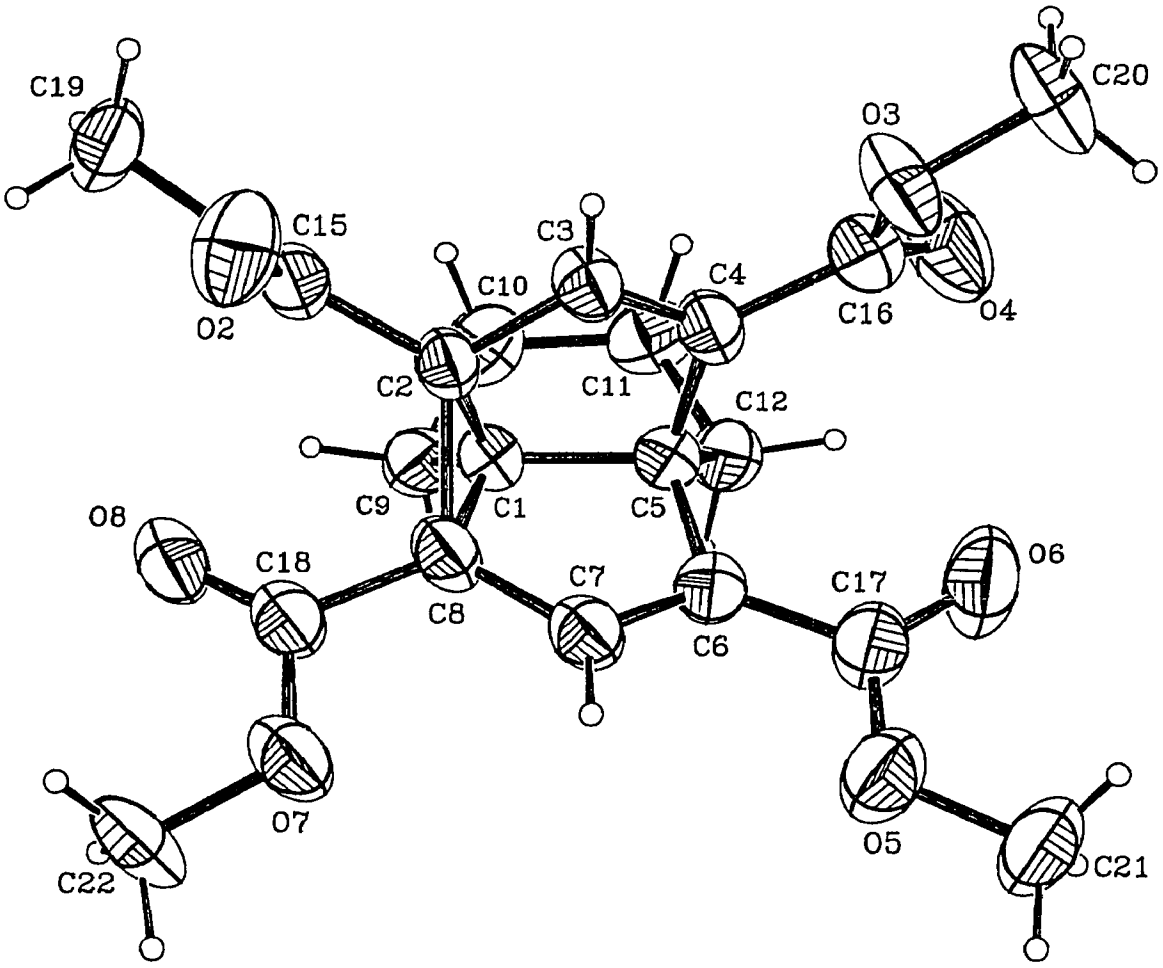


Figure 4–83. *ORTEP* drawing of Sb-6 (unprimed) at **335 K** with 50% thermal ellipsoids.

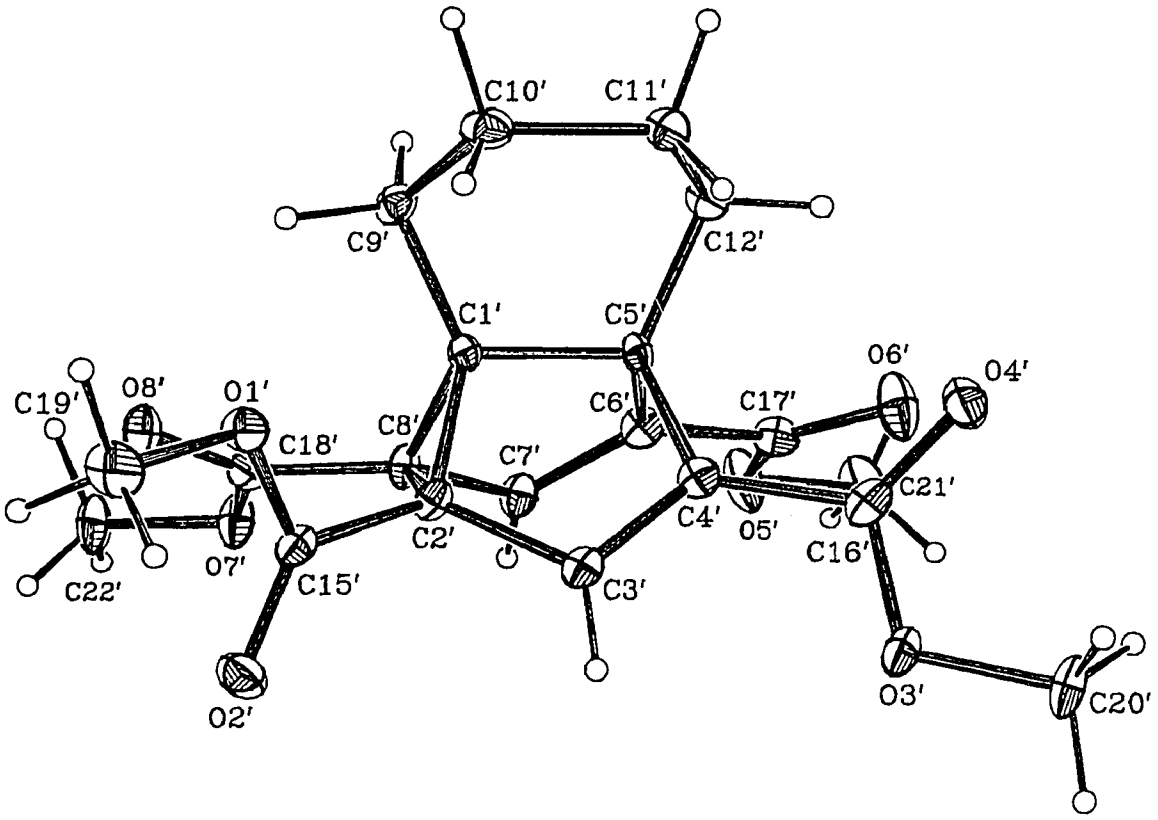


Figure 4–84. *ORTEP* drawing of Sb-6 (primed) at **115 K** with 50% thermal ellipsoids.

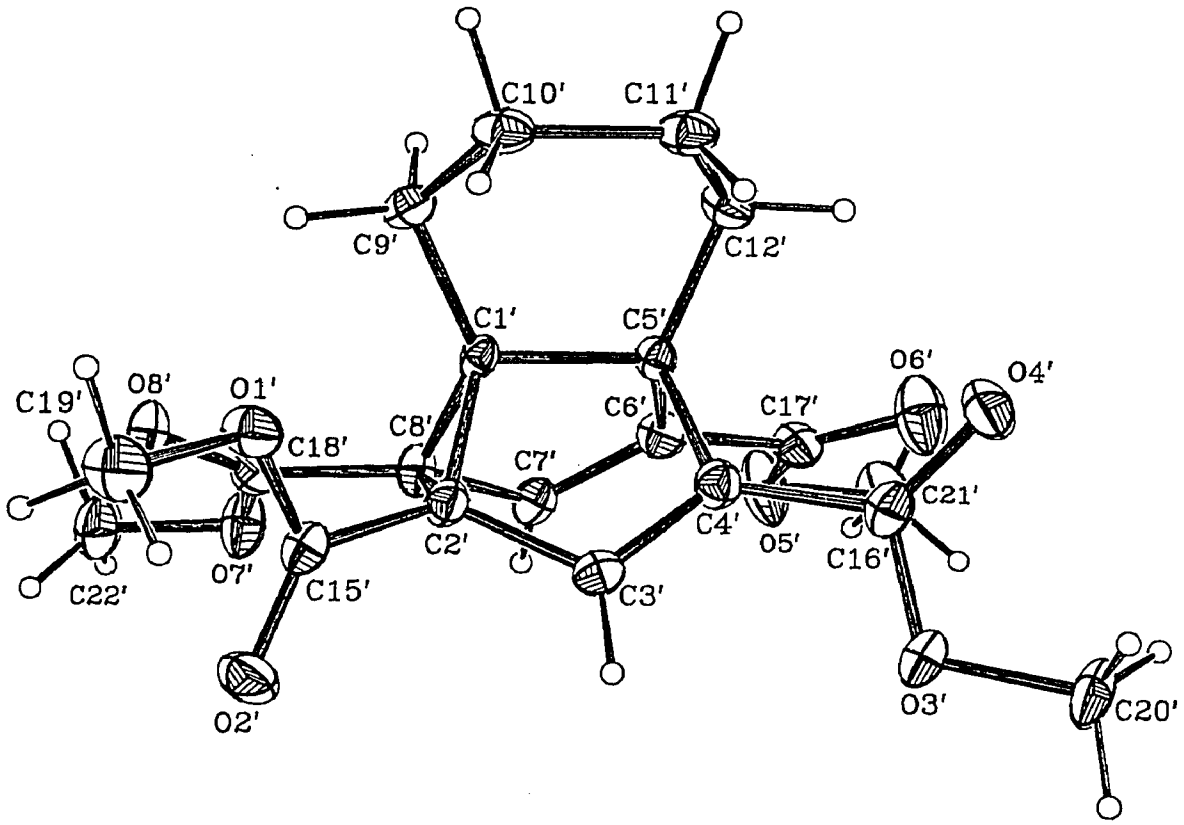


Figure 4–85. *ORTEP* drawing of Sb-6 (primed) at **153 K** with 50% thermal ellipsoids.

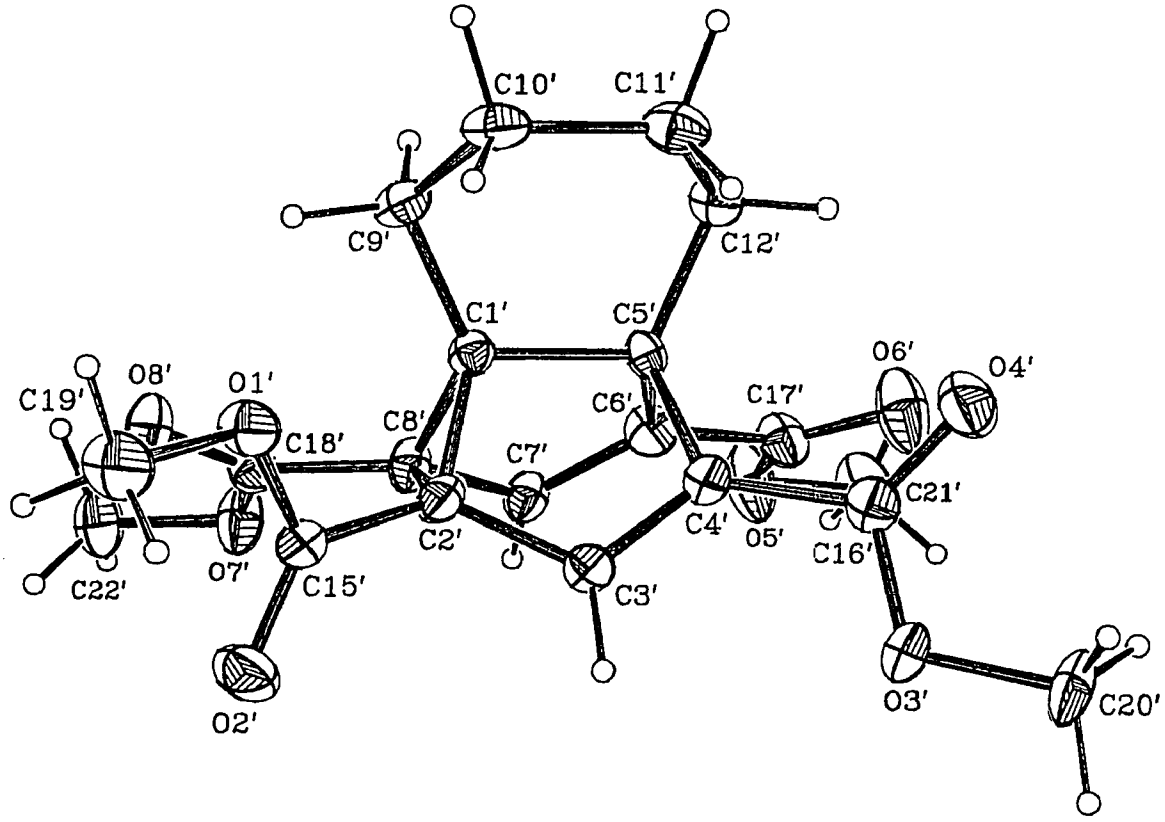


Figure 4–86. *ORTEP* drawing of Sb-6 (primed) at **181 K** with 50% thermal ellipsoids.

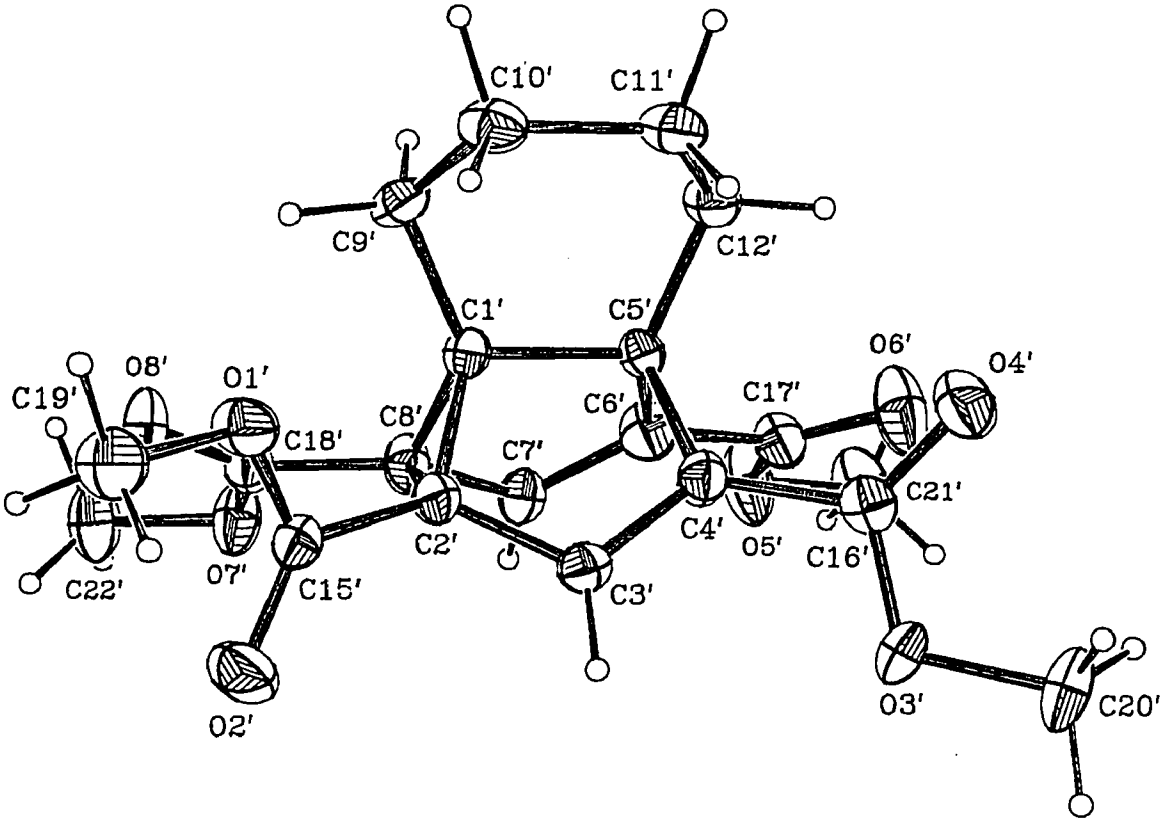


Figure 4–87. *ORTEP* drawing of Sb-6 (primed) at **208 K** with 50% thermal ellipsoids.

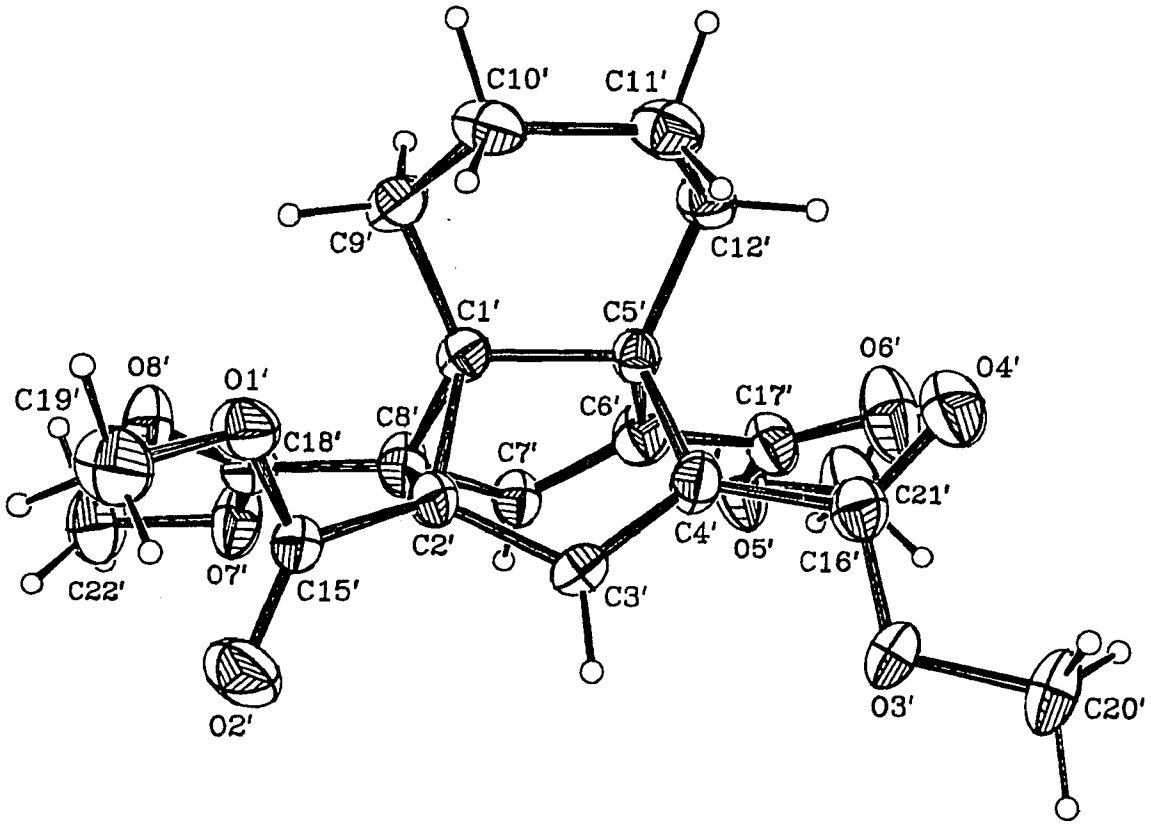


Figure 4–88. *ORTEP* drawing of Sb-6 (primed) at **236 K** with 50% thermal ellipsoids.

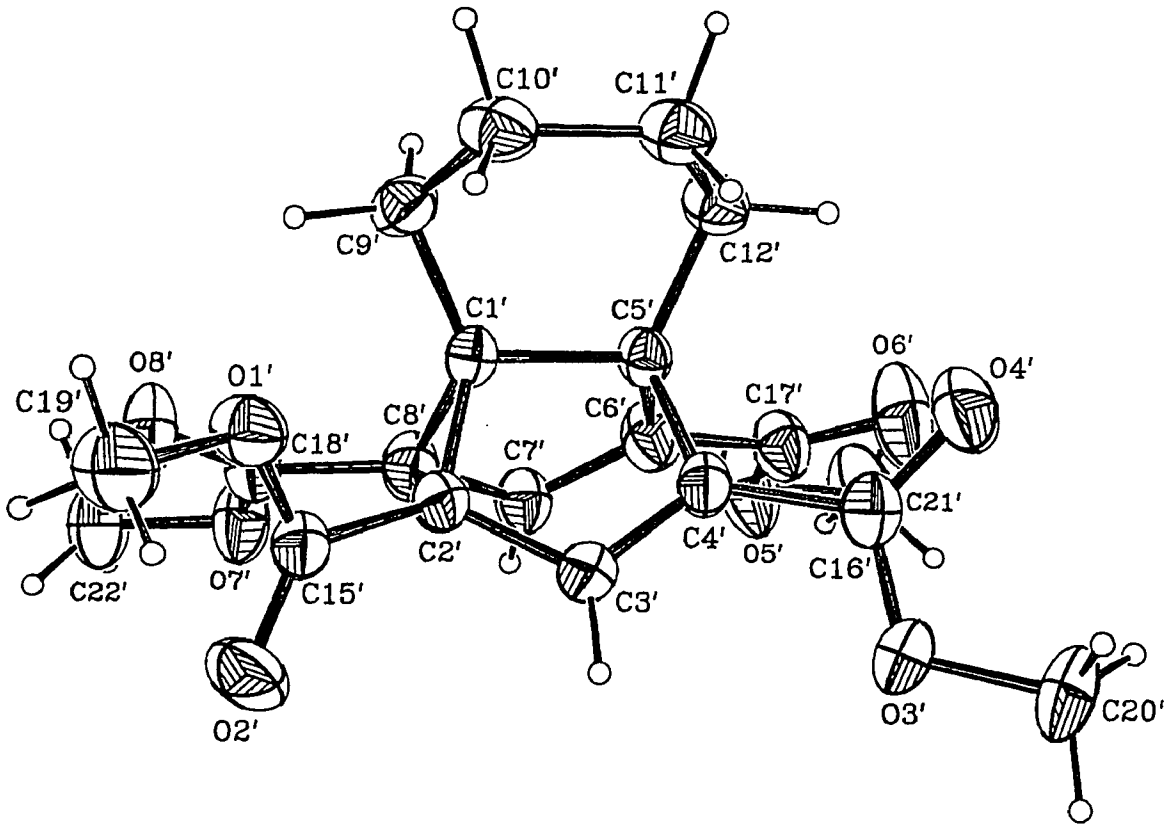


Figure 4–89. *ORTEP* drawing of Sb-6 (primed) at **265 K** with 50% thermal ellipsoids.

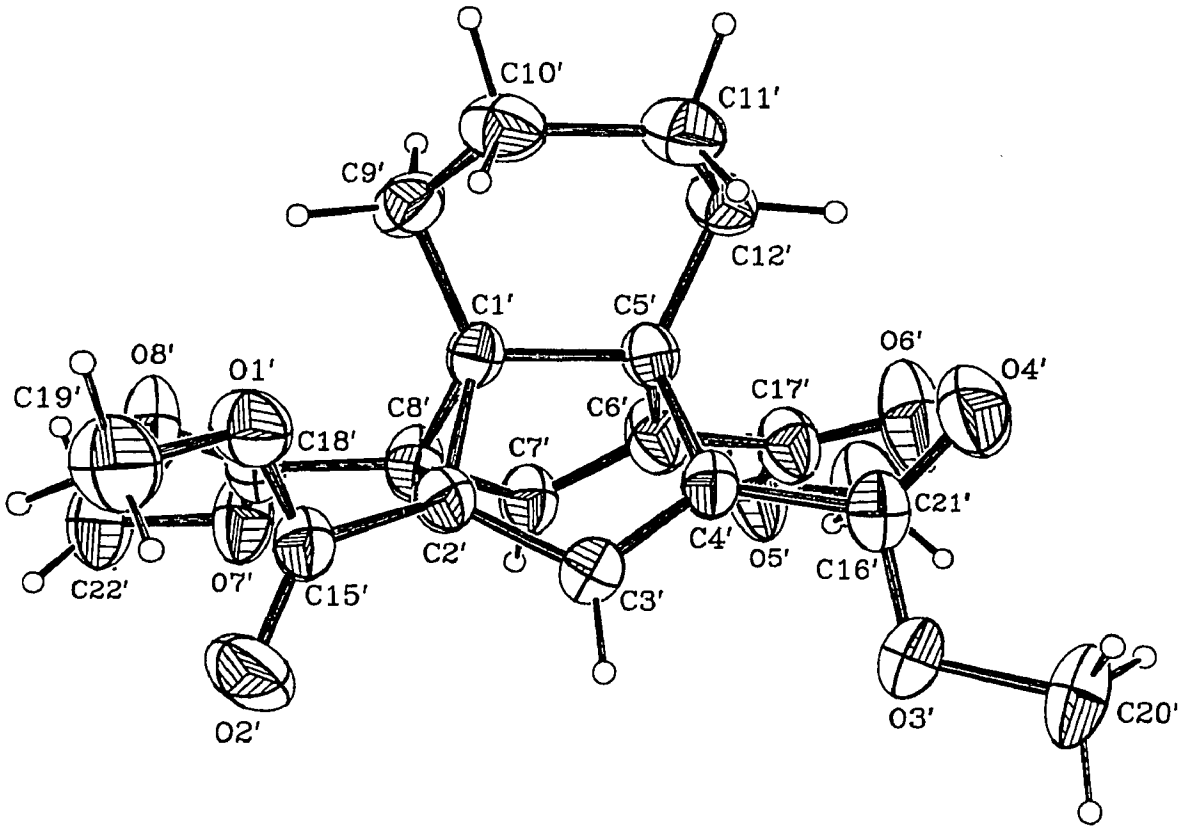


Figure 4–90. *ORTEP* drawing of Sb-6 (primed) at **294 K** with 50% thermal ellipsoids.

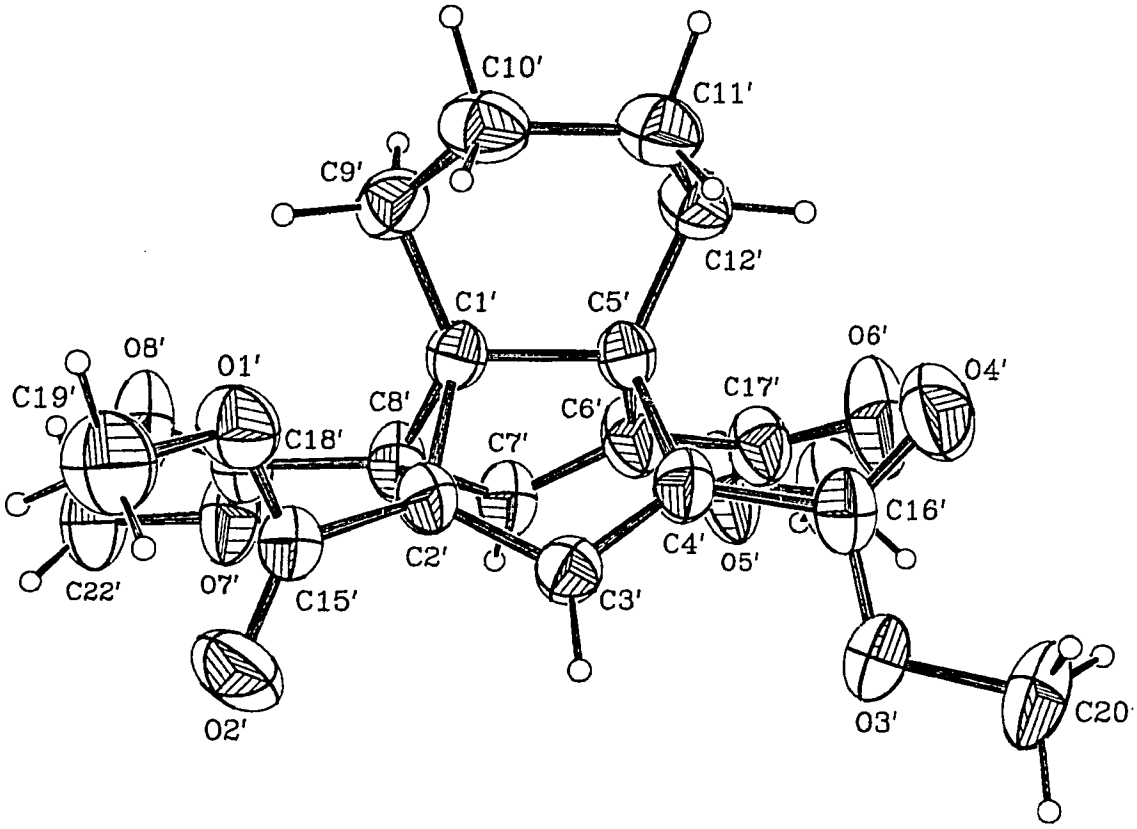


Figure 4–91. *ORTEP* drawing of Sb-6 (primed) at **322 K** with 50% thermal ellipsoids.

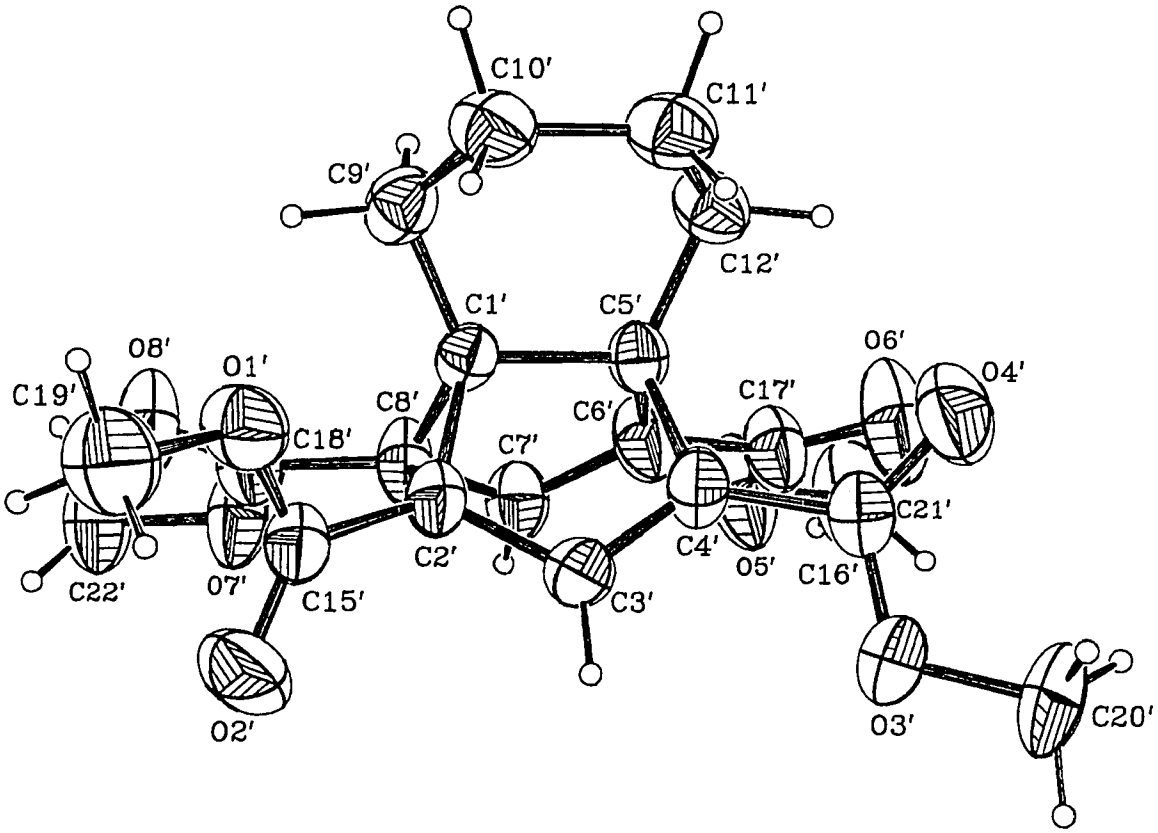


Figure 4–92. *ORTEP* drawing of Sb-6 (primed) at **335 K** with 50% thermal ellipsoids.

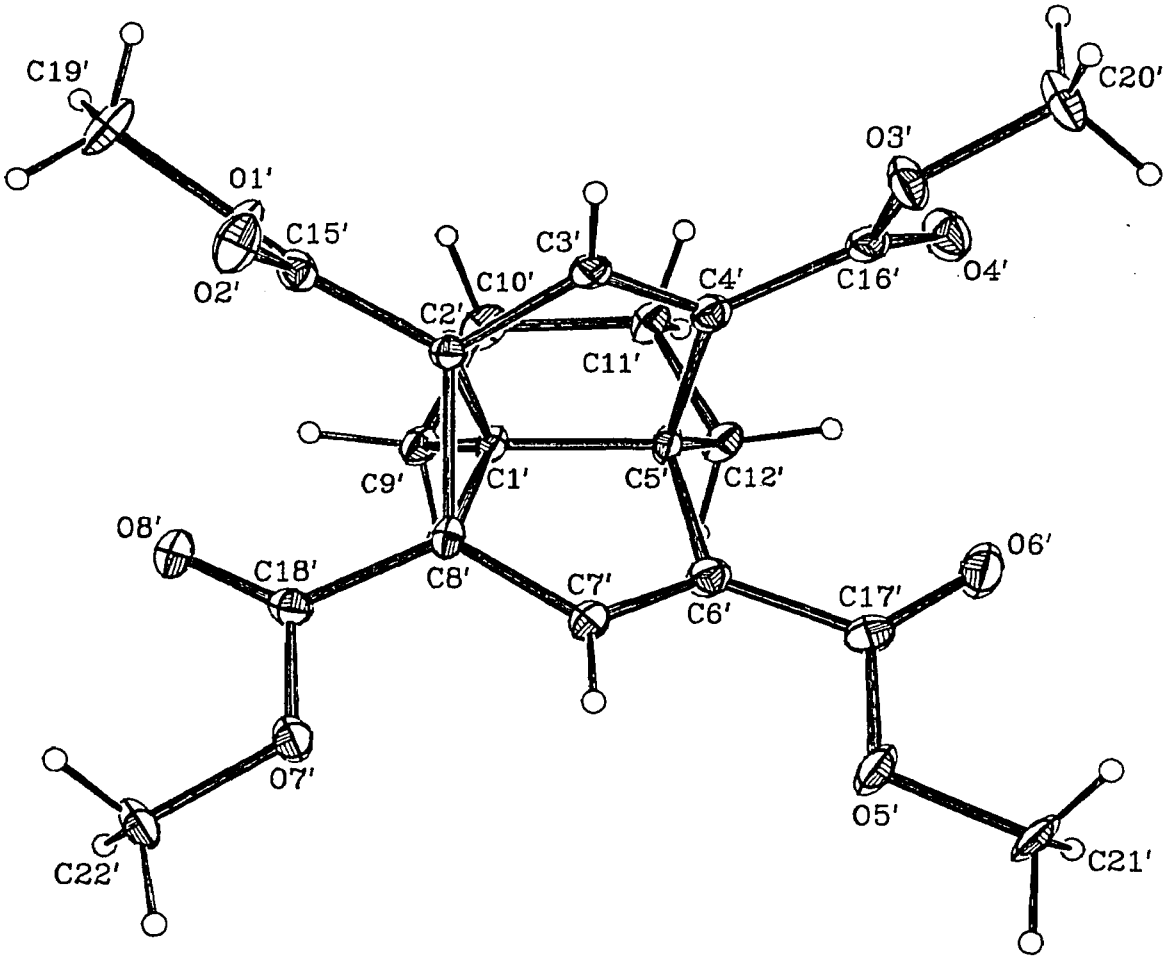


Figure 4–93. *ORTEP* drawing of Sb-6 (primed) at **115 K** with 50% thermal ellipsoids.

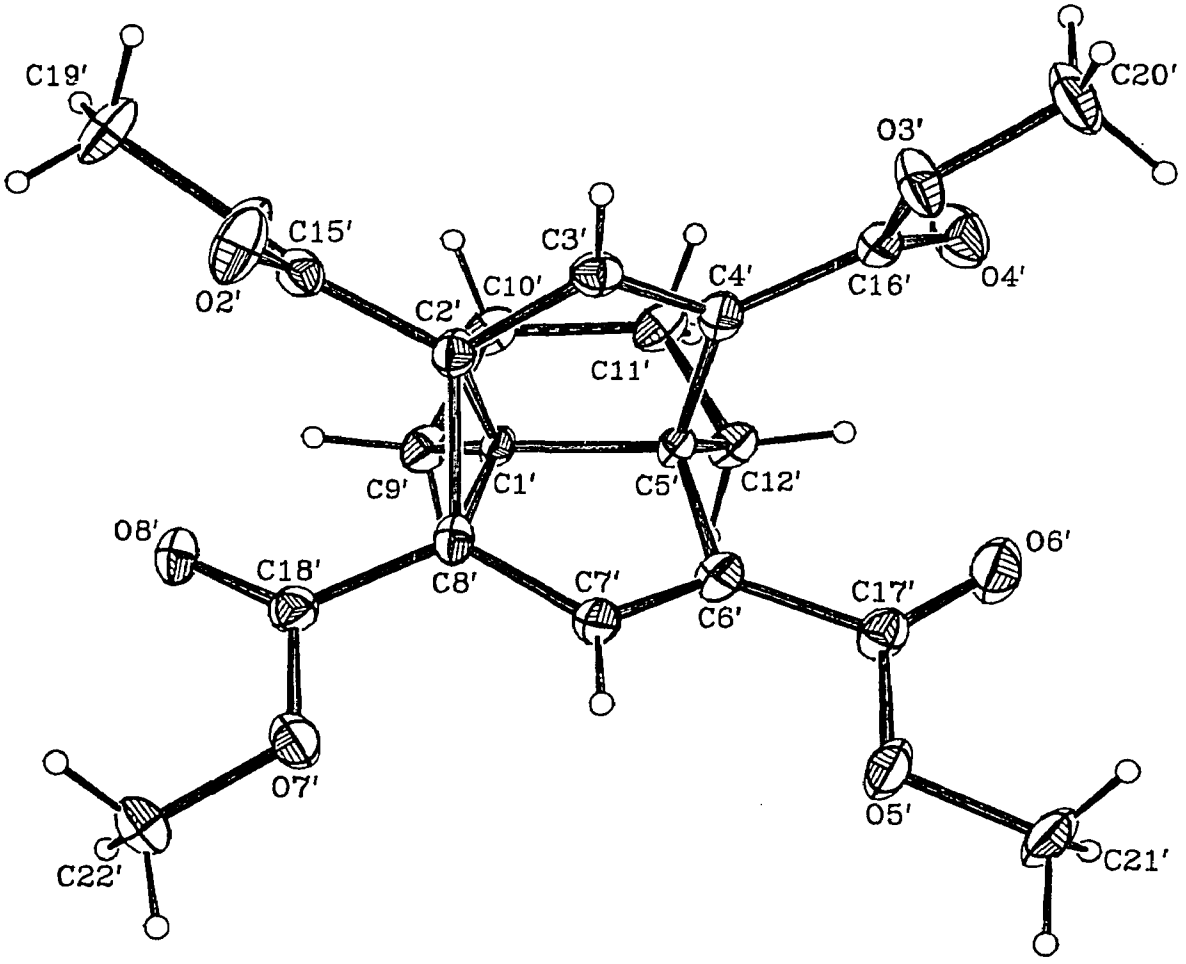


Figure 4–94. *ORTEP* drawing of Sb-6 (primed) at **153 K** with 50% thermal ellipsoids.

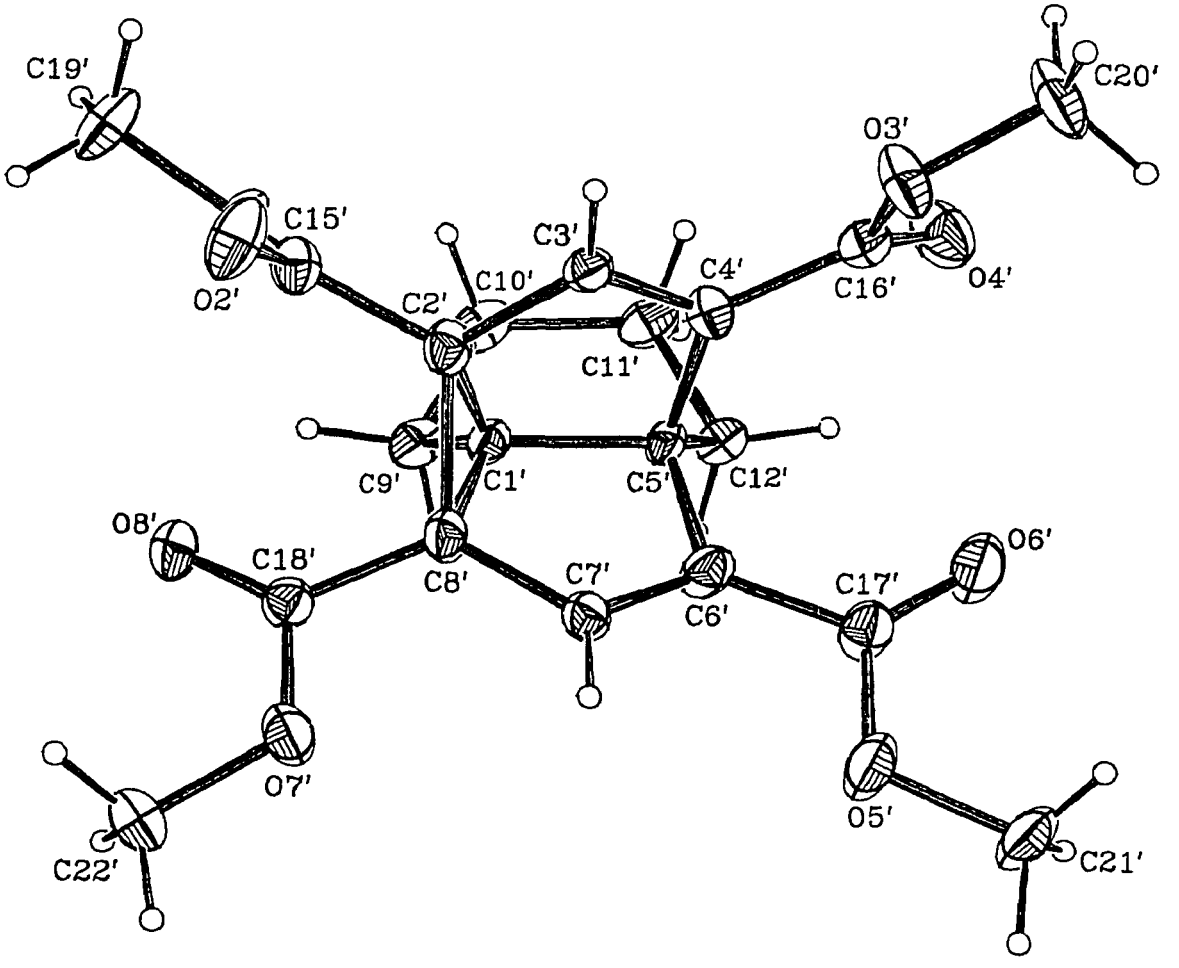


Figure 4–95. *ORTEP* drawing of Sb-6 (primed) at **181 K** with 50% thermal ellipsoids.

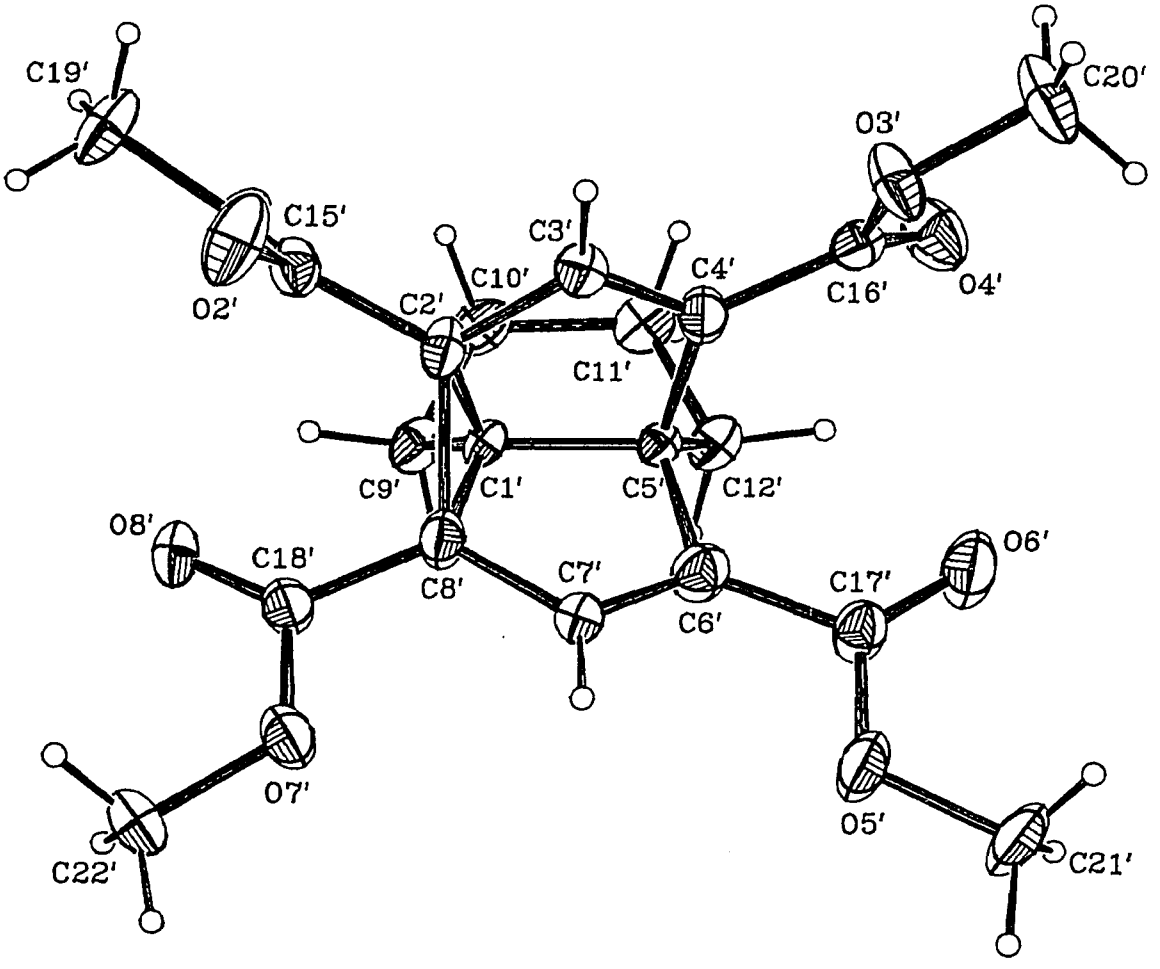


Figure 4–96. *ORTEP* drawing of Sb-6 (primed) at **208 K** with 50% thermal ellipsoids.

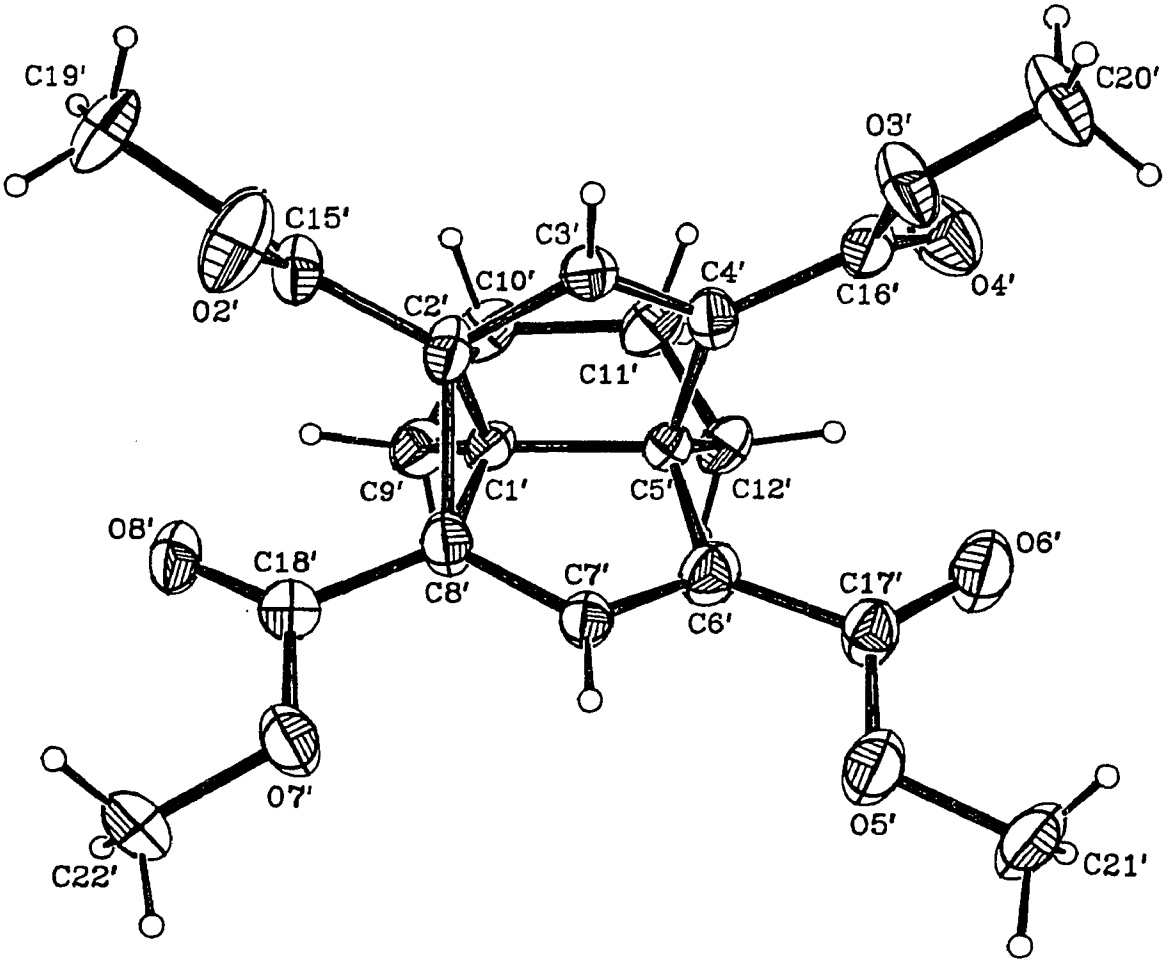


Figure 4–97. *ORTEP* drawing of Sb-6 (primed) at **236 K** with 50% thermal ellipsoids.

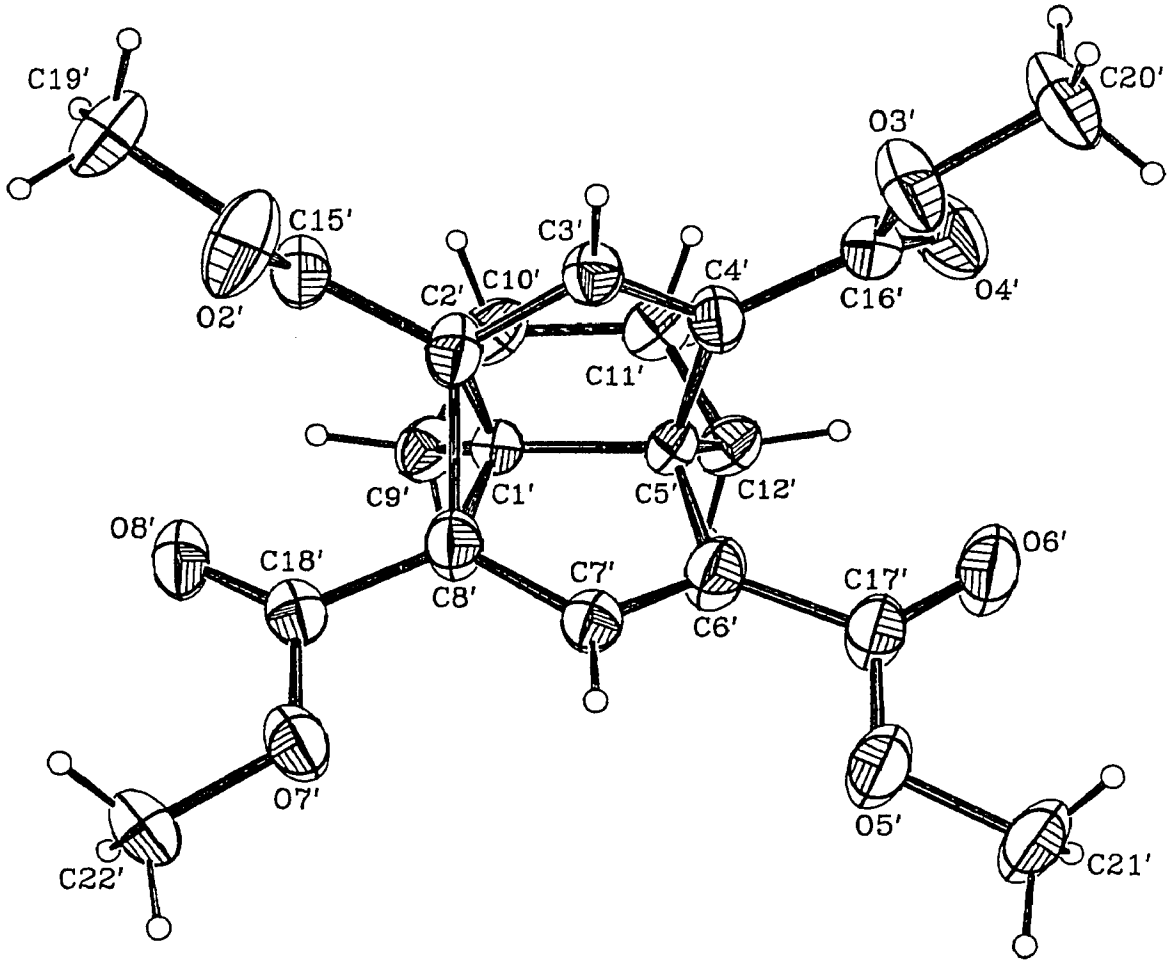


Figure 4–98. *ORTEP* drawing of Sb-6 (primed) at **265 K** with 50% thermal ellipsoids.

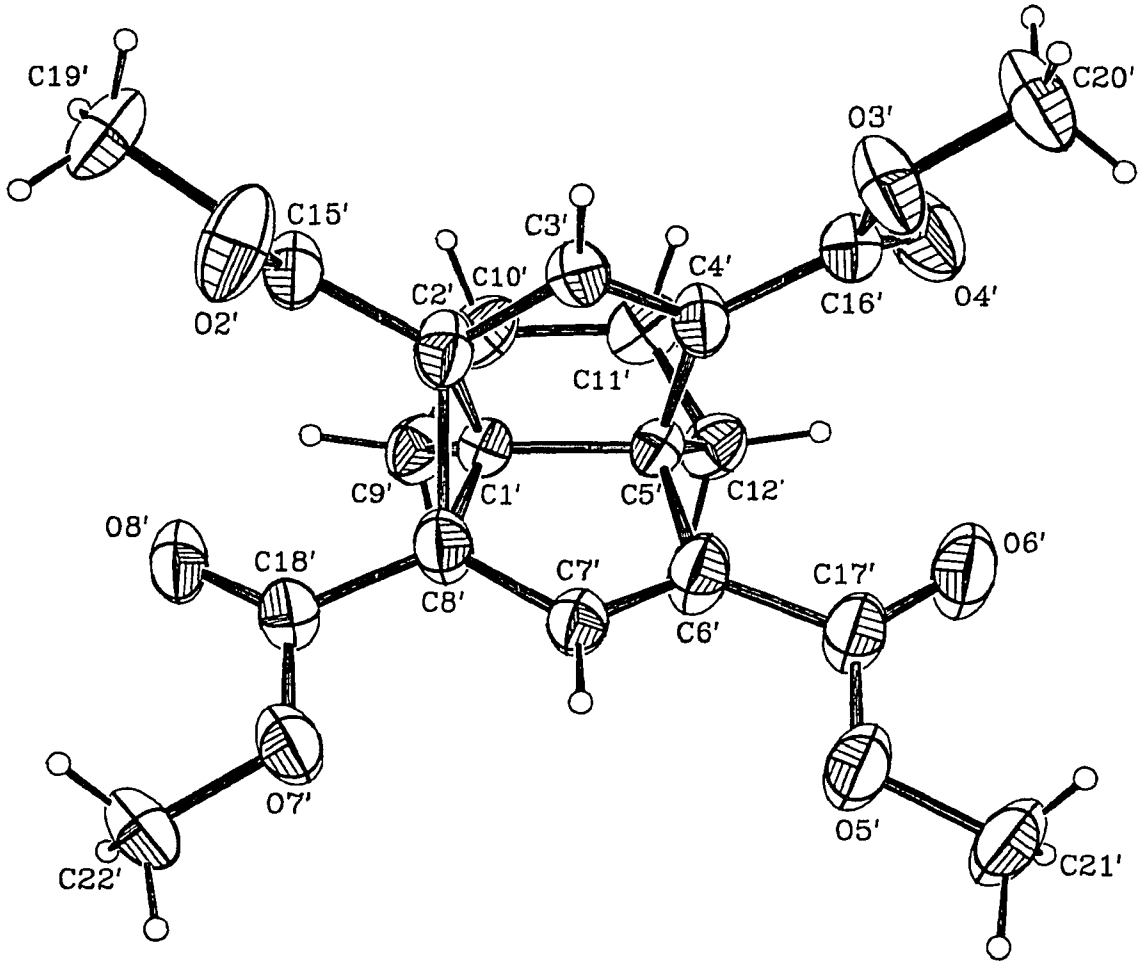


Figure 4–99. *ORTEP* drawing of Sb-6 (primed) at **294 K** with 50% thermal ellipsoids.

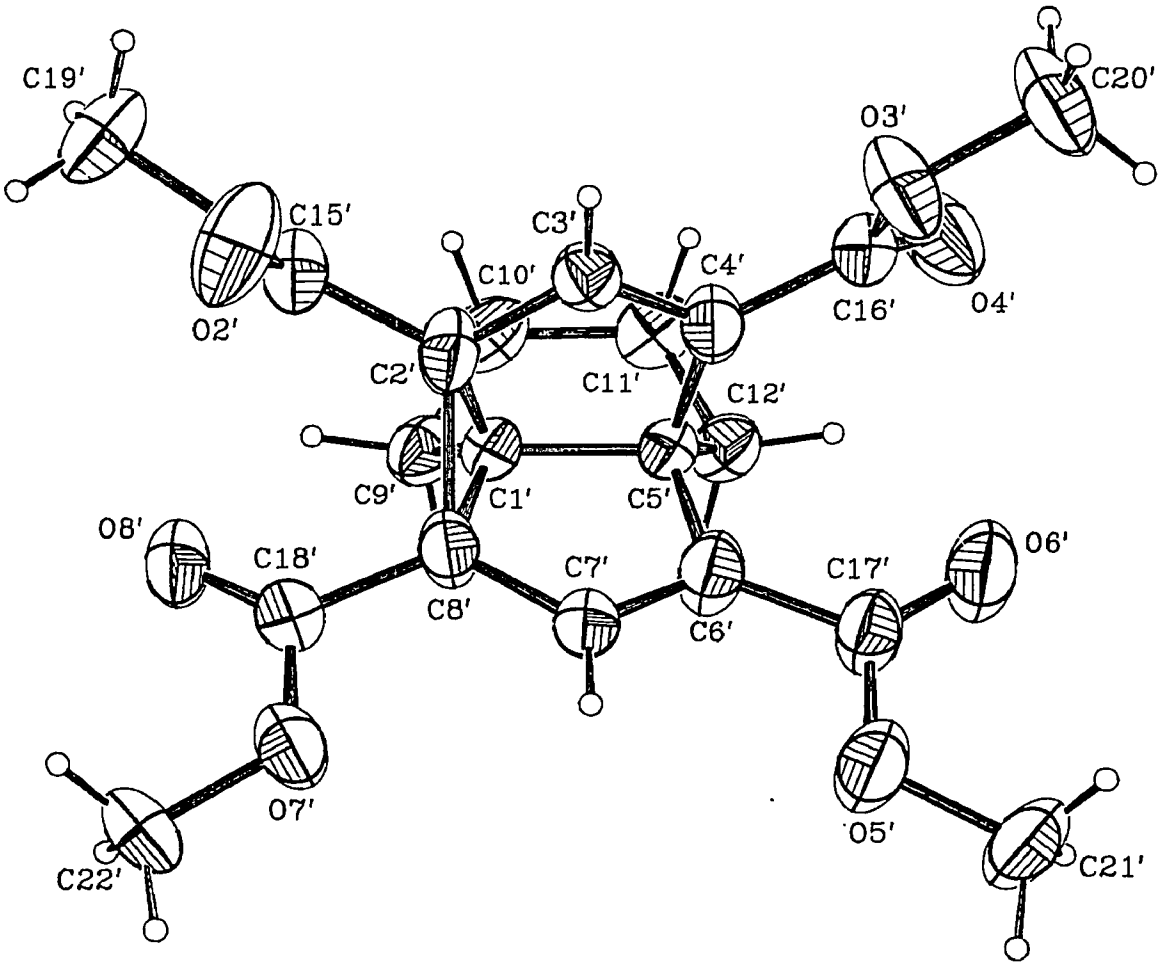


Figure 4–100. *ORTEP* drawing of Sb-6 (primed) at **322 K** with 50% thermal ellipsoids.

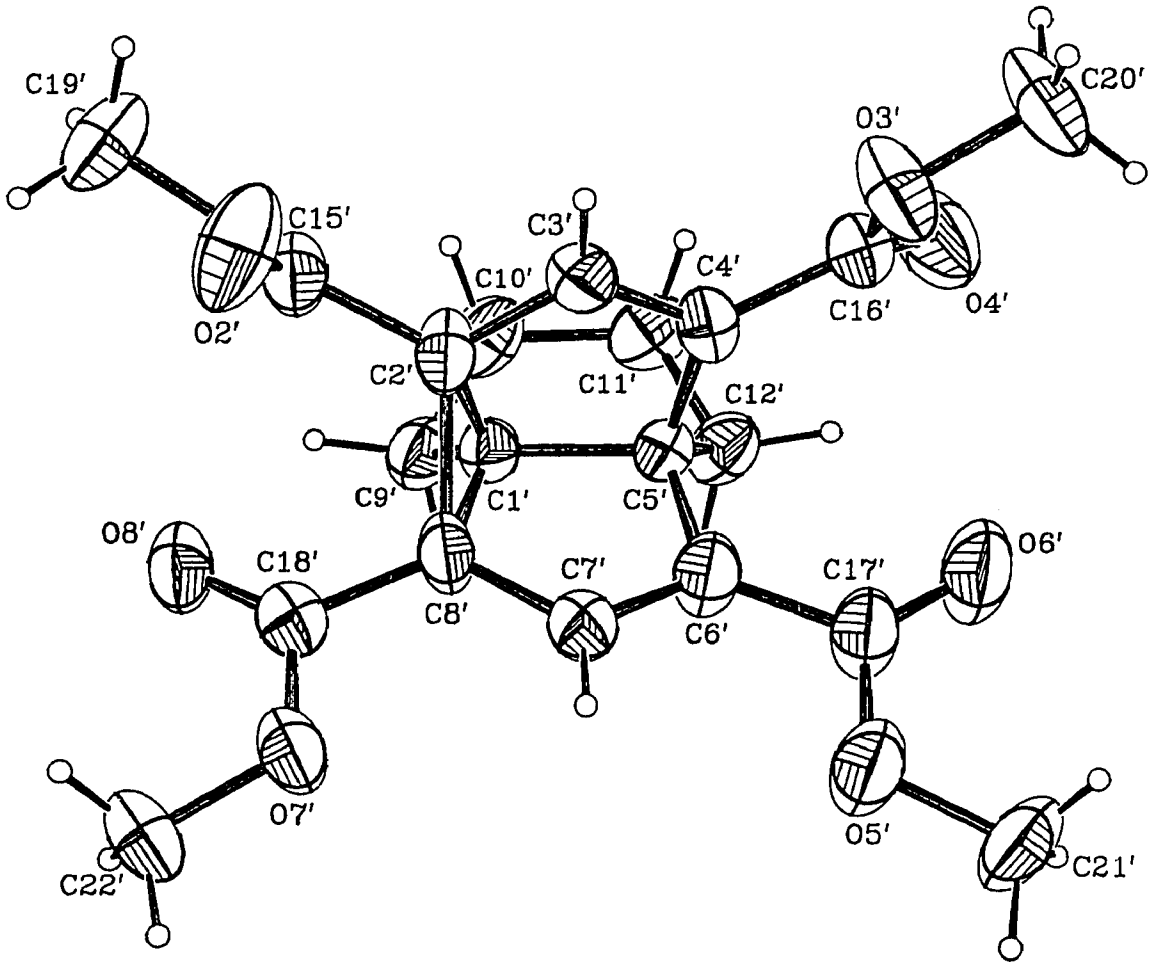


Figure 4–101. *ORTEP* drawing of Sb-6 (primed) at **335 K** with 50% thermal ellipsoids.

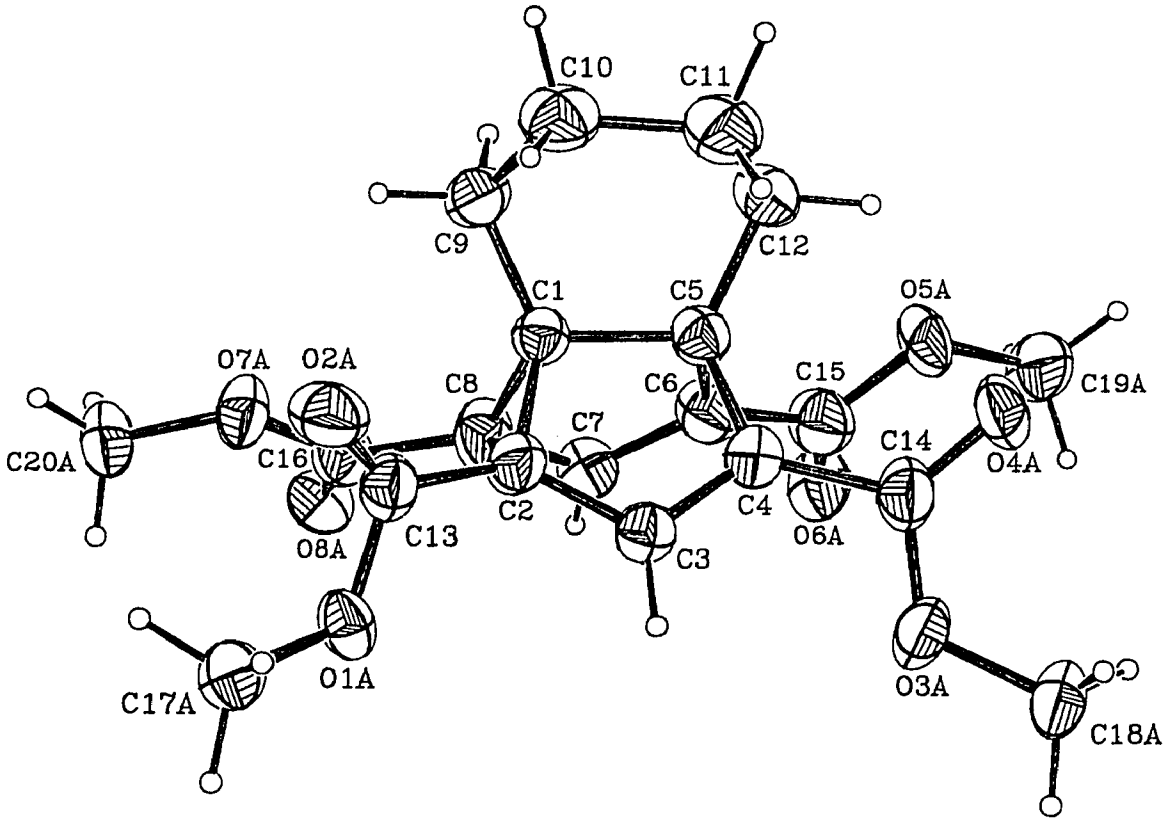


Figure 4–102. *ORTEP* drawing of polymorph of Sb-6, rotamer A, (50% occupancy) at **295 K** with 50% thermal ellipsoids.

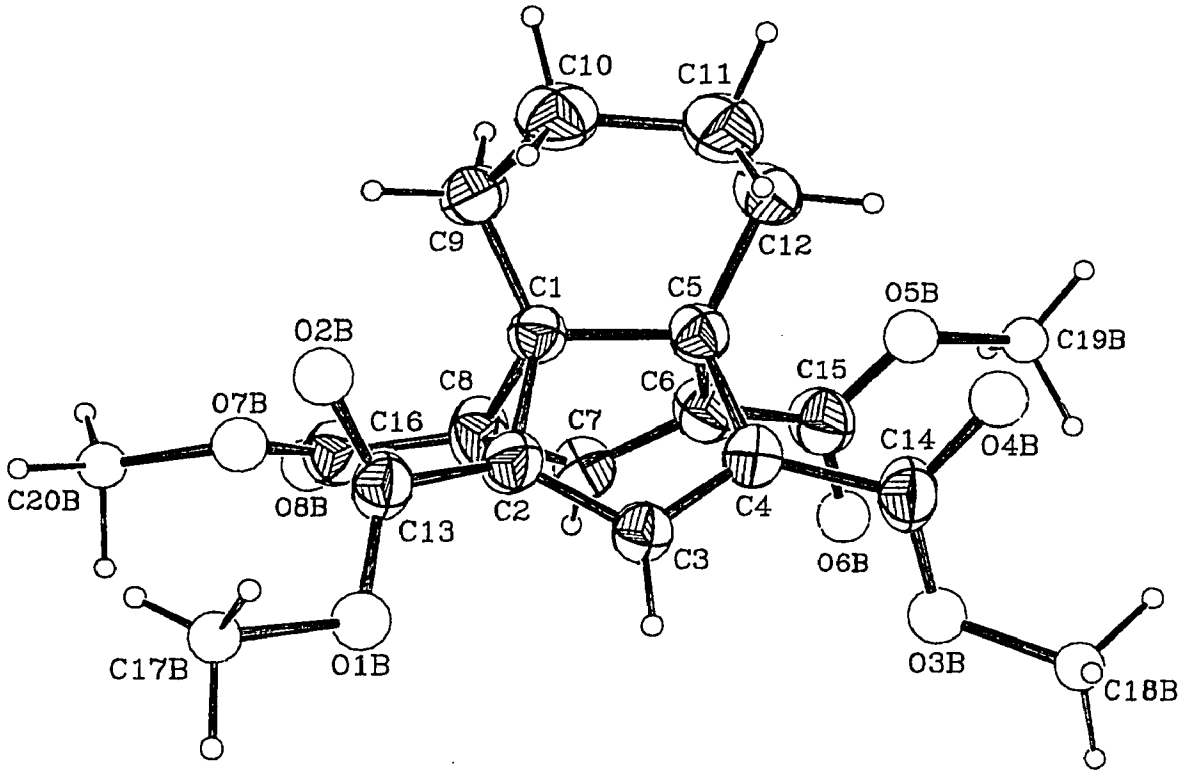


Figure 4–103. *ORTEP* drawing of polymorph of Sb-6, rotamer B, (25% occupancy) at **295 K** with 50% thermal ellipsoids.

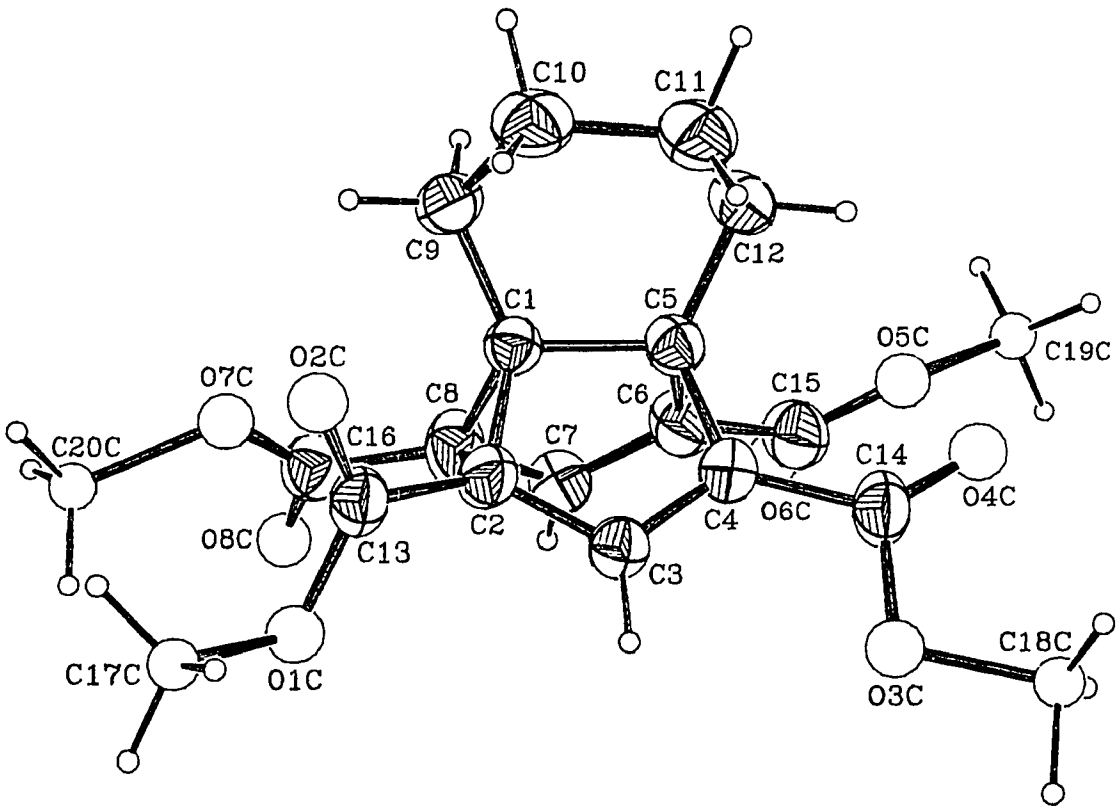


Figure 4–104. *ORTEP* drawing of polymorph of Sb-6, rotamer C, (25% occupancy) at **295 K** with 50% thermal ellipsoids.

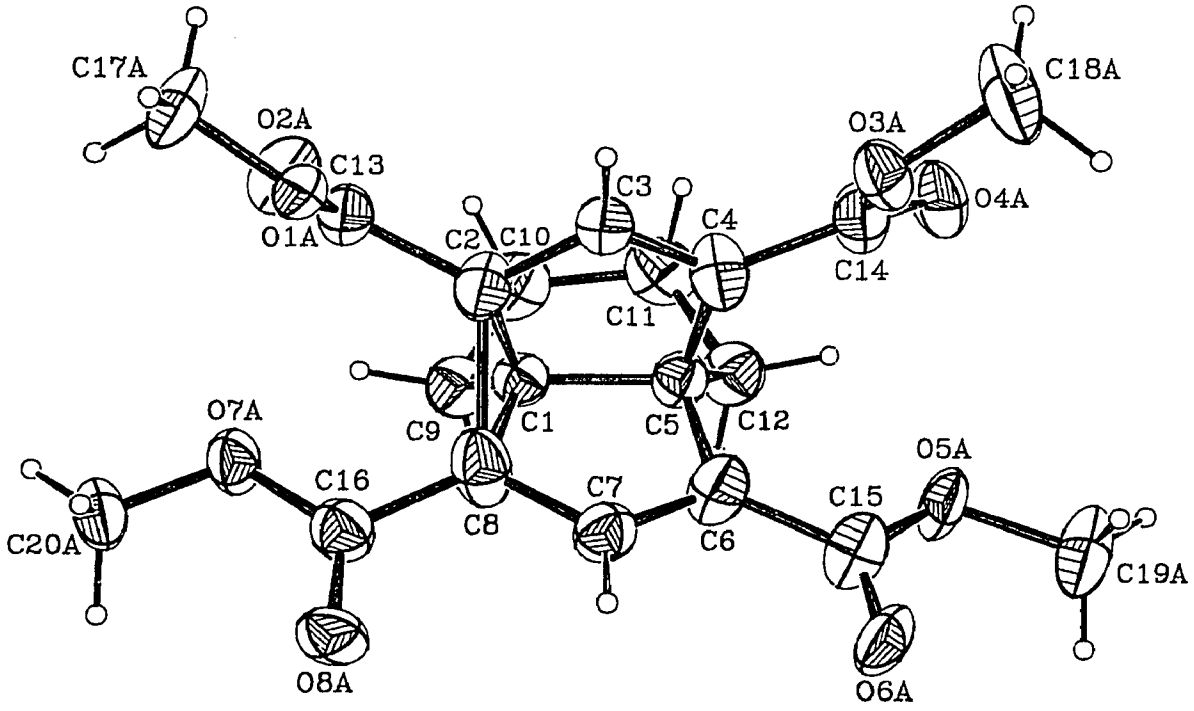


Figure 4–105. *ORTEP* drawing of polymorph of Sb-6, rotamer A, (50% occupancy) at **295 K** with 50% thermal ellipsoids.

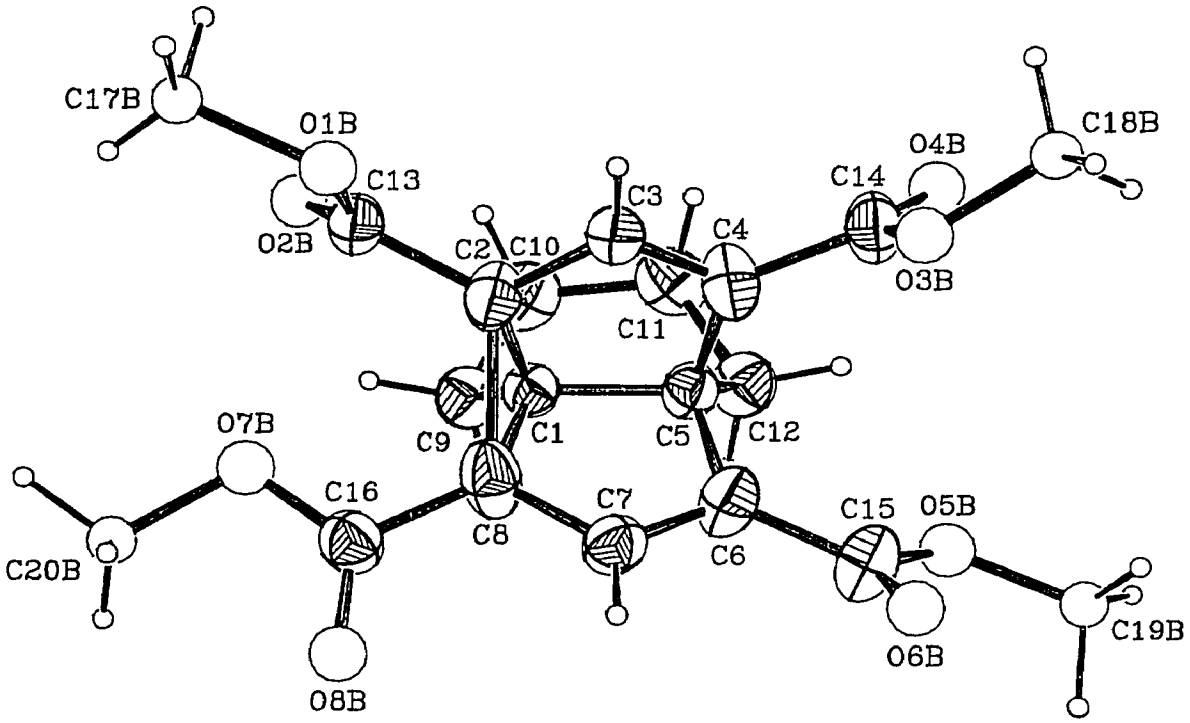


Figure 4–106. *ORTEP* drawing of polymorph of Sb-6, rotamer B, (25% occupancy) at **295 K** with 50% thermal ellipsoids.

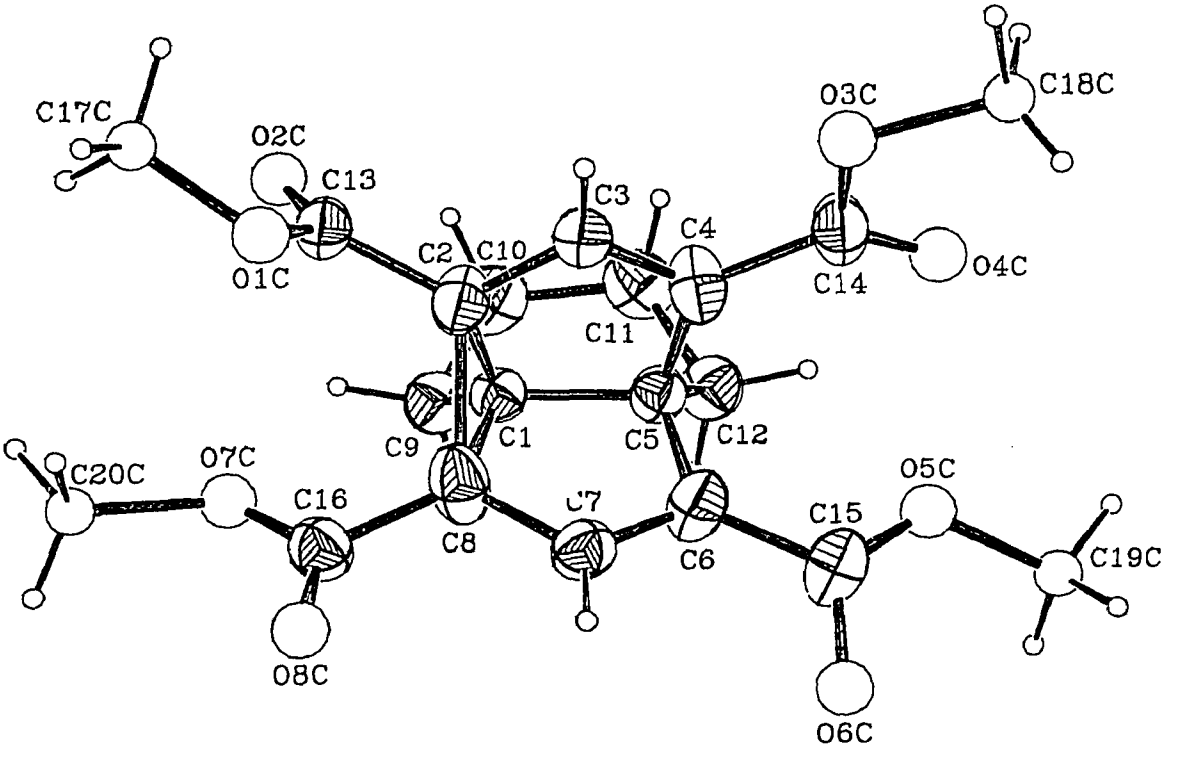
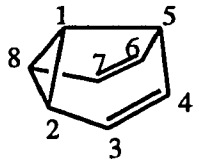


Figure 4–107. *ORTEP* drawing of polymorph of Sb-6, rotamer C, (25% occupancy) at **295 K** with 50% thermal ellipsoids.

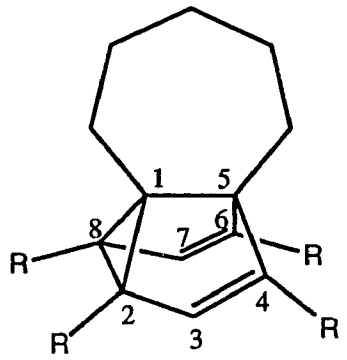
4.4 SB-7

If the hydrogens on the carbons, C1 and C5, in semibullvalene



Tricyclo[3.3.0.0^{2,8}]octa-3,6-diene
(Semibullvalene)

are replaced with a chain of five methylenes to form a seven-membered ring on top of semibullvalene and four ester groups replace the four hydrogens at C2, C4, C6, and C8, we obtain the annulated compound **1,5-cycloheptano-2,4,6,8-tetracarbomethoxy-semibullvalene** or simply Sb-7.



R = $COOCH_3$

1,5-Cycloheptano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-7)

The X-ray crystal data for Sb-7 are summarized in Table 4–17.

Table 4–17. X-ray Crystal Data for Sb-7 at Various Temperatures

	115 K	**127 K**	**153 K**
Formula	$C_{21}H_{24}O_8$	$C_{21}H_{24}O_8$	$C_{21}H_{24}O_8$
Formula weight	404.42	404.42	404.42
Melting point (°C)	99–100	99–100	99–100
Crystal size (mm)	0.16 x 0.24 x 0.50	0.16 x 0.24 x 0.50	0.16 x 0.24 x 0.50
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	11.118(1)	11.121(1)	11.128(1)
b (Å)	8.482(2)	8.498(5)	8.513(6)
c (Å)	20.453(1)	20.467(1)	20.502(1)
β (°)	90.20(1)	90.22(1)	90.29(1)
Cell volume (Å^3)	1928.65(0.37)	1934.22(1.22)	1942.27(1.38)
Z	4	4	4
d_{calc} (g cm^{-3})	1.395	1.389	1.383
μ(Cu $K\alpha$) (cm^{-1})	8.57	8.54	8.50
R	0.041	0.050	0.048
R_w	0.059	0.071	0.068

Table 4–17 (cont'd). X-ray Crystal Data for Sb-7 at Various Temperatures

	181 K	**208 K**	**236 K**
Formula	$C_{21}H_{24}O_8$	$C_{21}H_{24}O_8$	$C_{21}H_{24}O_8$
Formula weight	404.42	404.42	404.42
Melting point (°C)	99–100	99–100	99–100
Crystal size (mm)	0.16 x 0.24 x 0.50	0.16 x 0.24 x 0.50	0.16 x 0.24 x 0.50
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	11.133(1)	11.138(1)	11.142(1)
b (Å)	8.533(6)	8.557(6)	8.580(4)
c (Å)	20.538(13)	20.582(10)	20.633(1)
β (°)	90.39(1)	90.53(1)	90.72(1)
Cell volume (Å^3)	1950.98(1.42)	1961.61(1.30)	1972.21(0.92)
Z	4	4	4
d_{calc} (g cm^{-3})	1.377	1.369	1.362
μ(Cu $K\alpha$) (cm^{-1})	8.46	8.42	8.37
R	0.053	0.038	0.039
R_w	0.075	0.051	0.052

Table 4–17 (cont'd). X-ray Crystal Data for Sb-7 at Various Temperatures

	265 K	**294 K**	**294 K**
Formula	$C_{21}H_{24}O_8$	$C_{21}H_{24}O_8$	$C_{21}H_{24}O_8$
Formula weight	404.42	404.42	404.42
Melting point (°C)	99–100	99–100	99–100
Crystal size (mm)	0.16 x 0.24 x 0.50	0.16 x 0.24 x 0.50	0.26 x 0.28 x 0.48
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	11.144(1)	11.141(1)	11.142(1)
b (Å)	8.612(2)	8.647(1)	8.649(1)
c (Å)	20.694(1)	20.763(1)	20.763(1)
β (°)	91.03(1)	91.53(1)	91.53(1)
Cell volume (Å^3)	1985.73(0.37)	1999.57(0.21)	2000.14(0.25)
Z	4	4	4
d_{calc} (g cm^{-3})	1.353	1.343	1.343
μ(Cu $K\alpha$) (cm^{-1})	8.31	8.26	8.25
R	0.039	0.042	0.050
R_w	0.051	0.053	0.064

Table 4–17 (cont'd). X-ray Crystal Data for Sb-7 at Various Temperatures

	295 K	**308 K**	**315 K**
Formula	$C_{21}H_{24}O_8$	$C_{21}H_{24}O_8$	$C_{21}H_{24}O_8$
Formula weight	404.42	404.42	404.42
Melting point (°C)	99–100	99–100	99–100
Crystal size (mm)	0.17 x 0.20 x 0.47	0.16 x 0.20 x 0.80	0.16 x 0.20 x 0.80
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	11.140(1)	11.135(1)	11.131(1)
b (Å)	8.654(1)	8.670(1)	8.684(1)
c (Å)	20.770(2)	20.796(1)	20.820(1)
β (°)	91.65(1)	91.96(1)	92.25(1)
Cell volume (Å^3)	2001.56(0.40)	2006.55(0.47)	2010.95(0.31)
Z	4	4	4
d_{calc} (g cm^{-3})	1.342	1.339	1.336
μ(Cu $K\alpha$) (cm^{-1})	8.25	8.23	8.21
R	0.040	0.042	0.045
R_w	0.052	0.054	0.055

At 315 K (42 °C), crystals of Sb-7 showed signs of deterioration, as evident from the wide ω scans. At 335 K (62 °C), crystals of Sb-7 deteriorated immediately.

According to the slope in Figure 4–108, the unit-cell volume of Sb-7 expands at the rate of 4.1 $Å^3$ for every 10 °C rise in temperature for four molecules in the unit cell (116 non-H's, 96 H's)

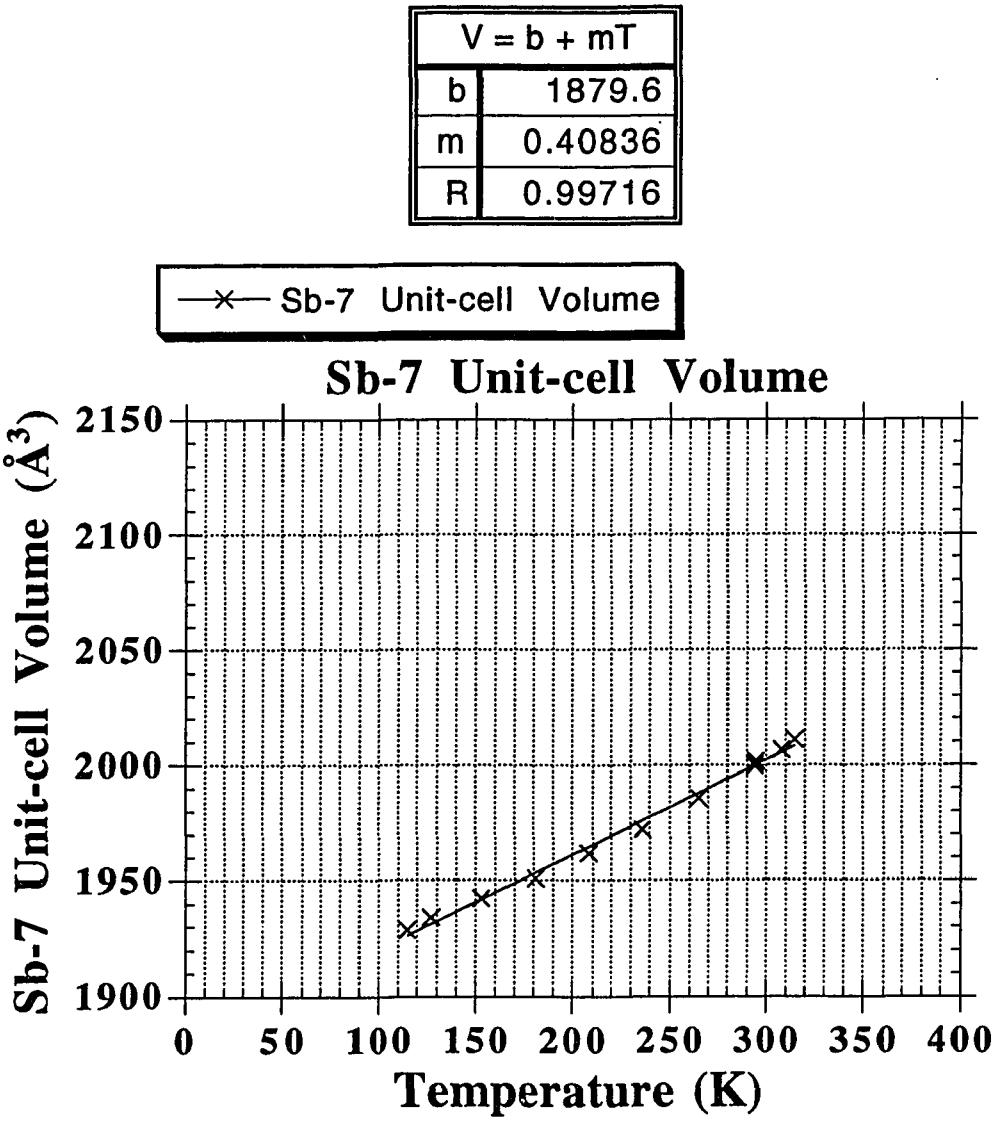


Figure 4–108. A plot of Sb-7 unit-cell volume versus temperature.

The density of Sb-7 (Figure 4–109) decreases as the volume of the unit cell expands.

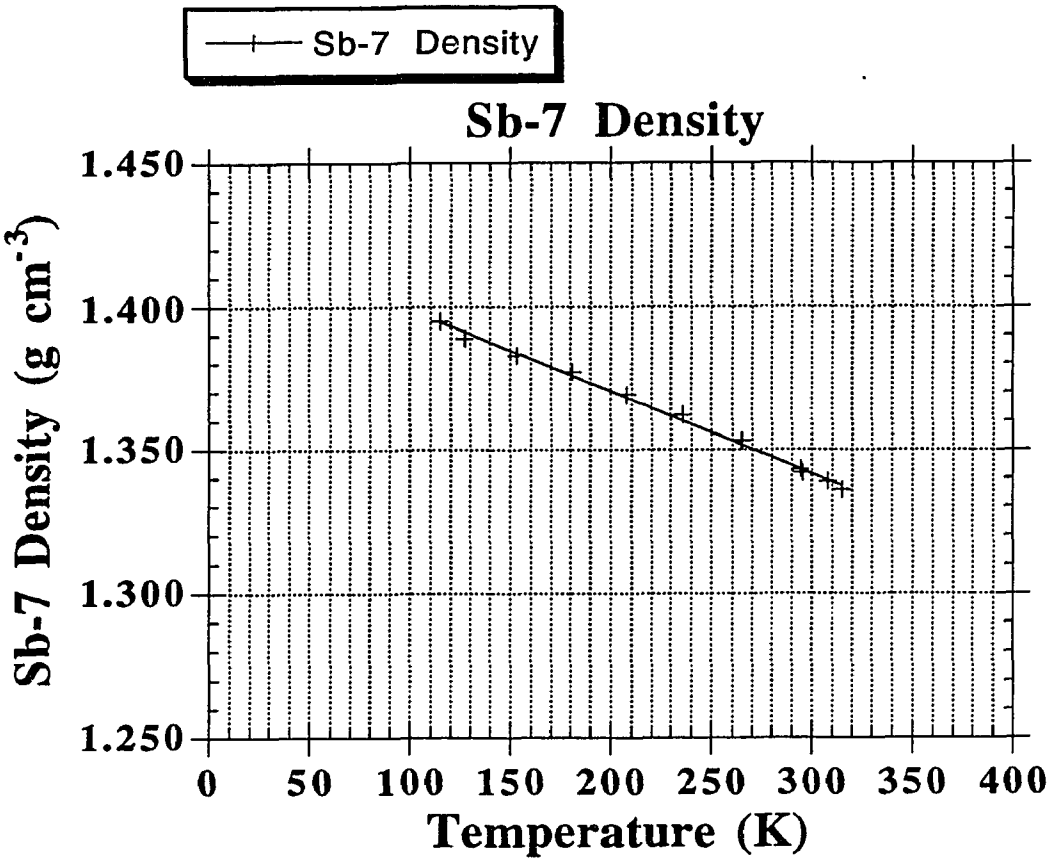


Figure 4–109. A plot of Sb-7 density versus temperature.

Selected interatomic distances in the semibullvalene ring of Sb-7 are listed in Table 4–18.

Table 4–18. Selected Interatomic Distances (Å) in the Semibullvalene Ring of Sb-7 at Various Temperatures.

	115 K	**127 K**	**153 K**	**181 K**	**208 K**	**236 K**
C1—C2	1.495(3)	1.507(4)	1.506(4)	1.498(4)	1.498(3)	1.495(3)
C1—C5	1.571(3)	1.575(4)	1.575(4)	1.574(4)	1.575(3)	1.574(3)
C1—C8	1.527(3)	1.529(4)	1.525(4)	1.519(4)	1.526(3)	1.523(3)
C2—C3	1.467(3)	1.469(4)	1.468(4)	1.466(4)	1.463(3)	1.462(3)
C2—C8	1.634(3)	1.636(4)	1.639(4)	1.638(4)	1.642(3)	1.648(3)
C3—C4	1.343(3)	1.335(4)	1.340(4)	1.338(4)	1.338(3)	1.340(3)
C3—C7	3.051(3)	3.053(4)	3.059(4)	3.055(4)	3.055(3)	3.052(3)
C4—C5	1.534(3)	1.544(4)	1.541(4)	1.537(4)	1.539(3)	1.537(3)
C4—C6	2.348(3)	2.351(4)	2.351(4)	2.350(4)	2.345(3)	2.335(3)
C5—C6	1.537(3)	1.539(4)	1.540(4)	1.537(4)	1.536(3)	1.532(3)
C6—C7	1.342(3)	1.333(4)	1.330(4)	1.336(4)	1.332(3)	1.334(3)
C7—C8	1.463(3)	1.465(4)	1.469(4)	1.469(4)	1.465(3)	1.461(3)
C2—C3 + C3—C4	2.810	2.804	2.808	2.804	2.801	2.802
C6—C7 + C7—C8	2.805	2.798	2.799	2.805	2.797	2.795
C2—C8 + C4—C6	3.982	3.987	3.990	3.989	3.987	3.983

Table 4–18 (cont'd). Selected Interatomic Distances (Å) in the Semibullvalene Ring of Sb-7 at Various Temperatures.

	265 K	294 K	294 K	295 K	308 K	315 K
C1—C2	1.494(3)	1.493(3)	1.496(4)	1.496(3)	1.500(4)	1.498(4)
C1—C5	1.572(3)	1.575(3)	1.572(4)	1.571(3)	1.572(4)	1.574(4)
C1—C8	1.523(3)	1.523(3)	1.521(4)	1.522(3)	1.522(4)	1.526(4)
C2—C3	1.457(3)	1.453(3)	1.449(4)	1.448(3)	1.443(4)	1.441(4)
C2—C8	1.660(3)	1.685(3)	1.677(4)	1.678(3)	1.691(4)	1.702(4)
C3—C4	1.345(3)	1.340(3)	1.345(4)	1.345(3)	1.342(4)	1.344(4)
C3—C7	3.051(3)	3.055(3)	3.046(4)	3.048(3)	3.048(4)	3.048(4)
C4—C5	1.538(3)	1.537(3)	1.538(4)	1.538(3)	1.537(4)	1.534(4)
C4—C6	2.325(3)	2.313(3)	2.309(4)	2.309(3)	2.291(4)	2.289(4)
C5—C6	1.529(3)	1.529(3)	1.529(4)	1.529(3)	1.526(4)	1.528(4)
C6—C7	1.334(3)	1.332(3)	1.331(4)	1.330(3)	1.332(4)	1.328(4)
C7—C8	1.457(3)	1.455(3)	1.449(4)	1.454(3)	1.450(4)	1.448(4)
C2—C3 + C3—C4	2.802	2.793	2.794	2.793	2.785	2.785
C6—C7 + C7—C8	2.791	2.787	2.780	2.784	2.782	2.776
C2—C8 + C4—C6	3.985	3.998	3.986	3.987	3.983	3.991

To compare distinguishing features of interatomic distances of ring atoms in Sb-7, they are plotted together against temperature in Figure 4–110, but congestion results. To clear up this congestion in the plots of interatomic distances, we will also display them in separate sets to bring out more clearly the changes which take place in the semibullvalene ring system as the temperature is varied. We will even resort to a change of scale to emphasize or to show more clearly those changes in interatomic distances which accompany or occur with the variation of temperature.

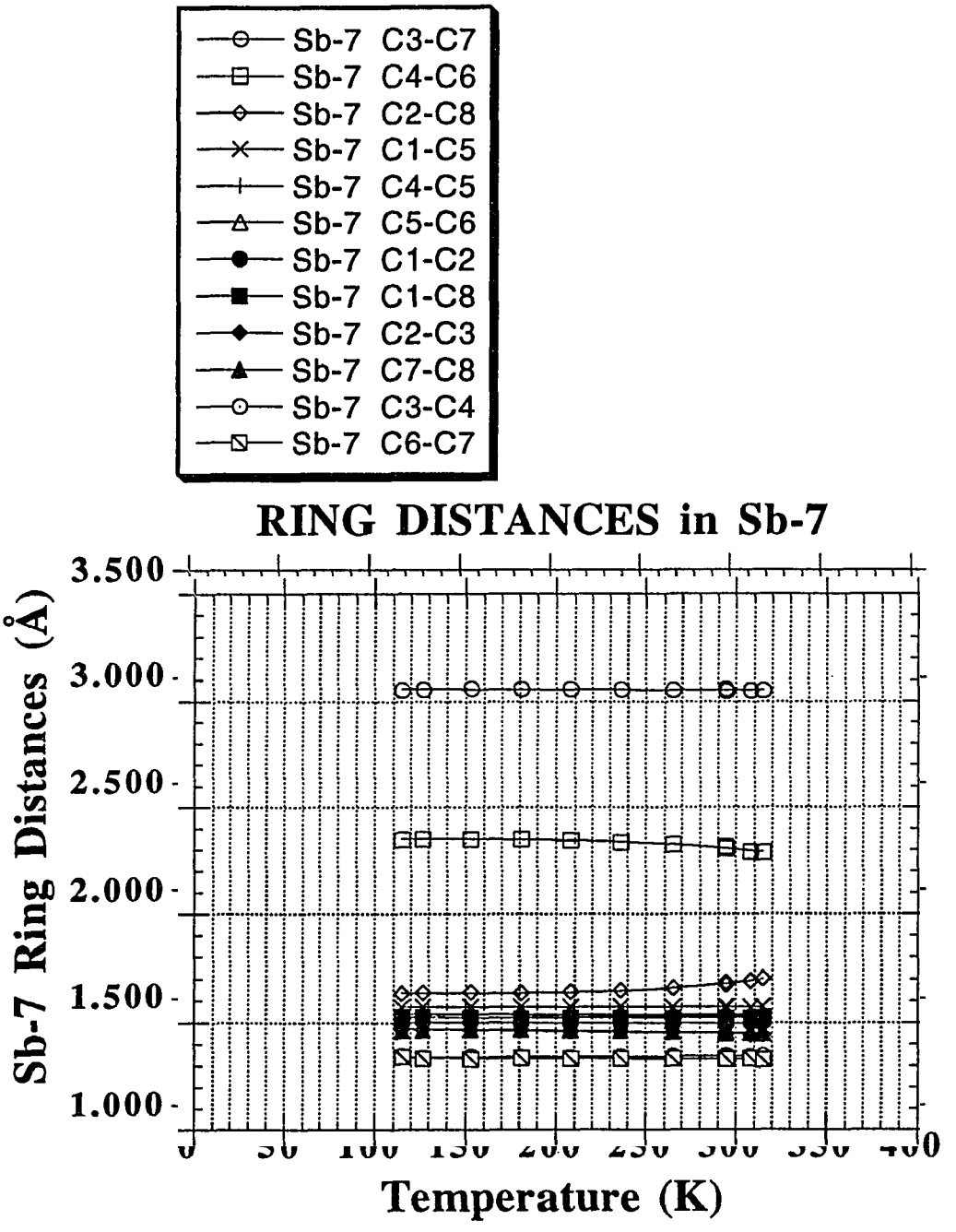


Figure 4–110. Plots of selected interatomic distances in the semibullvalene ring of Sb-7 versus temperature.

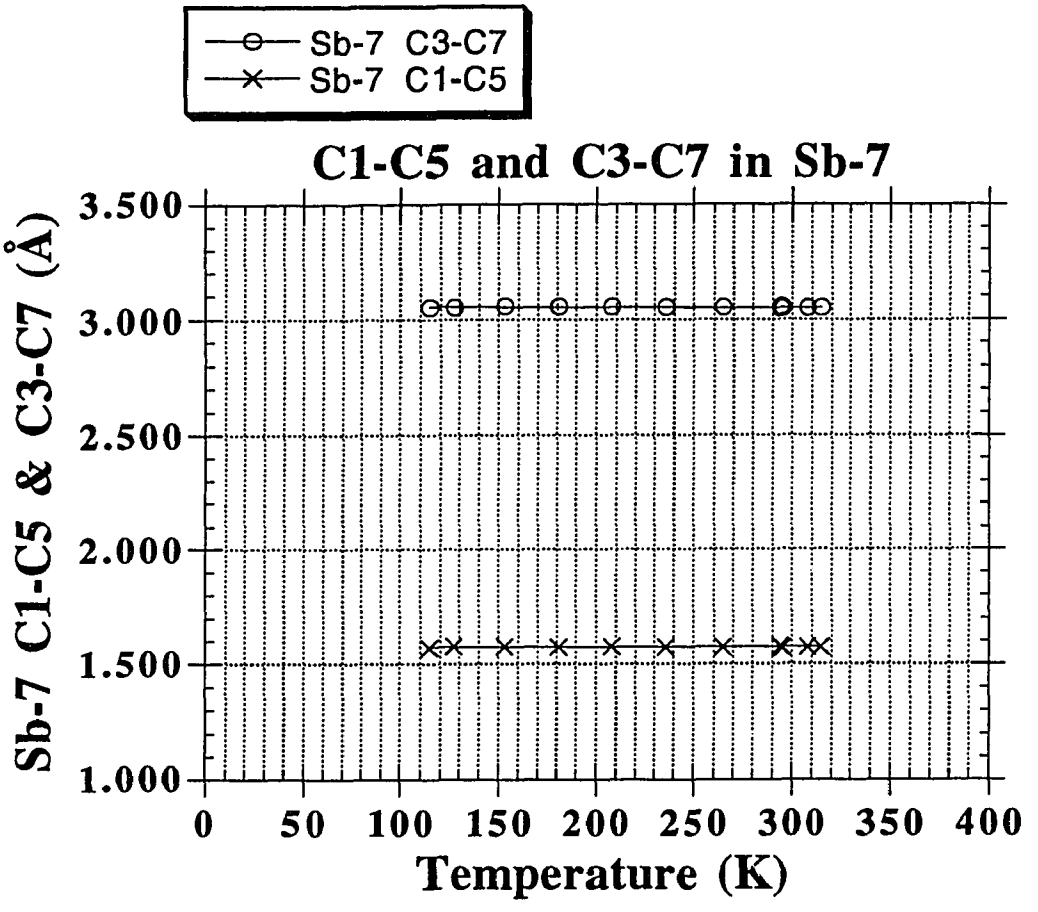


Figure 4–111. Plots of C1—C5 and C3—C7 distances in Sb-7 versus temperature.

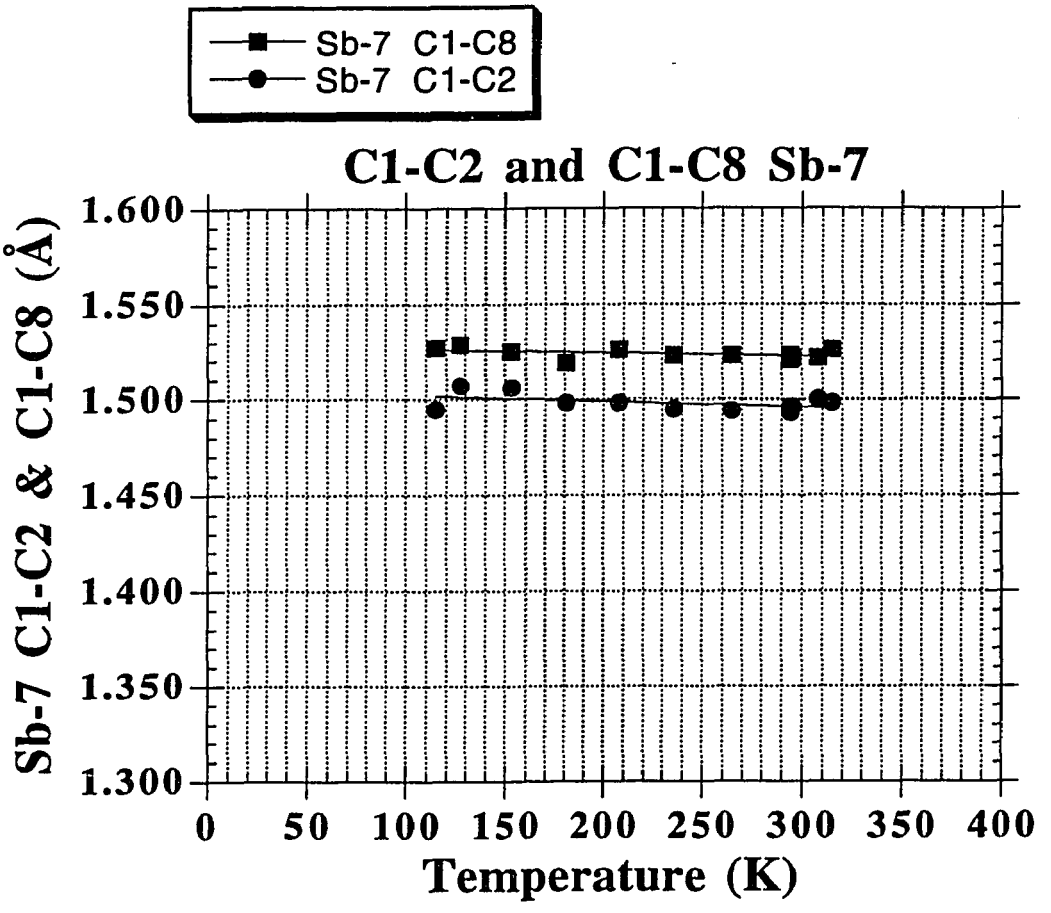


Figure 4–112. Plots of C1—C2 and C1—C8 distances in Sb-7 versus temperature.

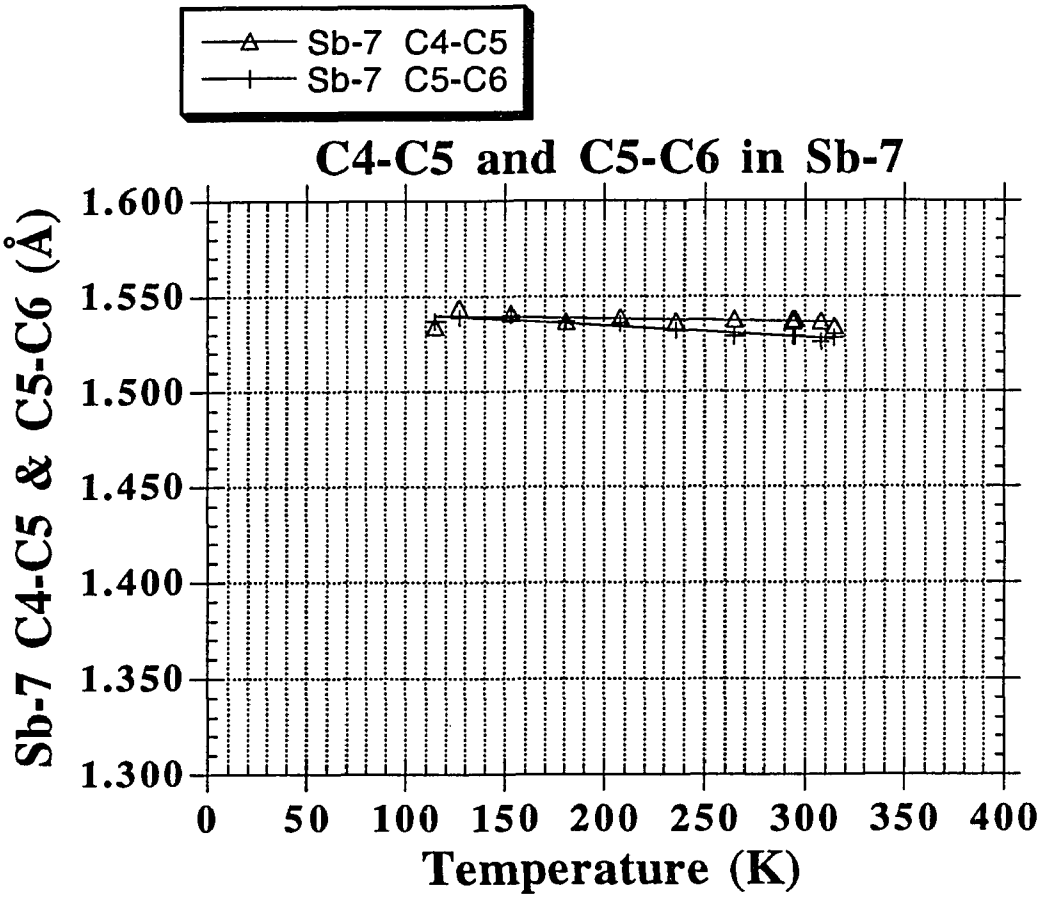


Figure 4–113. Plots of C4—C5 and C5—C6 distances in Sb-7 versus temperature.

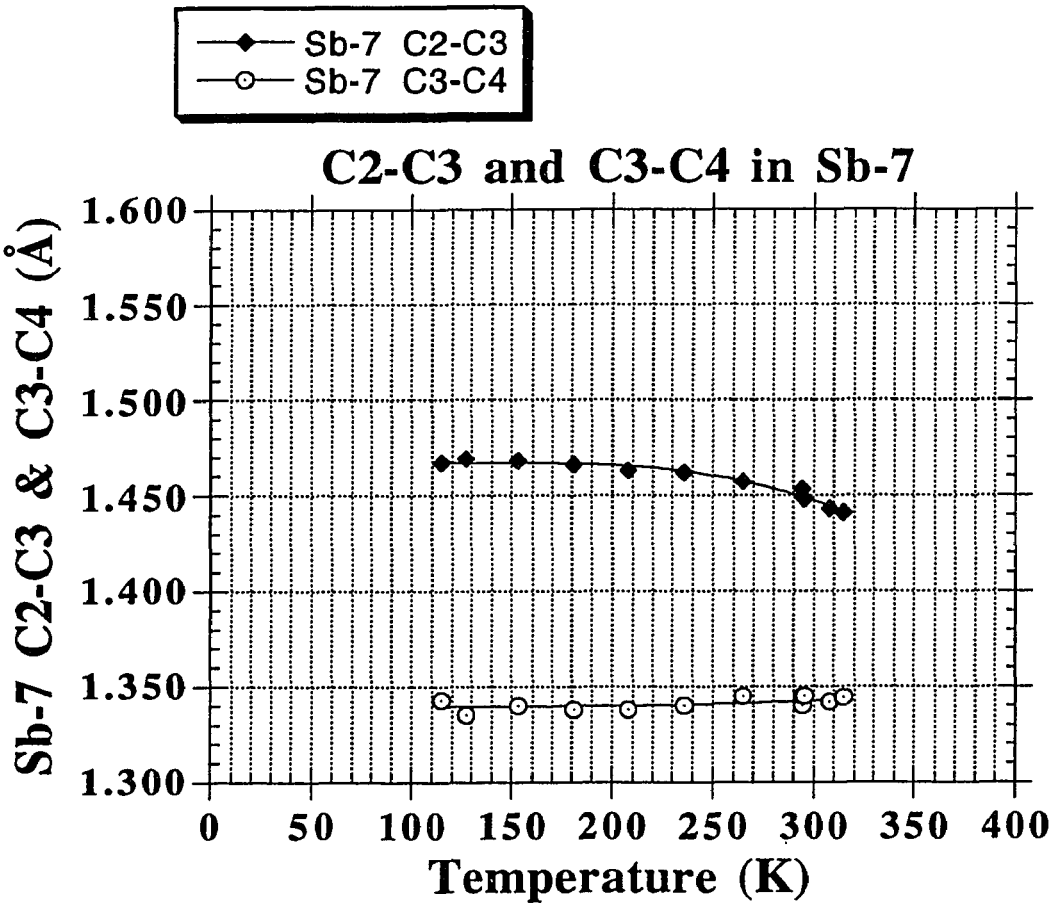


Figure 4–114. Plots of C2—C3 and C3—C4 distances in Sb-7 versus temperature.

The sum of the distances C2—C3 and C3—C4 in Sb-7 is nearly constant as the temperature is varied (Figure 4–1115).

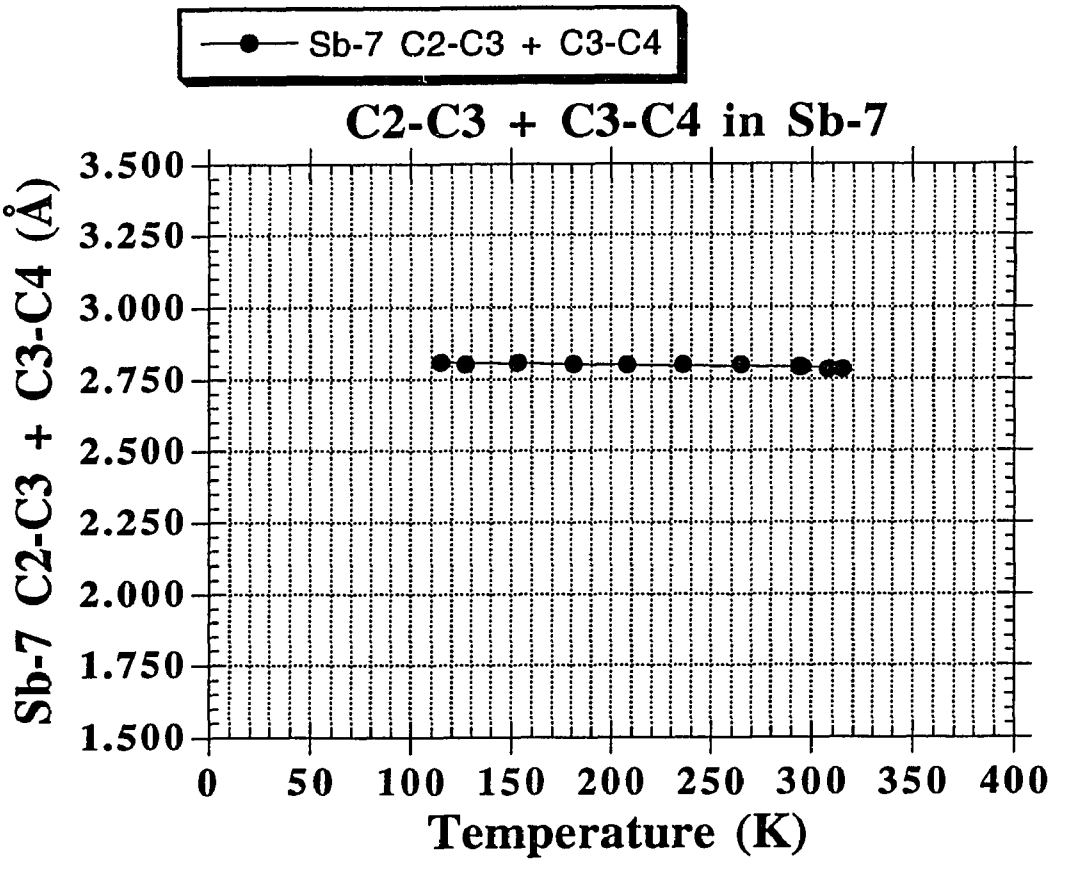


Figure 4–115. A plot of the sum of the distances C2—C3 and C3—C4 in Sb-7 versus temperature.

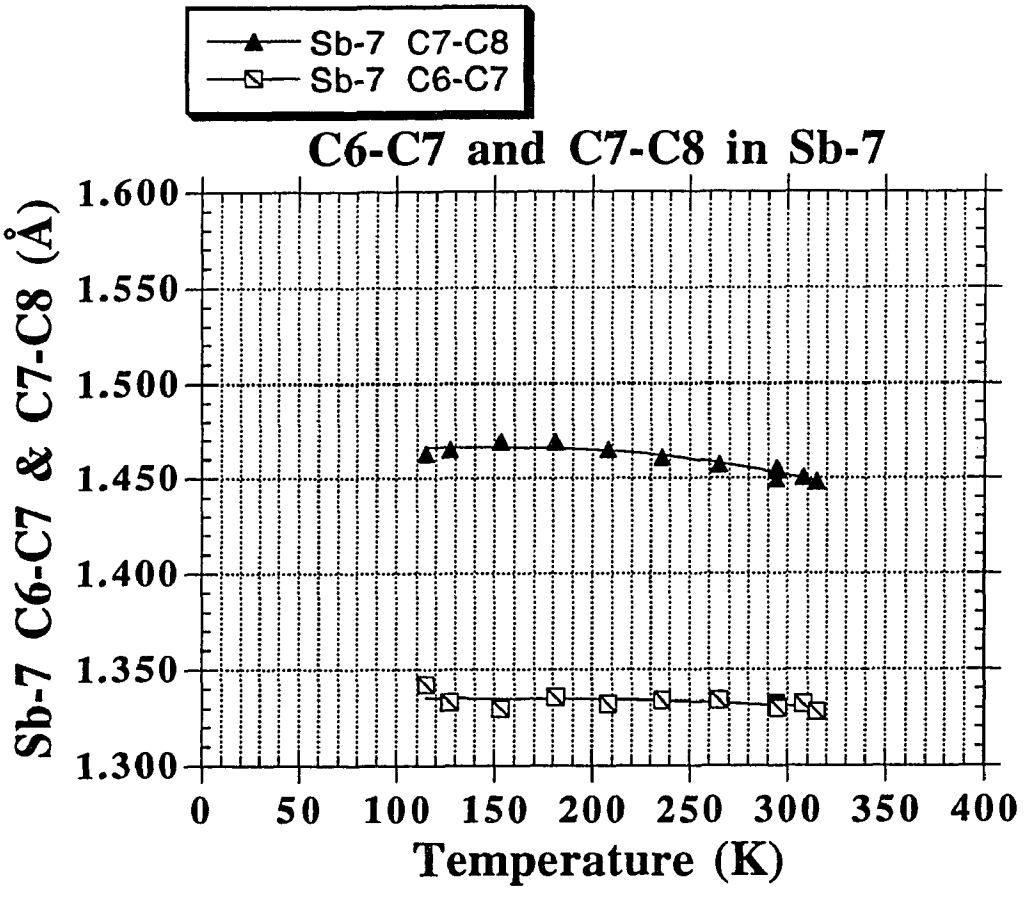


Figure 4–116. Plots of C6—C7 and C7—C8 distances in Sb-7 versus temperature.

The sum of the distances C6—C7 and C7—C8 in Sb-7 is nearly constant as the temperature is varied (Figure 4–117).

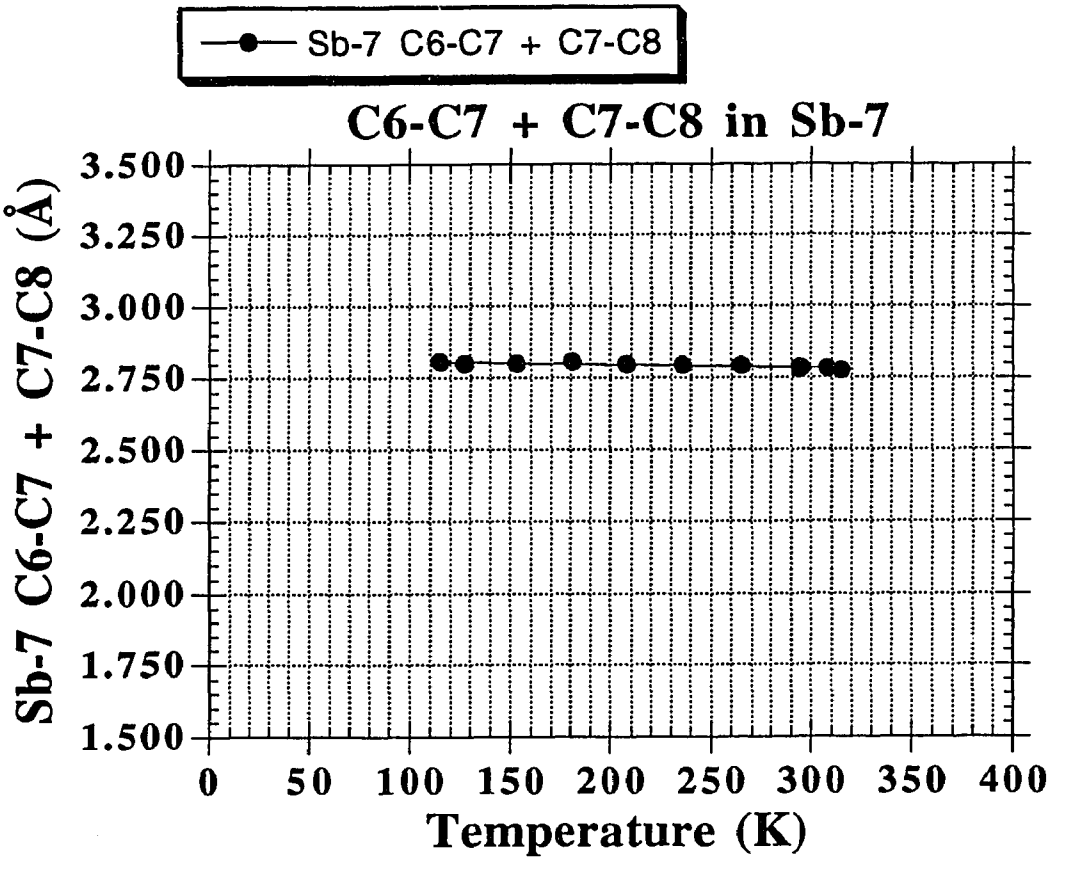


Figure 4–117. A plot of the sum of the distances C6—C7 and C7—C8 in Sb-7 versus temperature.

Figure 4-118 clearly illustrates that as the bond distance C2—C8 in Sb-7 becomes longer with increasing temperature, the interatomic distance C4—C6 becomes shorter.

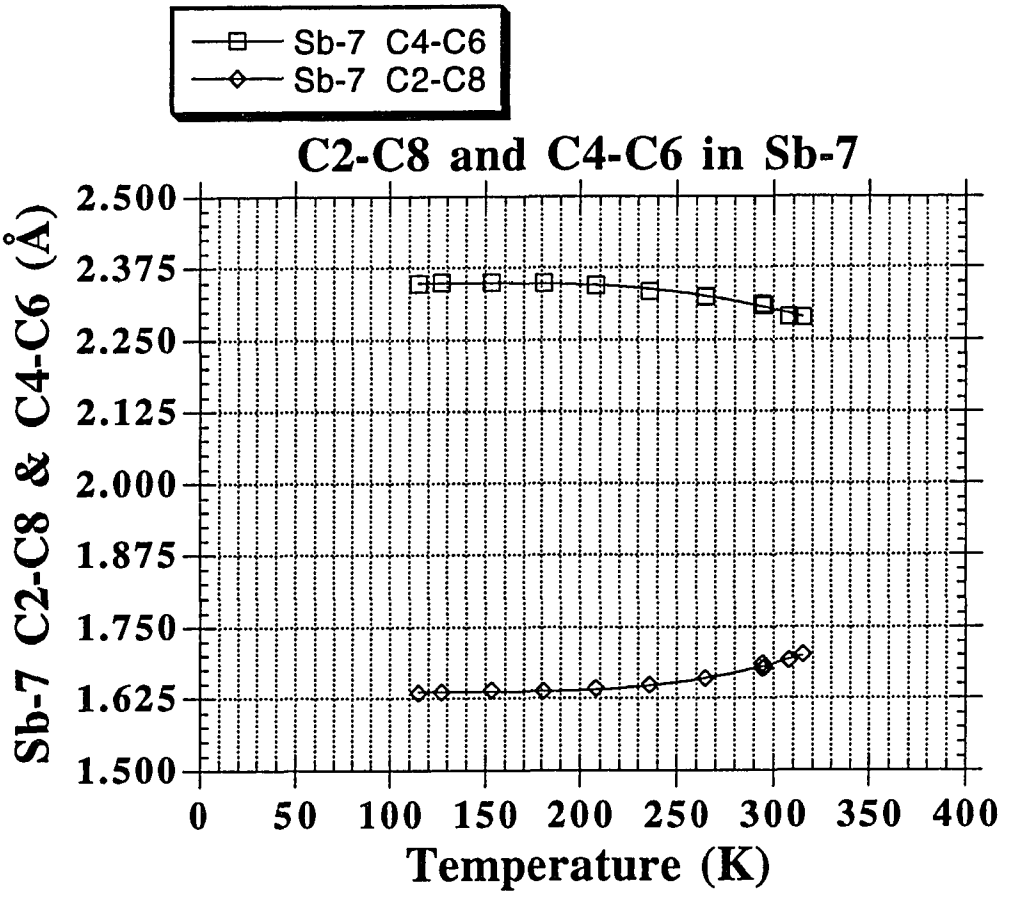


Figure 4–118. Plots of C2—C8 and C4—C6 distances in Sb-7 versus temperature.

Even though C2—C8 and C4—C6 change with temperature, their sum remains constant (Figure 4–119).

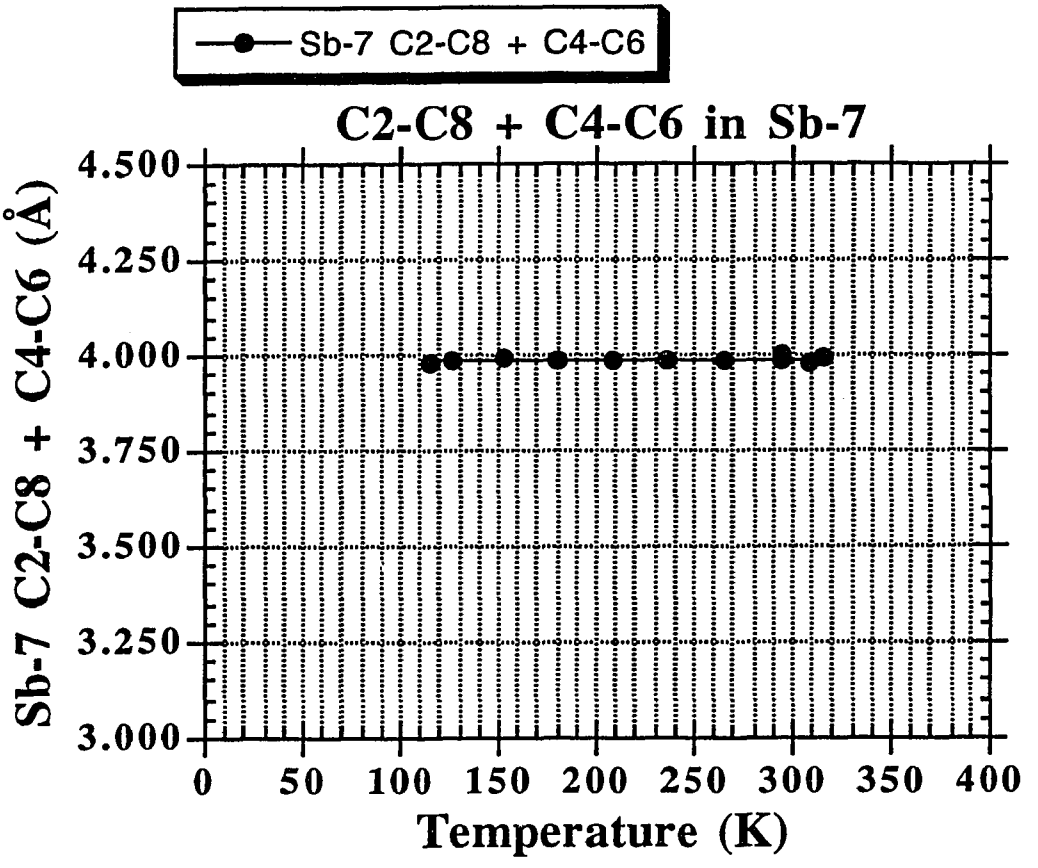


Figure 4–119. A plot of the sum of the distances C2—C8 and C4—C6 in Sb-7 versus temperature.

Selected angles in the semibullvalene ring of Sb-7 are in Table 4–19. These angles remain essentially constant as the temperature is varied, except those of the cyclopropyl ring and the corresponding angles opposite to the cyclopropyl ring, formed by the atoms, C4, C5, and C6. The angles of the cyclopropyl ring must change to accommodate the elongation of the C2—C8 bond.

Table 4–19. Selected Angles (°) in the Semibullvalene Ring of Sb-7 at Various Temperatures.

	115 K	**127 K**	**153 K**	**181 K**	**208 K**	**236 K**
C2—C1—C5	104.7(2)	104.5(2)	104.7(2)	104.7(2)	104.7(2)	104.9(2)
C2—C1—C8	65.4(1)	65.2(2)	65.4(2)	65.7(2)	65.8(1)	66.2(1)
C5—C1—C8	103.4(1)	103.0(2)	103.3(2)	103.5(2)	103.3(2)	103.4(2)
C1—C2—C3	108.2(2)	108.1(2)	108.0(2)	108.1(2)	108.2(2)	108.2(2)
C1—C2—C8	58.2(1)	58.0(2)	57.8(2)	57.8(2)	57.9(1)	57.7(1)
C3—C2—C8	116.9(2)	116.7(2)	116.8(2)	116.7(2)	116.8(2)	116.5(2)
C2—C3—C4	110.9(2)	111.2(3)	111.1(2)	111.1(3)	111.2(2)	111.1(2)
C3—C4—C5	111.3(2)	111.5(2)	111.6(2)	111.4(2)	111.4(2)	111.5(2)
C5—C4—C6	40.2(1)	40.2(1)	40.3(1)	40.1(1)	40.2(1)	40.4(1)
C1—C5—C4	102.5(1)	102.3(2)	102.1(2)	102.3(2)	102.1(2)	102.1(2)
C1—C5—C6	102.6(1)	102.5(2)	102.3(2)	102.3(2)	102.4(2)	102.4(2)
C4—C5—C6	99.7(2)	99.4(2)	99.4(2)	99.7(2)	99.4(2)	99.1(2)
C4—C6—C5	40.1(1)	40.4(1)	40.3(1)	40.1(2)	40.4(1)	40.6(1)
C5—C6—C7	110.5(2)	110.9(2)	111.2(2)	111.1(3)	111.0(2)	111.1(2)
C6—C7—C8	111.6(2)	111.4(2)	111.3(2)	111.0(3)	111.5(2)	111.5(2)
C1—C8—C2	56.3(1)	56.7(2)	56.7(2)	56.5(2)	56.3(1)	56.1(1)
C1—C8—C7	107.5(2)	107.7(2)	107.7(2)	107.8(2)	107.5(2)	107.6(2)
C2—C8—C7	120.9(2)	121.0(2)	121.0(2)	121.0(2)	120.9(2)	120.8(2)
$(\alpha+\beta)/2$[a]	82.6	82.3	82.4	82.7	82.6	82.7
C3—M[b]—C7	85.1	84.9	85.1	85.2	85.2	85.3

[a] α = C2—C1—C8, β = C4—C5—C6.
[b] M = midpoint between C1 and C5 bond.

Table 4–19 (cont'd). Selected Angles (°) in the Semibullvalene Ring of Sb-7 at Various Temperatures.

	265 K	294 K	294 K	295 K	308 K	315 K
C2—C1—C5	105.1(2)	105.1(2)	104.9(2)	104.8(2)	104.6(2)	104.5(2)
C2—C1—C8	66.8(1)	67.9(2)	67.6(2)	67.5(2)	68.0(2)	68.5(2)
C5—C1—C8	103.4(2)	103.1(2)	103.2(2)	103.3(2)	103.5(2)	103.4(2)
C1—C2—C3	108.3(2)	108.5(2)	108.7(2)	108.7(2)	108.8(2)	109.0(2)
C1—C2—C8	57.5(1)	56.9(2)	56.9(2)	57.0(1)	56.6(2)	56.5(2)
C3—C2—C8	116.3(2)	115.7(2)	116.3(2)	116.1(2)	116.0(2)	115.9(2)
C2—C3—C4	111.1(2)	111.2(2)	110.9(2)	111.1(2)	111.3(2)	111.1(3)
C3—C4—C5	111.3(2)	111.5(2)	111.5(2)	111.3(2)	111.4(2)	111.6(2)
C5—C4—C6	40.5(1)	40.9(1)	41.0(1)	41.0(1)	41.4(1)	41.5(1)
C1—C5—C4	102.1(2)	101.8(2)	102.0(2)	102.1(2)	102.3(2)	102.2(2)
C1—C5—C6	102.7(2)	102.9(2)	102.8(2)	102.8(2)	102.7(2)	102.8(2)
C4—C5—C6	98.6(2)	98.0(2)	97.7(2)	97.7(2)	96.9(2)	96.8(2)
C4—C6—C5	40.8(1)	41.2(1)	41.3(1)	41.3(1)	41.7(1)	41.7(1)
C5—C6—C7	111.0(2)	111.2(2)	111.0(2)	111.0(2)	111.0(2)	111.1(2)
C6—C7—C8	111.6(2)	111.4(2)	111.7(2)	111.8(2)	112.0(2)	112.2(3)
C1—C8—C2	55.8(1)	55.2(1)	55.5(2)	55.5(1)	55.4(2)	55.0(2)
C1—C8—C7	107.6(2)	108.1(2)	108.0(2)	107.8(2)	107.5(2)	107.6(2)
C2—C8—C7	120.6(2)	120.5(2)	120.0(2)	120.2(2)	119.9(2)	119.5(2)
$(\alpha+\beta)/2$[a]	82.7	82.9	82.7	82.6	82.4	82.7
C3—M[b]—C7	85.3	85.4	85.1	85.2	85.3	85.3

[a] α = C2—C1—C8, β = C4—C5—C6.
[b] M = midpoint between C1 and C5 bond.

Graphs based on the previous table illustrate the changes which occur in the semibullvalene ring of Sb-7 as C2—C8 elongates while C4—C6 contracts with increasing temperature.

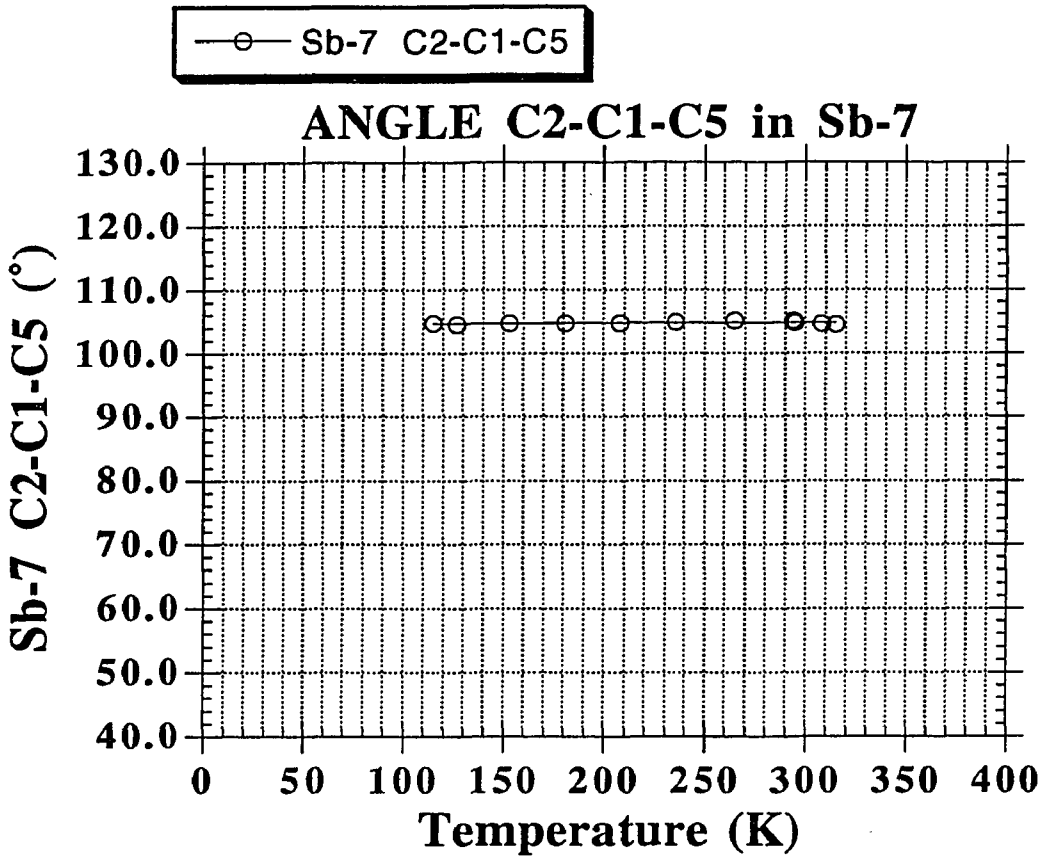


Figure 4–120. A plot of the angle C2—C1—C5 in Sb-7 versus temperature.

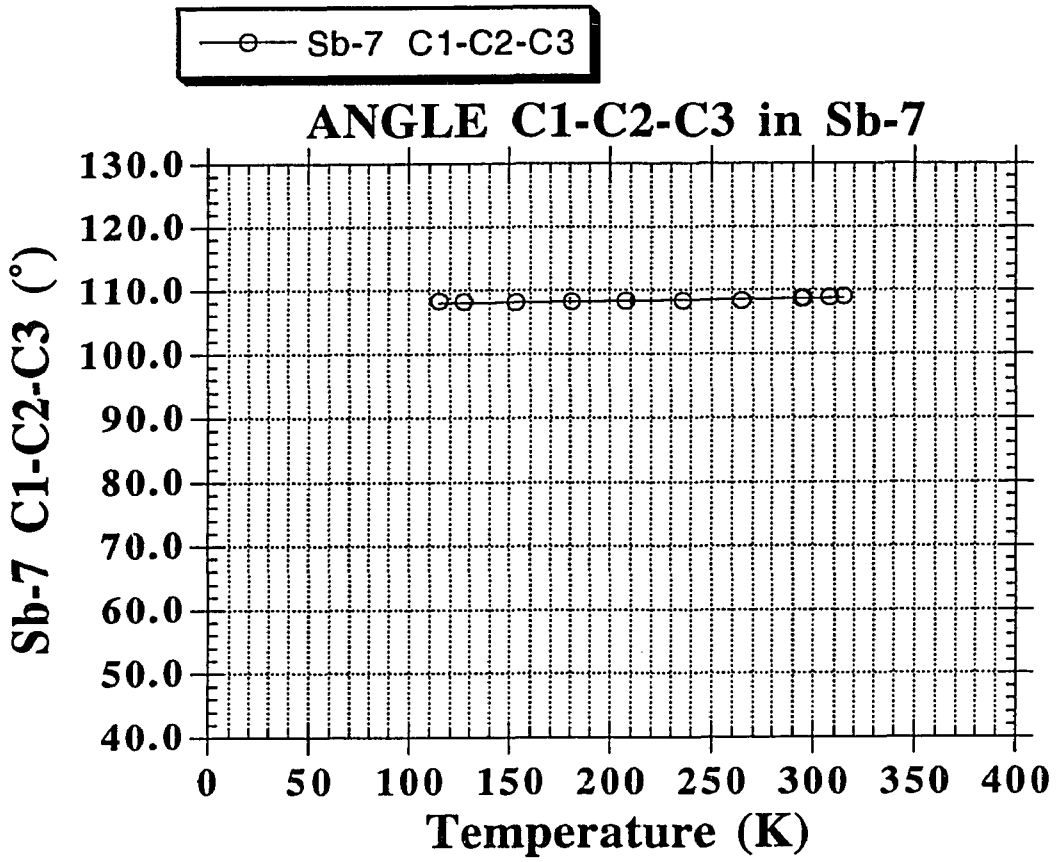


Figure 4–121. A plot of the angle C1—C2—C3 in Sb-7 versus temperature.

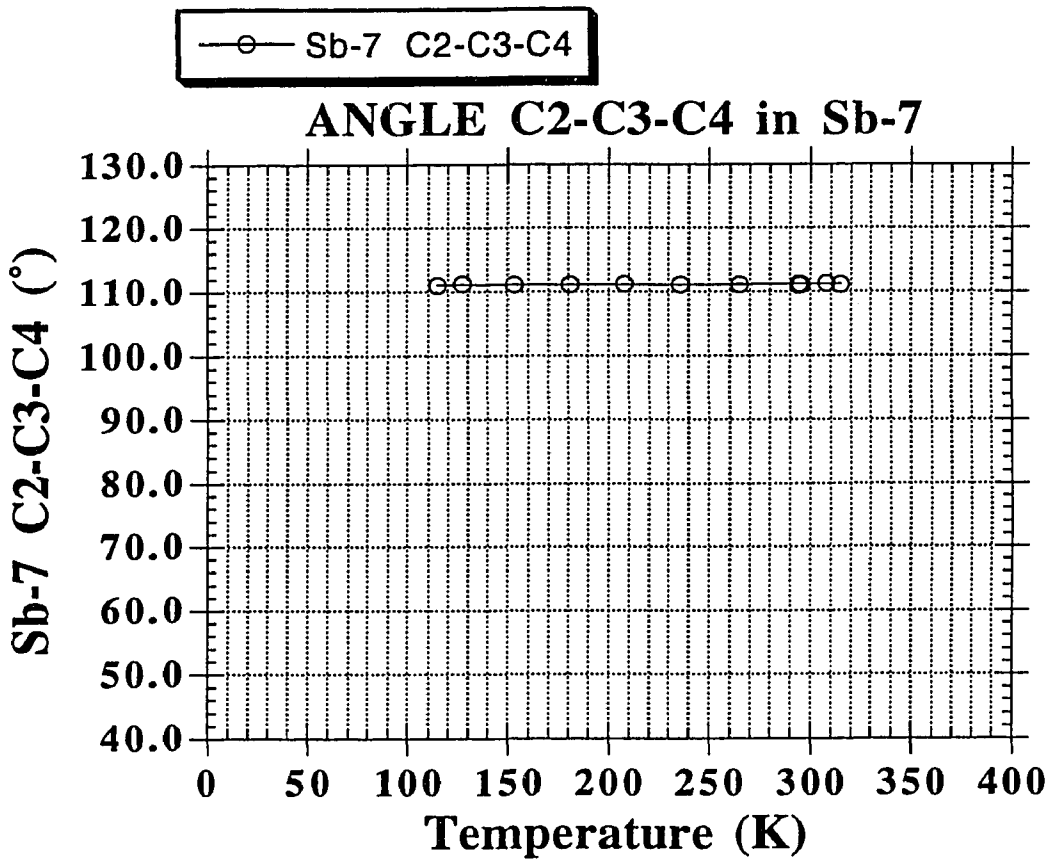


Figure 4–122. A plot of the angle C2—C3—C4 in Sb-7 versus temperature.

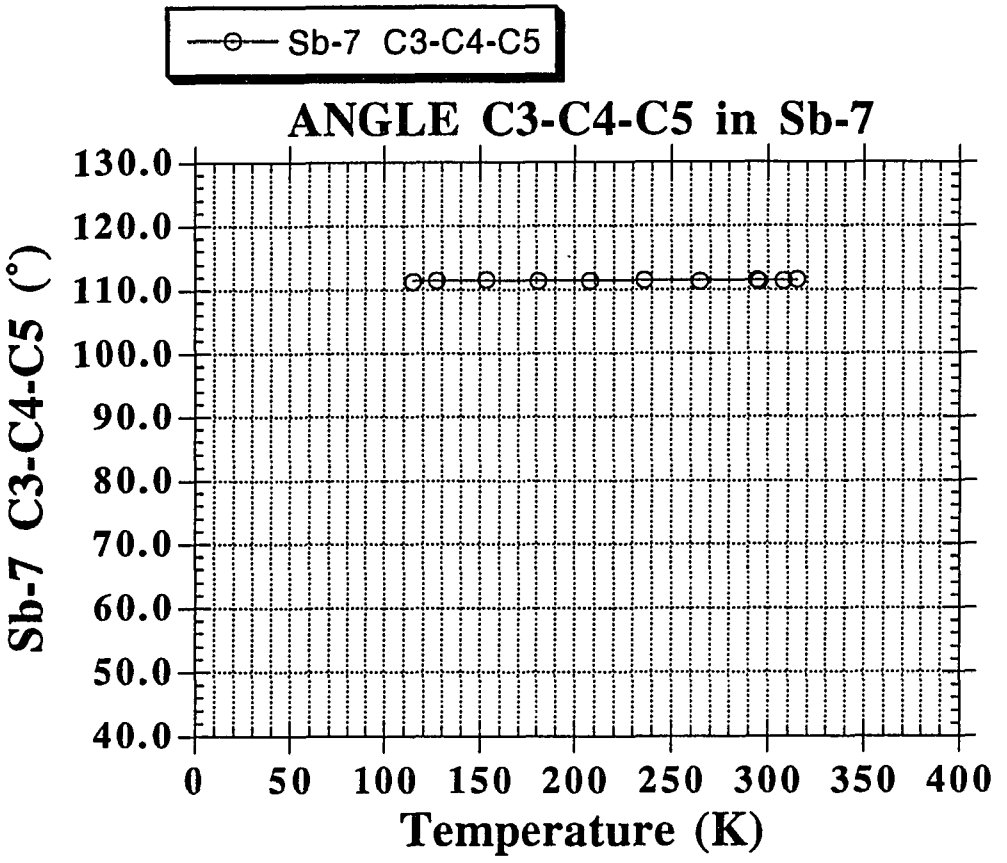


Figure 4–123. A plot of the angle C2—C4—C5 in Sb-7 versus temperature.

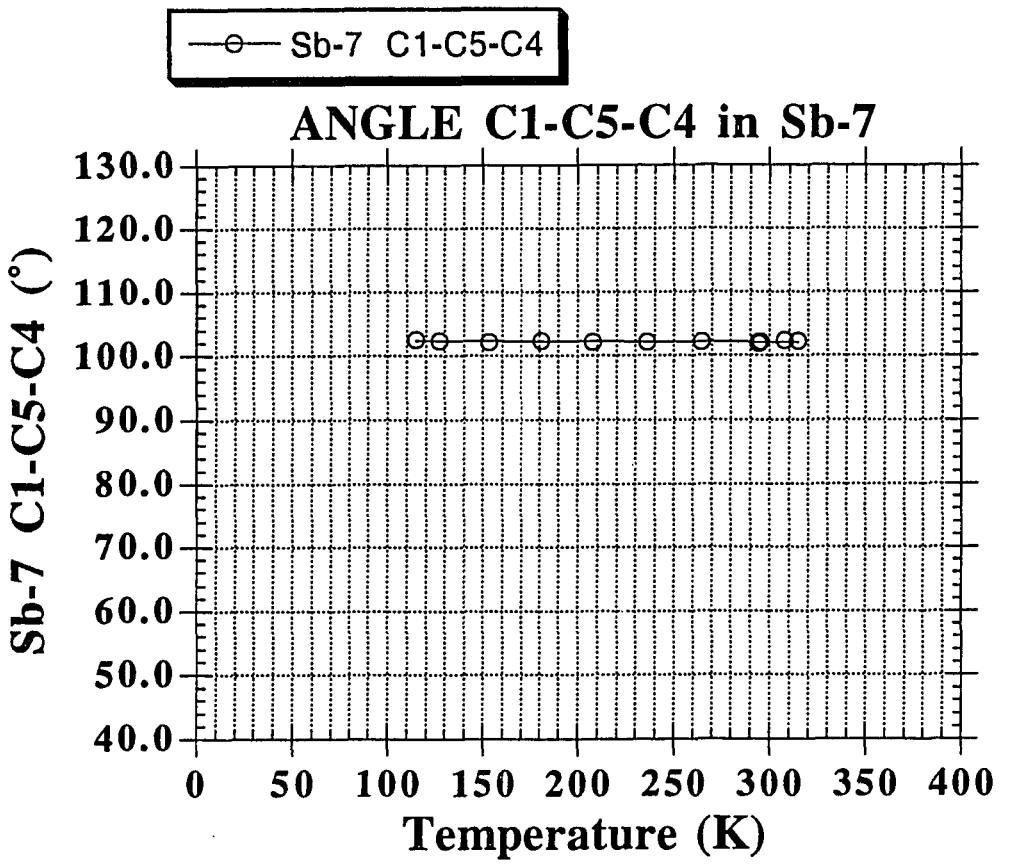


Figure 4–124. A plot of the angle C1—C5—C4 in Sb-7 versus temperature.

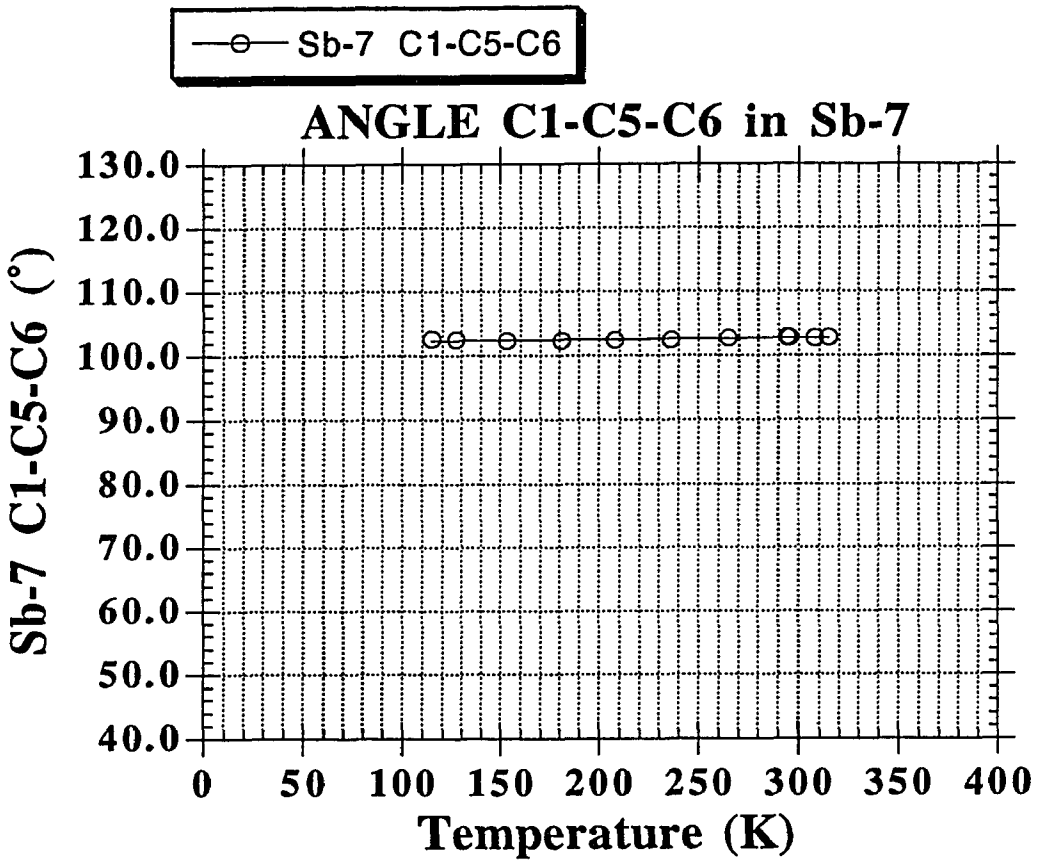


Figure 4–125. A plot of the angle C1—C5—C6 in Sb-7 versus temperature.

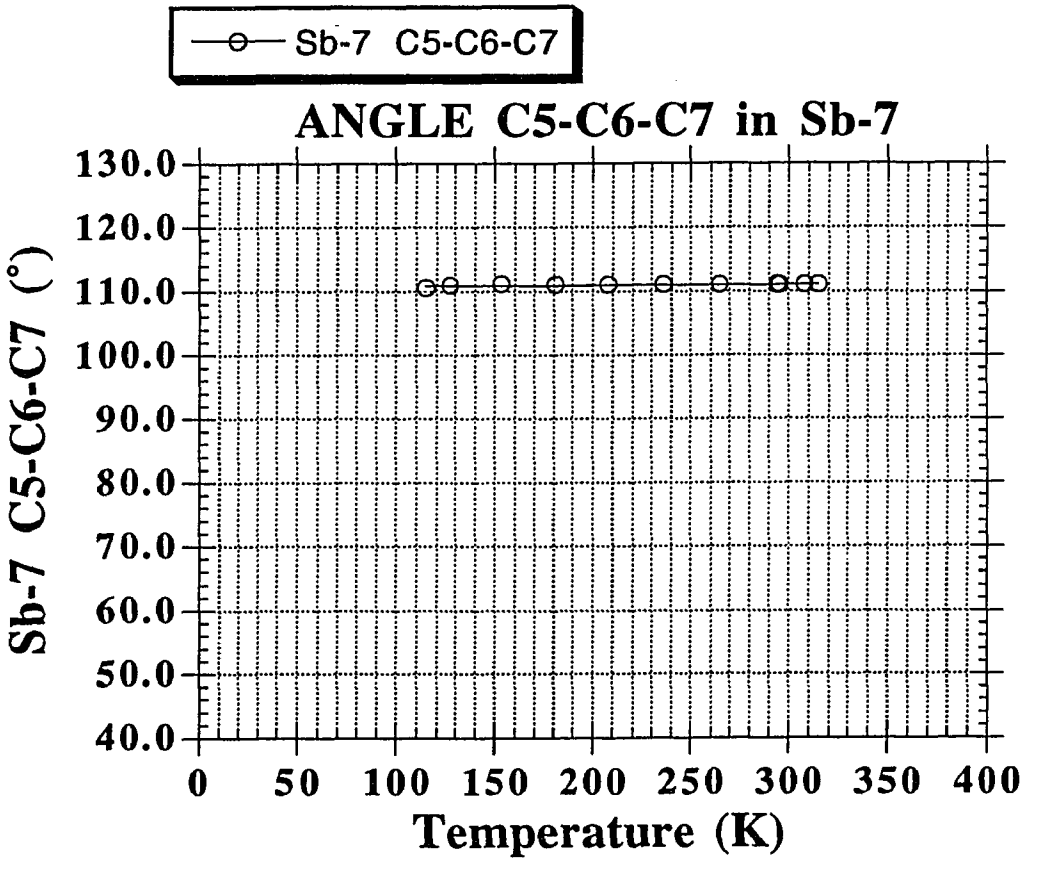


Figure 4–126. A plot of the angle C5—C6—C7 in Sb-7 versus temperature.

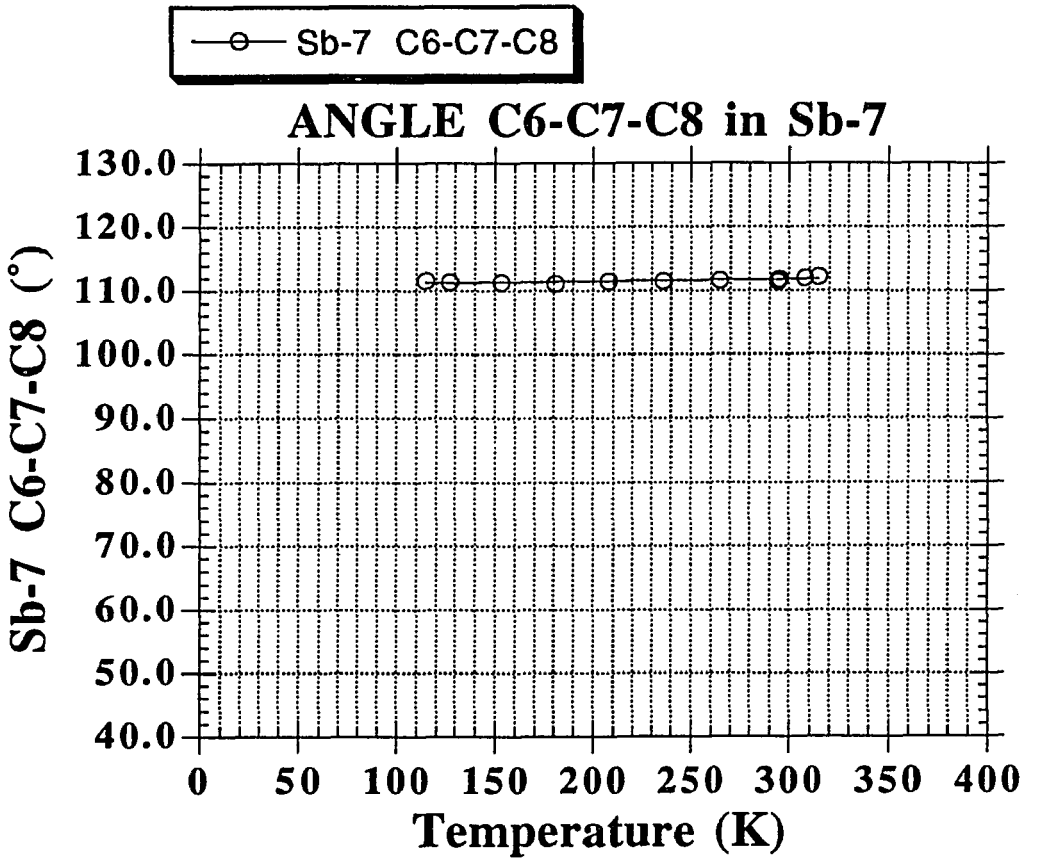


Figure 4–127. A plot of the angle C6—C7—C8 in Sb-7 versus temperature.

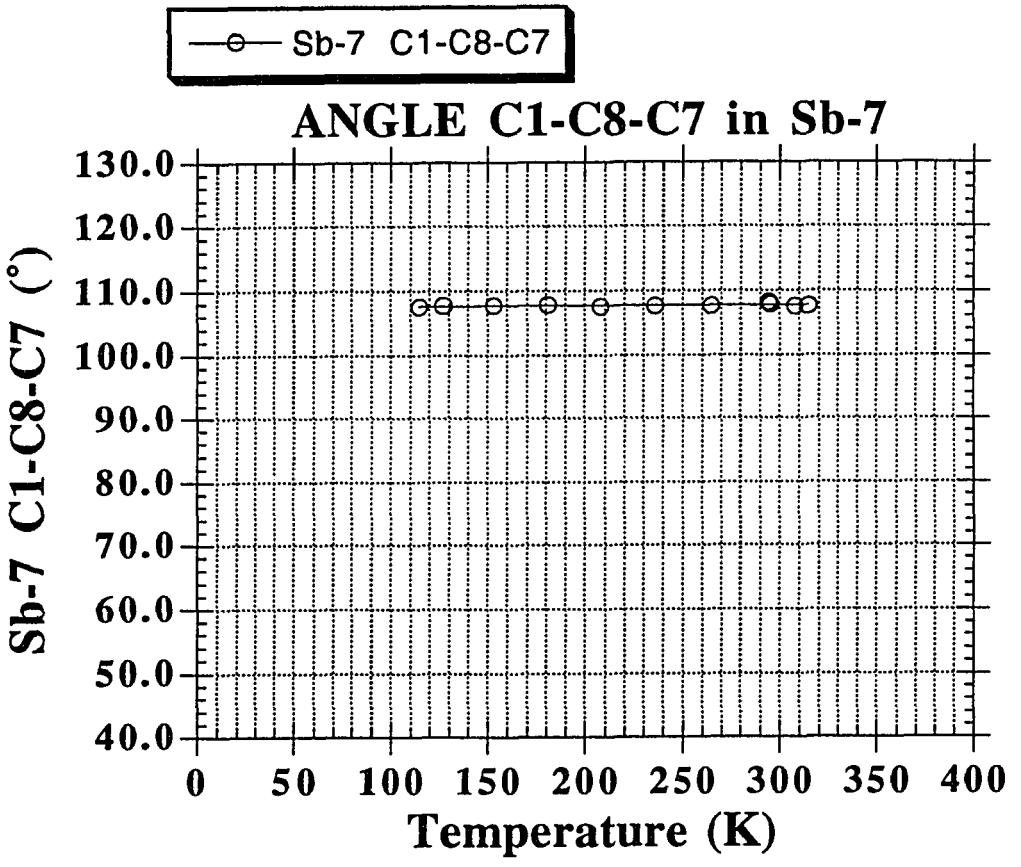


Figure 4–128. A plot of the angle C1—C8—C7 in Sb-7 versus temperature.

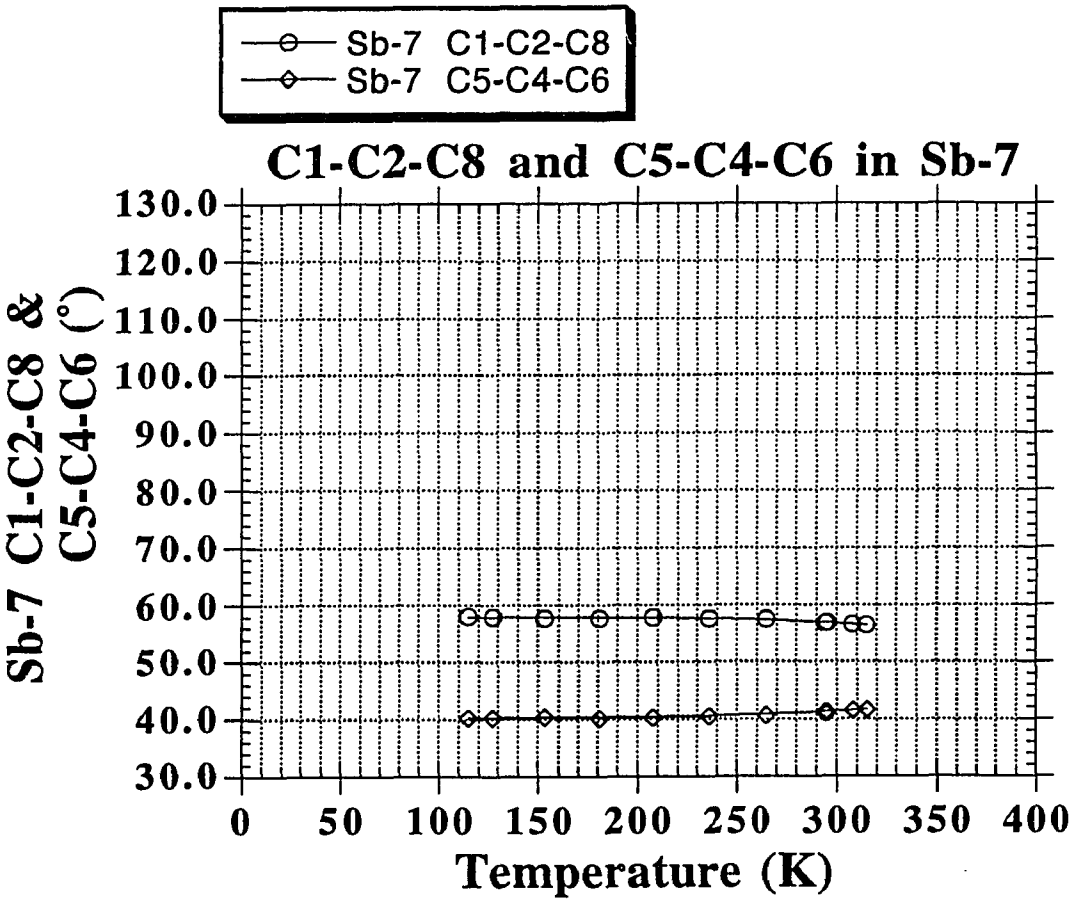


Figure 4–129. Plots of the angles C1—C2—C8 and C5—C4—C6 in Sb-7 versus temperature.

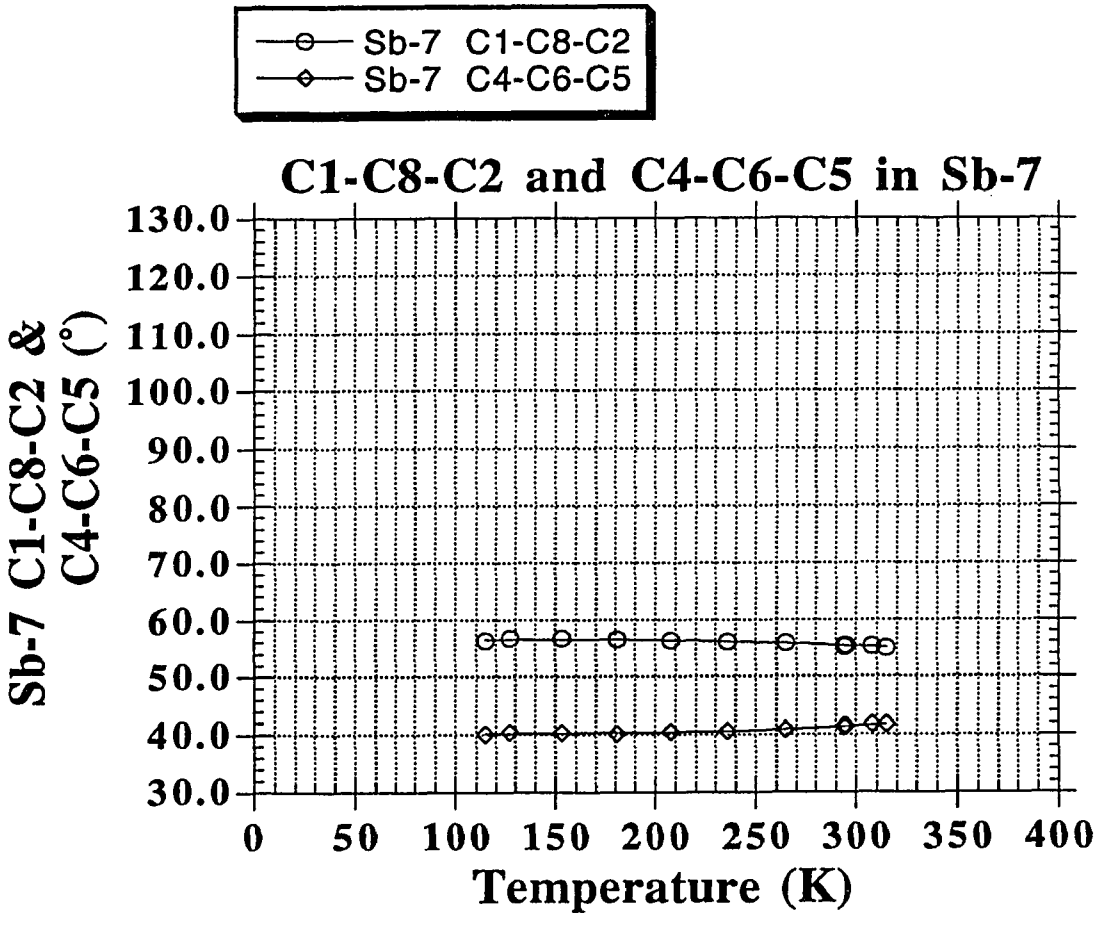


Figure 4–130. Plots of the angles C1—C8—C2 and C4—C6—C5 in Sb-7 versus temperature.

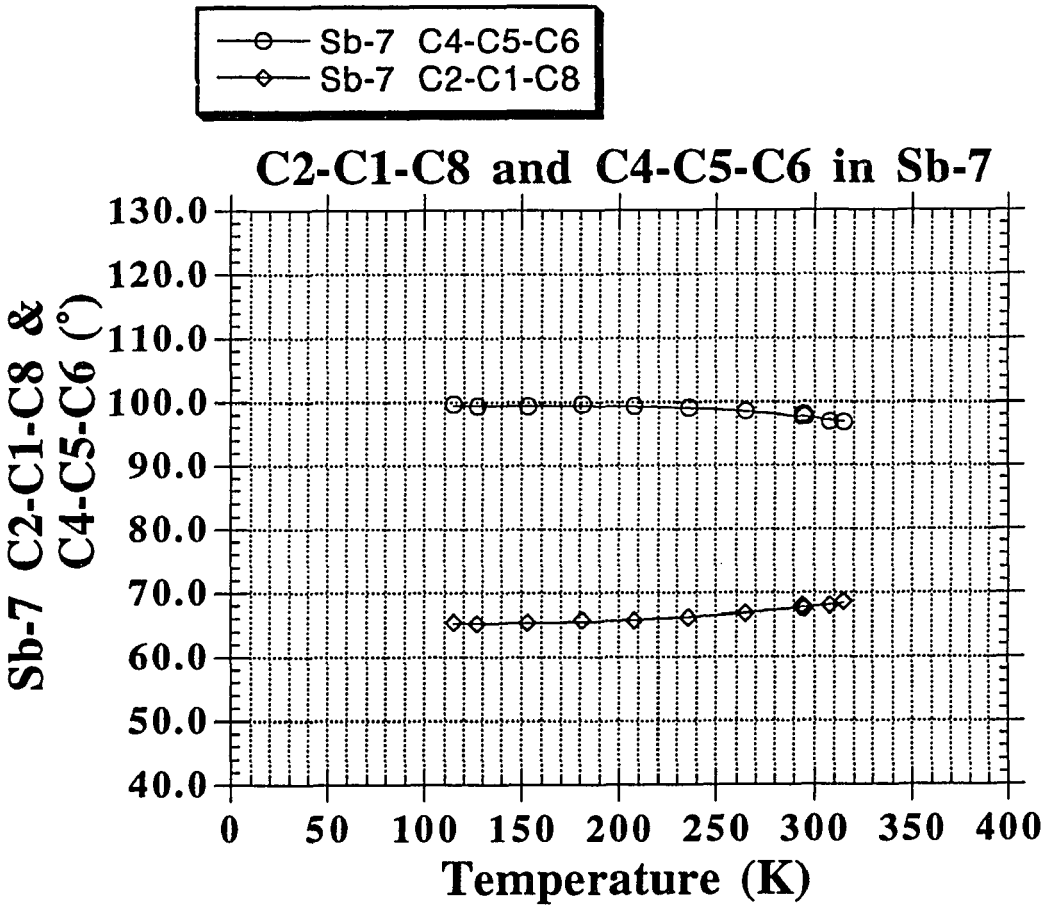


Figure 4–131. Plots of the angles C2—C1—C8 and C4—C5—C6 in Sb-7 versus temperature.

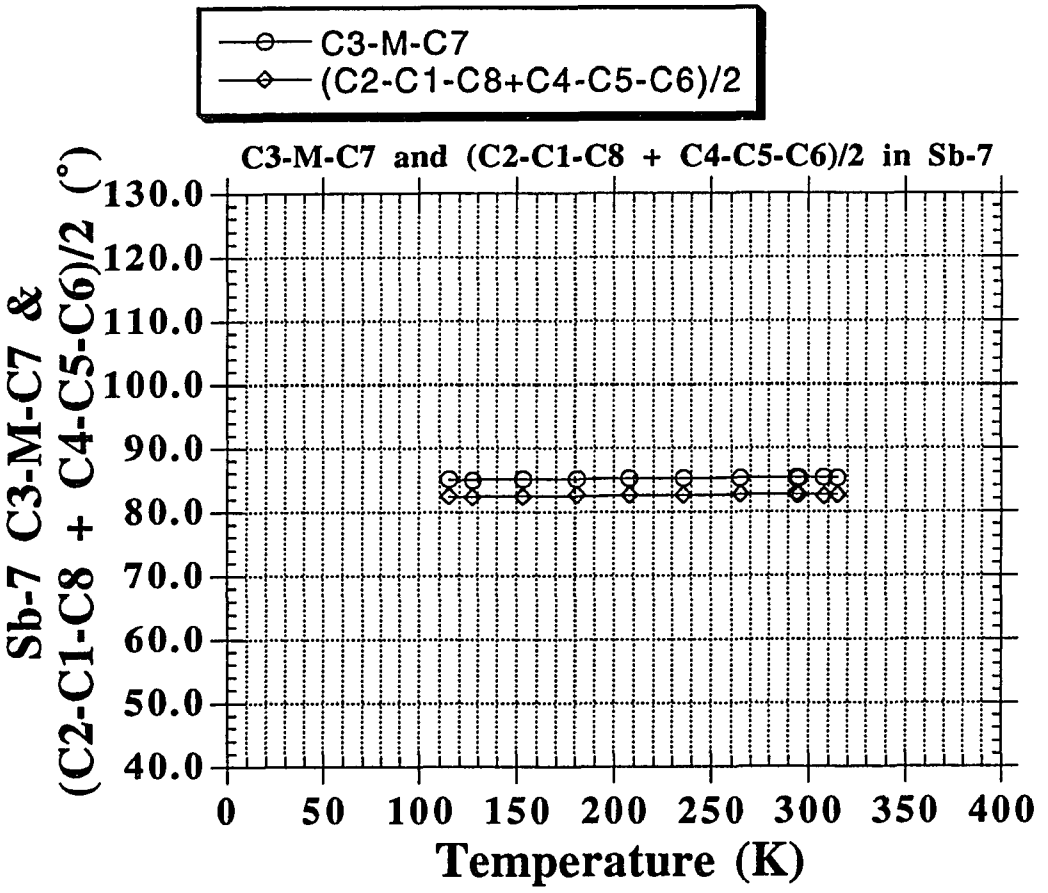


Figure 4–132. Plots of the angle C3—M—C7 (M = midpoint between C1 and C5) and the average angle of C2—C1—C8 and C4—C5—C6 in Sb-7 versus temperature.

The root-mean-square displacements in Table 4–20 say very little to shed any light on the changes that occur in the distances C2—C 8 and C4—C6.

Table 4–20. Selected Root-Mean-Square Amplitudes (Å) of Thermal Vibrations in the Semibullvalene Ring of Sb-7 at Various Temperatures

		Min.	Int'med	Max.
115 K	C1	0.099	0.123	0.128
	C2	0.106	0.120	0.126
	C3	0.103	0.127	0.133
	C4	0.091	0.129	0.133
	C5	0.109	0.125	0.128
	C6	0.094	0.128	0.141
	C7	0.103	0.122	0.135
	C8	0.107	0.125	0.138
127 K	C1	0.114	0.123	0.162
	C2	0.115	0.128	0.158
	C3	0.109	0.128	0.174
	C4	0.117	0.124	0.152
	C5	0.117	0.131	0.139
	C6	0.113	0.123	0.159
	C7	0.117	0.128	0.167
	C8	0.118	0.129	0.160
153 K	C1	0.124	0.133	0.169
	C2	0.122	0.140	0.162
	C3	0.128	0.137	0.169
	C4	0.129	0.139	0.151
	C5	0.123	0.138	0.147
	C6	0.124	0.134	0.164
	C7	0.130	0.134	0.167
	C8	0.133	0.136	0.165
181 K	C1	0.130	0.146	0.170
	C2	0.131	0.146	0.173
	C3	0.137	0.148	0.187
	C4	0.138	0.147	0.160
	C5	0.137	0.146	0.160
	C6	0.134	0.144	0.171
	C7	0.136	0.152	0.176
	C8	0.135	0.153	0.174

Table 4–20 (cont'd). Selected Root-Mean-Square Amplitudes (Å) of Thermal Vibrations in the Semibullvalene Ring of Sb-7 at Various Temperatures

		Min.	Int'med	Max.
181 K	C1	0.130	0.146	0.170
	C2	0.131	0.146	0.173
	C3	0.137	0.148	0.187
	C4	0.138	0.147	0.160
	C5	0.137	0.146	0.160
	C6	0.134	0.144	0.171
	C7	0.136	0.152	0.176
	C8	0.135	0.153	0.174
208 K	C1	0.148	0.152	0.162
	C2	0.148	0.158	0.165
	C3	0.154	0.159	0.166
	C4	0.155	0.158	0.167
	C5	0.144	0.158	0.163
	C6	0.140	0.158	0.168
	C7	0.149	0.158	0.170
	C8	0.153	0.164	0.166
236 K	C1	0.157	0.162	0.171
	C2	0.164	0.172	0.176
	C3	0.161	0.168	0.179
	C4	0.164	0.164	0.180
	C5	0.150	0.168	0.177
	C6	0.154	0.167	0.185
	C7	0.163	0.169	0.179
	C8	0.165	0.171	0.182
265 K	C1	0.168	0.178	0.188
	C2	0.170	0.183	0.195
	C3	0.167	0.185	0.195
	C4	0.179	0.181	0.200
	C5	0.166	0.181	0.192
	C6	0.168	0.179	0.202
	C7	0.176	0.184	0.197
	C8	0.175	0.186	0.206
294 K	C1	0.178	0.194	0.204
	C2	0.181	0.194	0.219
	C3	0.185	0.197	0.210
	C4	0.190	0.193	0.227
	C5	0.182	0.195	0.208
	C6	0.183	0.192	0.224
	C7	0.187	0.201	0.208
	C8	0.185	0.207	0.229

Table 4–20 (cont'd). Selected Root-Mean-Square Amplitudes (Å) of Thermal Vibrations in the Semibullvalene Ring of Sb-7 at Various Temperatures

		Min.	Int'med	Max.
294 K	C1	0.176	0.196	0.200
	C2	0.184	0.198	0.217
	C3	0.185	0.199	0.207
	C4	0.184	0.211	0.222
	C5	0.180	0.193	0.209
	C6	0.186	0.195	0.218
	C7	0.188	0.195	0.216
	C8	0.178	0.210	0.227
295 K	C1	0.179	0.193	0.207
	C2	0.187	0.198	0.222
	C3	0.187	0.201	0.213
	C4	0.194	0.198	0.229
	C5	0.177	0.197	0.211
	C6	0.186	0.199	0.218
	C7	0.190	0.202	0.214
	C8	0.193	0.203	0.230
308 K	C1	0.190	0.207	0.214
	C2	0.197	0.207	0.229
	C3	0.186	0.212	0.228
	C4	0.196	0.204	0.245
	C5	0.189	0.200	0.224
	C6	0.196	0.204	0.232
	C7	0.202	0.209	0.221
	C8	0.201	0.216	0.250
315 K	C1	0.196	0.213	0.222
	C2	0.206	0.206	0.243
	C3	0.197	0.221	0.226
	C4	0.207	0.214	0.248
	C5	0.194	0.215	0.230
	C6	0.203	0.209	0.240
	C7	0.204	0.218	0.228
	C8	0.206	0.225	0.255

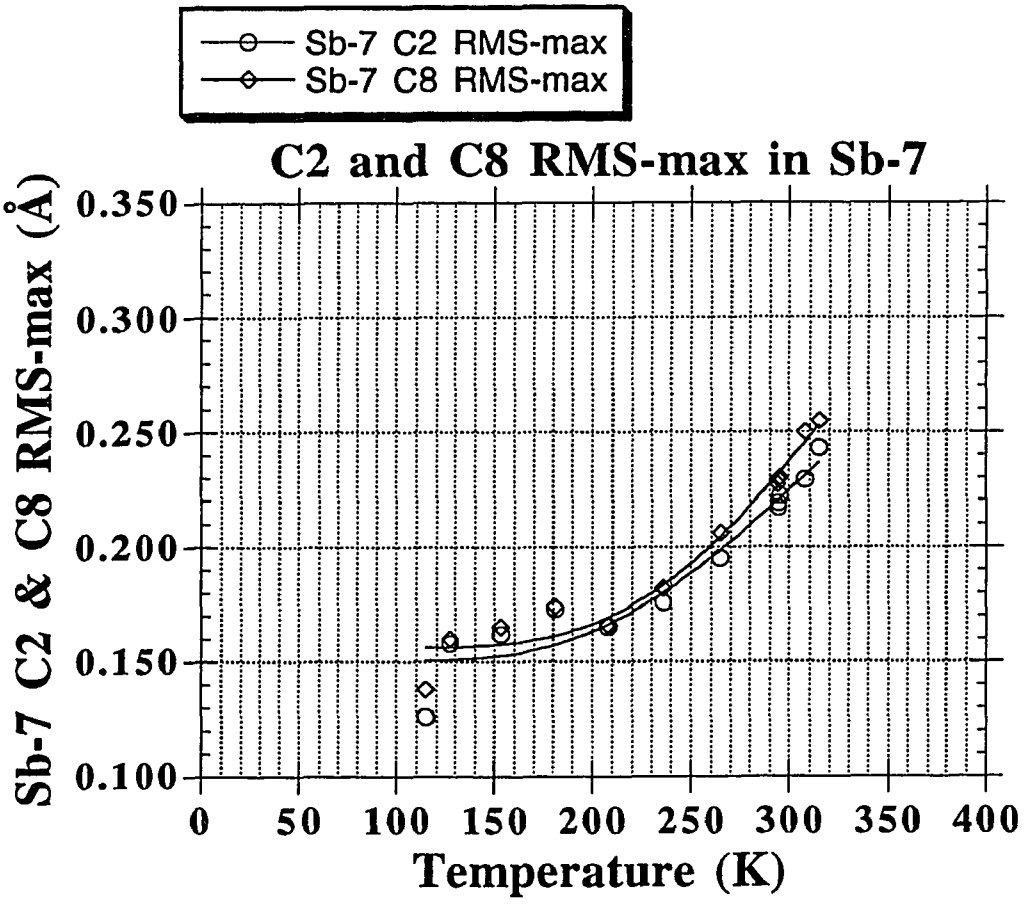


Figure 4–133. Plots of C2 RMS-max and C8 RMS-max in Sb-7 versus temperature.

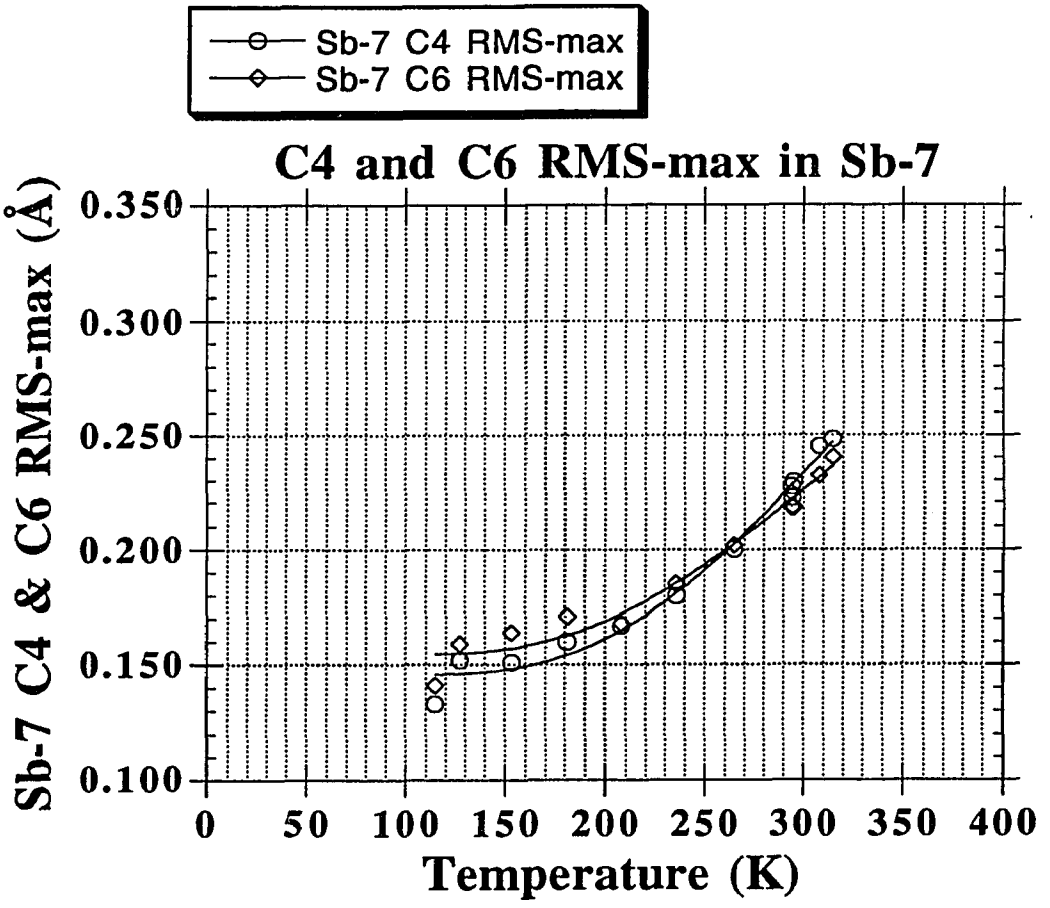


Figure 4–134. Plots of C4 RMS-max and C6 RMS-max in Sb-7 versus temperature.

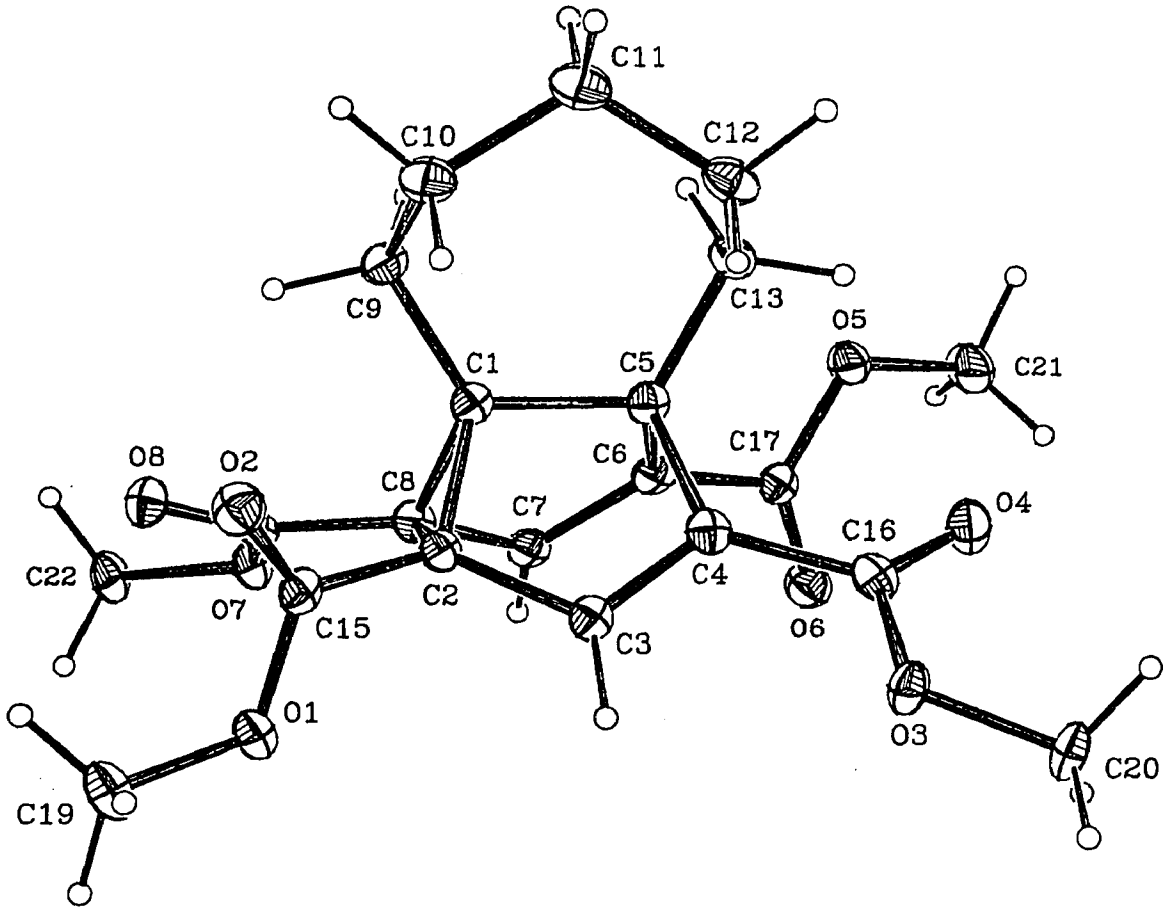


Figure 4–135. *ORTEP* drawing of Sb-7 at **115 K** with 50% thermal ellipsoids.

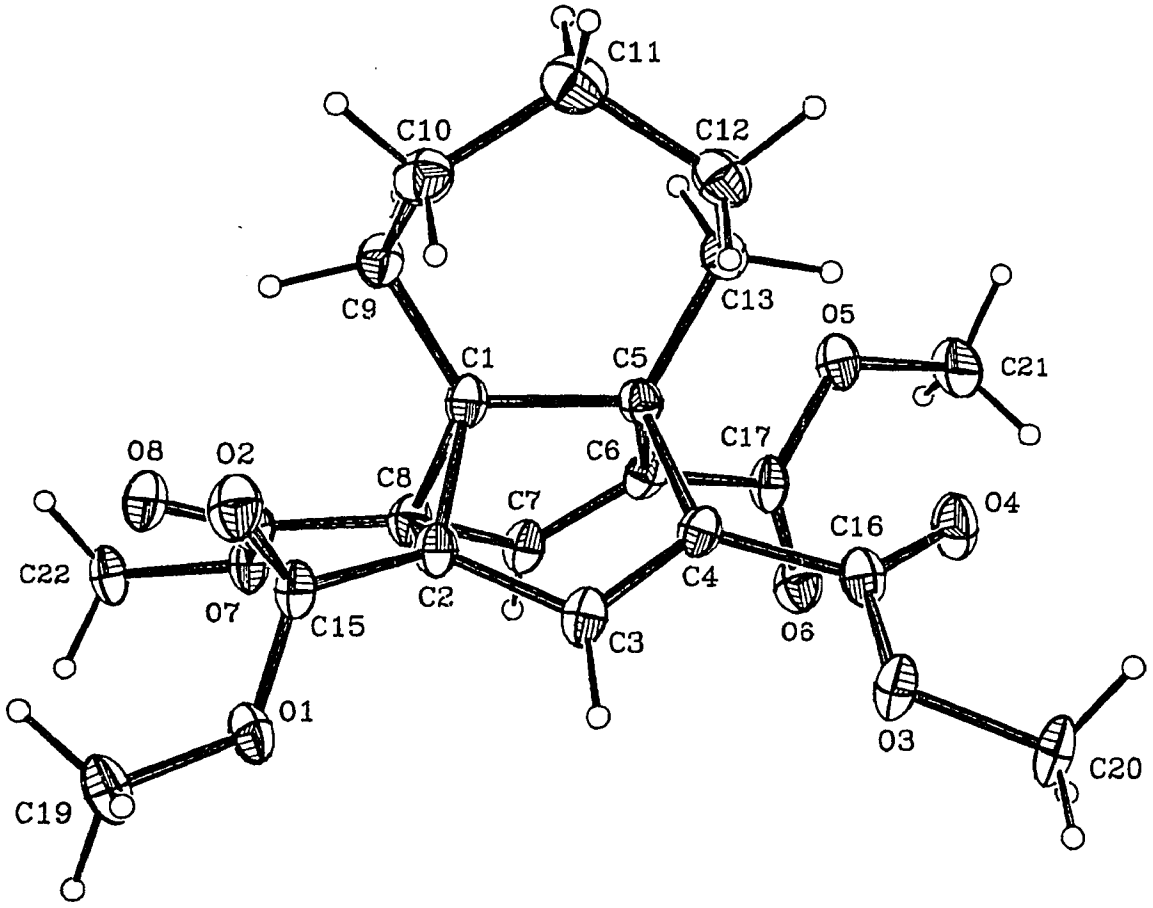


Figure 4–136. *ORTEP* drawing of Sb-7 at **127 K** with 50% thermal ellipsoids.

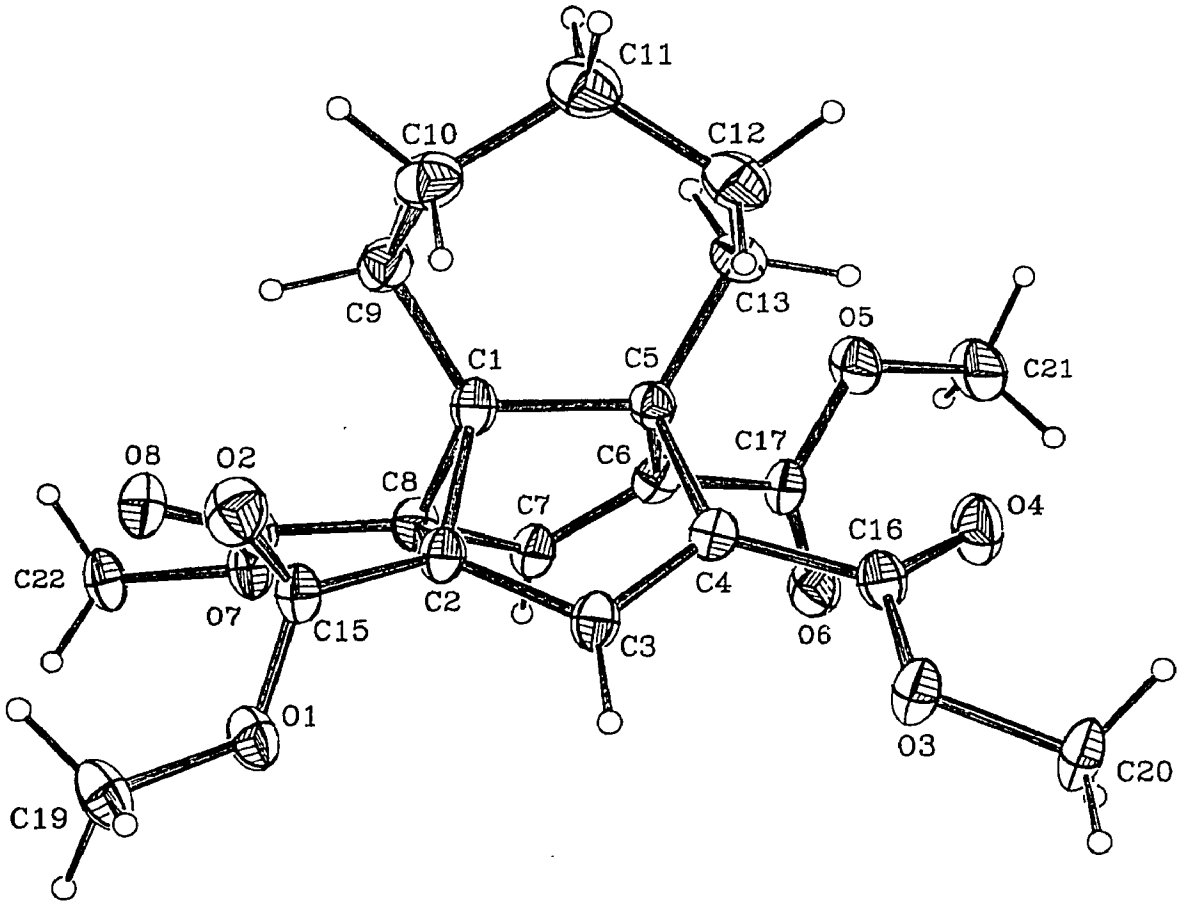


Figure 4–137. *ORTEP* drawing of Sb-7 at **153 K** with 50% thermal ellipsoids.

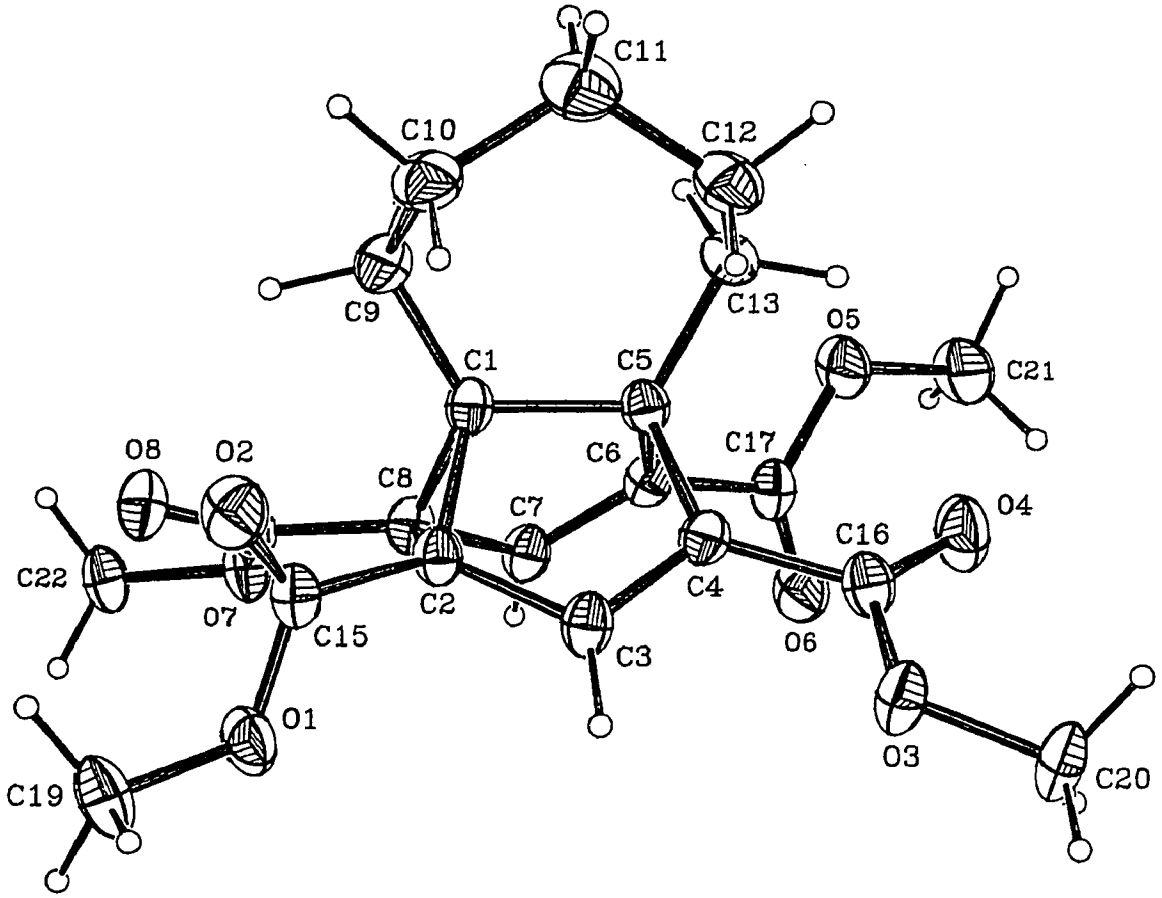


Figure 4–138. *ORTEP* drawing of Sb-7 at **181 K** with 50% thermal ellipsoids.

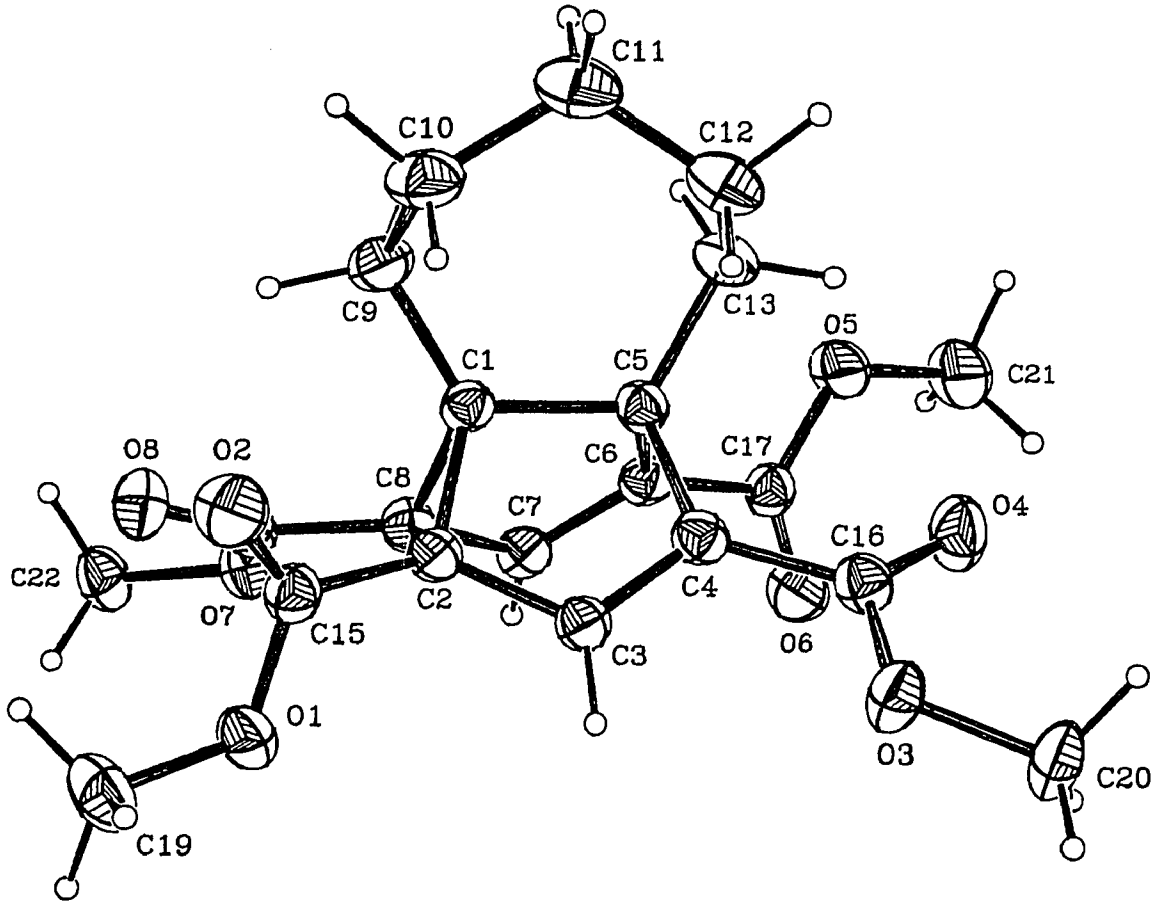


Figure 4–139. *ORTEP* drawing of Sb-7 at **208 K** with 50% thermal ellipsoids.

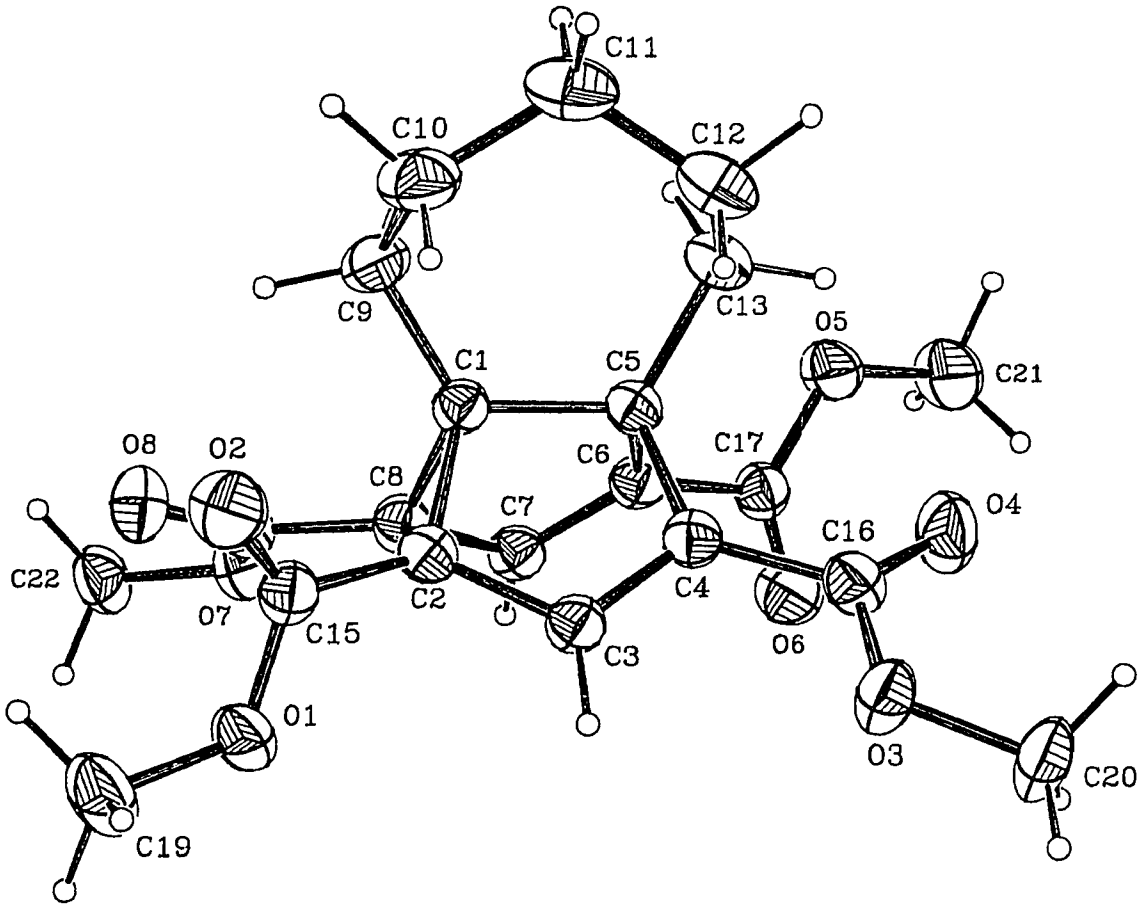


Figure 4–140. *ORTEP* drawing of Sb-7 at **236 K** with 50% thermal ellipsoids.

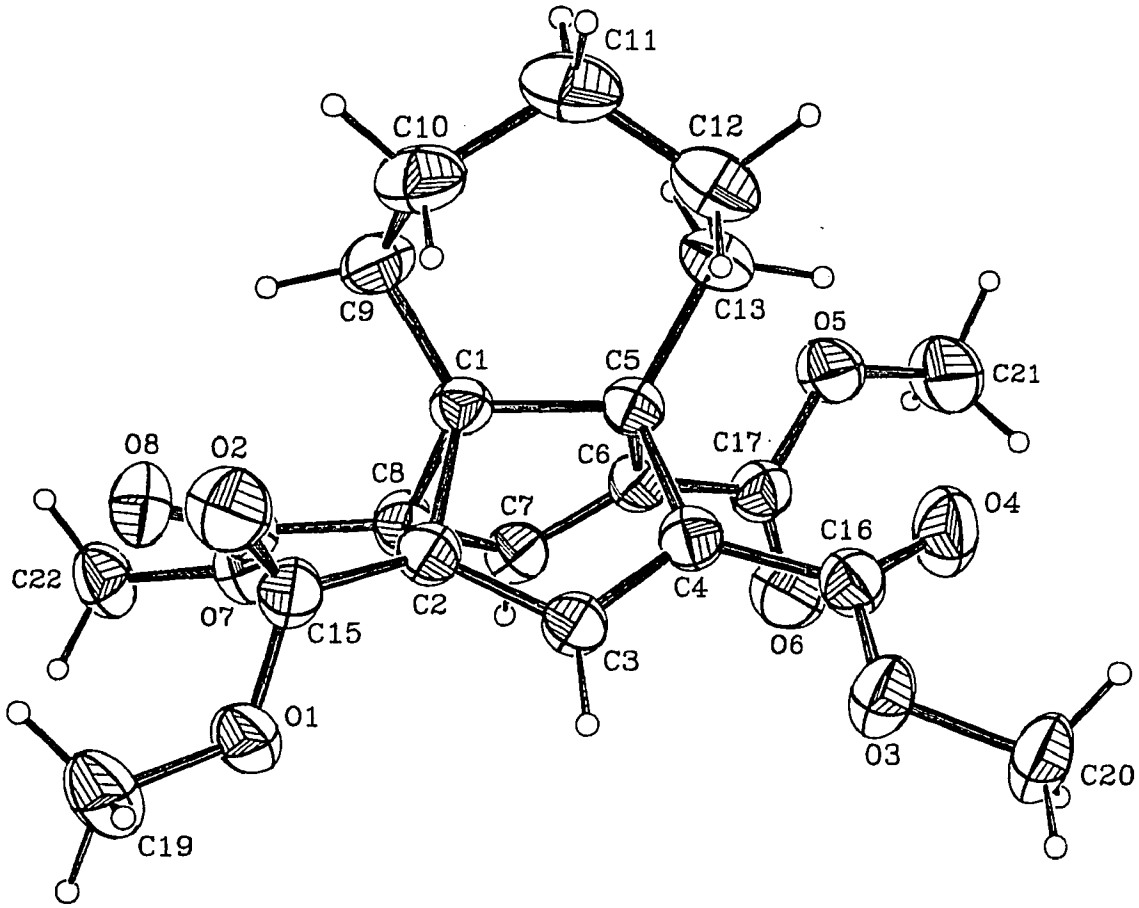


Figure 4–141. *ORTEP* drawing of Sb-7 at **265 K** with 50% thermal ellipsoids.

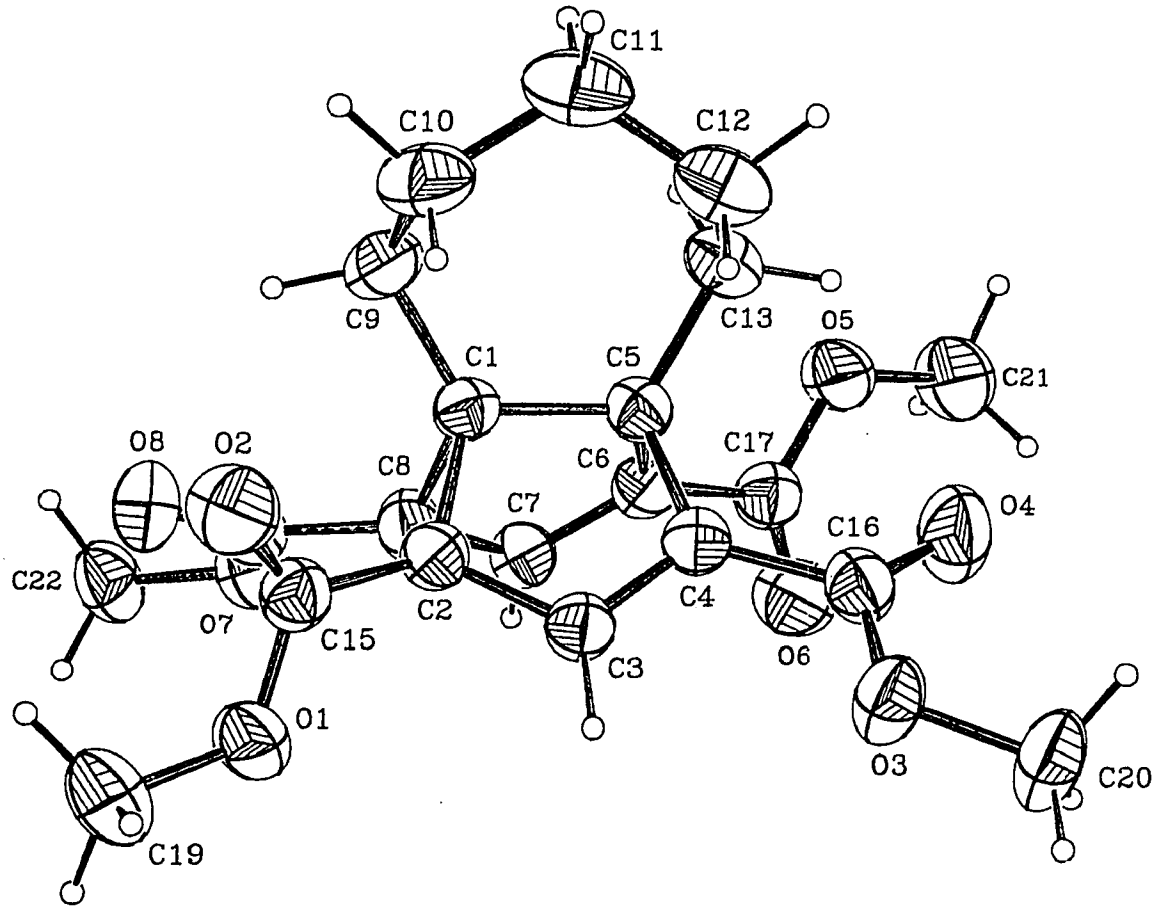


Figure 4–142. *ORTEP* drawing of Sb-7 at **294 K** with 50% thermal ellipsoids.

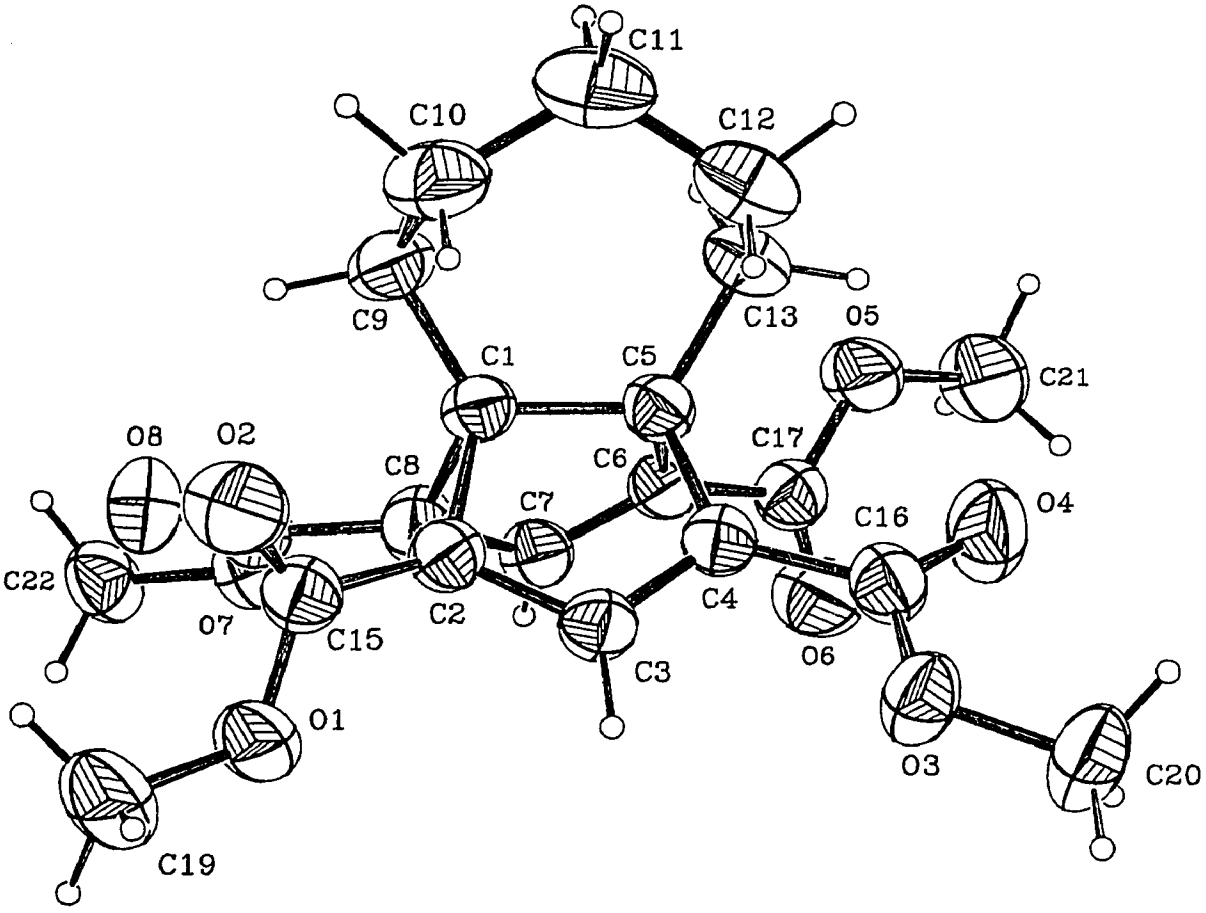


Figure 4–143. *ORTEP* drawing of Sb-7 at **308 K** with 50% thermal ellipsoids.

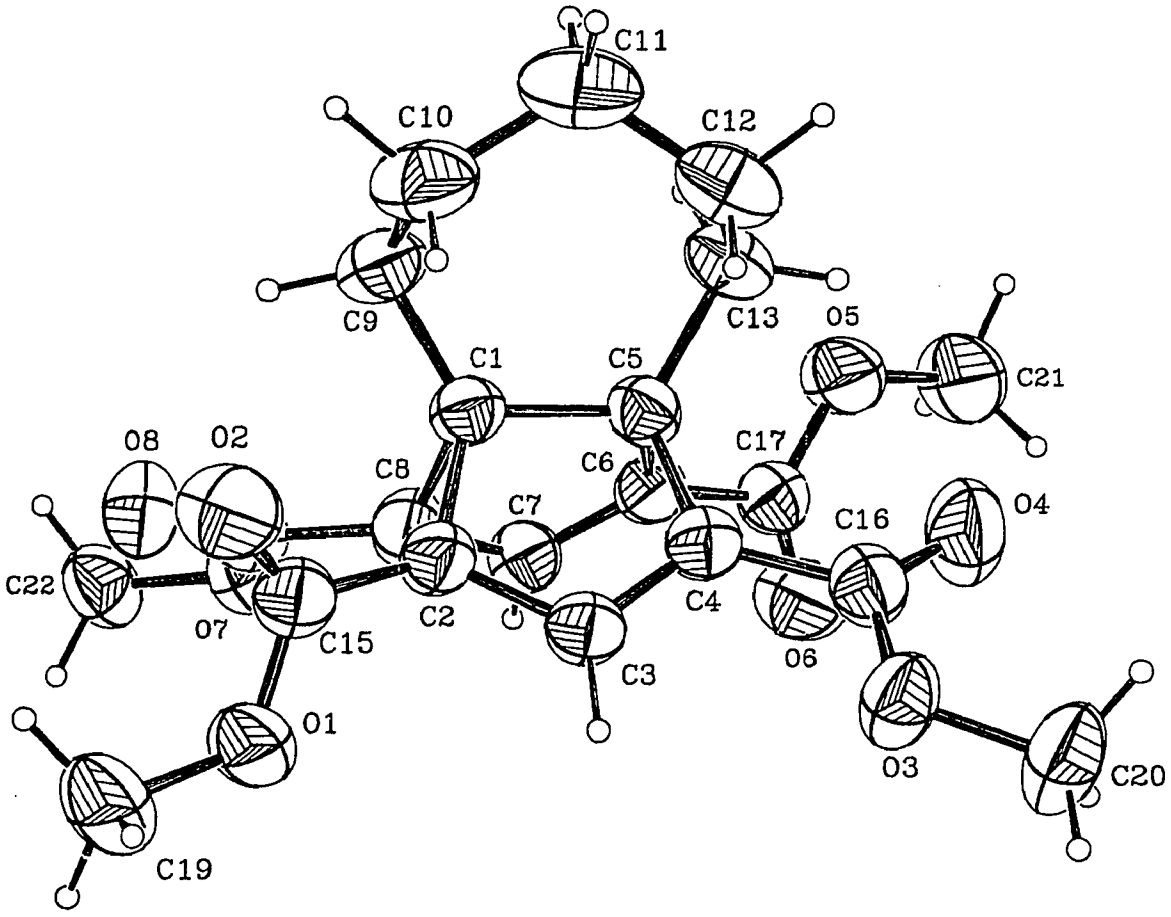


Figure 4–144. *ORTEP* drawing of Sb-7 at **315 K** with 50% thermal ellipsoids.

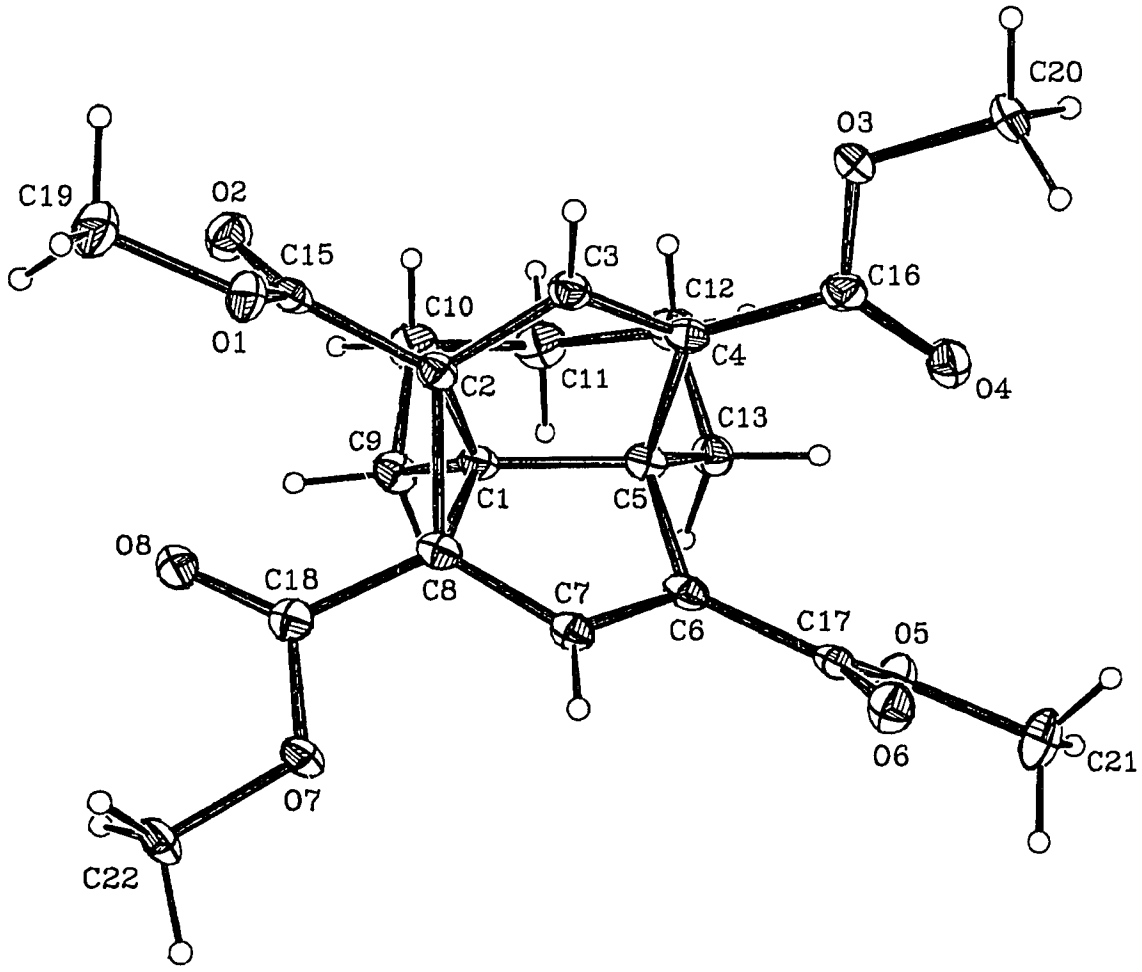


Figure 4–145. *ORTEP* drawing of Sb-7 at **115 K** with 50% thermal ellipsoids.

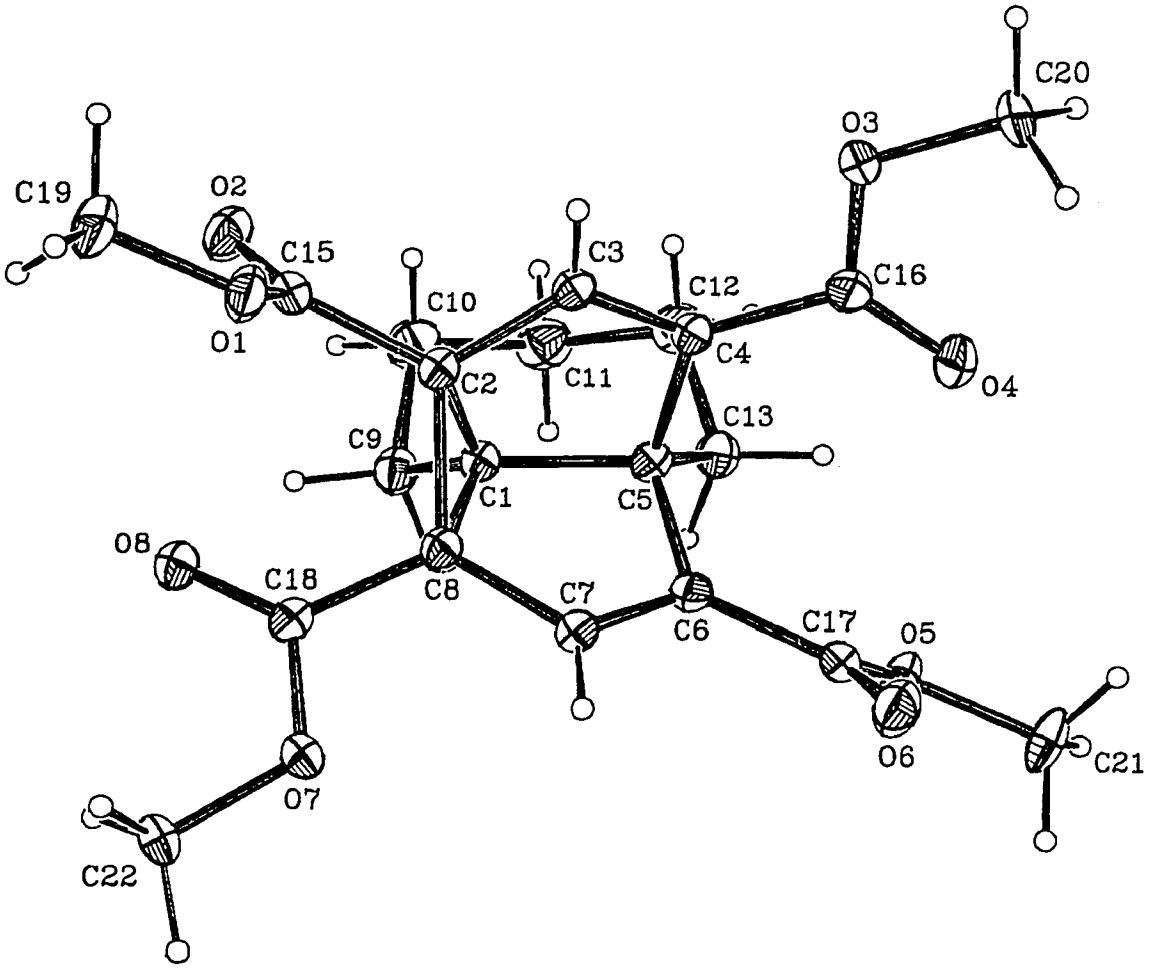


Figure 4–146. *ORTEP* drawing of Sb-7 at **127 K** with 50% thermal ellipsoids.

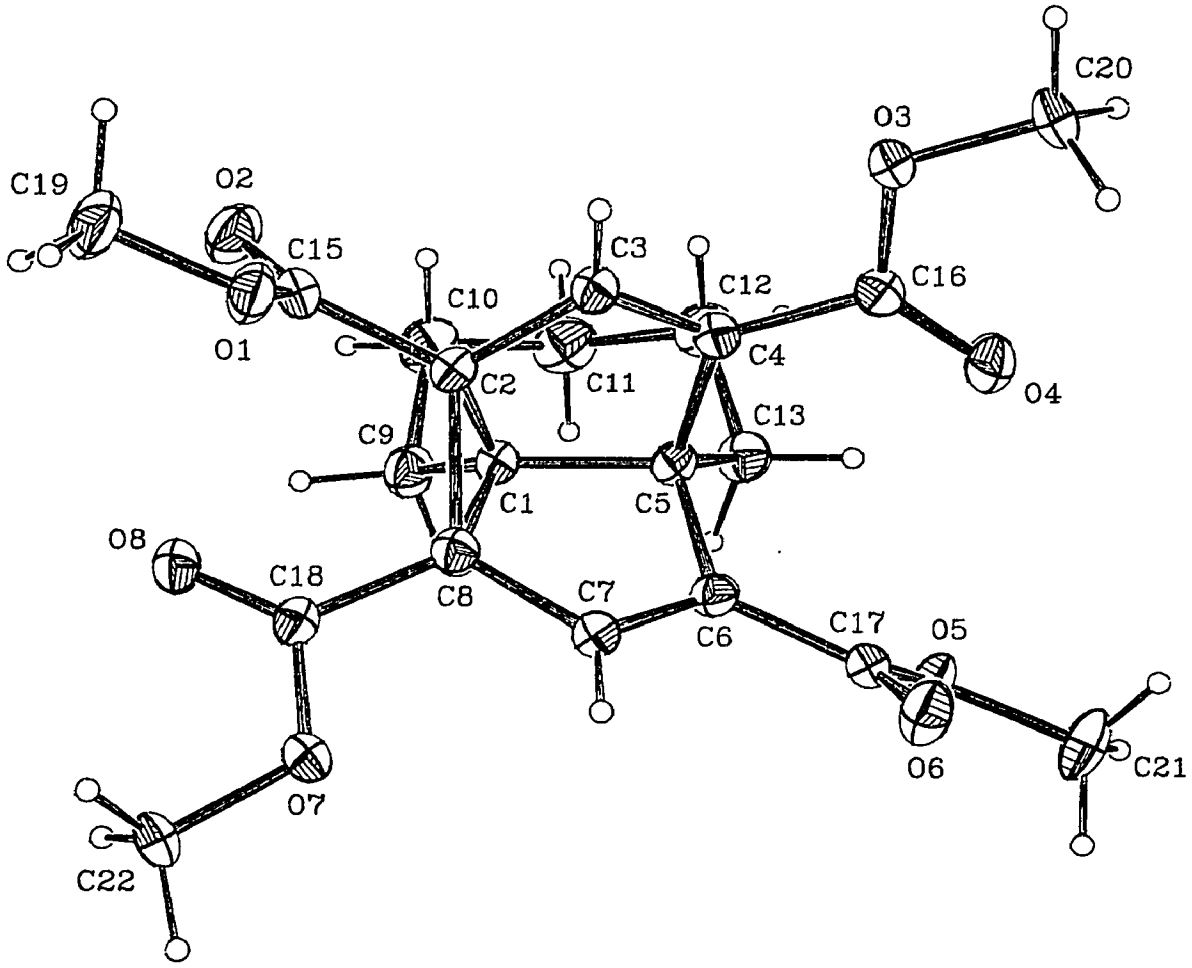


Figure 4–147. *ORTEP* drawing of Sb-7 at **153 K** with 50% thermal ellipsoids.

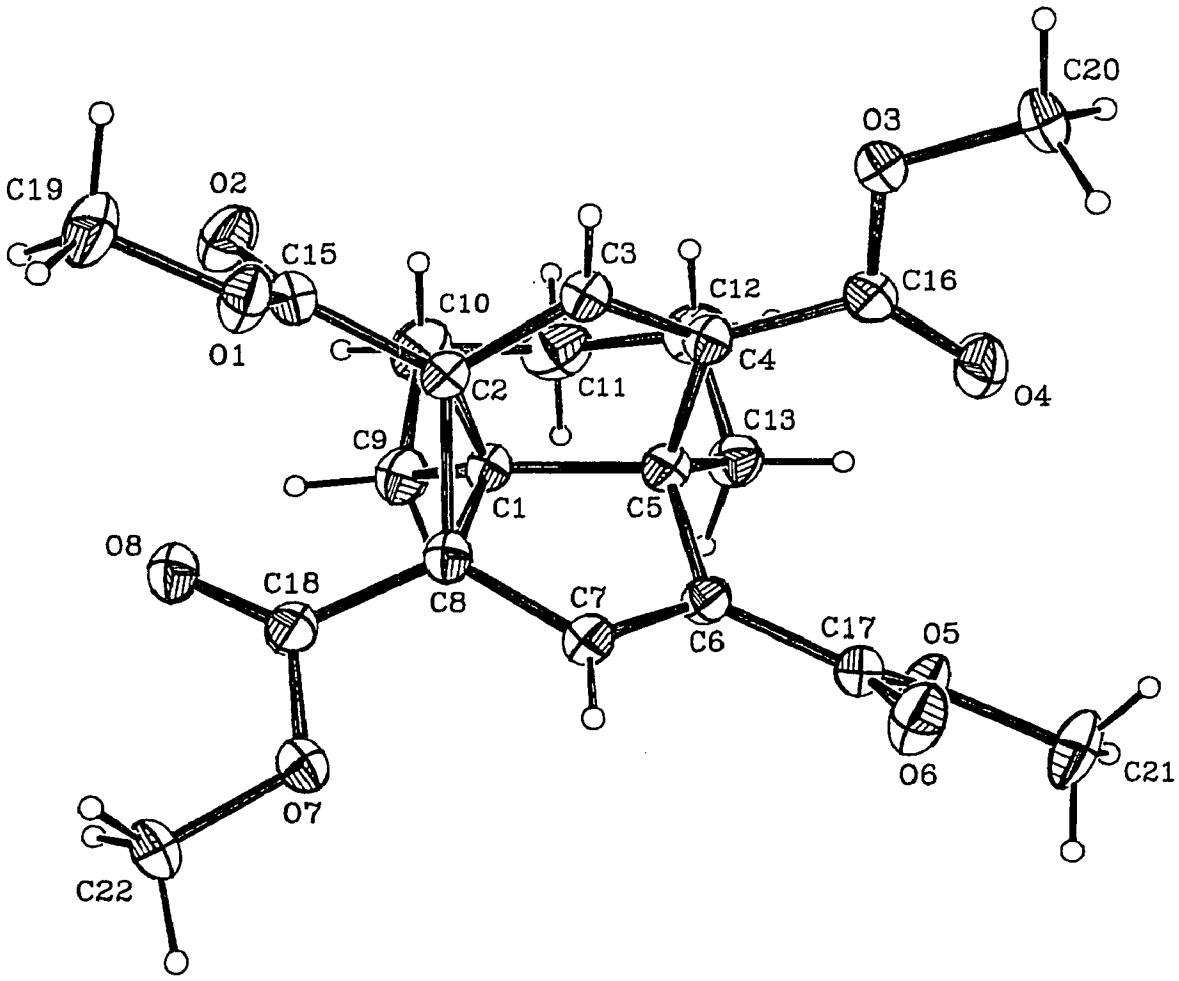


Figure 4–148. *ORTEP* drawing of Sb-7 at **181 K** with 50% thermal ellipsoids.

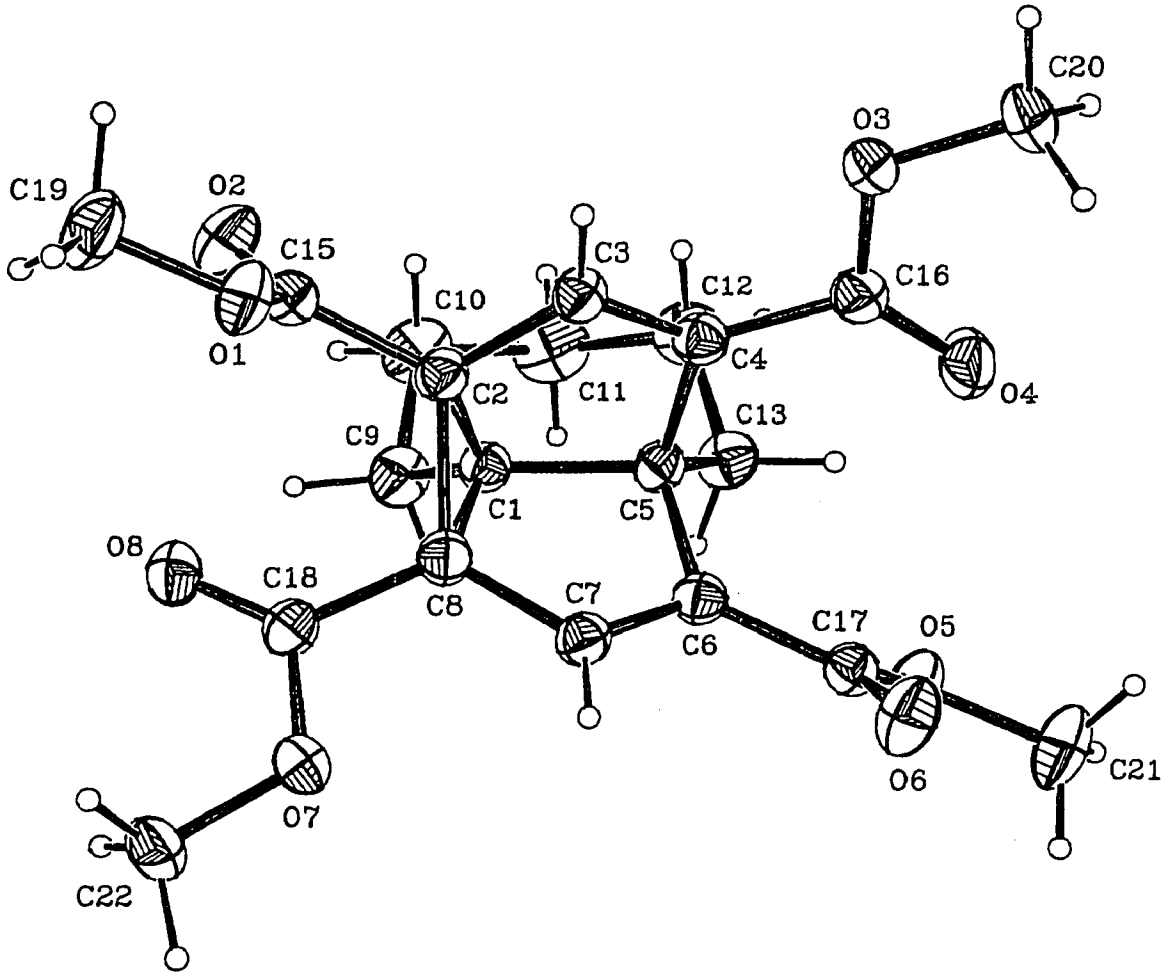


Figure 4–149. *ORTEP* drawing of Sb-7 at **208 K** with 50% thermal ellipsoids.

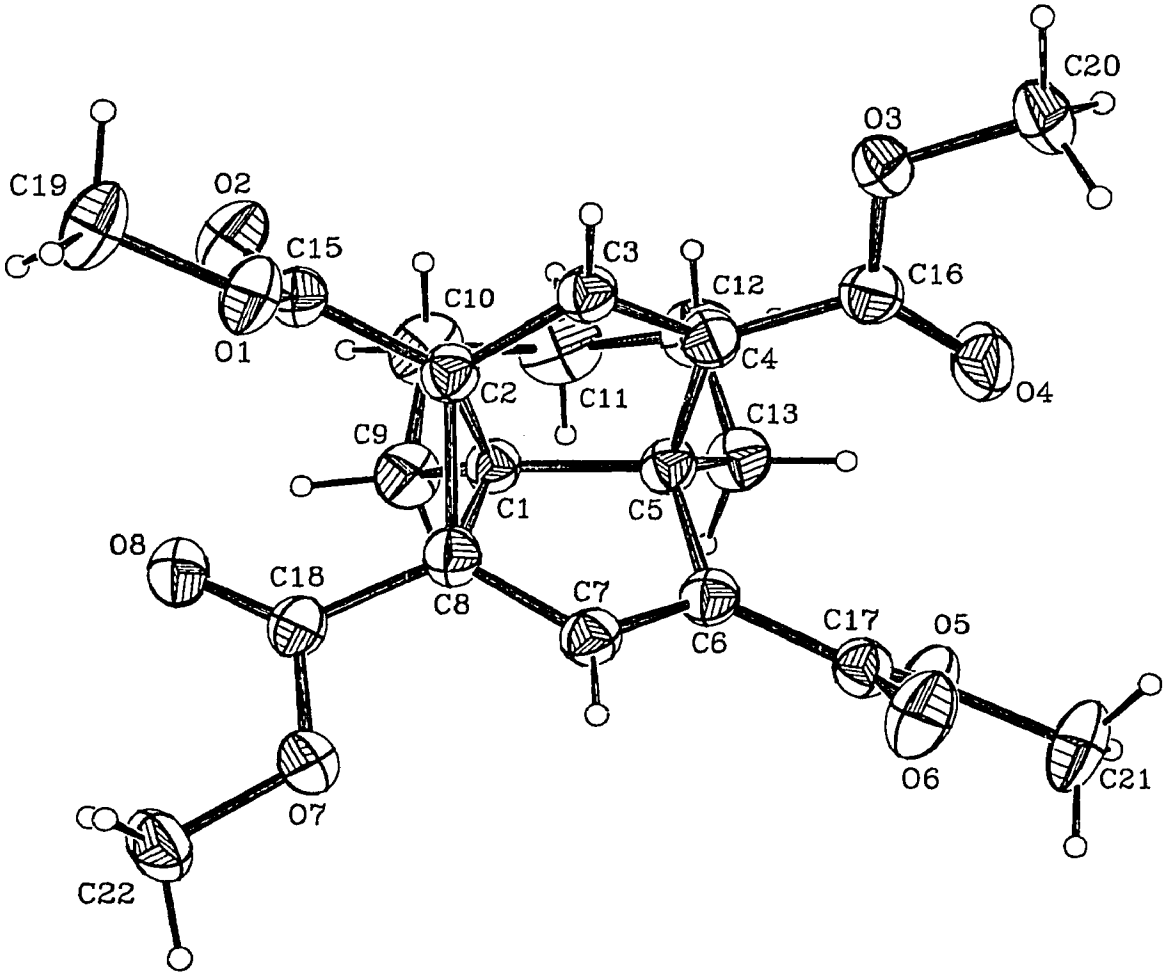


Figure 4–150. *ORTEP* drawing of Sb-7 at **236 K** with 50% thermal ellipsoids.

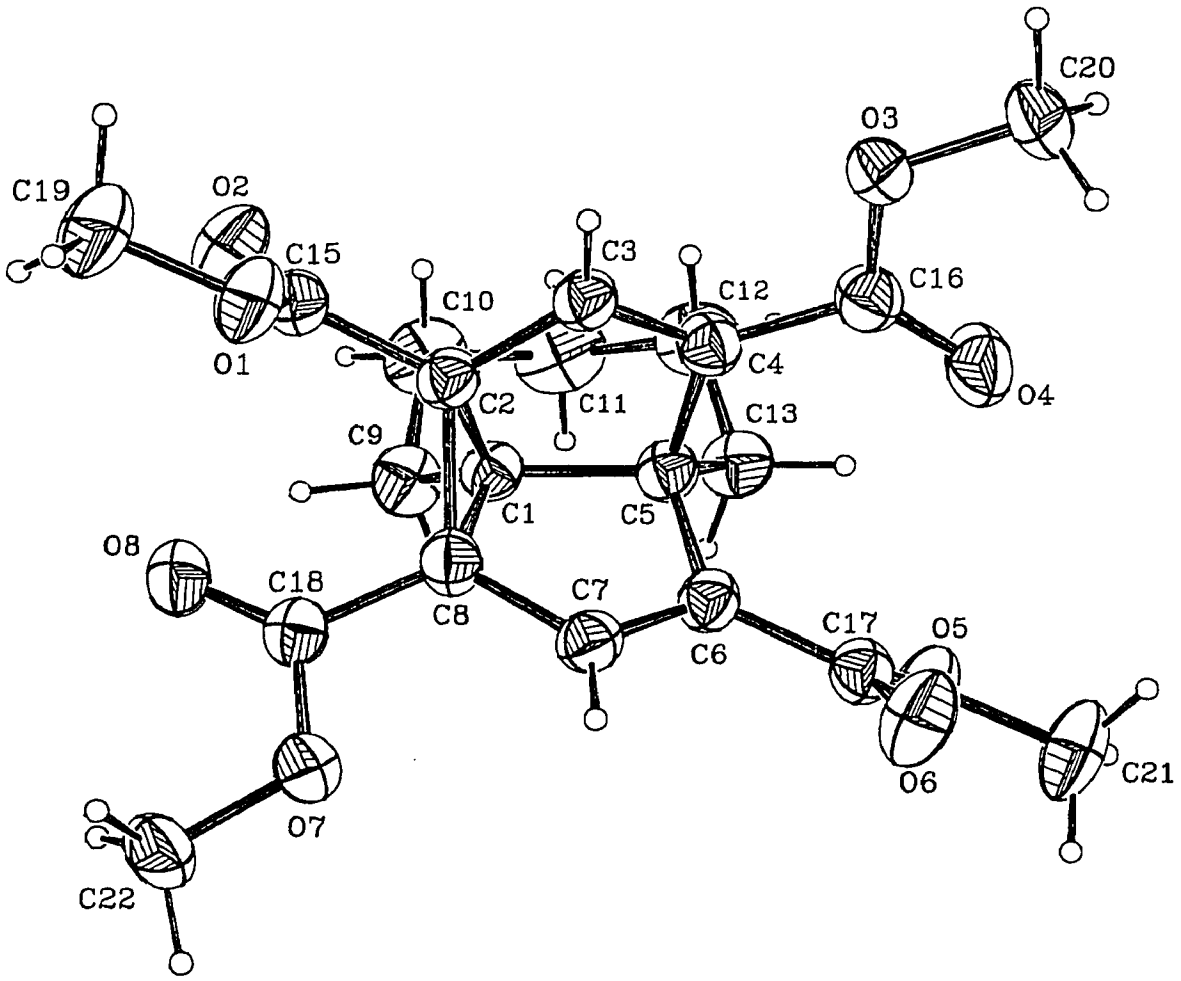


Figure 4–151. *ORTEP* drawing of Sb-7 at **265 K** with 50% thermal ellipsoids.

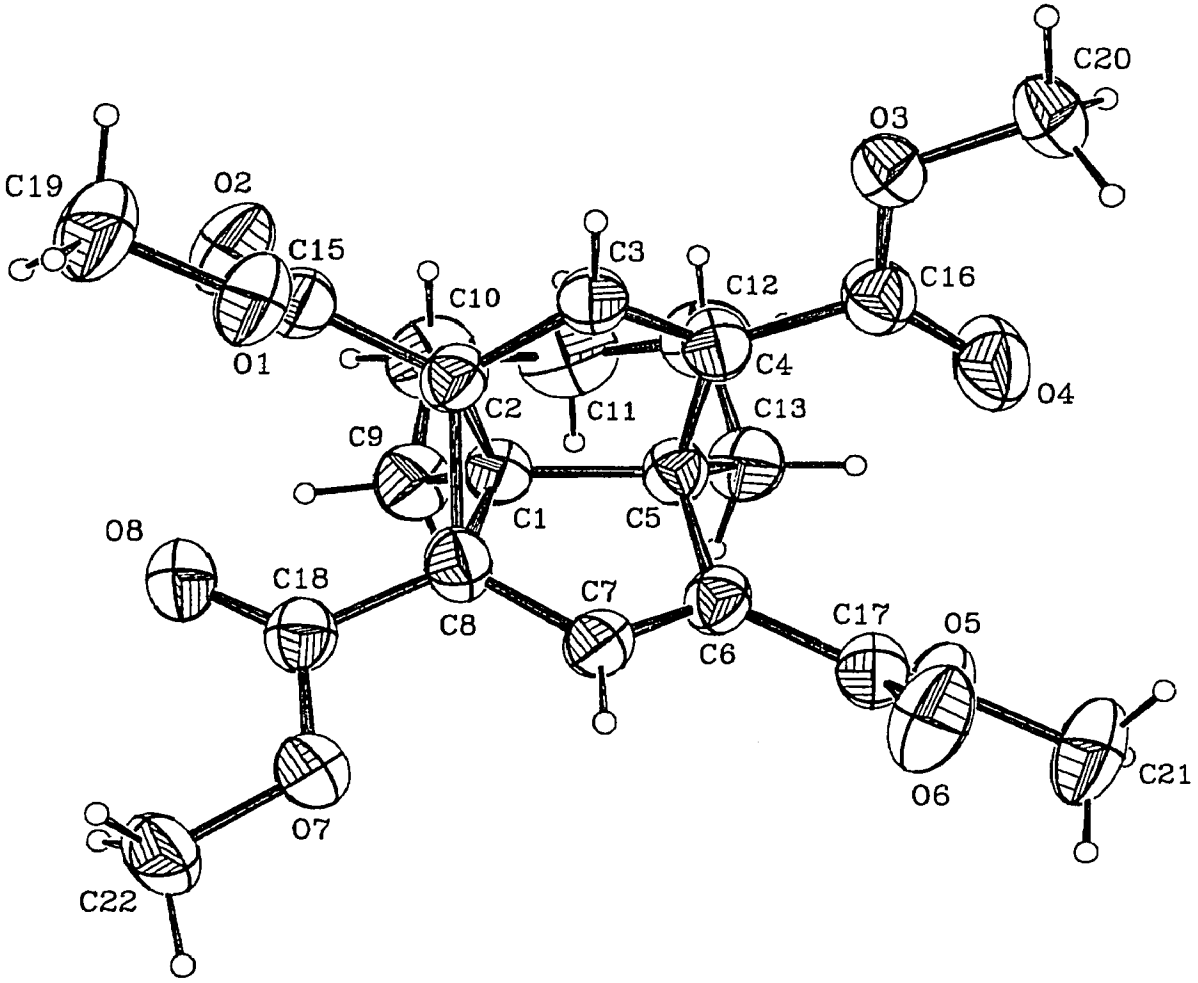


Figure 4–152. *ORTEP* drawing of Sb-7 at **294 K** with 50% thermal ellipsoids.

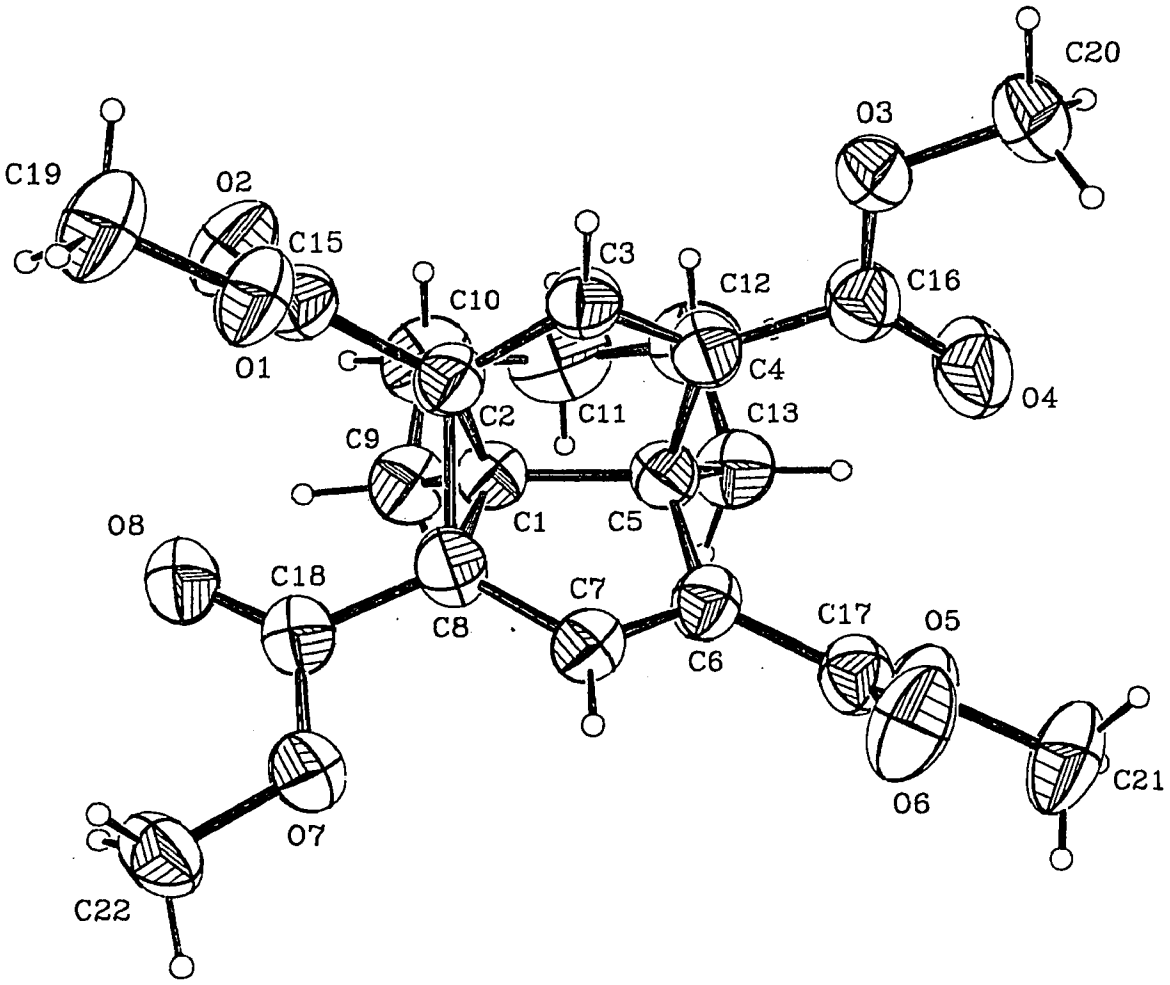


Figure 4–153. *ORTEP* drawing of Sb-7 at **308 K** with 50% thermal ellipsoids.

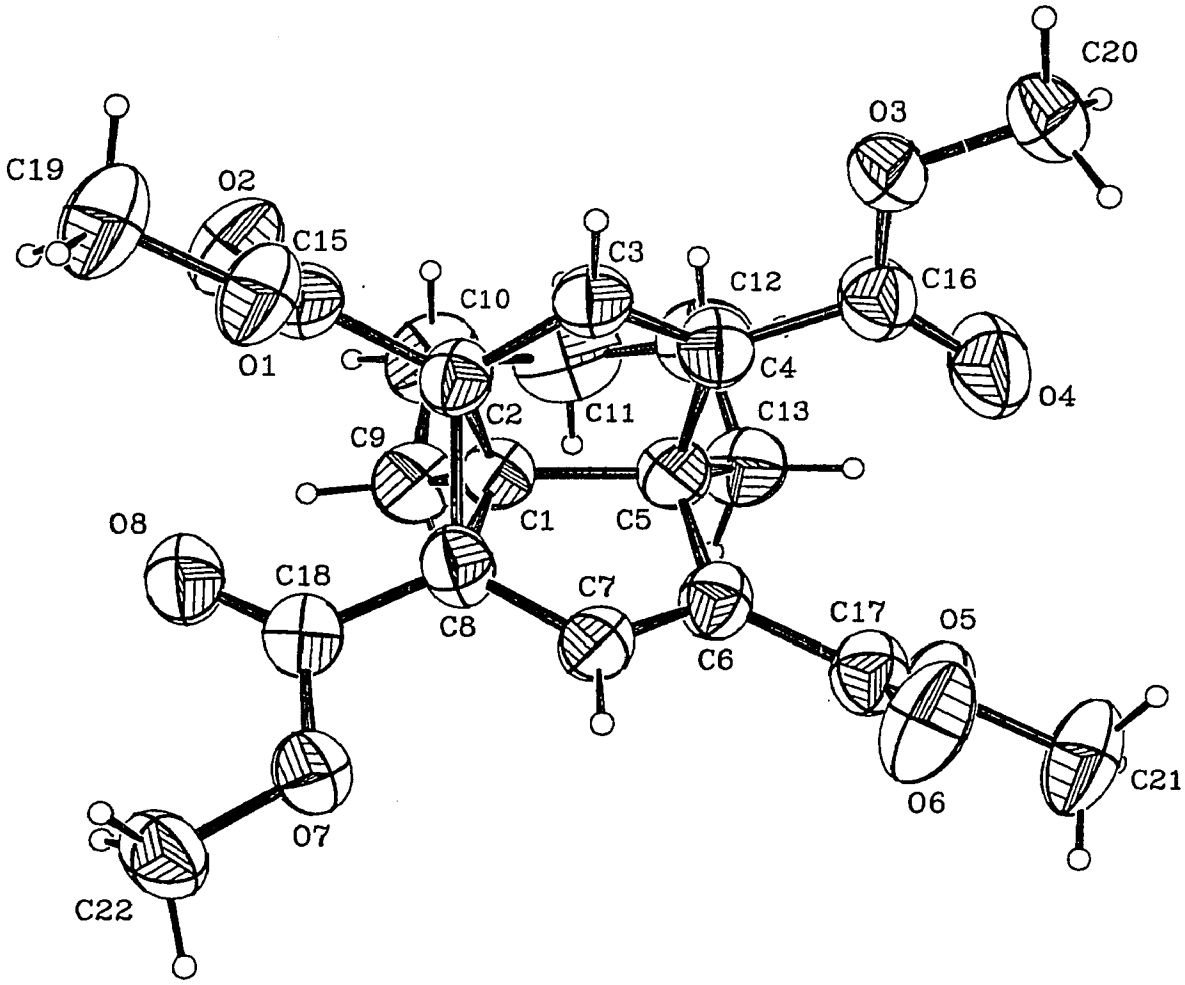


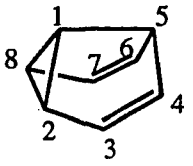
Figure 4–154. *ORTEP* drawing of Sb-7 at **315 K** with 50% thermal ellipsoids.



Figure 4–155. ^1H NMR spectra of Sb-7 at 20.4 °C in CD_2Cl_2.

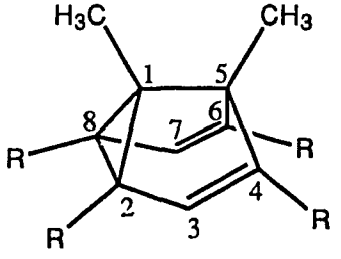
4.5 SB-ME2

If the hydrogens on the carbons, C1 and C5, in semibullvalene



Tricyclo[3.3.0.0^{2,8}]octa-3,6-diene
(Semibullvalene)

are replaced with two methyl groups and four ester groups replace the four hydrogens at C2, C4, C6, and C8, we obtain the annulated compound **1,5-dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene** or simply Sb-Me$_2$



R = COOCH$_3$
1,5-dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-Me$_2$)

The X-ray crystal data for Sb-Me$_2$ is listed in Table 4–21.

Table 4–21. X-ray Crystal Data for Sb-Me_2 at Various Temperatures

	20 K	**115 K[a]**	**127 K[a]**
Formula	$C_{18}H_{20}O_8$	$C_{18}H_{20}O_8$	$C_{18}H_{20}O_8$
Formula weight	364.36	364.36	364.36
Melting point (°C)	102-103	102-103	102-103
Crystal size (mm)	0.25 x 0.38 x 0.63	0.23 x 0.25 x 0.37	0.23 x 0.25 x 0.37
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	6.490(2)	6.510(2)	6.514(2)
b (Å)	10.749(4)	10.763(1)	10.767(1)
c (Å)	24.296(8)	24.331(3)	24.346(2)
Cell volume (Å^3)	1694.93	1704.75(0.69)	1707.46(0.54)
Z	4	4	4
d_{calc} (g cm^{-3})	1.428	1.420	1.417
μ(Cu $K\alpha$) (cm^{-1})	1.06 (Mo $K\alpha$)	9.08	9.07
R	0.036	0.035	0.037
R_w	0.043	0.049	0.048

Table 4–21 (cont'd). X-ray Crystal Data for Sb-Me_2 at Various Temperatures

	153 K	**181 K**	**208 K**
Formula	$C_{18}H_{20}O_8$	$C_{18}H_{20}O_8$	$C_{18}H_{20}O_8$
Formula weight	364.36	364.36	364.36
Melting point (°C)	102-103	102-103	102-103
Crystal size (mm)	0.23 x 0.25 x 0.37	0.23 x 0.25 x 0.37	0.23 x 0.25 x 0.37
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	6.524(2)	6.540(1)	6.557(1)
b (Å)	10.779(1)	10.790(1)	10.801(1)
c (Å)	24.393(2)	24.442(2)	24.490(2)
Cell volume (Å^3)	1715.50(0.45)	1724.72(0.34)	1734.33(0.30)
Z	4	4	4
d_{calc} (g cm^{-3})	1.411	1.403	1.395
μ(Cu $K\alpha$) (cm^{-1})	9.03	8.98	8.93
R	0.037	0.037	0.038
R_w	0.049	0.049	0.050

Table 4–21 (cont'd). X-ray Crystal Data for Sb-Me_2 at Various Temperatures

	236 K	**265 K**	**294 K**
Formula	$C_{18}H_{20}O_8$	$C_{18}H_{20}O_8$	$C_{18}H_{20}O_8$
Formula weight	364.36	364.36	364.36
Melting point (°C)	102-103	102-103	102-103
Crystal size (mm)	0.23 x 0.25 x 0.37	0.23 x 0.25 x 0.37	0.23 x 0.25 x 0.37
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	6.577(1)	6.598(1)	6.624(1)
b (Å)	10.812(2)	10.823(1)	10.834(1)
c (Å)	24.539(1)	24.590(1)	24.641(1)
Cell volume (Å^3)	1744.79(0.25)	1755.87(0.17)	1768.24(0.17)
Z	4	4	4
d_{calc} (g cm^{-3})	1.387	1.378	1.369
μ(Cu $K\alpha$) (cm^{-1})	8.88	8.82	8.76
R	0.039	0.039	0.042
R_w	0.051	0.050	0.054

Table 4–21 (cont'd). X-ray Crystal Data for Sb-Me_2 at Various Temperatures

	295 K	**322 K**	**335 K**
Formula	$C_{18}H_{20}O_8$	$C_{18}H_{20}O_8$	$C_{18}H_{20}O_8$
Formula weight	364.36	364.36	364.36
Melting point (°C)	102-103	102-103	102-103
Crystal size (mm)	0.23 x 0.25 x 0.37	0.14 x 0.24 x 0.50	0.14 x 0.24 x 0.50
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	6.623(1)	6.639(3)	6.652(4)
b (Å)	10.835(1)	10.835(1)	10.8421)
c (Å)	24.6482)	24.664(2)	24.695(3)
Cell volume (Å^3)	1768.64(0.42)	1774.22(0.88)	1781.04(0.97)
Z	4	4	4
d_{calc} (g cm^{-3})	1.368	1.364	1.359
μ(Cu $K\alpha$) (cm^{-1})	8.76	8.73	8.70
R	0.042	0.039	0.041
R_w	0.059	0.045	0.047

Sb-Me_2 crystallizes in the noncentric space group $P2_12_12_1$, while the other five candidates belong to centric space groups. The significance or implications of this fact are not clear at this time.

The unit-cell volume of Sb-Me_2 is plotted against temperature in Figure 4–156. From 0 to about 100 K, this curve is relatively flat. From then on, it rises linearly.

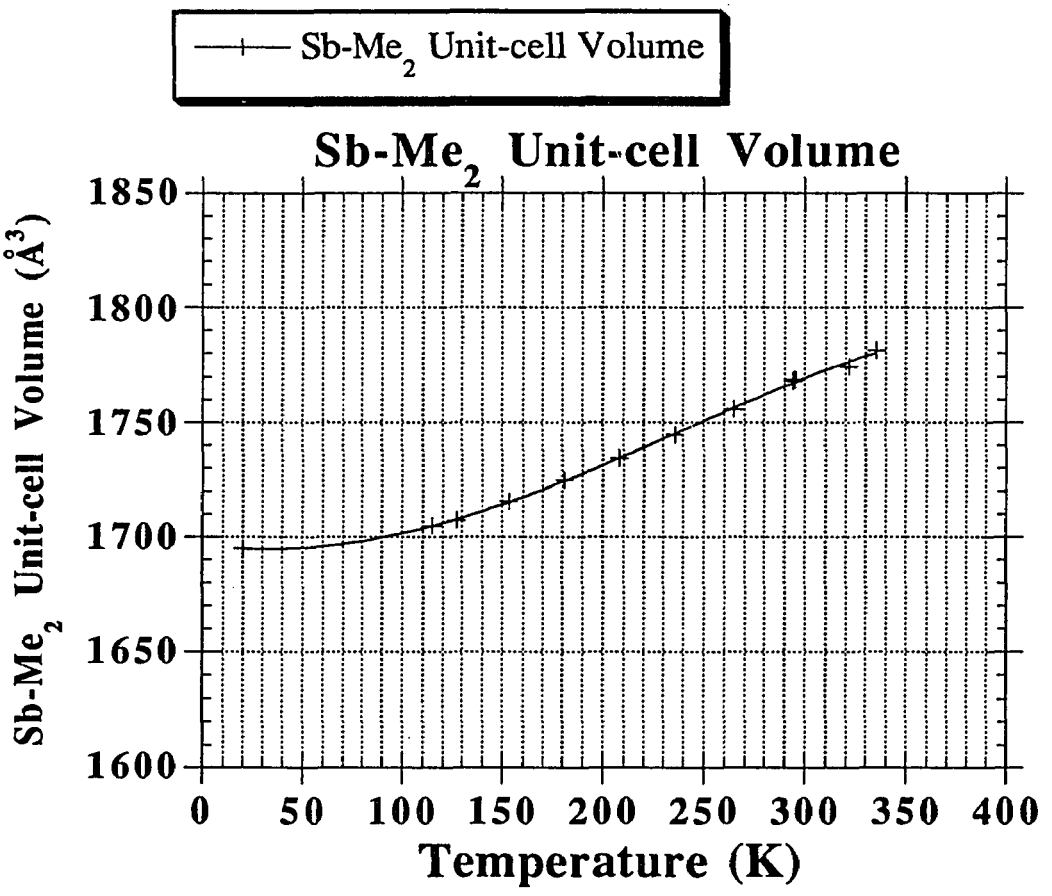


Figure 4–156. A plot of Sb-Me_2 unit-cell volume versus temperature.

For the purpose of comparing Sb-Me_2 with the other five compounds, we eliminate the point at the 20 K and fit the remaining volume-temperature data points of Sb-Me_2 with a straight line as in Figure 4–157.

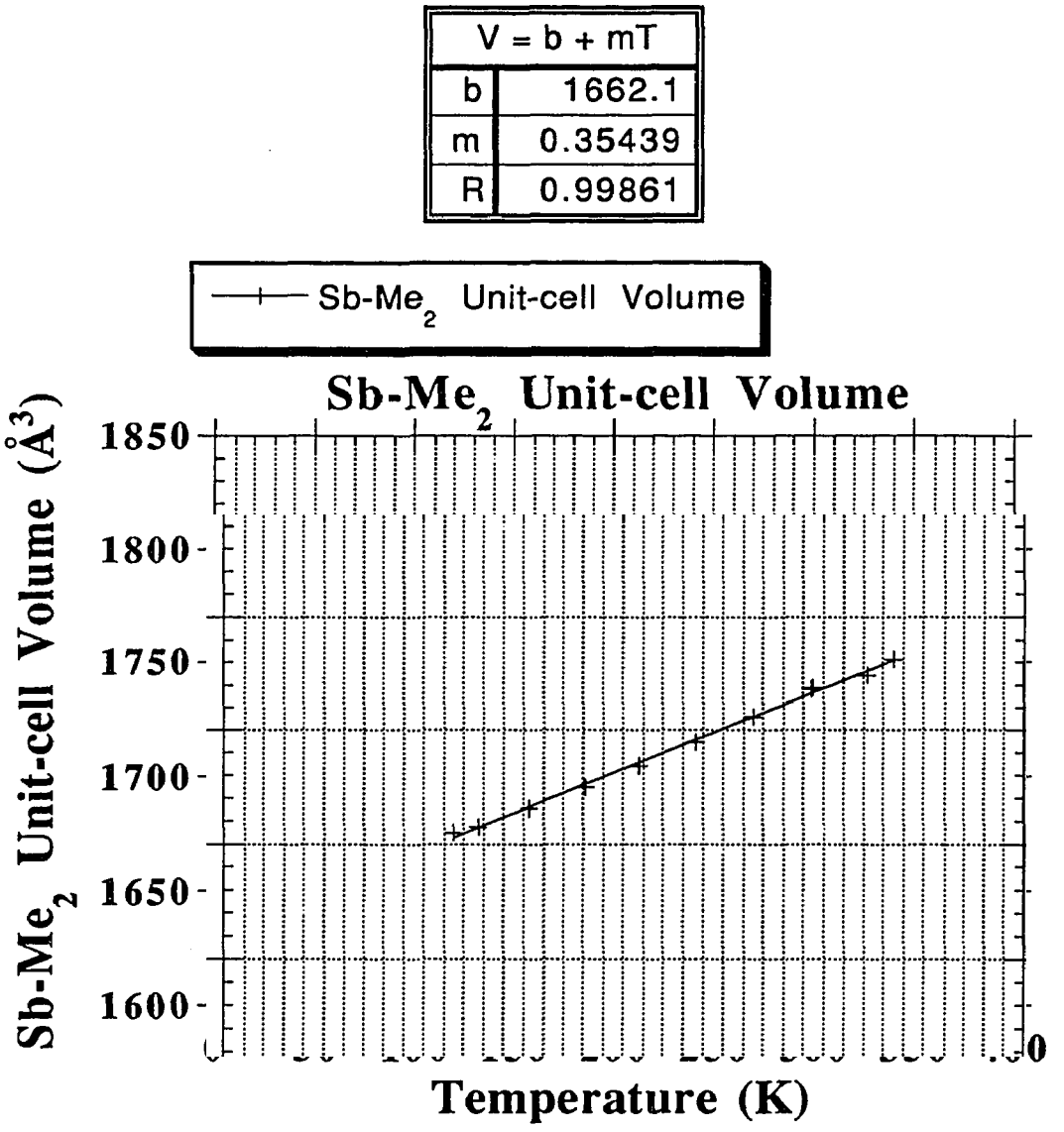


Figure 4–157. A plot of Sb-Me_2 unit-cell volume versus temperature.

According to the slope in Figure 4–157, the unit-cell volume of Sb-Me_2 expands at the rate of 3.5 $Å^3$ for every 10 °C rise in temperature for four molecules in the unit cell (104 non-H's and 80 H's).

The volume expands but the density of Sb-Me_2 decreases as shown in Figure 4–158.

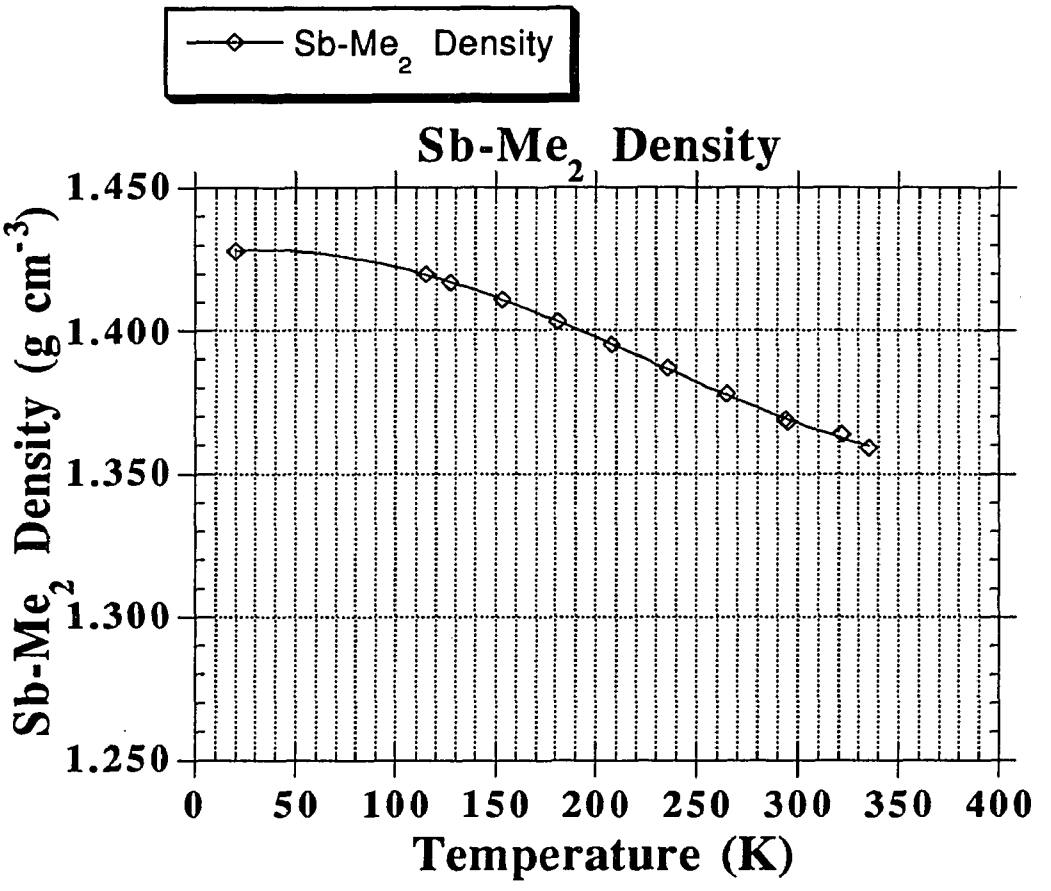


Figure 4–158. A plot of Sb-Me_2 density versus temperature.

The interatomic distances for Sb-Me_2 in Table 4–22 tell the same story as the corresponding data in the previous compounds, that is, the bond distance C2—C8 elongates and the interatomic distance C4—C6 becomes shorter as the temperature increases. At the same time, the double bonds, C3—C4 and C6—C7, become more delocalized and the single bonds, C2—C3 and C7—C8, acquire more double bond character. The single bonds, C1—C5 and C3—C7, meanwhile remain unchanged throughout the same temperature range. The graphs based on Table 4–22 illustrate this behavior in Sb-M_2.

Table 4–22. Selected Interatomic Distances (Å) in the Ring of Sb-Me_2 at Various Temperatures

	20 K	**115 K**	**127 K**	**153 K**	**181 K**	**208 K**
C1—C2	1.498(4)	1.488(3)	1.487(3)	1.481(3)	1.482(4)	1.483(4)
C1—C5	1.588(4)	1.578(3)	1.582(3)	1.582(3)	1.581(3)	1.582(3)
C1—C8	1.526(3)	1.525(2)	1.524(3)	1.522(3)	1.523(3)	1.525(3)
C2—C3	1.464(4)	1.469(3)	1.468(3)	1.466(3)	1.462(3)	1.454(4)
C2—C8	1.651(3)	1.660(3)	1.667(3)	1.674(4)	1.696(4)	1.715(4)
C3—C4	1.336(4)	1.344(3)	1.342(3)	1.342(3)	1.340(3)	1.341(3)
C3—C7	3.045	3.052(3)	3.053(3)	3.049(3)	3.053(3)	3.049(3)
C4—C5	1.540(4)	1.526(3)	1.524(3)	1.521(4)	1.519(3)	1.515(4)
C4—C6	2.339(4)	2.313(3)	2.312(3)	2.296(4)	2.279(4)	2.263(4)
C5—C6	1.539(4)	1.533(3)	1.536(3)	1.534(3)	1.533(3)	1.531(3)
C6—C7	1.343(4)	1.351(3)	1.349(3)	1.349(3)	1.351(3)	1.351(3)
C7—C8	1.461(4)	1.452(3)	1.448(3)	1.443(3)	1.437(3)	1.431(3)
C2—C3 + C3—C4	2.800	2.813	2.810	2.808	2.802	2.795
C6—C7 + C7—C8	2.804	2.803	2.797	2.792	2.788	2.782
C2—C8 + C4—C6	3.990	3.973	3.979	3.970	3.975	3.978

Table 4–22 (cont'd). Selected Interatomic Distances (Å) in the Ring of Sb-Me_2 at Various Temperatures

	236 K	265 K	294 K	295 K	322 K	335 K
C1—C2	1.483(4)	1.480(4)	1.480(5)	1.479(4)	1.487(6)	1.481(7)
C1—C5	1.580(3)	1.583(3)	1.577(4)	1.580(3)	1.572(5)	1.572(6)
C1—C8	1.523(3)	1.528(3)	1.522(4)	1.526(3)	1.524(5)	1.524(6)
C2—C3	1.449(4)	1.440(4)	1.430(5)	1.433(4)	1.407(6)	1.411(6)
C2—C8	1.731(4)	1.756(4)	1.781(5)	1.768(4)	1.815(7)	1.827(7)
C3—C4	1.343(4)	1.340(4)	1.345(4)	1.344(4)	1.348(6)	1.349(6)
C3—C7	3.051(4)	3.046(4)	3.051(4)	3.046(4)	3.038(6)	3.046(6)
C4—C5	1.516(4)	1.519(4)	1.516(4)	1.512(4)	1.500(6)	1.509(7)
C4—C6	2.247(4)	2.234(4)	2.215(5)	2.216(4)	2.174(6)	2.173(7)
C5—C6	1.532(3)	1.530(3)	1.531(4)	1.532(3)	1.522(5)	1.515(6)
C6—C7	1.347(3)	1.344(3)	1.347(4)	1.344(3)	1.353(5)	1.351(6)
C7—C8	1.429(3)	1.421(4)	1.418(4)	1.422(3)	1.417(6)	1.405(6)
C2—C3 + C3—C4	2.792	2.780	2.775	2.777	2.755	2.760
C6—C7 + C7—C8	2.776	2.765	2.765	2.766	2.770	2.756
C2—C8 + C4—C6	3.978	3.990	3.996	3.984	3.989	4.000

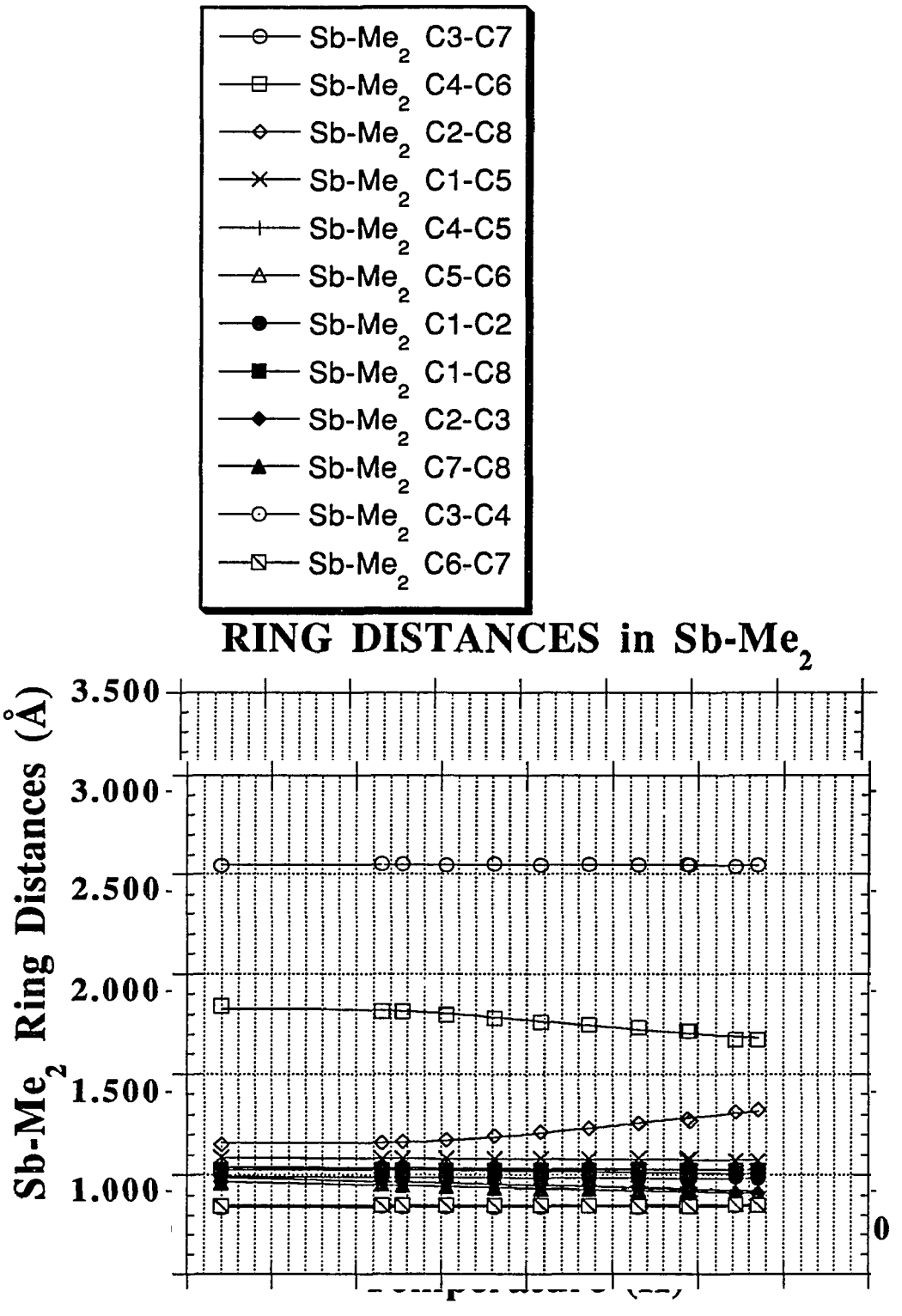


Figure 4–159. Plots of selected interatomic distances in the ring of $Sb\text{-}Me_2$ versus temperature.

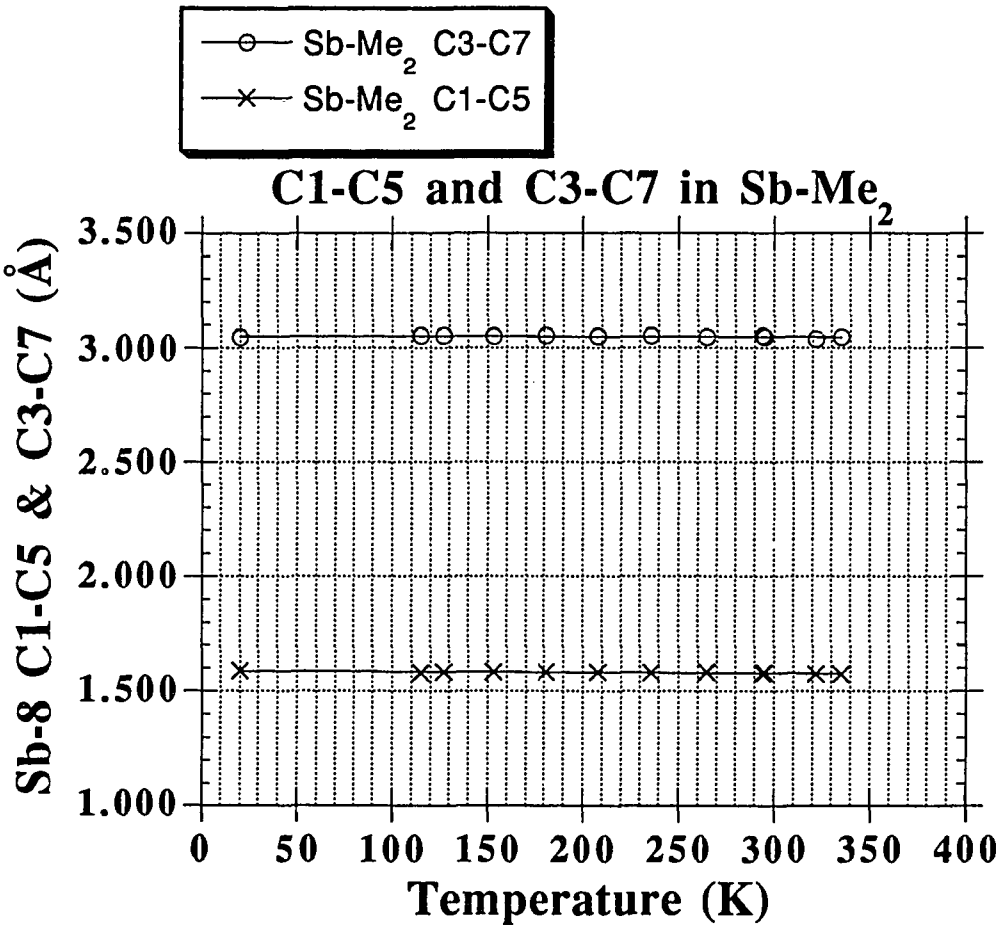


Figure 4–160. Plots of C1—C5 and C3—C7 distances in Sb-Me_2 versus temperature.

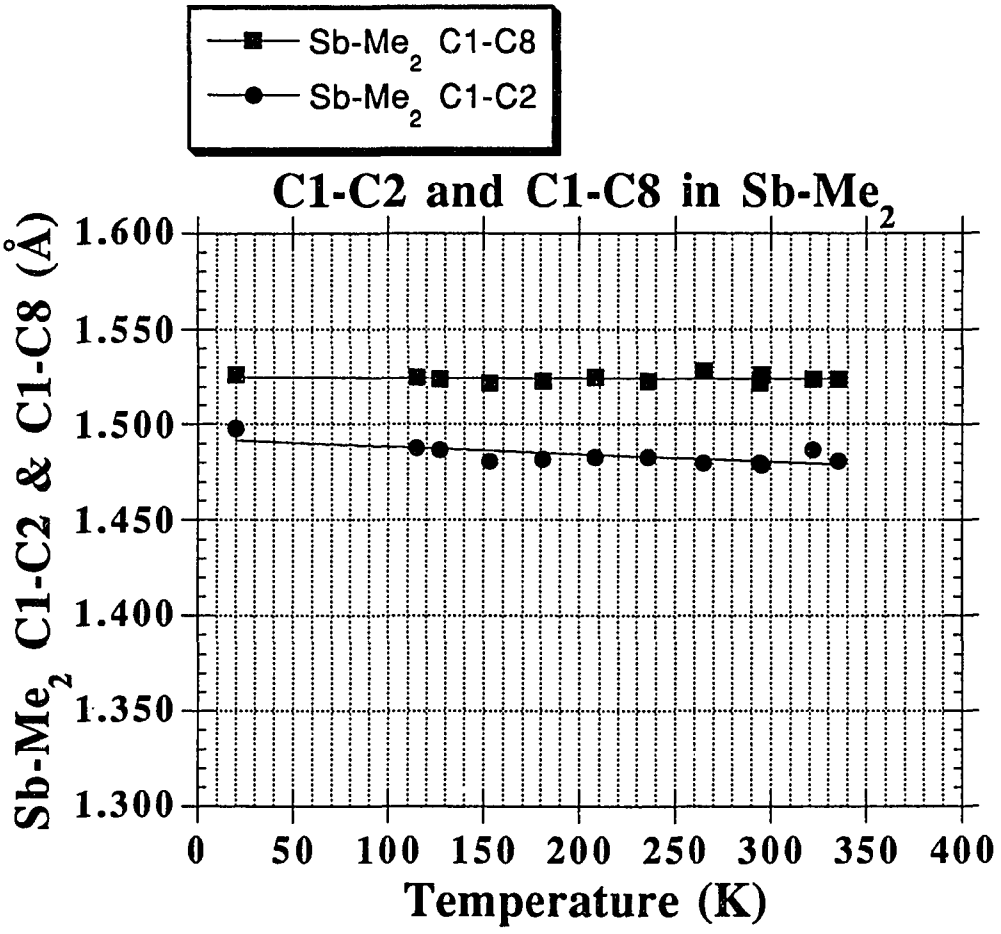


Figure 4–161. Plots of C1—C2 and C1—C8 distances in Sb-Me_2 versus temperature.

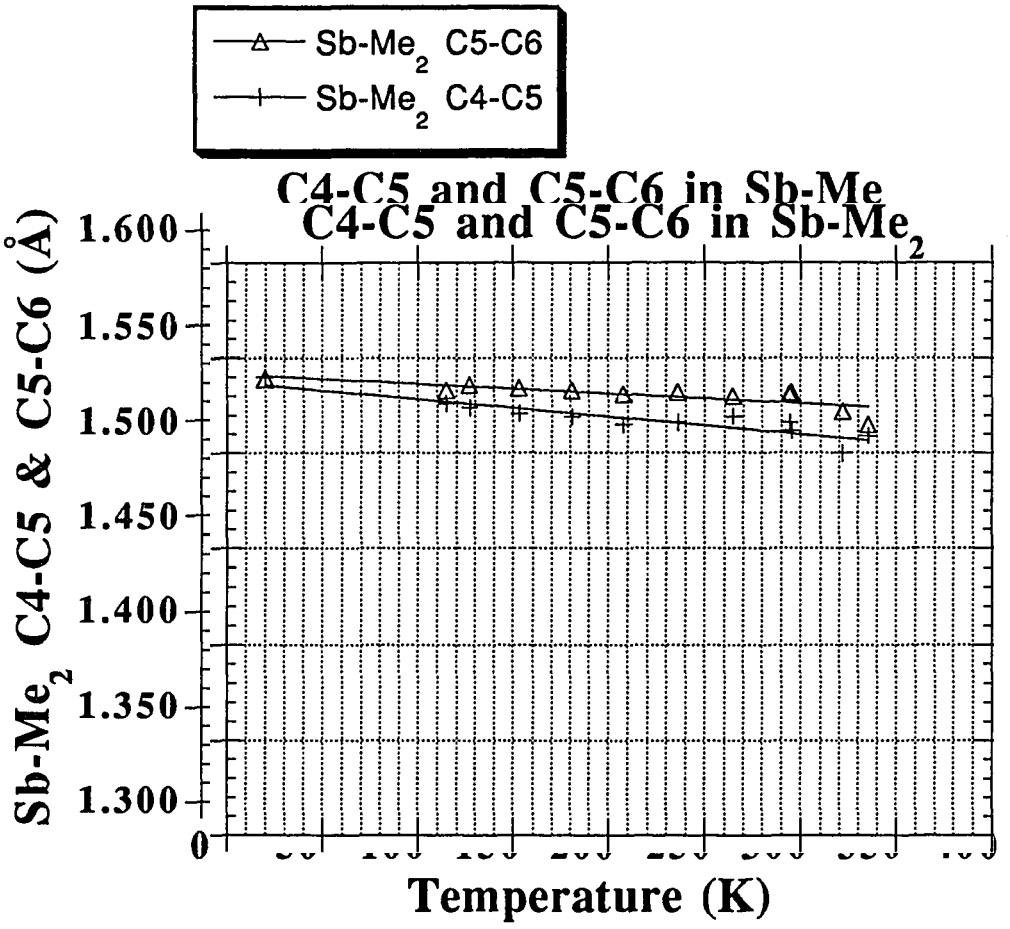


Figure 4–162. Plots of C4—C5 and C5—C6 distances in $Sb\text{-}Me_2$ versus temperature.

The graphs in Figure 4–163 indicate that the single bond C2—C3 becomes shorter "faster" than the double bond C3—C4 becomes longer. The same type of behavior was evident in the cyclooctatetraenes, which were discussed in Chapter 1.

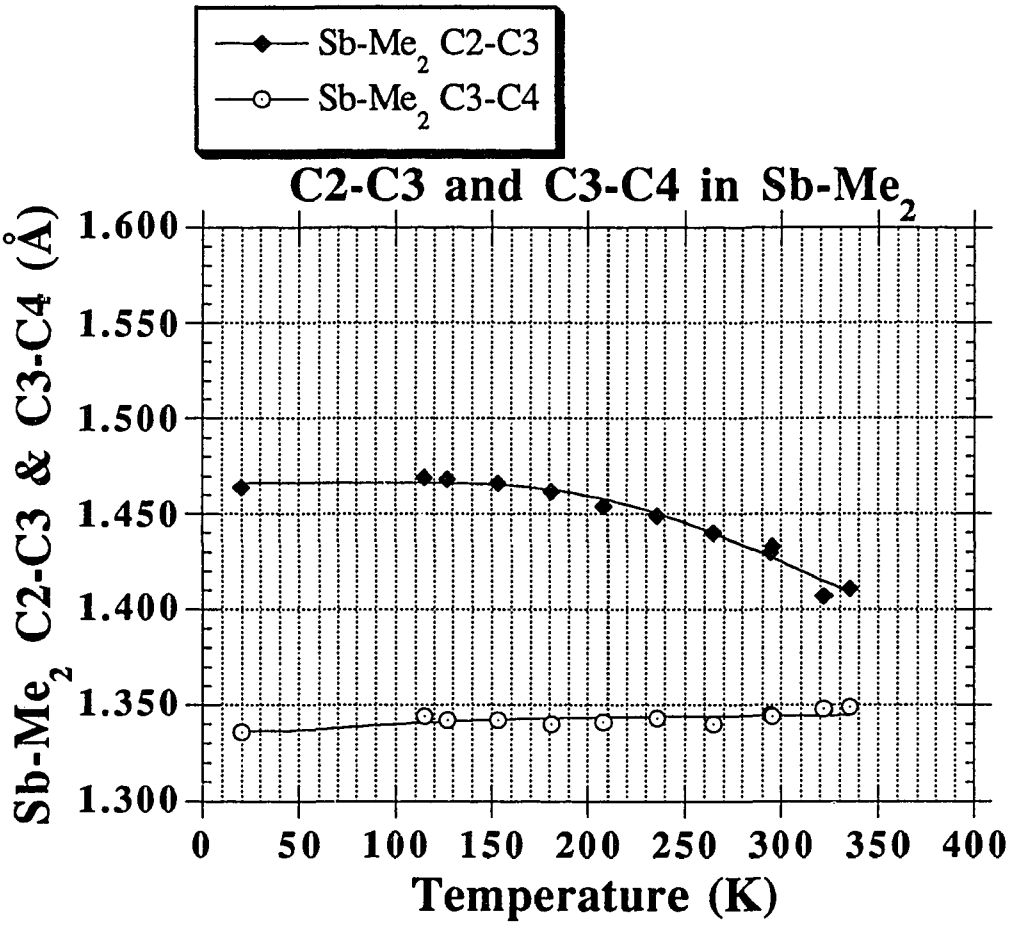


Figure 4–163. Plots of C2—C3 and C3—C4 distances in Sb-Me_2 versus temperature.

Since C2—C3 and C3—C4 do not compensate each other equally, their sum is not altogether constant.

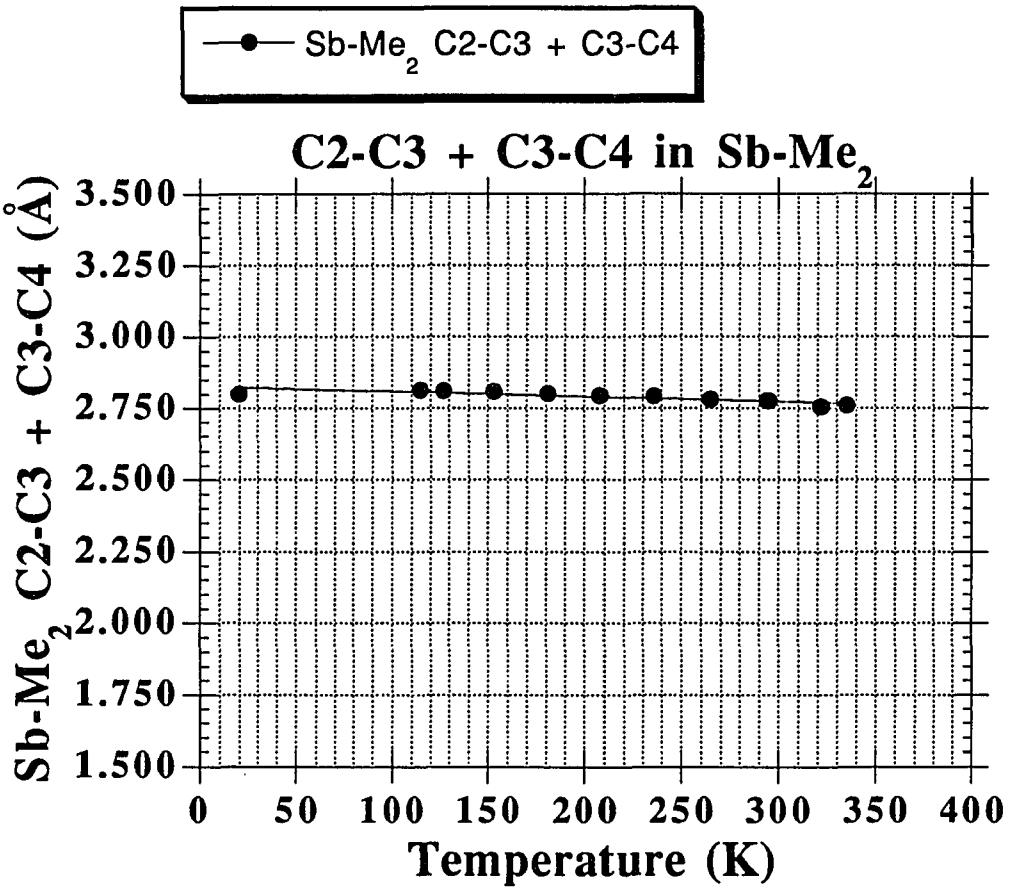


Figure 4–164. A plot of the sum of C2—C3 and C3—C4 distances in Sb-Me_2 versus temperature.

The bond distances C6—C7 and C7—C8 behave similarly to C2—C3 and C7—C8.

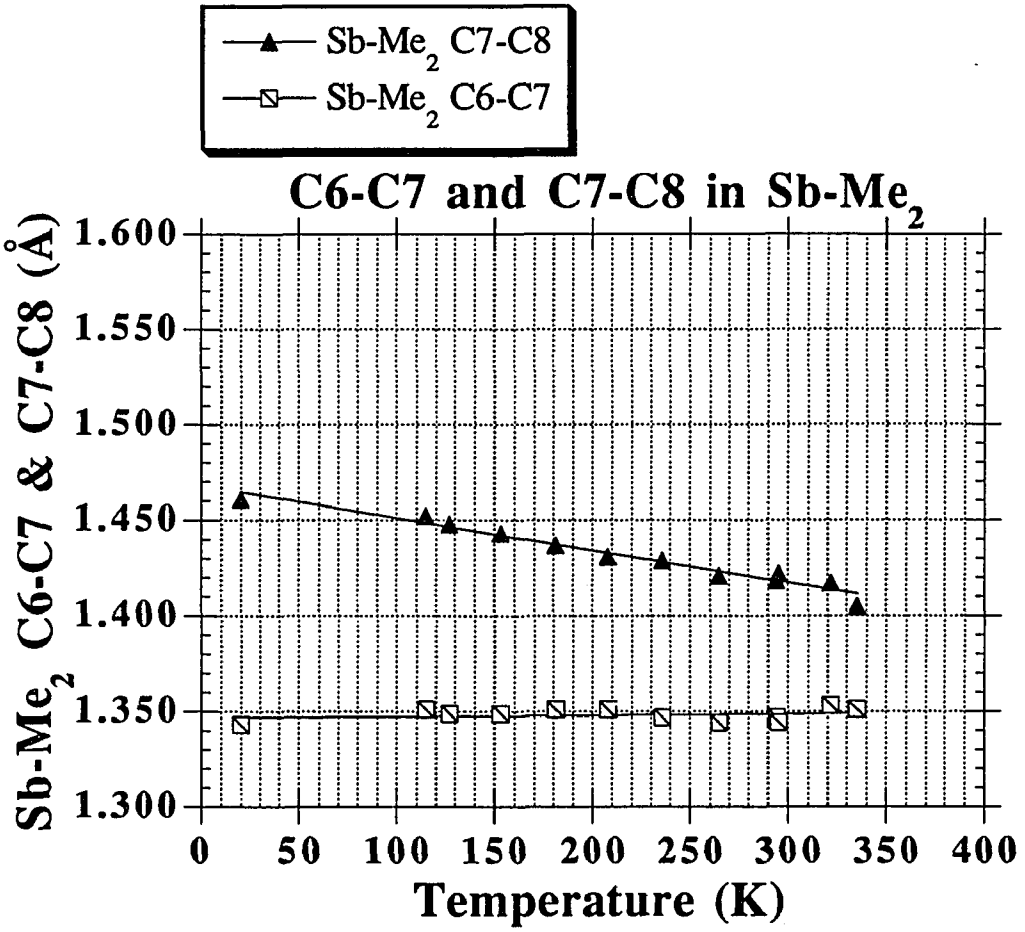


Figure 4–165. Plots of C6—C7 and C7—C8 distances in $Sb\text{-}Me_2$ versus temperature.

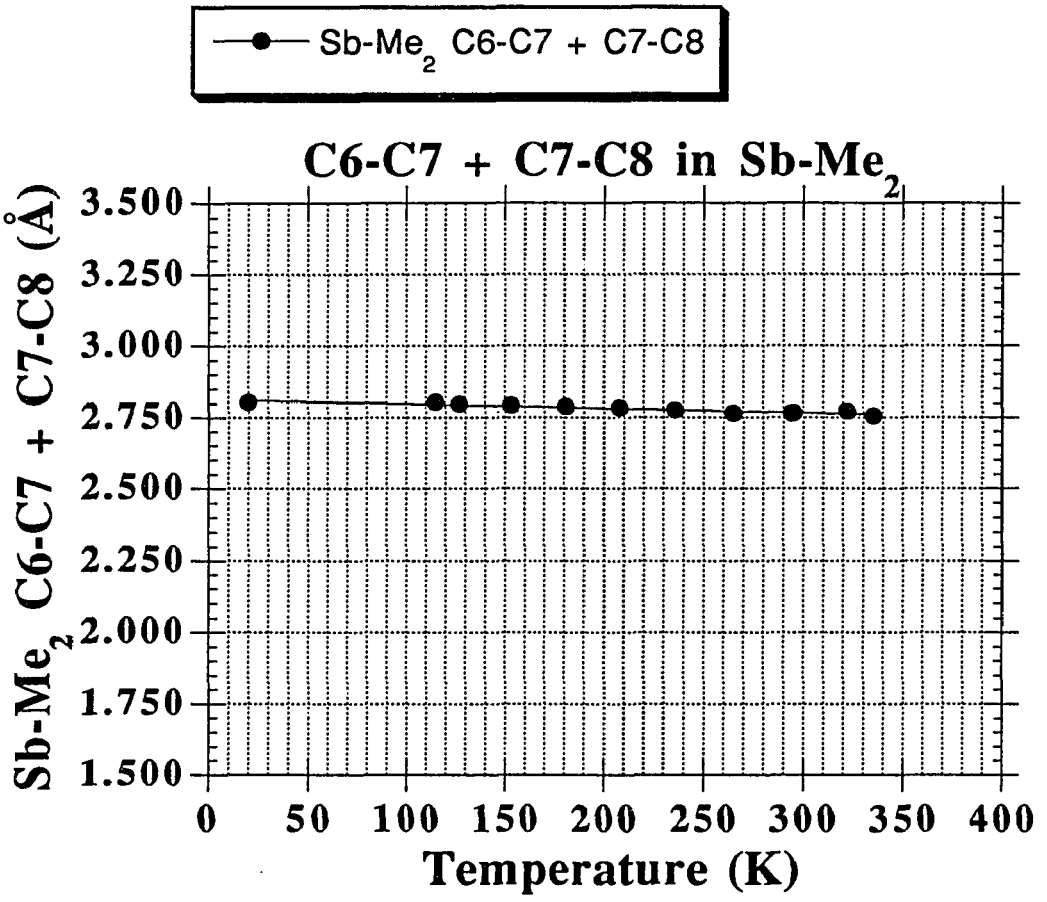


Figure 4–166. A plot of the sum of C6—C7 and C7—C8 distances in Sb-Me_2 versus temperature.

The distances C2—C8 and C4—C6 in Figure 4–167 compensate each other equally. C2—C8 becomes longer and C4—C6 becomes shorter by the same amount. Their sum is constant (Figure 4–168).

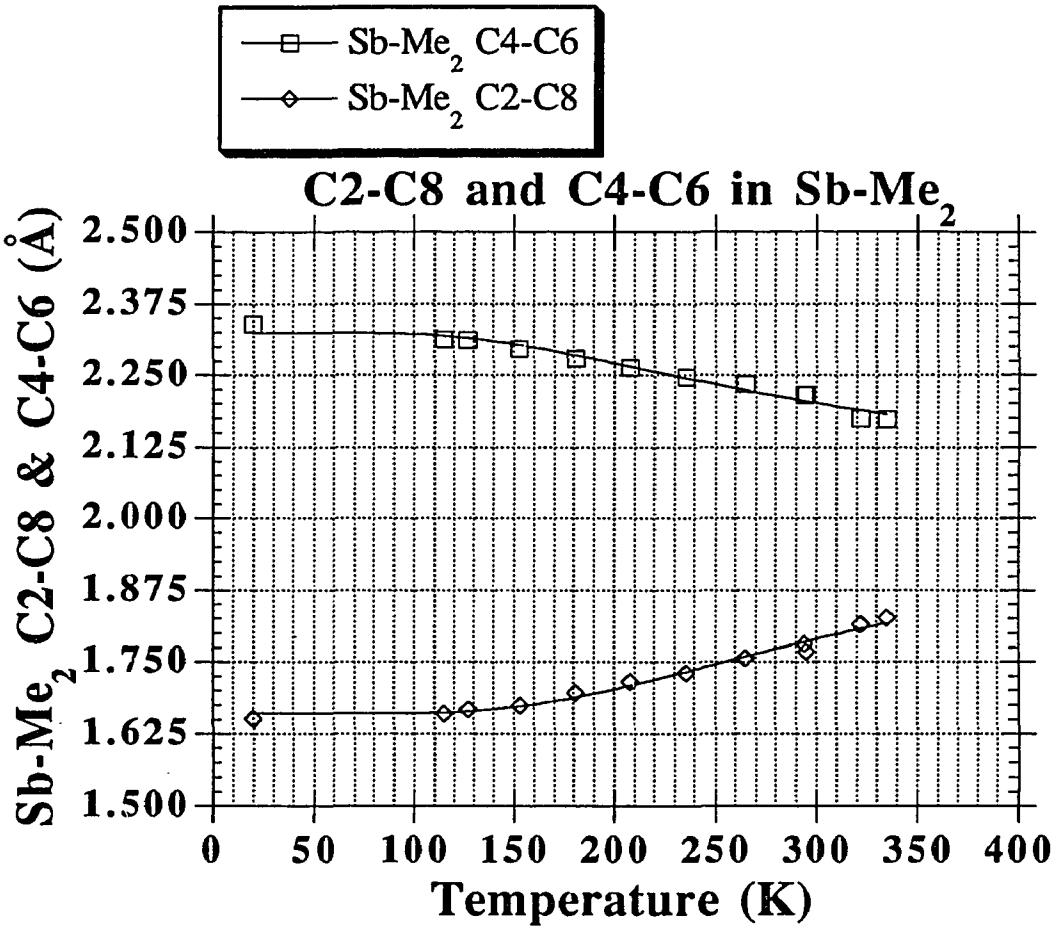


Figure 4–167. Plots of C2—C8 and C4—C6 distances in Sb-Me2 versus temperature.

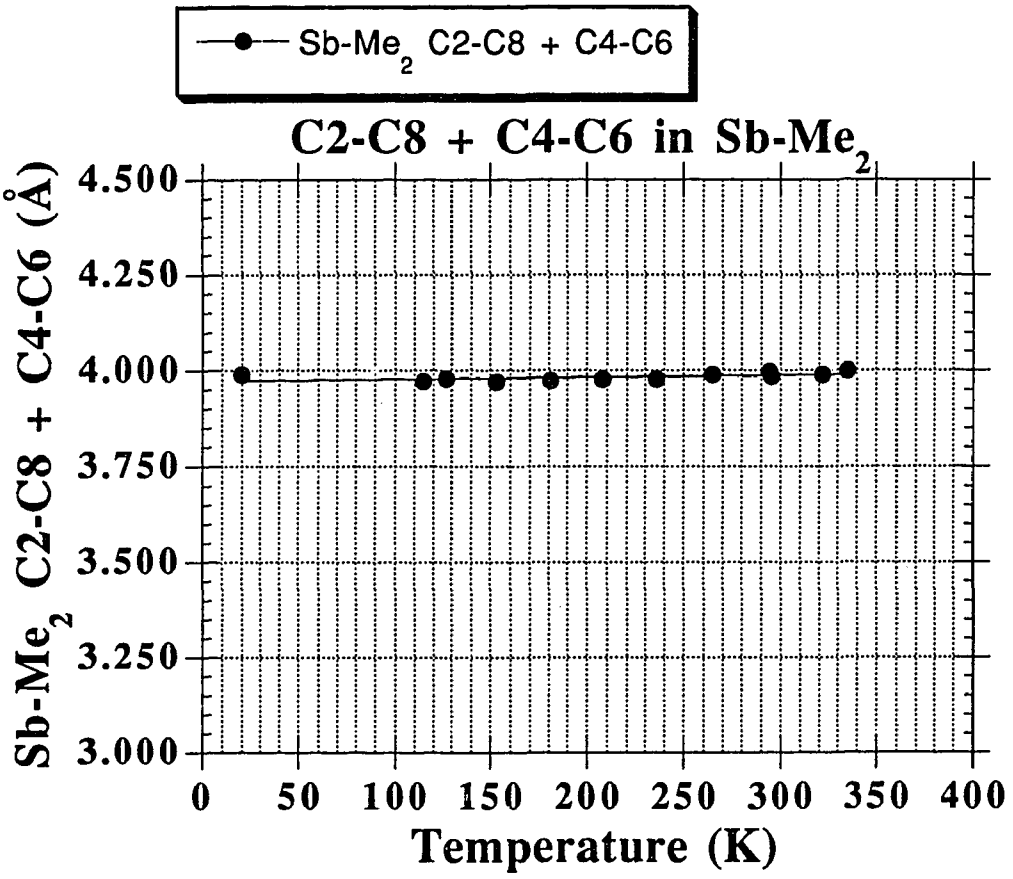


Figure 4–168. A plot of the sum of the distances C2—C8 and C4—C6 in $Sb\text{-}Me_2$ versus temperature.

The angles of the ring atoms in Table 4–23 reflect the elongations and contractions of distances in the ring of Sb-Me_2.

Table 4–23. Selected Angles (°) in the Ring of Sb-Me_2 at Various Temperatures

	20 K	**115 K**	**127 K**	**153 K**	**181 K**	**208 K**
C2—C1—C5	103.7(2)	104.0(2)	103.8(2)	104.0(2)	104.0(2)	103.9(2)
C2—C1—C8	66.2(2)	66.8(1)	67.2(2)	67.8(2)	68.7(2)	69.5(2)
C5—C1—C8	103.9(2)	103.9(1)	103.6(2)	103.6(2)	103.7(2)	103.4(2)
C1—C2—C3	108.3(2)	108.5(2)	108.7(2)	108.7(2)	108.7(2)	108.9(2)
C1—C2—C8	57.8(2)	57.6(1)	57.4(1)	57.3(1)	56.8(1)	56.4(2)
C3—C2—C8	118.8(2)	118.9(2)	118.8(2)	118.7(2)	118.5(2)	118.3(2)
C2—C3—C4	111.6(2)	110.6(2)	110.6(2)	110.6(2)	110.7(2)	110.9(2)
C3—C4—C5	110.4(2)	110.9(2)	110.9(2)	111.1(2)	111.2(2)	111.2(2)
C5—C4—C6	40.6(2)	41.0(1)	41.1(1)	41.5(1)	41.9(1)	42.3(1)
C1—C5—C4	102.2(2)	102.4(2)	102.6(2)	102.4(2)	102.5(2)	102.6(2)
C1—C5—C6	102.4(2)	102.6(1)	102.5(2)	102.7(2)	102.7(2)	102.8(2)
C4—C5—C6	98.8(2)	98.3(1)	98.1(2)	97.5(2)	96.7(2)	95.9(2)
C4—C6—C5	40.6(2)	40.8(1)	40.7(1)	41.1(1)	41.4(1)	41.8(1)
C5—C6—C7	111.7(2)	111.9(2)	111.8(2)	111.7(2)	111.7(2)	111.7(2)
C6—C7—C8	111.5(2)	110.8(2)	110.9(2)	111.0(2)	111.1(2)	111.2(2)
C1—C8—C2	56.1(2)	55.5(1)	55.3(1)	55.0(1)	54.5(1)	54.1(2)
C1—C8—C7	108.0(2)	108.6(2)	109.0(2)	109.1(2)	109.2(2)	109.4(2)
C2—C8—C7	118.1(2)	118.1(2)	117.9(2)	117.7(2)	117.3(2)	116.8(2)
$(\alpha+\beta)/2$[a]	82.5	82.6	82.7	82.7	82.7	82.7
C3—M[b]—C7	84.8	84.9	85.0	85.0	85.3	85.2

[a] α = C2—C1—C8, β = C4—C5—C6.

[b] M = midpoint between C1 and C5 bond.

Table 4–23 (cont'd). Selected Angles (°) in the Ring of Sb-Me_2 at Various Temperatures

	236 K	**265 K**	**294 K**	**295 K**	**322 K**	**335 K**
C2—C1—C5	104.1(2)	104.0(2)	104.1(2)	104.1(2)	103.5(3)	103.7(3)
C2—C1—C8	70.3(2)	71.4(2)	72.8(2)	72.1(2)	74.1(3)	74.9(3)
C5—C1—C8	103.6(2)	103.5(2)	103.6(2)	103.5(2)	103.4(3)	103.3(3)
C1—C2—C3	108.9(2)	109.2(2)	109.5(3)	109.3(2)	109.9(4)	110.4(4)
C1—C2—C8	55.9(2)	55.6(2)	54.7(2)	55.2(2)	53.9(2)	53.6(3)
C3—C2—C8	118.0(2)	117.7(2)	117.4(2)	117.6(2)	116.4(3)	116.5(4)
C2—C3—C4	110.9(2)	111.3(3)	111.0(3)	111.1(3)	111.0(4)	110.6(4)
C3—C4—C5	111.2(2)	111.1(2)	111.2(3)	111.2(2)	111.3(4)	111.4(4)
C5—C4—C6	42.8(1)	43.1(1)	43.6(2)	43.6(1)	44.4(2)	44.2(2)
C1—C5—C4	102.6(2)	102.4(2)	102.5(2)	102.4(2)	102.8(3)	102.6(3)
C1—C5—C6	102.6(2)	102.5(2)	102.6(2)	102.4(2)	103.4(3)	103.2(3)
C4—C5—C6	95.0(2)	94.2(2)	93.3(2)	93.4(2)	92.0(3)	91.9(3)
C4—C6—C5	42.2(1)	42.7(1)	43.1(2)	42.9(1)	43.6(2)	44.0(2)
C5—C6—C7	112.0(2)	112.2(2)	112.2(2)	112.6(2)	111.7(3)	111.8(4)
C6—C7—C8	111.0(2)	111.3(2)	111.0(2)	110.8(2)	111.2(3)	111.4(4)
C1—C8—C2	53.8(2)	53.0(2)	52.5(2)	52.7(2)	52.0(2)	51.5(3)
C1—C8—C7	109.5(2)	109.5(2)	109.9(2)	109.9(2)	109.8(3)	109.8(3)
C2—C8—C7	116.6(2)	115.9(2)	115.5(3)	115.6(2)	114.9(3)	114.7(4)
$(\alpha+\beta)/2$[a]	82.7	82.8	83.1	82.8	83.1	83.4
C3—M[b]—C7	85.3	85.2	85.4	85.2	85.2	85.5

[a] α = C2—C1—C8, β = C4—C5—C6.
[b] M = midpoint between C1 and C5 bond.

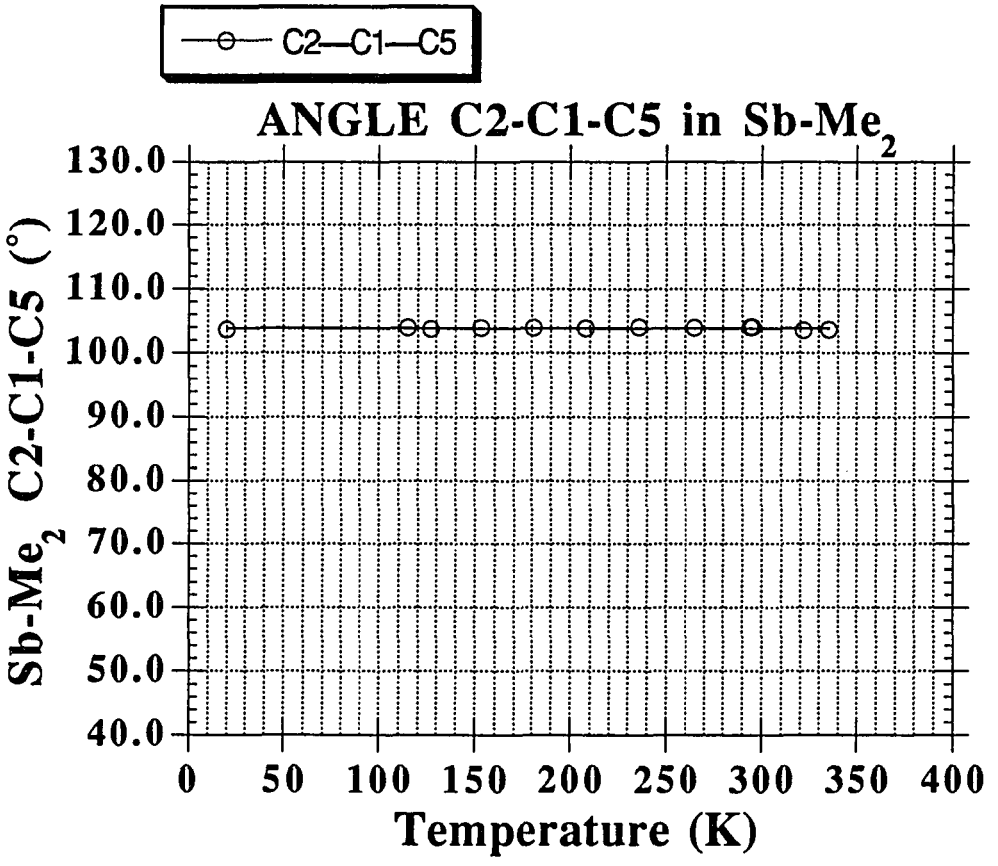


Figure 4–169. A plot of the angle C2—C1—C5 in Sb-Me_2 versus temperature.

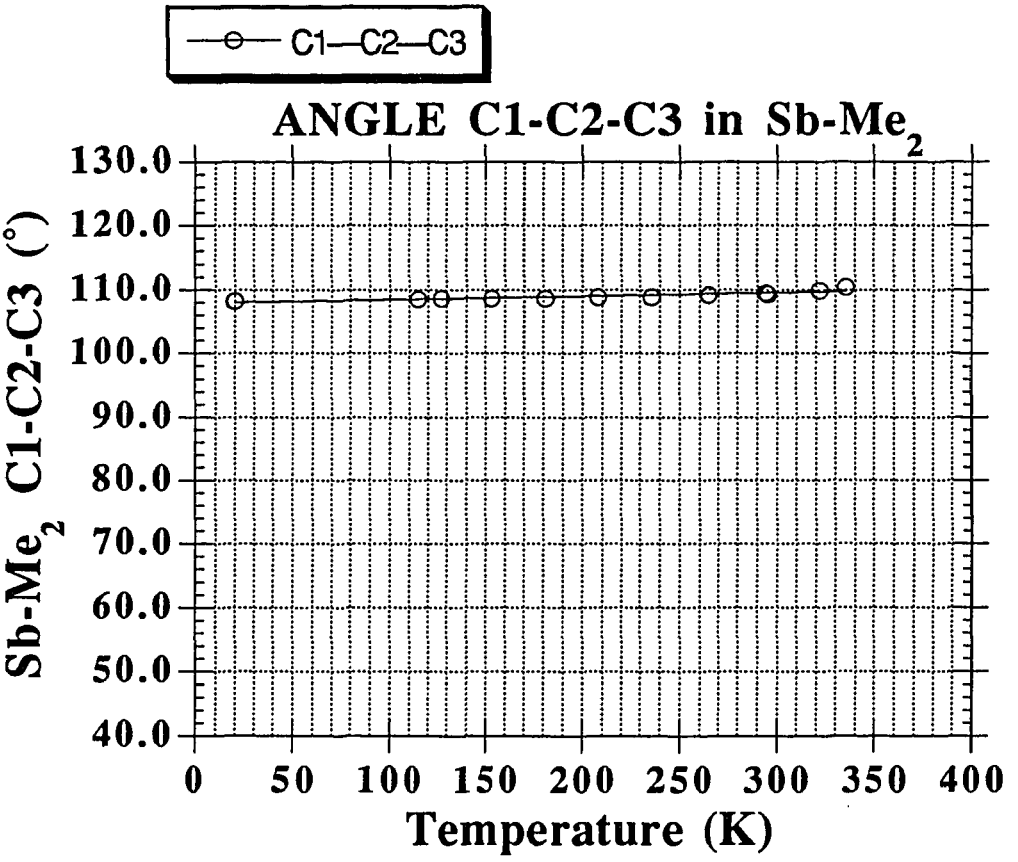


Figure 4–170. A plot of the angle C1—C2—C3 in Sb-Me_2 versus temperature.

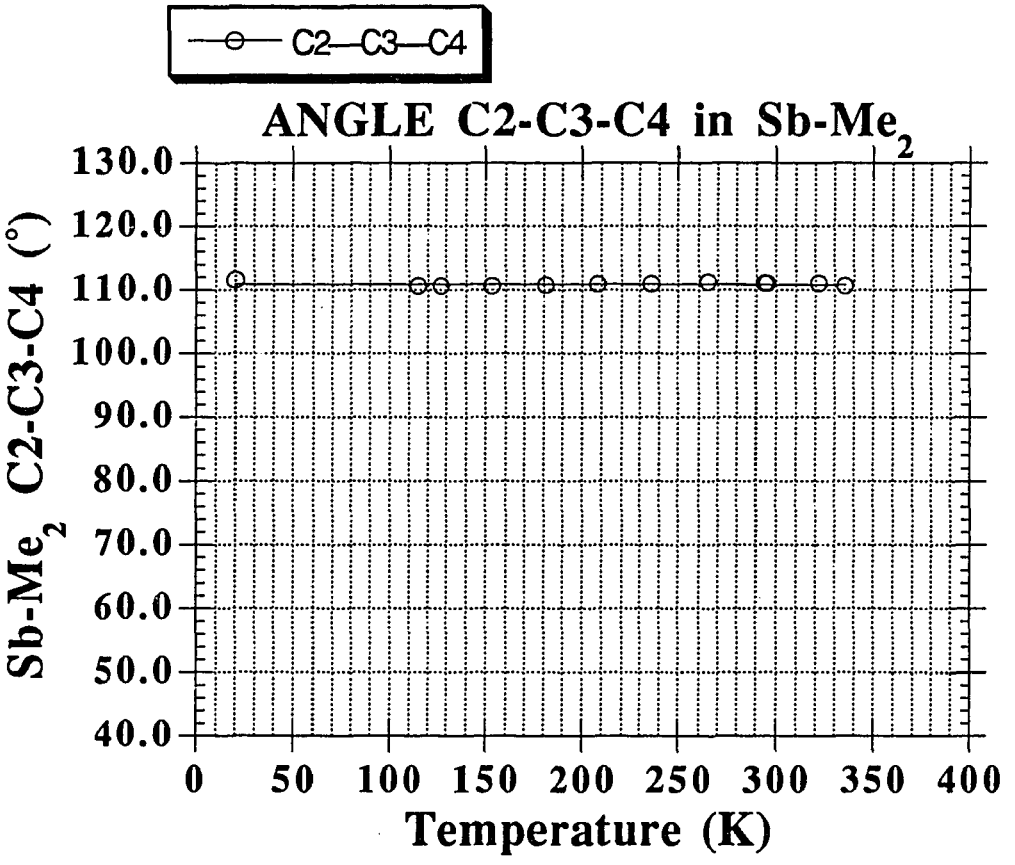


Figure 4–171. A plot of the angle C2—C3—C4 in Sb-Me_2 versus temperature.

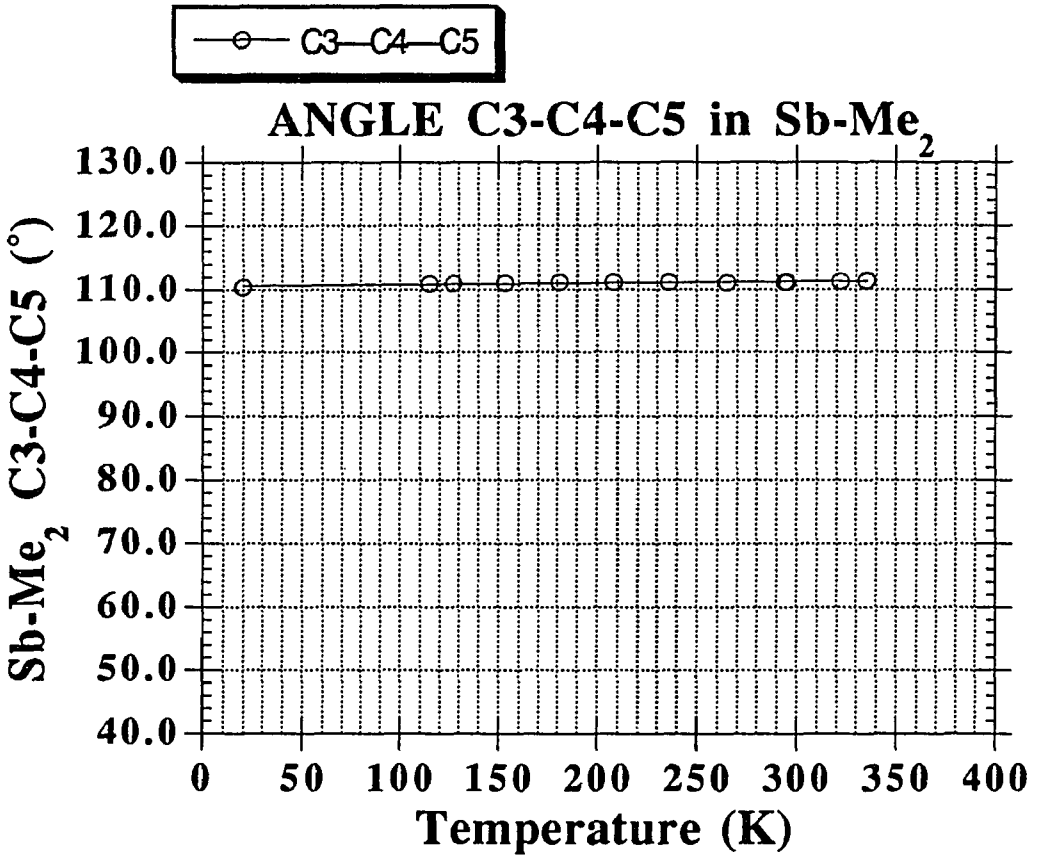


Figure 4–172. A plot of the angle C3—C4—C5 in Sb-Me_2 versus temperature.

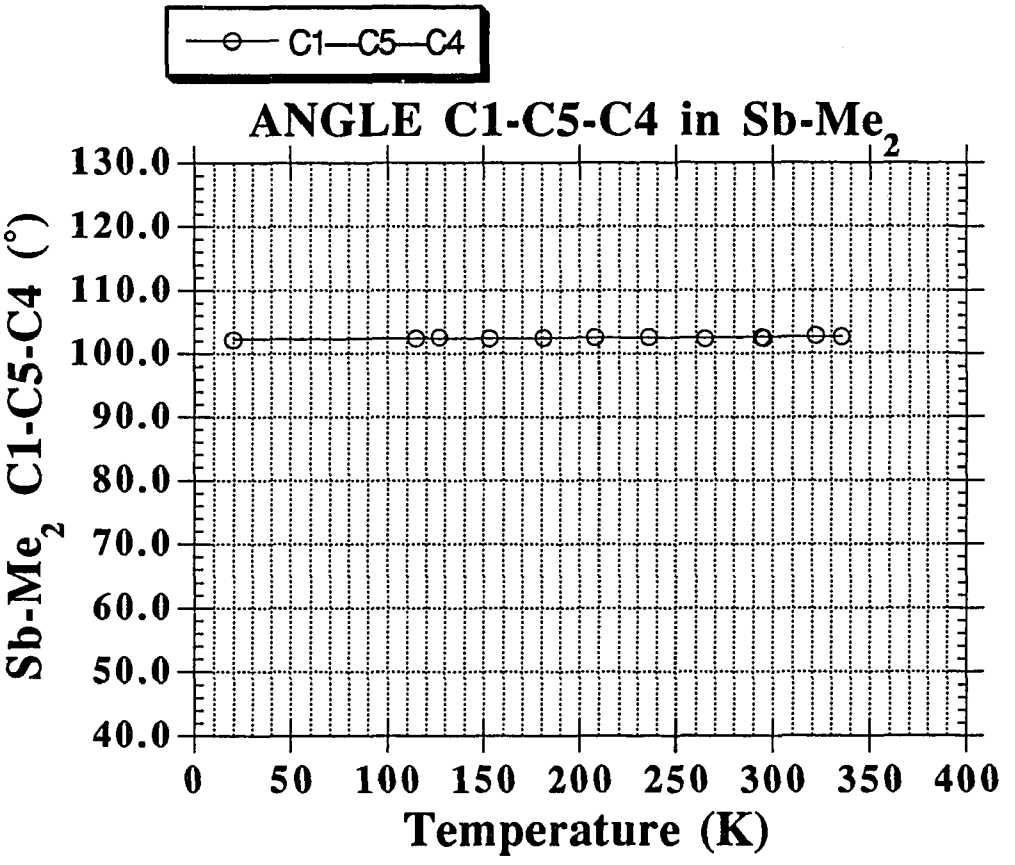


Figure 4–173. A plot of the angle C1—C5—C4 in Sb-Me_2 versus temperature.

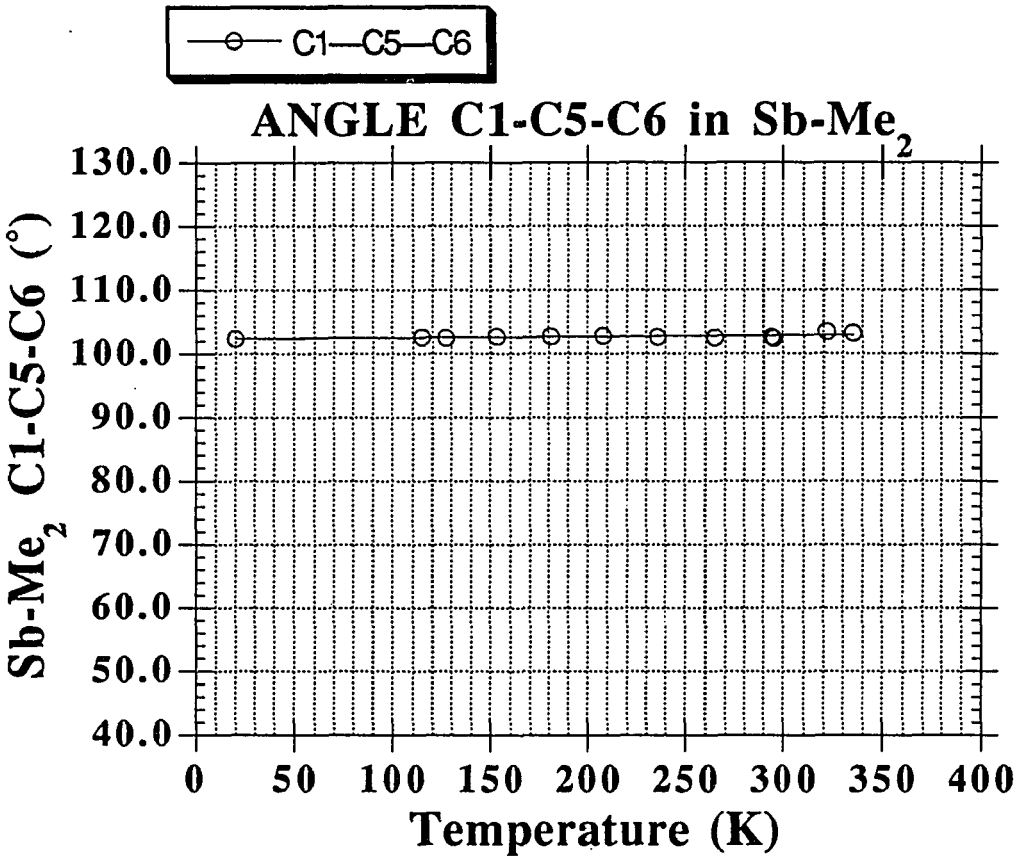


Figure 4–174. A plot of the angle C1—C5—C6 in Sb-Me_2 versus temperature.

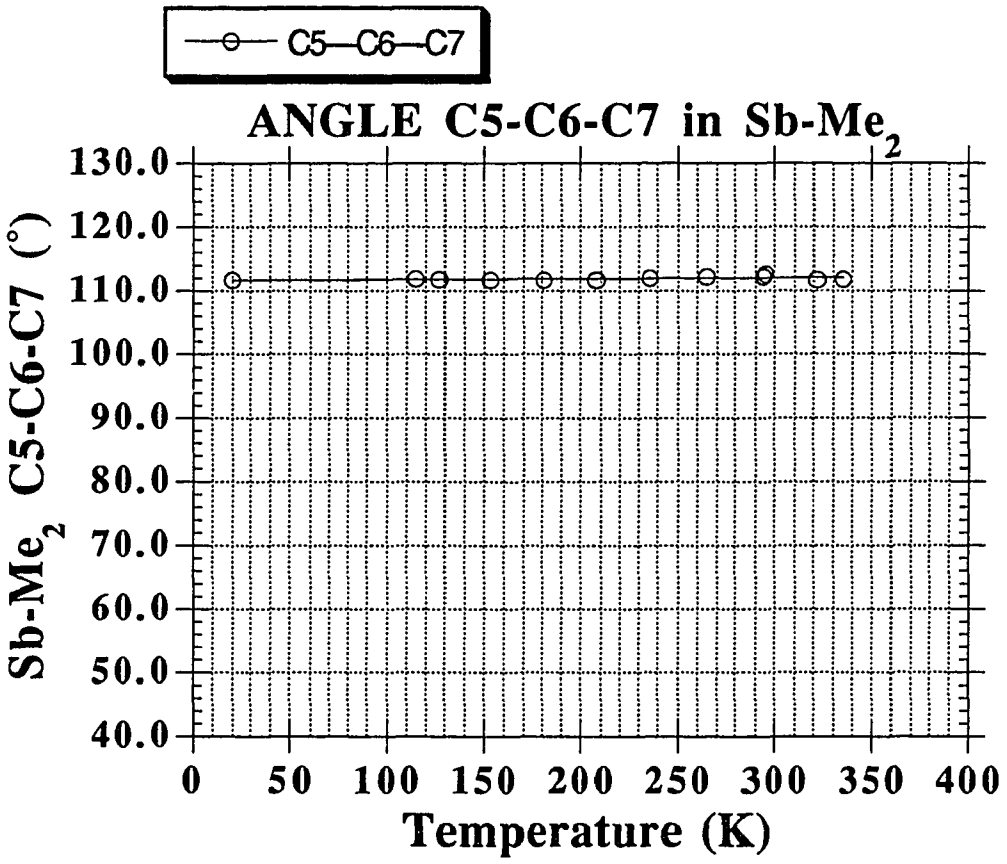


Figure 4–175. A plot of the angle C5—C6—C7 in Sb-Me_2 versus temperature.

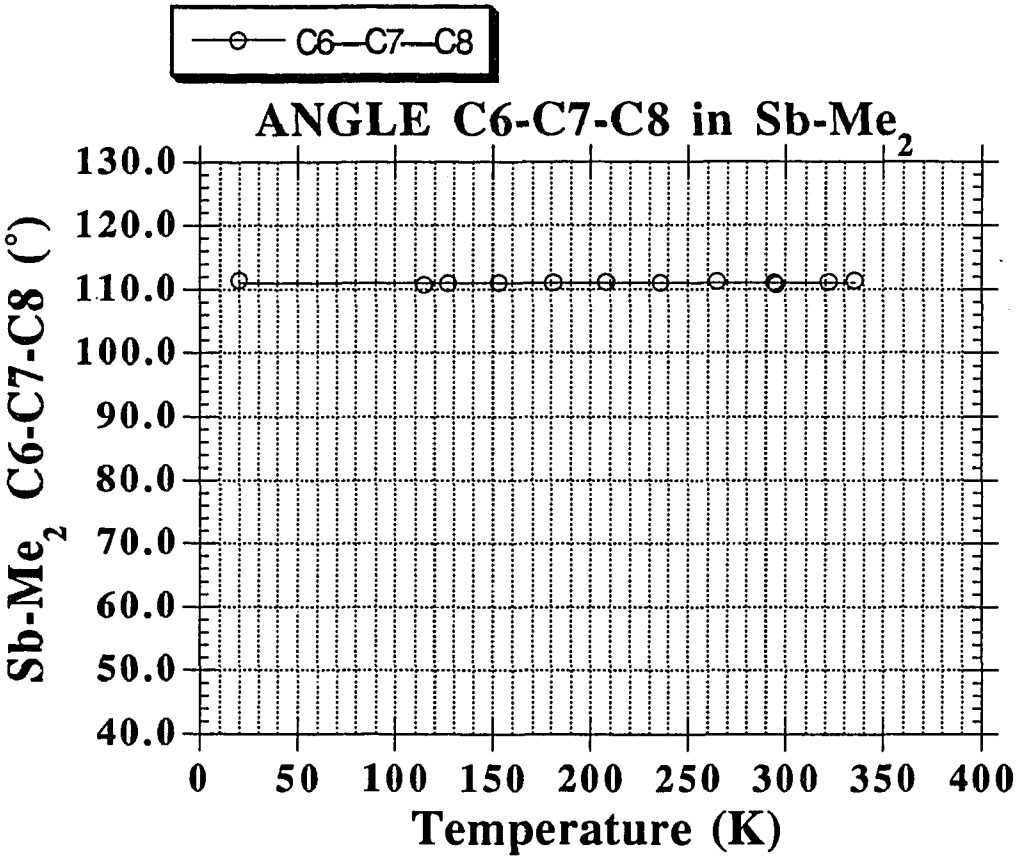


Figure 4–176. A plot of the angle C6—C7—C8 in Sb-Me_2 versus temperature.

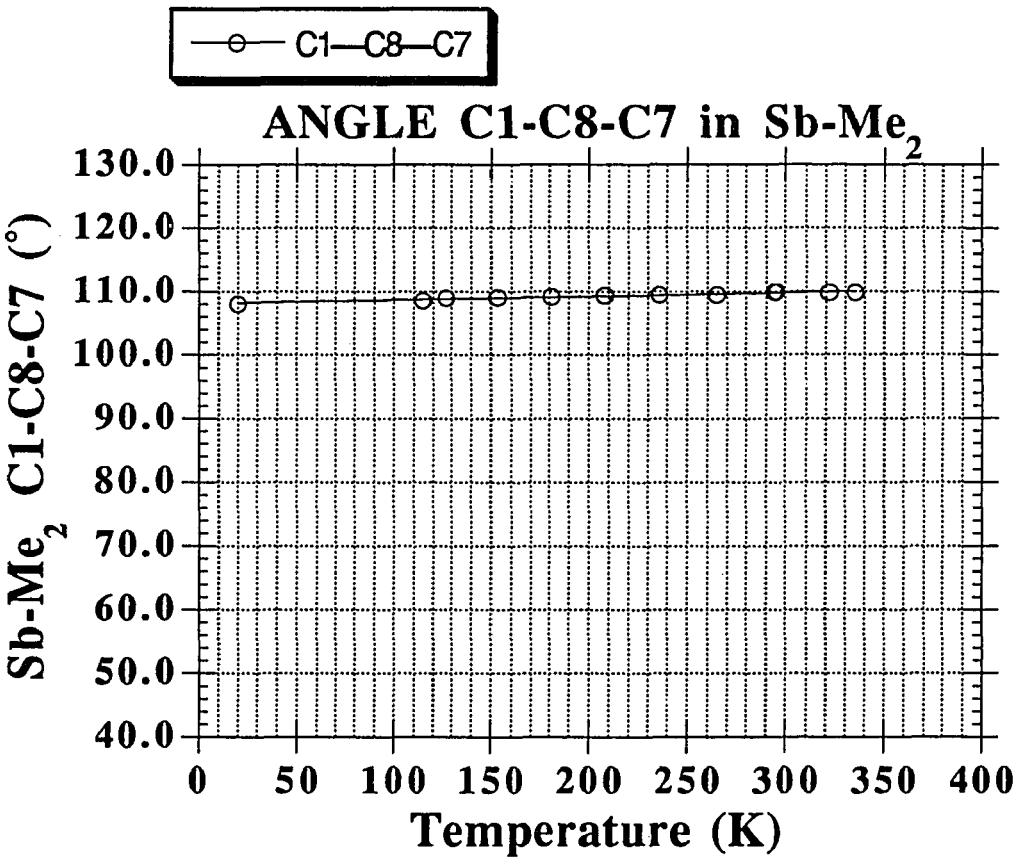


Figure 4–177. A plot of the angle C1—C8—C7 in Sb-Me_2 versus temperature.

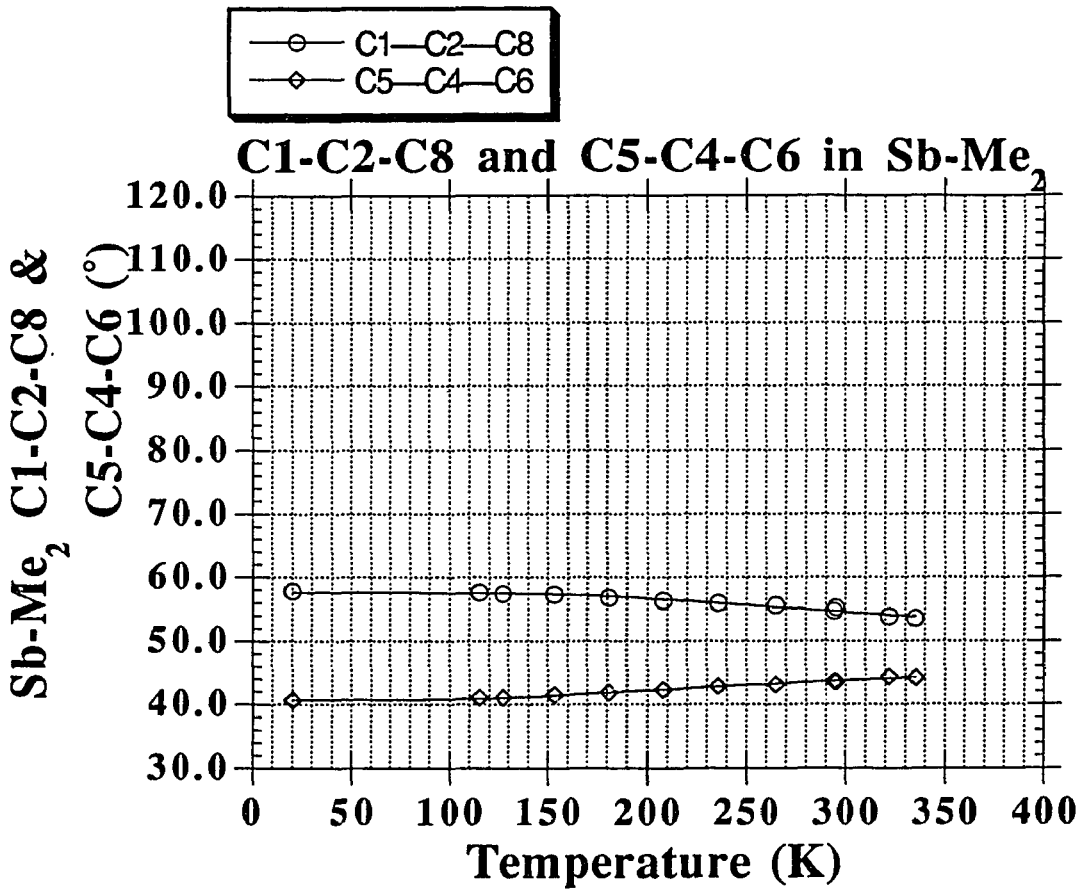


Figure 4–178. Plots of the angles C1—C2—C8 and C5—C4—C6 in Sb-Me_2 versus temperature.

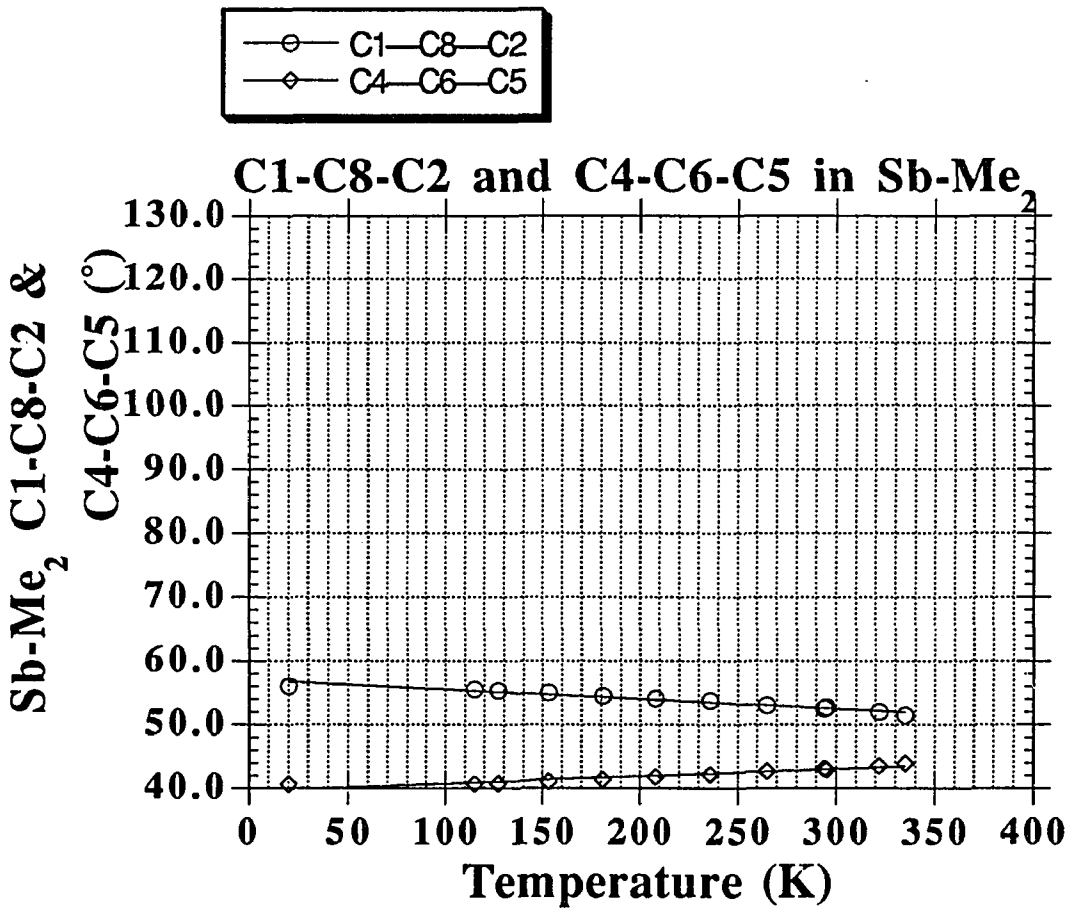


Figure 4–179. Plots of the angles C1—C8—C2 and C4—C6—C5 in Sb-Me_2 versus temperature.

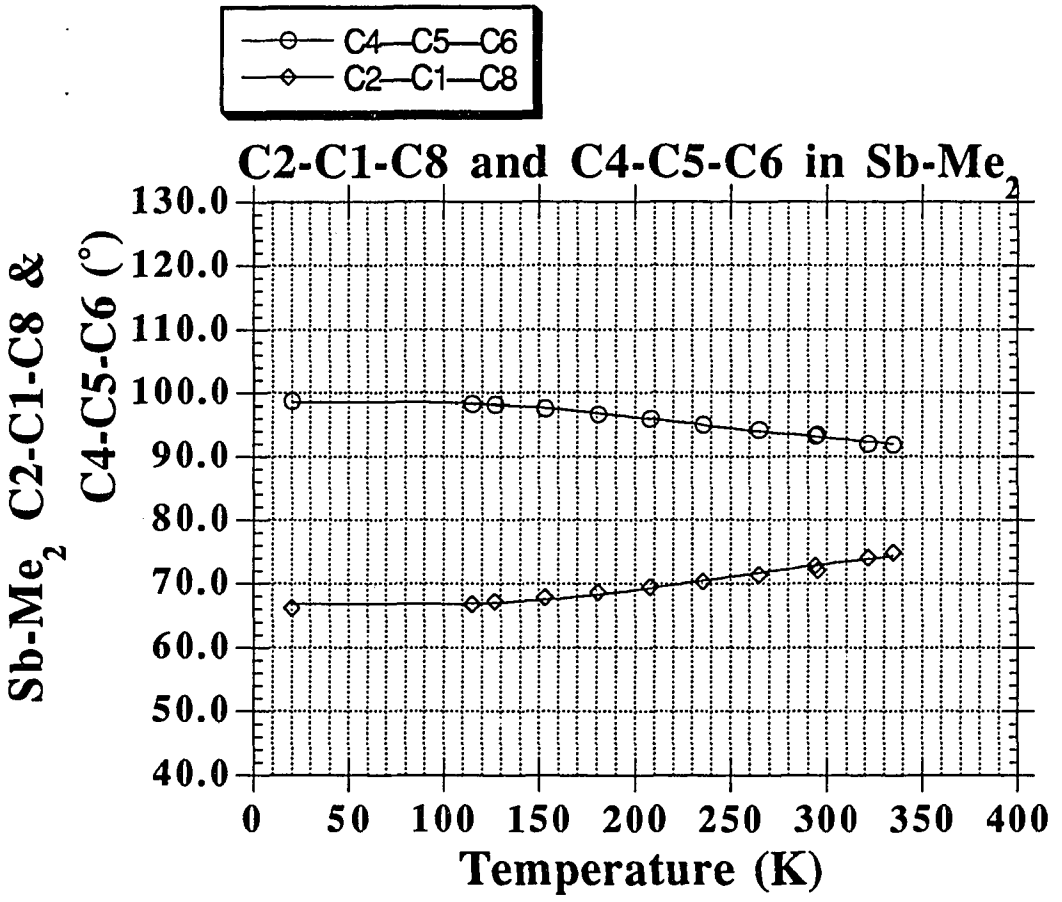


Figure 4–180. Plots of the angles C2—C1—C8 and C4—C4—C6 in Sb-Me_2 versus temperature.

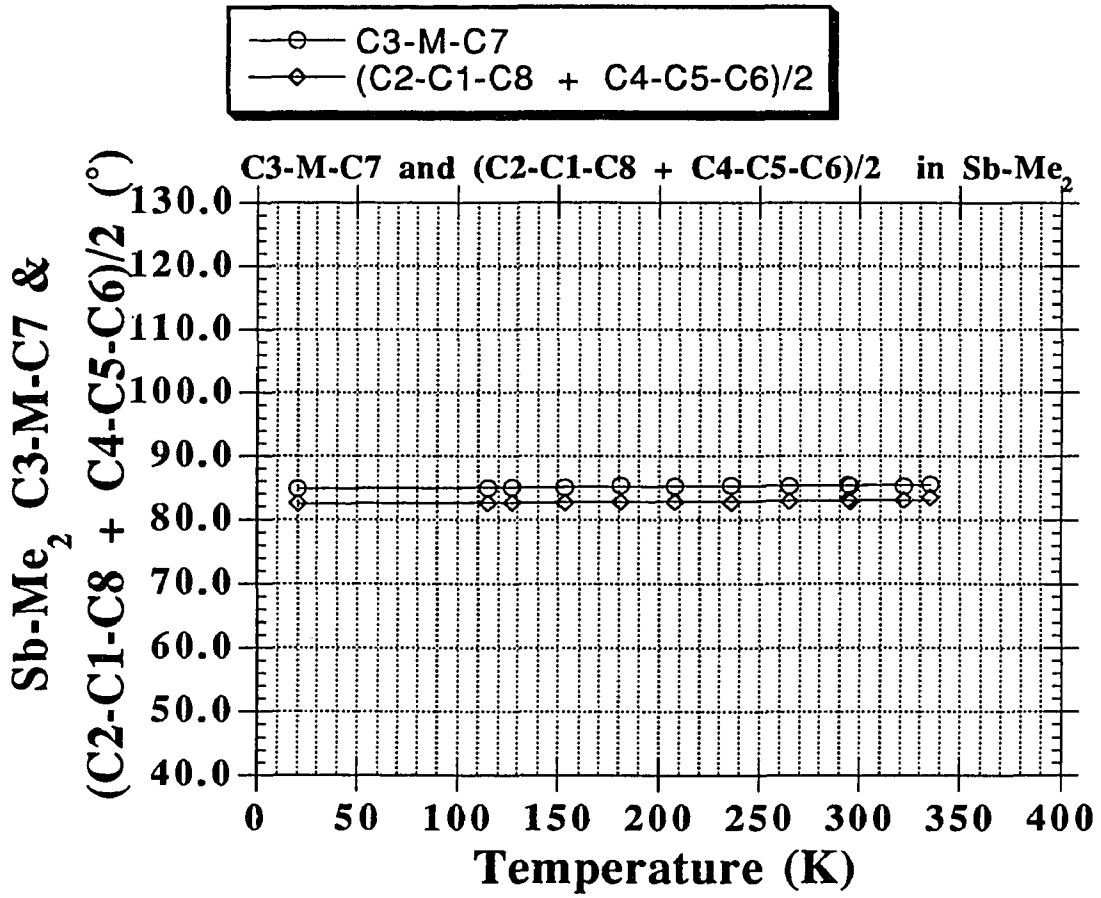


Figure 4–181. Plots of the angle C3—M—C7 (M = midpoint between C1 and C5) and the average angle of C2—C1—C8 and C4—C5—C6 in Sb-Me_2 versus temperature.

From the root-mean-square amplitudes in Table 4–24 and the *ORTEP* drawings of Sb-Me_2 at the end of this section, we can see, especially at higher temperatures, that the maximum vibrations of atoms C2, C4, C6, and C8 are greater than other atoms in the semibullvalene ring and that the direction of vibration is parallel to the plane of the cyclopropyl ring. All this, of course, is consistent with the Cope rearrangement at work. Furthermore, Sb-Me_2 is predisposed to structural changes more so than the first four candidates because of its low activation energy of 3.8 kcal/mole in the solid state, which is significantly lower than that of semibullvalene (5.5 kcal/mole).

Table 4–24. Selected Root-Mean-Square Amplitudes (Å) of Thermal Vibrations in the Ring of Sb-Me_2 at Various Temperatures

		Min.	Int'med	Max.
20 K	C1	0.095	0.102	0.122
	C2	0.093	0.108	0.129
	C3	0.096	0.107	0.126
	C4	0.099	0.116	0.123
	C5	0.091	0.101	0.125
	C6	0.070	0.124	0.141
	C7	0.070	0.119	0.127
	C8	0.082	0.113	0.123
115 K	C1	0.112	0.119	0.148
	C2	0.127	0.136	0.159
	C3	0.114	0.133	0.152
	C4	0.120	0.128	0.148
	C5	0.107	0.115	0.149
	C6	0.114	0.127	0.159
	C7	0.115	0.124	0.147
	C8	0.111	0.122	0.160
127 K	C1	0.117	0.129	0.157
	C2	0.133	0.146	0.167
	C3	0.118	0.144	0.158
	C4	0.125	0.140	0.161
	C5	0.114	0.124	0.160
	C6	0.120	0.134	0.177
	C7	0.123	0.130	0.153
	C8	0.116	0.131	0.174
153 K	C1	0.128	0.142	0.161
	C2	0.143	0.169	0.184
	C3	0.133	0.159	0.165
	C4	0.140	0.156	0.169
	C5	0.122	0.139	0.165
	C6	0.135	0.146	0.194
	C7	0.132	0.140	0.166
	C8	0.131	0.142	0.192

Table 4–24 (cont'd). Selected Root-Mean-Square Amplitudes (Å) of Thermal Vibrations in the Ring of Sb-Me_2 at Various Temperatures

		Min.	Int'med	Max.
181 K	C1	0.142	0.144	0.167
	C2	0.151	0.174	0.203
	C3	0.146	0.165	0.171
	C4	0.151	0.165	0.178
	C5	0.133	0.147	0.169
	C6	0.145	0.152	0.206
	C7	0.142	0.150	0.173
	C8	0.136	0.147	0.203
208 K	C1	0.153	0.156	0.175
	C2	0.159	0.183	0.221
	C3	0.158	0.170	0.186
	C4	0.161	0.182	0.182
	C5	0.145	0.159	0.174
	C6	0.156	0.163	0.224
	C7	0.148	0.160	0.181
	C8	0.150	0.160	0.216
236 K	C1	0.163	0.165	0.181
	C2	0.172	0.196	0.243
	C3	0.171	0.183	0.192
	C4	0.170	0.190	0.200
	C5	0.158	0.163	0.189
	C6	0.164	0.171	0.235
	C7	0.160	0.166	0.194
	C8	0.162	0.170	0.228
265 K	C1	0.172	0.178	0.188
	C2	0.174	0.208	0.265
	C3	0.180	0.196	0.202
	C4	0.180	0.203	0.211
	C5	0.170	0.178	0.192
	C6	0.176	0.183	0.246
	C7	0.169	0.177	0.208
	C8	0.168	0.182	0.245

Table 4–24 (cont'd). Selected Root-Mean-Square Amplitudes (Å) of Thermal Vibrations in the Ring of Sb-Me_2 at Various Temperatures

		Min.	Int'med	Max.
294 K	C1	0.183	0.192	0.201
	C2	0.185	0.221	0.281
	C3	0.190	0.214	0.214
	C4	0.182	0.214	0.230
	C5	0.180	0.187	0.206
	C6	0.184	0.194	0.266
	C7	0.177	0.195	0.215
	C8	0.183	0.198	0.259
295 K	C1	0.181	0.197	0.213
	C2	0.189	0.228	0.291
	C3	0.204	0.216	0.222
	C4	0.193	0.221	0.234
	C5	0.183	0.196	0.219
	C6	0.185	0.201	0.275
	C7	0.178	0.199	0.225
	C8	0.182	0.196	0.271
322 K	C1	0.190	0.198	0.209
	C2	0.181	0.233	0.296
	C3	0.202	0.220	0.235
	C4	0.189	0.233	0.233
	C5	0.196	0.196	0.208
	C6	0.195	0.211	0.264
	C7	0.185	0.199	0.223
	C8	0.183	0.222	0.264
335 K	C1	0.187	0.213	0.219
	C2	0.202	0.233	0.305
	C3	0.195	0.221	0.239
	C4	0.193	0.226	0.245
	C5	0.191	0.204	0.229
	C6	0.199	0.208	0.276
	C7	0.189	0.213	0.219
	C8	0.198	0.216	0.261

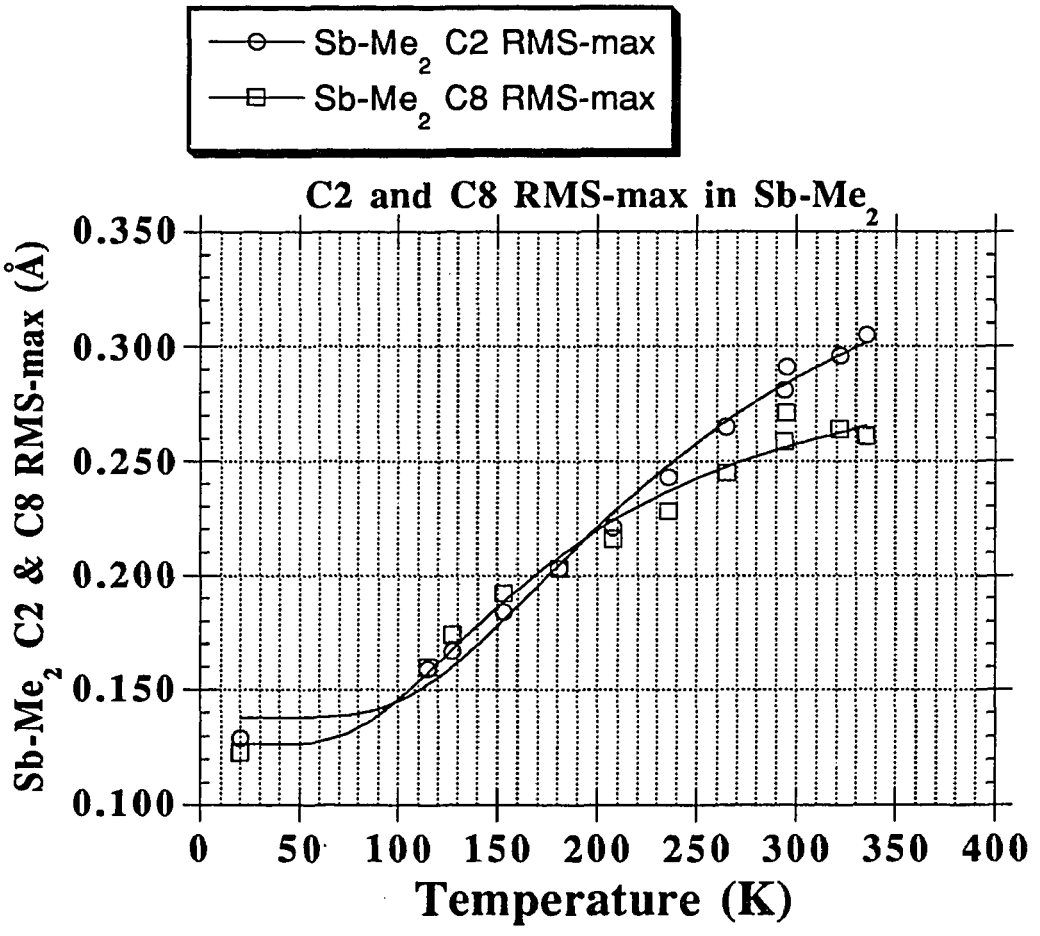


Figure 4–182. Plots of C2 RMS-max and C8 RMS-max in $Sb\text{-}Me_2$ versus temperature.

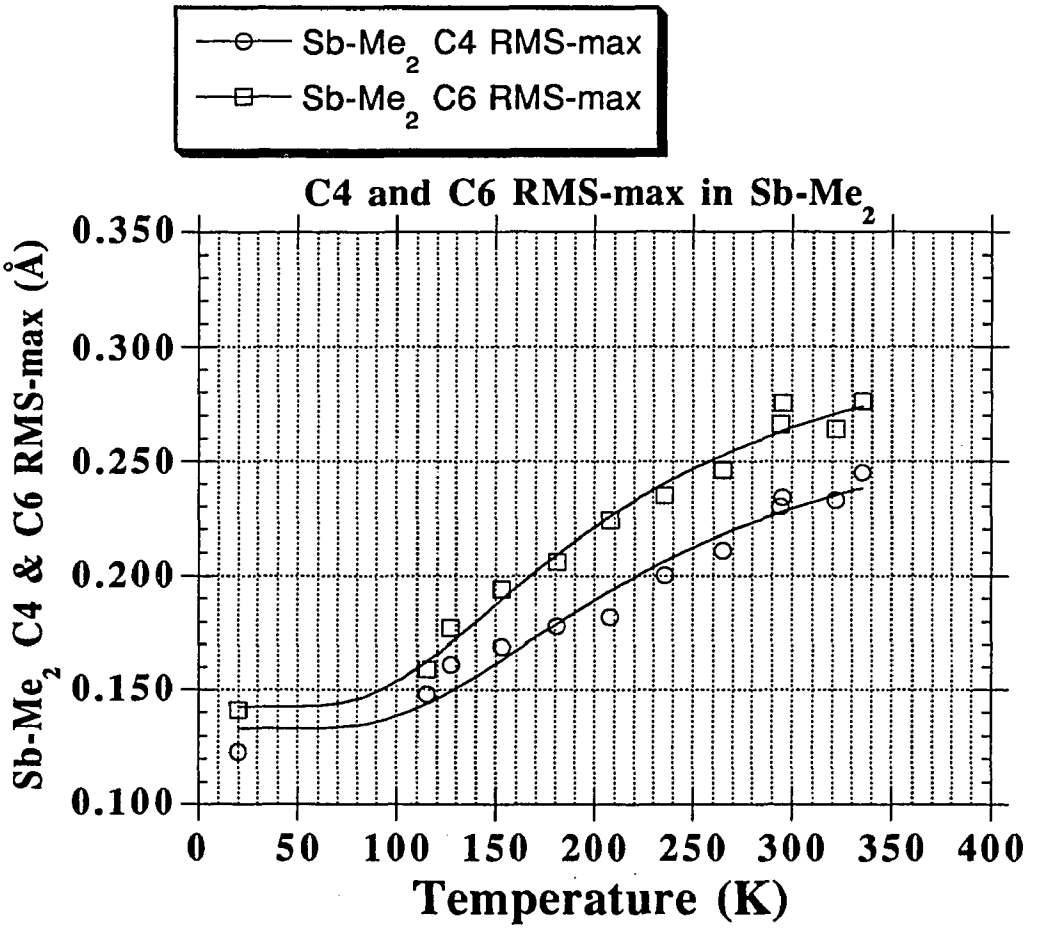


Figure 4–183. Plots of C4 RMS-max and C6 RMS-max in Sb-Me_2 versus temperature.

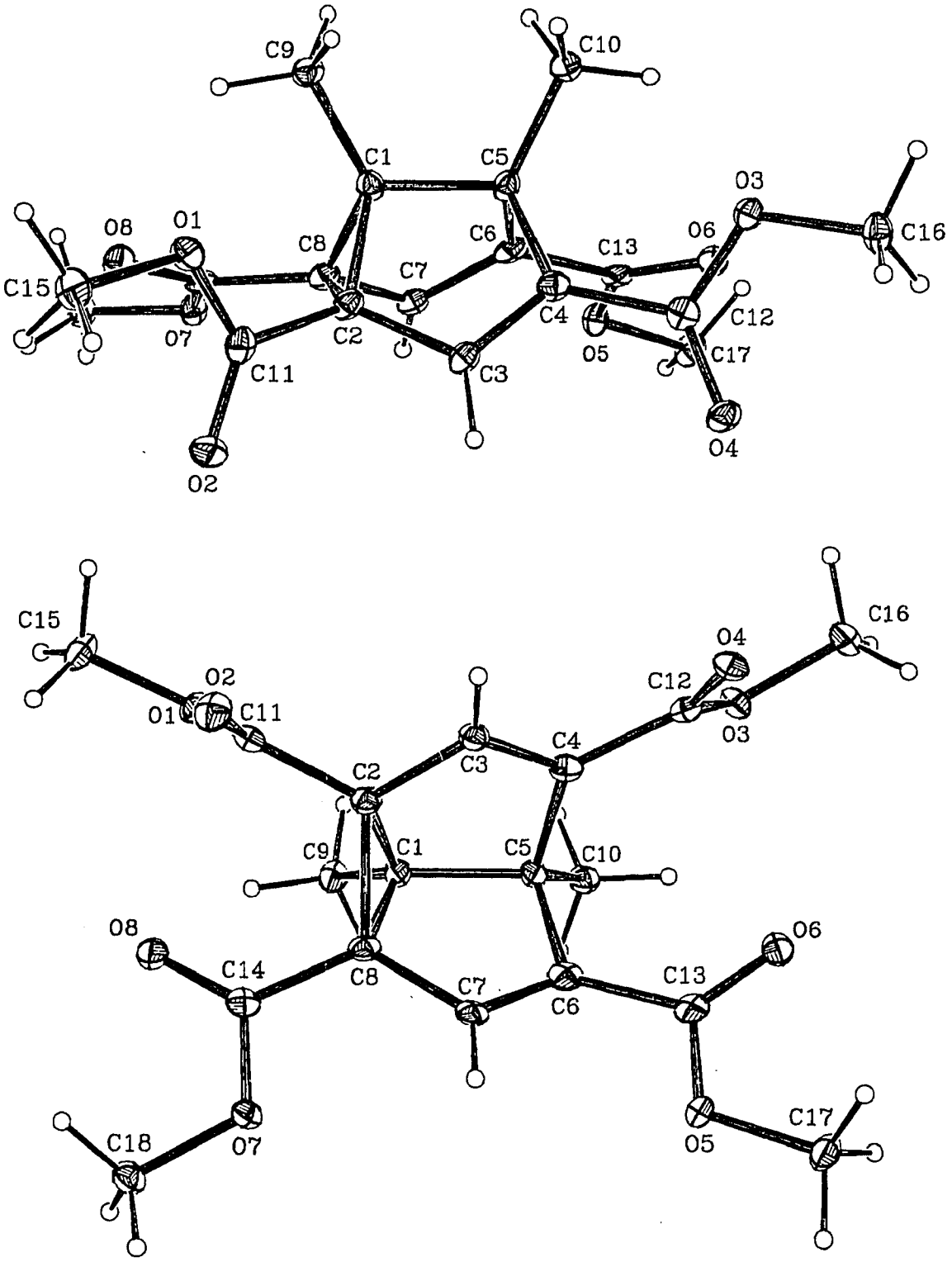


Figure 4–184. *ORTEP* drawings of Sb-Me_2 at **20 K** with 50% thermal ellipsoids.

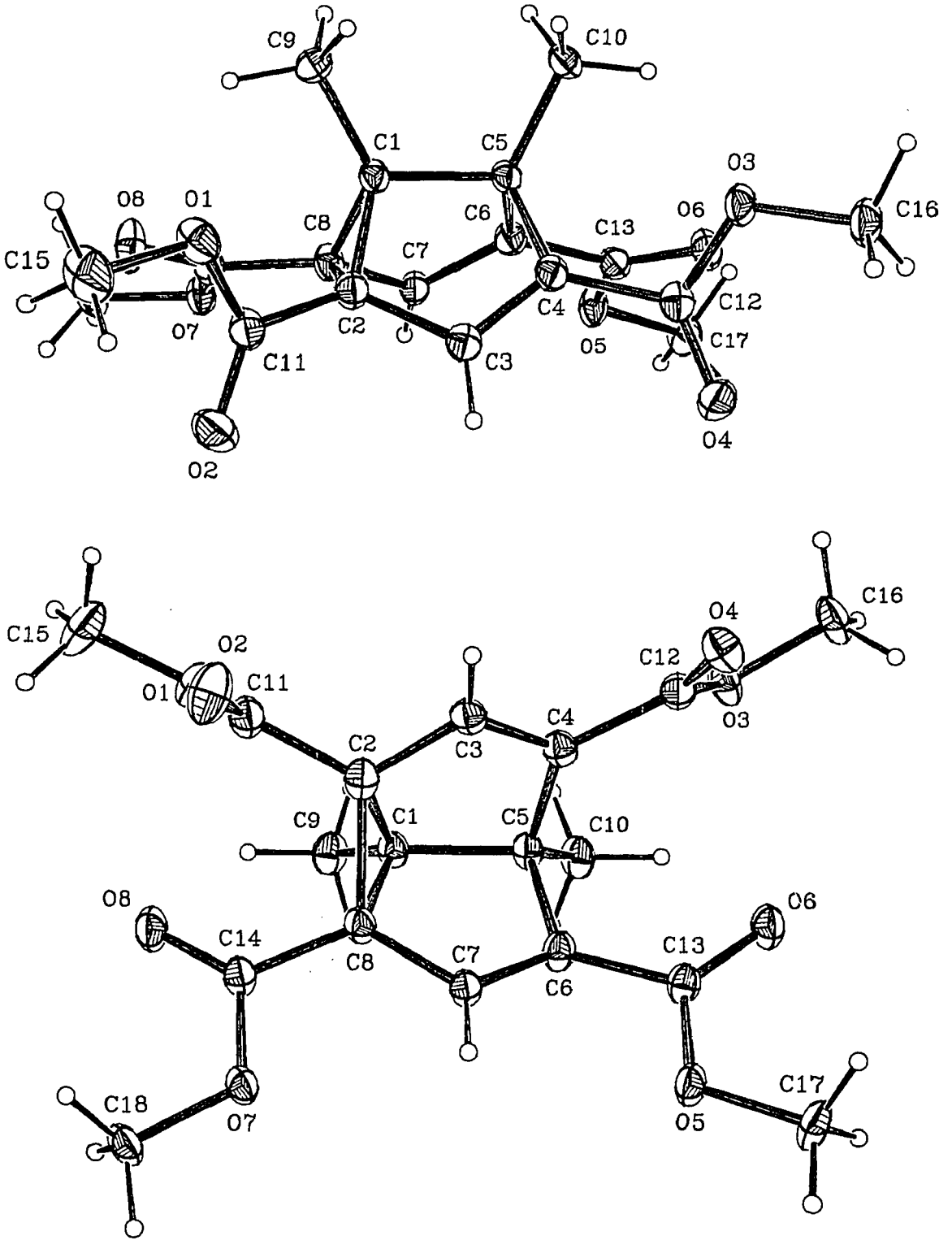


Figure 4–185. *ORTEP* drawings of Sb-Me_2 at **115 K** with 50% thermal ellipsoids.

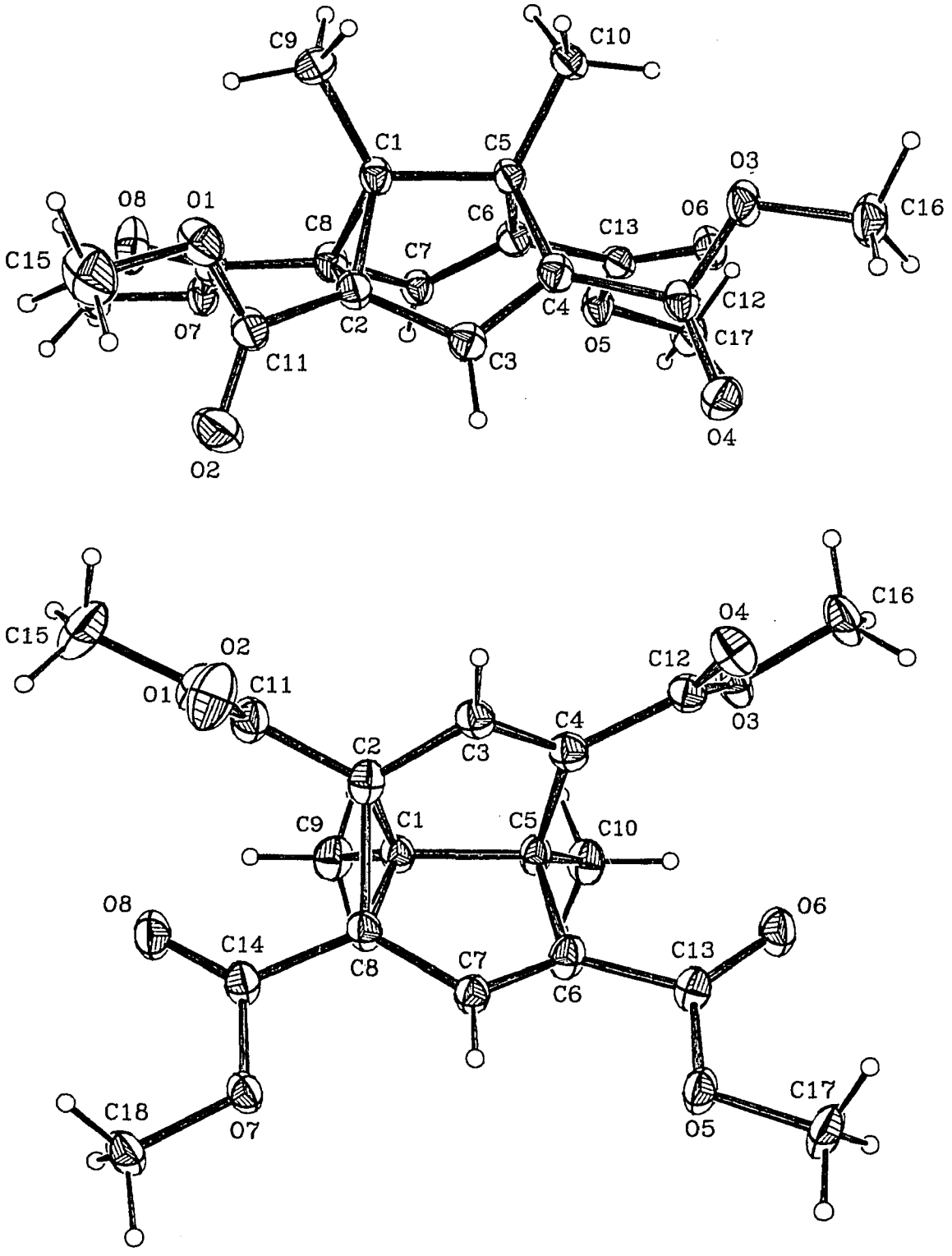


Figure 4–186. *ORTEP* drawings of Sb-Me_2 at **127 K** with 50% thermal ellipsoids.

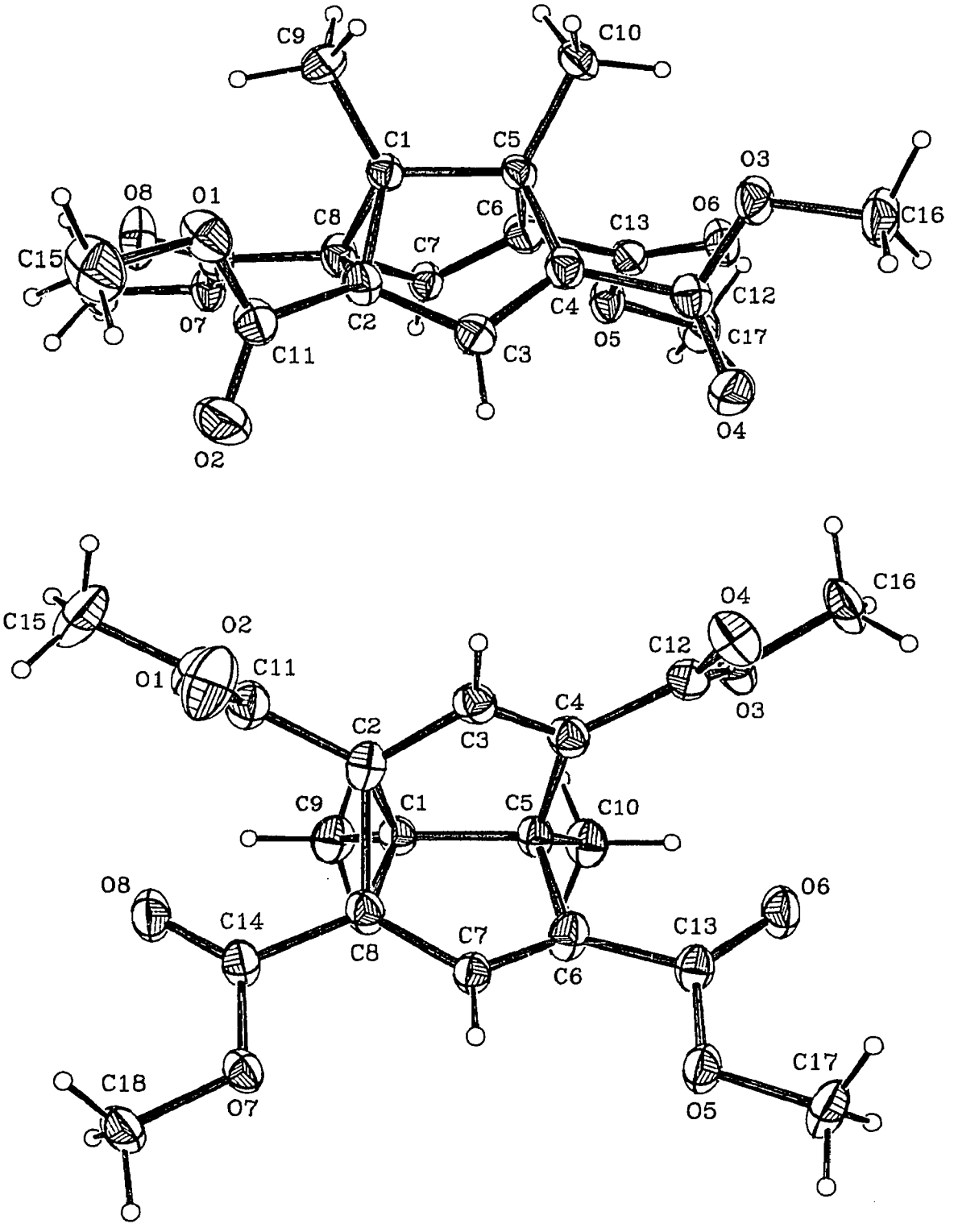


Figure 4–187. *ORTEP* drawings of Sb-Me_2 at **153 K** with 50% thermal ellipsoids.

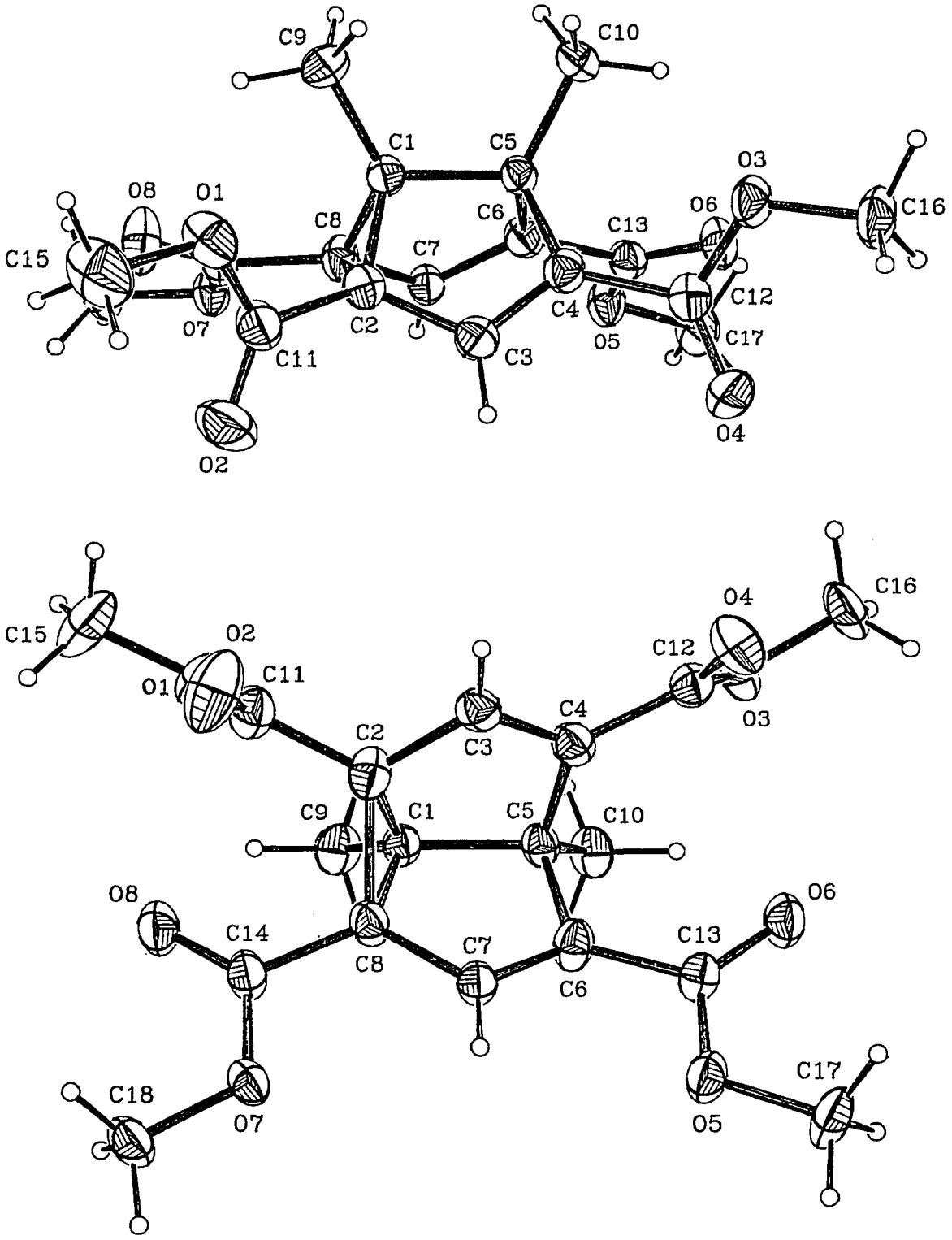


Figure 4–188. *ORTEP* drawings of Sb-Me_2 at **181 K** with 50% thermal ellipsoids.

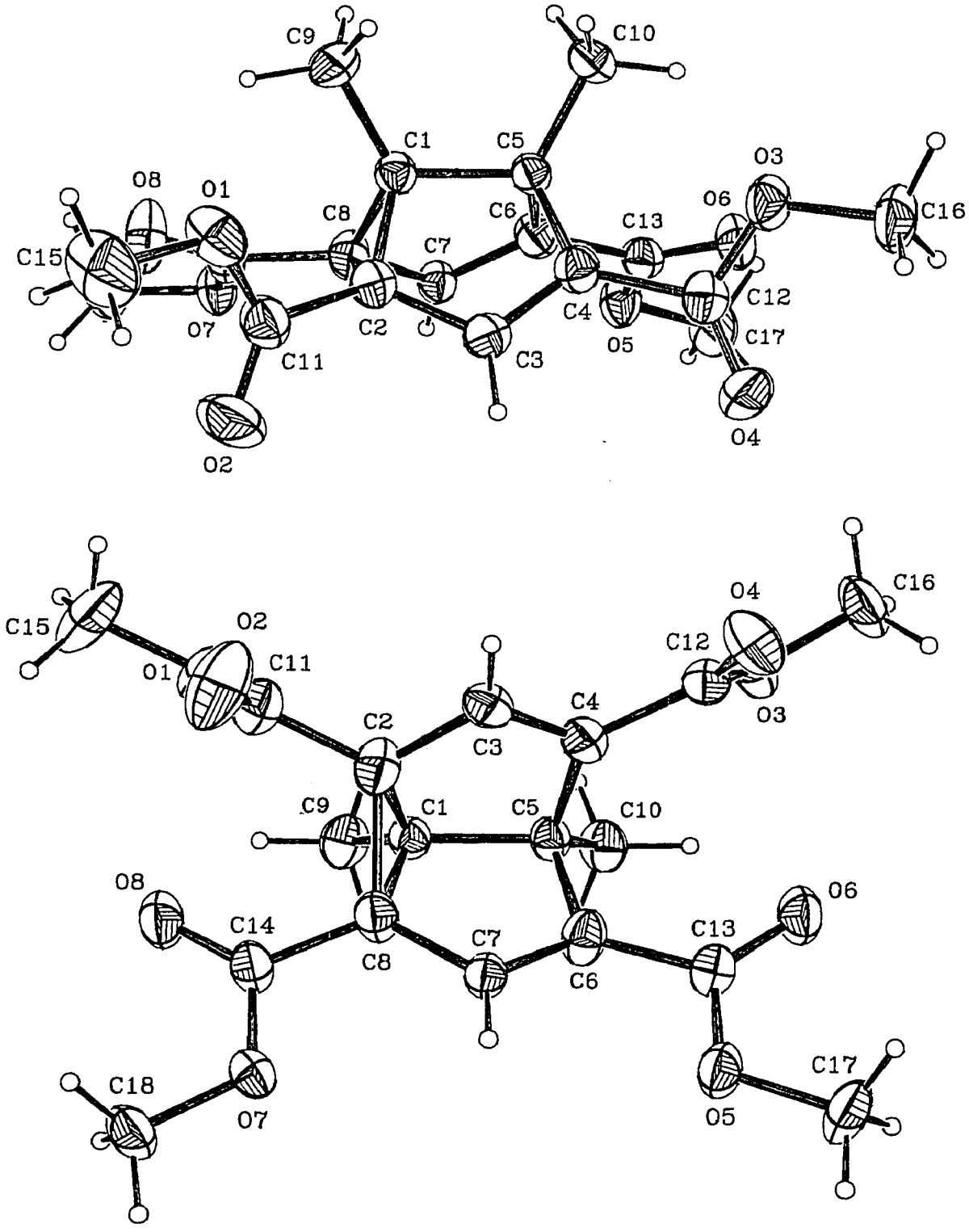


Figure 4–189. *ORTEP* drawings of Sb-Me_2 at **208 K** with 50% thermal ellipsoids.

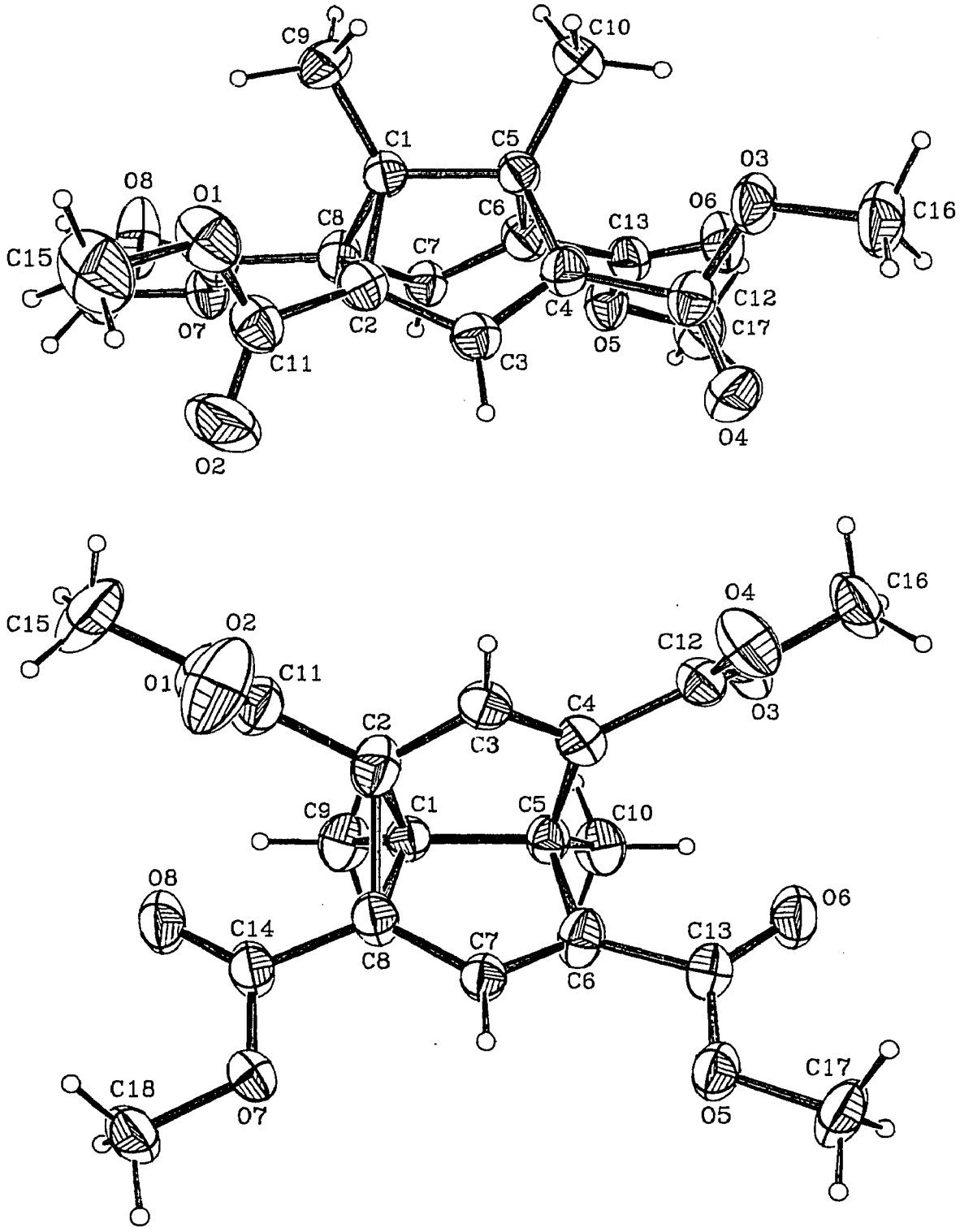


Figure 4–190. *ORTEP* drawings of Sb-Me_2 at **236 K** with 50% thermal ellipsoids.

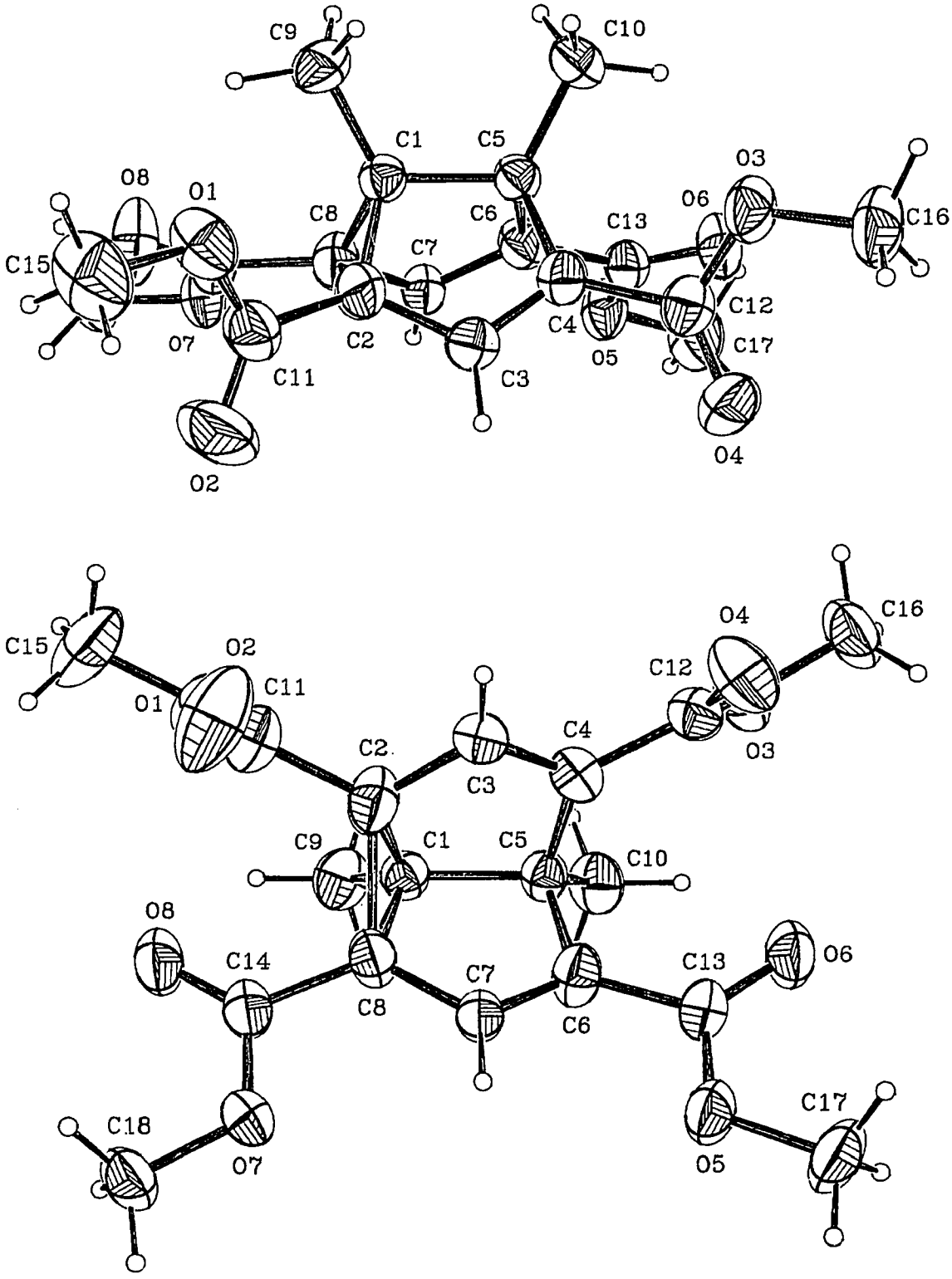


Figure 4–191. *ORTEP* drawings of Sb-Me_2 at **265 K** with 50% thermal ellipsoids.

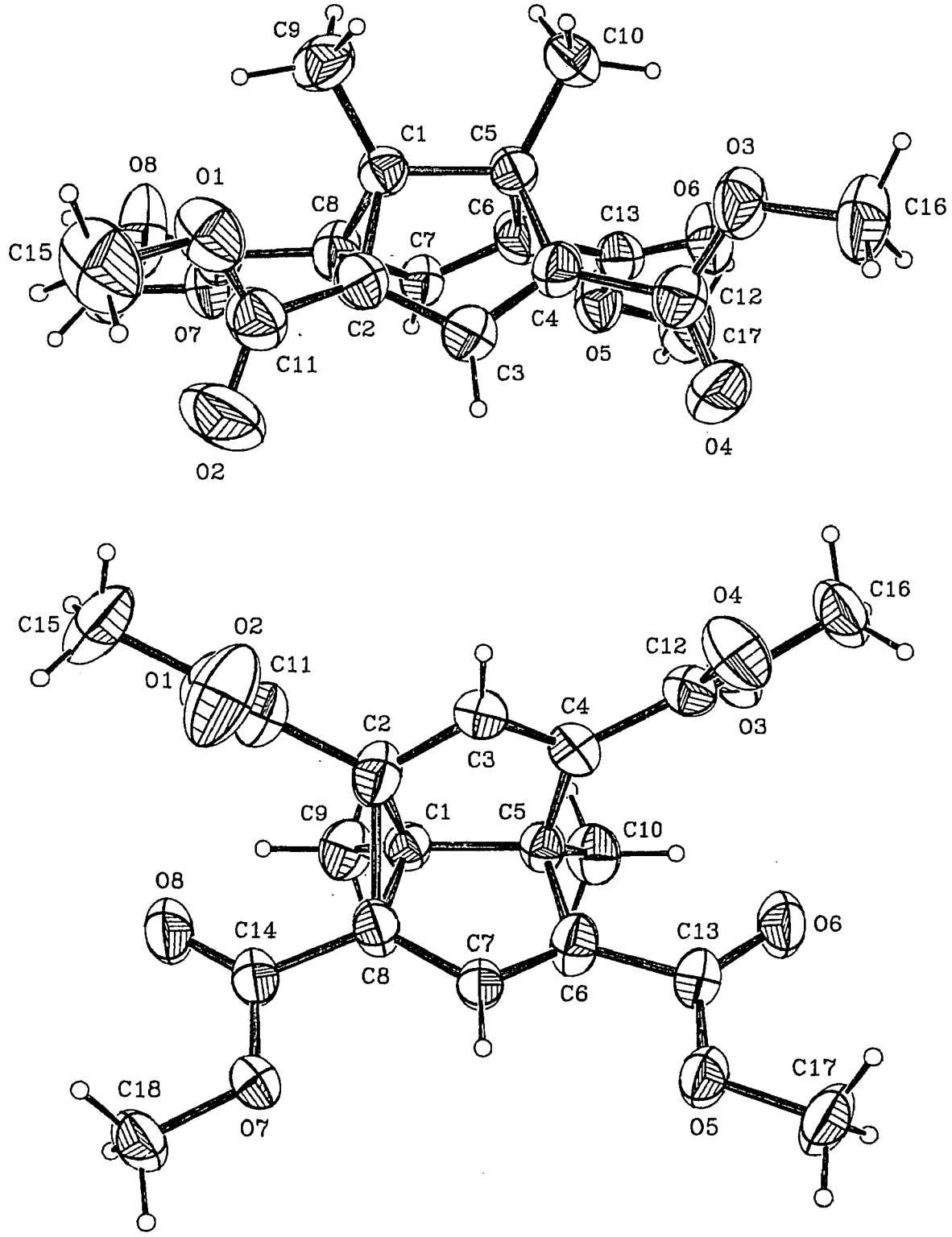


Figure 4–192. *ORTEP* drawings of Sb-Me_2 at **294 K** with 50% thermal ellipsoids.

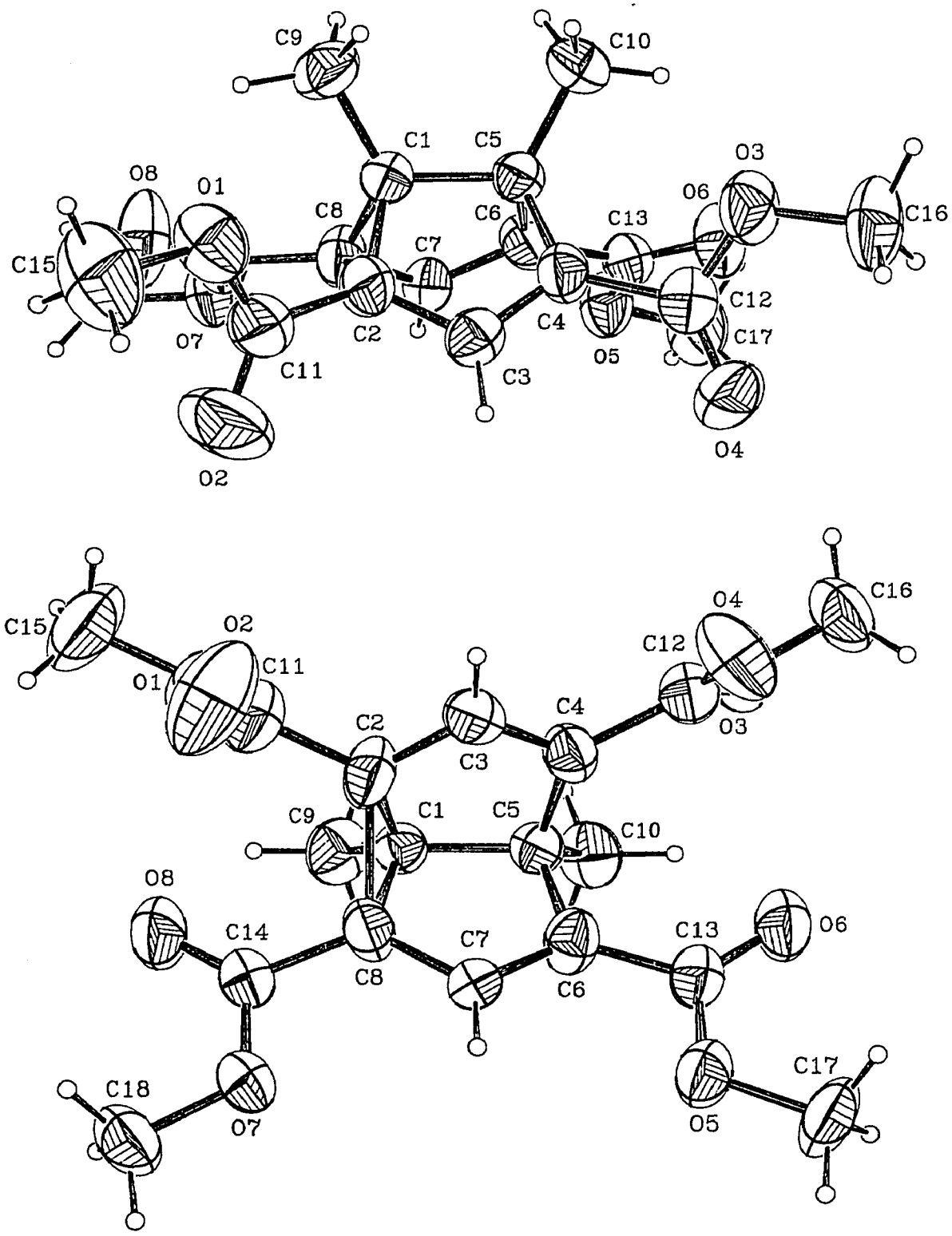


Figure 4–193. *ORTEP* drawings of Sb-Me_2 at **322 K** with 50% thermal ellipsoids.

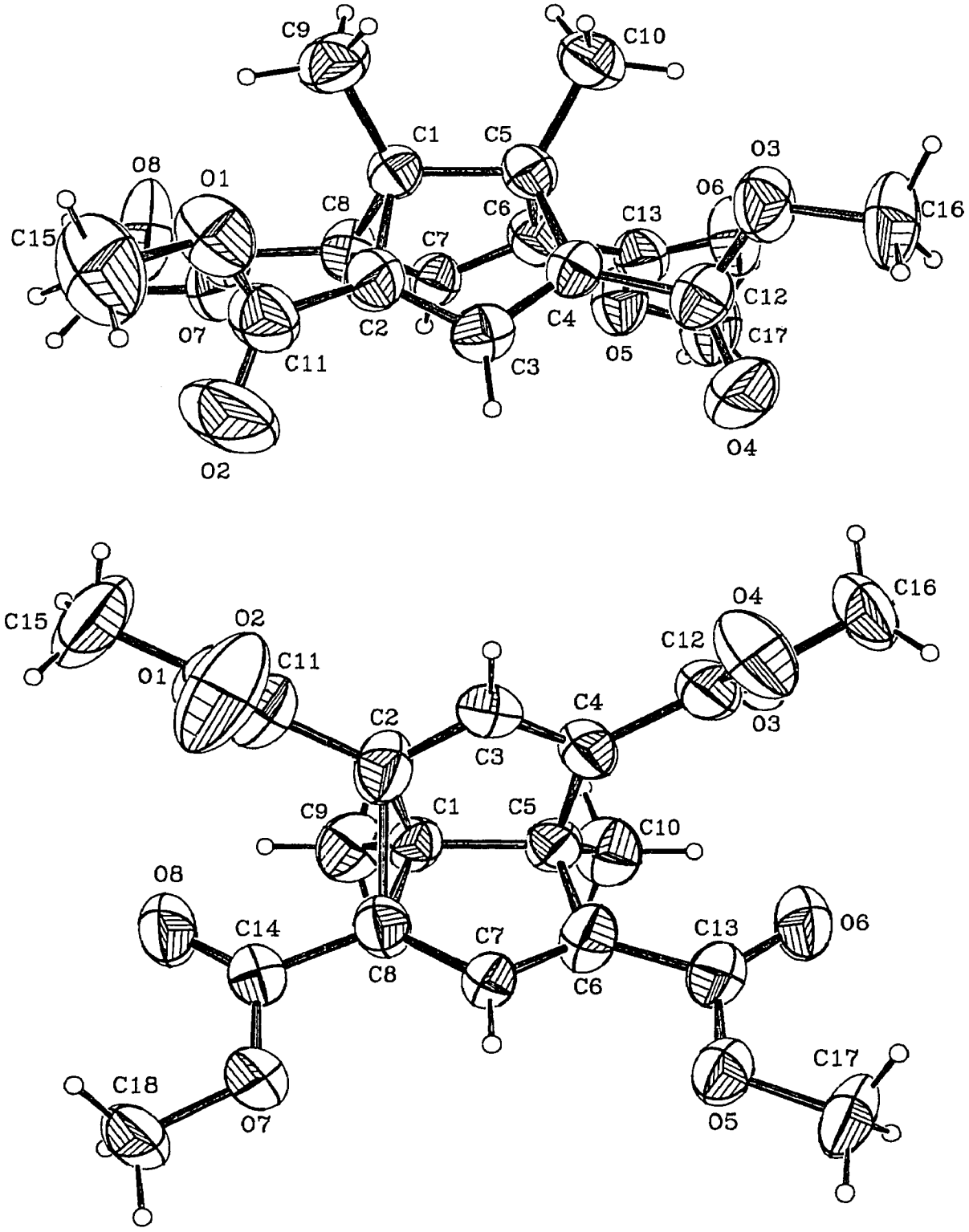


Figure 4–194. *ORTEP* drawings of Sb-Me_2 at **335 K** with 50% thermal ellipsoids.

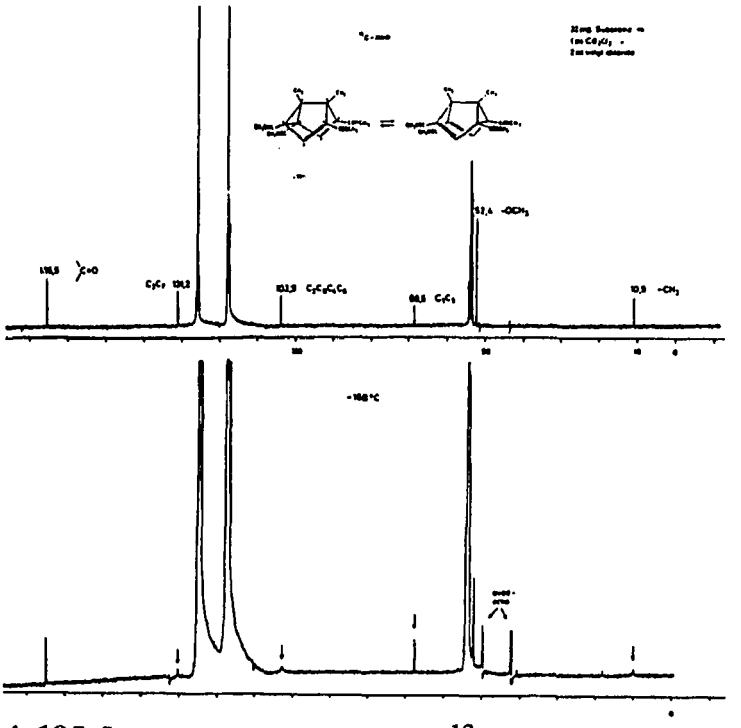


Figure 4–195. Low-temperature solution ^{13}C NMR spectra of Sb-Me_2.

^{13}C-CP-MAS-SPECTRUM OF 1,5-DIMETHYL-2,4,6,8-TETRACARBOMETHOXYSEMIBULLVALENE

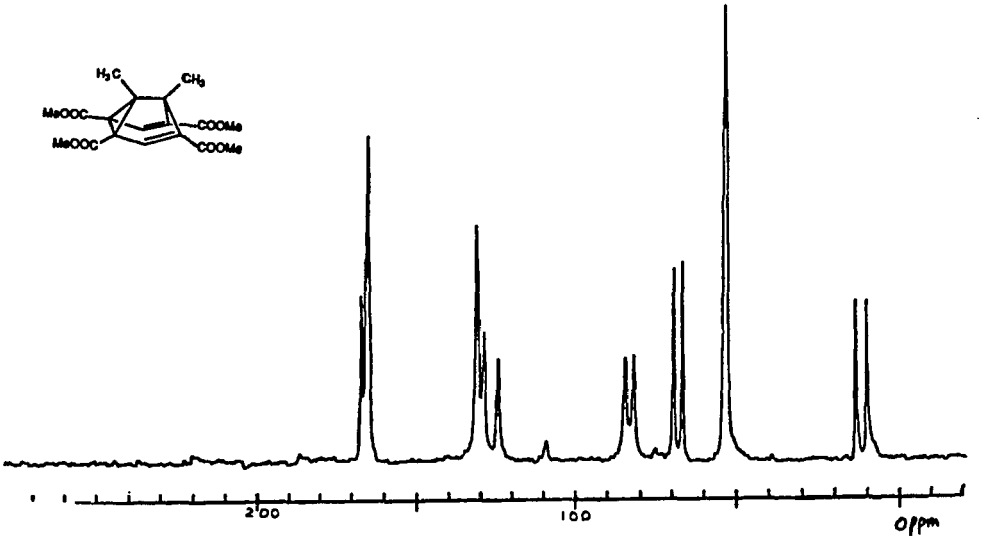
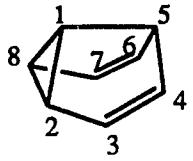


Figure 4–196. CP-MAS ^{13}C NMR spectrum of Sb-Me_2.

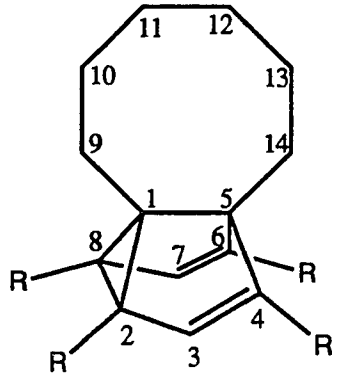
4.6 SB-8

If the hydrogens on the carbons, C1 and C5, in semibullvalene



Tricyclo[3.3.0.0^{2,8}]octa-3,6-diene
(Semibullvalene)

are replaced with a chain of six methylenes to form a eight-membered ring on top of semibullvalene and four ester groups replace the four hydrogens at C2, C4, C6, and C8, we obtain the annulated compound **1,5-cyclooctano-2,4,6,8-tetracarbomethoxy semibullvalene** or simply Sb-8.



R = $COOCH_3$
1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

The X-ray crystal data for Sb-8 are summarized in Table 4–25.

Table 4–25. X-ray Crystal Data for Sb-8 at Various Temperatures

	20 K	**115 K[a]**	**115 K[b]**
Formula	$C_{22}H_{26}O_8$	$C_{22}H_{26}O_8$	$C_{22}H_{26}O_8$
Formula weight	418.45	418.45	418.45
Melting point (°C)	170–171	170–171	170–171
Crystal size (mm)	0.32 x 0.40 x 0.50	0.08 x 0.10 x 0.59	0.08 x 0.10 x 0.59
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	10.498(8)	10.529(4)	10.531(1)
b (Å)	14.388(13)	14.481(3)	14.4971)
c (Å)	14.129(11)	14.121(9)	14.099(5)
β (°)	109.21(2)	109.36(4)	109.20(1)
Cell volume (Å^3)	2015.21	2031.37(25.47)	2032.69(6.9)
Z	4	4	4
d_{calc} (g cm^{-3})	1.379	1.365	1.367
μ(Cu $K\alpha$) (cm^{-1})	0.98 (Mo)	8.28	8.29
R	0.055	0.036	0.051
R_w	0.064	0.046	0.063

[a] This data collection at **115 K** was first in the sequence **115 K,** 153 K, 181 K, 208 K, 236 K, 265 K, 279 K, 294 K, 140 K, 127 K, 115 K.

[b] This data collection at **115 K** was last in the sequence 115 K, 153 K, 181 K, 208 K, 236 K, 265 K, 279 K, 294 K, 140 K, 127 K, **115 K.**

Table 4–25 (cont'd). X-ray Crystal Data for Sb-8 at Various Temperatures

	127 K	**140 K**	**153 K**
Formula	$C_{22}H_{26}O_8$	$C_{22}H_{26}O_8$	$C_{22}H_{26}O_8$
Formula weight	418.45	418.45	418.45
Melting point (°C)	170–171	170–171	170–171
Crystal size (mm)	0.08 x 0.10 x 0.59	0.08 x 0.10 x 0.59	0.08 x 0.10 x 0.59
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	10.538(1)	10.548(1)	10.554(1)
b (Å)	14.528(1)	14.563(1)	14.598(1)
c (Å)	14.106(6)	14.101(3)	14.108(4)
β (°)	109.21(1)	109.30(1)	109.33(1)
Cell volume (Å^3)	2039.23(7.76)	2044.33(7.94)	2051.15(8.75)
Z	4	4	4
d_{calc} (g cm^{-3})	1.363	1.359	1.355
μ(Cu $K\alpha$) (cm^{-1})	8.26	8.24	8.22
R	0.042	0.040	0.040
R_w	0.053	0.047	0.046

Table 4–25 (cont'd). X-ray Crystal Data for Sb-8 at Various Temperatures

	181 K	**208 K**	**236 K**
Formula	$C_{22}H_{26}O_8$	$C_{22}H_{26}O_8$	$C_{22}H_{26}O_8$
Formula weight	418.45	418.45	418.45
Melting point (°C)	170–171	170–171	170–171
Crystal size (mm)	0.08 x 0.10 x 0.59	0.08 x 0.10 x 0.59	0.08 x 0.10 x 0.59
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	10.567(1)	10.578(1)	10.587(1)
b (Å)	14.663(1)	14.726(1)	14.784(1)
c (Å)	14.118(3)	14.145(2)	14.170(2)
β (°)	109.40(1)	109.47(1)	109.53(1)
Cell volume (Å^3)	2063.38(7.25)	2077.44(5.74)	2090.40(4.57)
Z	4	4	4
d_{calc} (g cm^{-3})	1.347	1.338	1.330
μ(Cu $K\alpha$) (cm^{-1})	8.17	8.11	8.06
R	0.040	0.041	0.042
R_w	0.047	0.048	0.048

Table 4–25 (cont'd). X-ray Crystal Data for Sb-8 at Various Temperatures

	265 K	**279 K**	**294 K**
Formula	$C_{22}H_{26}O_8$	$C_{22}H_{26}O_8$	$C_{22}H_{26}O_8$
Formula weight	418.45	418.45	418.45
Melting point (°C)	170–171	170–171	170–171
Crystal size (mm)	0.08 x 0.10 x 0.59	0.08 x 0.10 x 0.59	0.08 x 0.10 x 0.59
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	10.597(1)	10.602(1)	10.607(1)
b (Å)	14.841(1)	14.870(1)	14.899(1)
c (Å)	14.200(1)	14.215(2)	14.230(1)
β (°)	109.60(1)	109.64(1)	109.68(1)
Cell volume (Å^3)	2103.84(3.53)	2110.61(3.69)	2117.40(3.19)
Z	4	4	4
d_{calc} (g cm^{-3})	1.321	1.317	1.313
μ(Cu $K\alpha$) (cm^{-1})	8.01	7.98	7.96
R	0.043	0.044	0.044
R_w	0.048	0.050	0.049

Table 4–25 (cont'd). X-ray Crystal Data for Sb-8 at Various Temperatures

	295 K	**295 K**	**335 K**
Formula	$C_{22}H_{26}O_8$	$C_{22}H_{26}O_8$	$C_{22}H_{26}O_8$
Formula weight	418.45	418.45	418.45
Melting point (°C)	170–171	170–171	170–171
Crystal size (mm)	0.12 x 0.20 x 0.67	0.18 x 0.33 x 0.40	0.12 x 0.24 x 0.40
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	10.607(1)	10.602(2)	10.616(1)
b (Å)	14.890(1)	14.893(2)	14.963(1)
c (Å)	14.228(1)	14.223(3)	14.27(6)
β (°)	109.72(1)	109.66(2)	109.80(1)
Cell volume (Å^3)	2115.34(16.8)	2114.91(11.94)	2132.88(11.08)
Z	4	4	4
d_{calc} (g cm^{-3})	1.314	1.314	1.303
μ(Cu $K\alpha$) (cm^{-1})	7.97	7.97	7.90
R	0.046	0.052	0.053
R_w	0.059	0.064	0.058

Table 4–25 (cont'd). X-ray Crystal Data for Sb-8 at Various Temperatures

	360 K
Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170–171
Crystal size (mm)	0.10 x 0.25 x 0.27
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.631(1)
b (Å)	15.018(3)
c (Å)	14.290(4)
β (°)	109.88(1)
Cell volume (Å^3)	2145.55(10.51)
Z	4
d_{calc} (g cm^{-3})	1.295
μ(Cu $K\alpha$) (cm^{-1})	7.85
R	0.046
R_w	0.052

The unit-cell volume of Sb-8 in Figure 4–197 is flat from 0 to about 75 K but thereafter expands linearly with temperature.

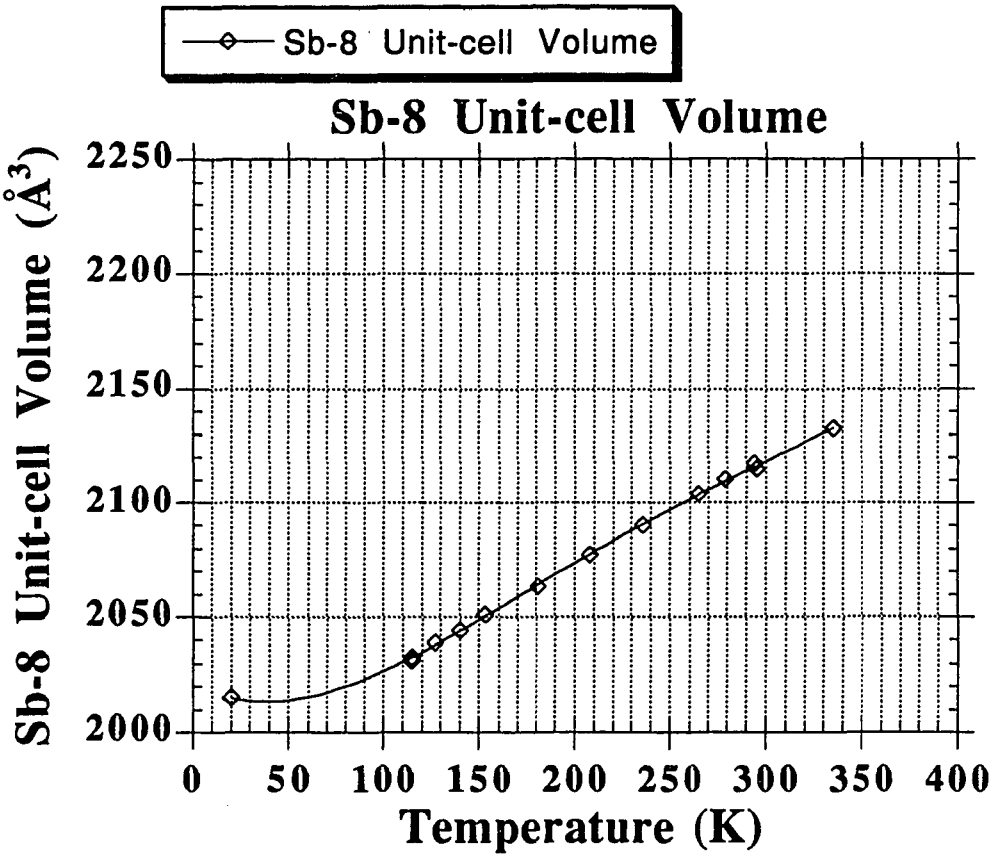


Figure 4–197. A plot of Sb-8 unit-cell volume versus temperature.

For the purpose of comparing Sb-8 with the other five compounds, we eliminate the point at the 20 K and fit the remaining volume-temperature data points of Sb-8 with a straight line as in Figure 4–198.

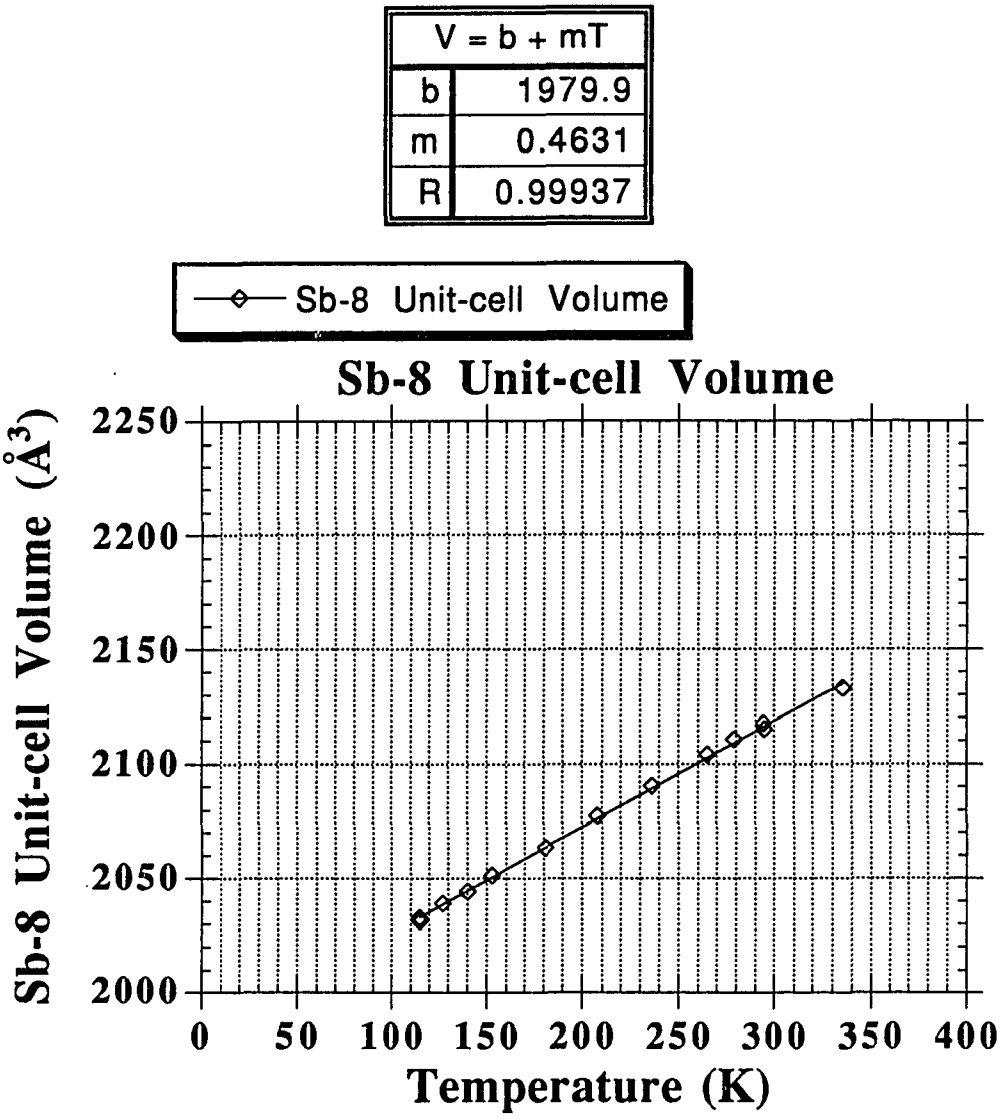


Figure 4–198. A linear plot of Sb-8 unit-cell volume versus temperature.

According to the slope in Figure 4–198, the unit-cell volume of Sb-6 expands at the rate of 4.6 $Å^3$ for every 10 °C rise in temperature for four molecules in the unit cell (120 non-H's and 104 H's).

As expected, the density of Sb-8 in Figure 4–199 decreases with increasing temperature as the volume expands.

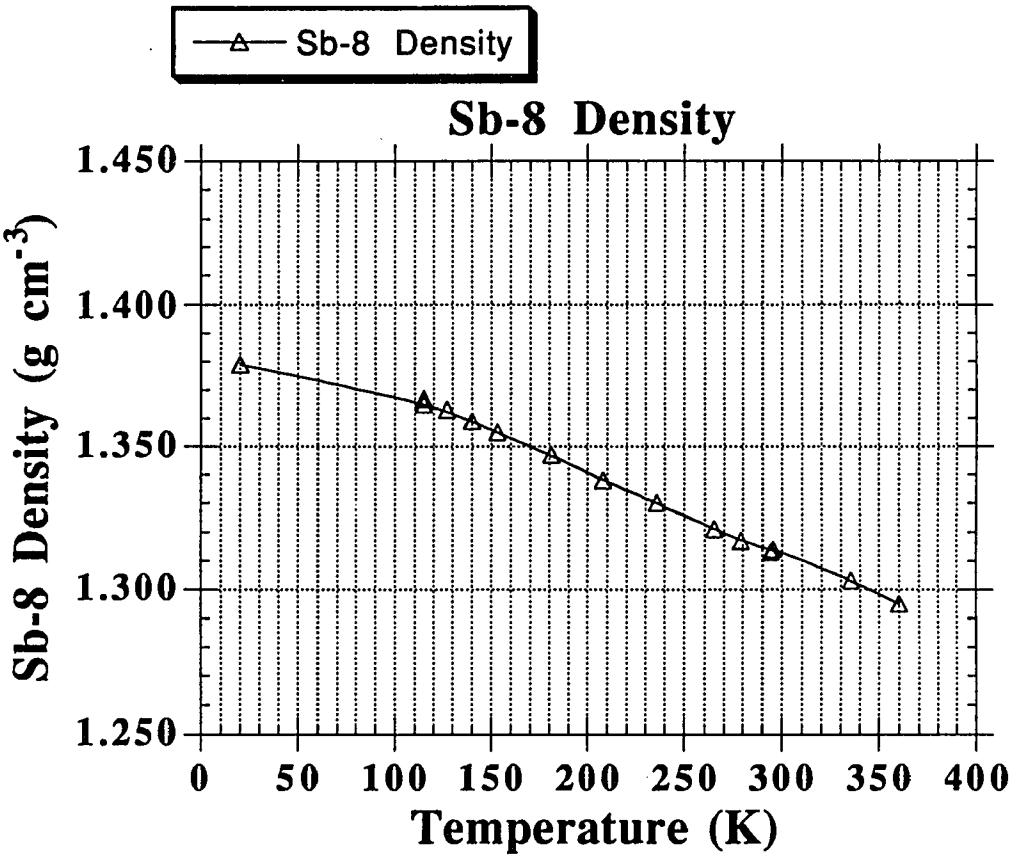


Figure 4–199. A plot of Sb-8 density versus temperature.

The interatomic distances in the semibullvalene ring of Sb-8 in Table 4–26 tell the same story as the corresponding data in the previous compounds, that is, the bond distance C2—C8 elongates and C4—C6 becomes shorter as the temperature increases. At the same time, the double bonds C3—C4 and C6—C7 become more delocalized and the single bonds C2—C3 and C7—C8 acquire more double bond character. The single bonds C1—C5 and C3—C7 meanwhile remain unchanged throughout the same temperature range. The graphs based on Tables 4–26 depict this behavior in Sb-8.

Table 4–26. Selected Interatomic Distances (Å) in the Ring of Sb-8 at Various Temperatures

	20 K	**115 K**	**115 K**	**127 K**	**140 K**	**153 K**
C1—C2	1.526(4)	1.523(3)	1.518(5)	1.519(4)	1.517(4)	1.514(4)
C1—C5	1.585(5)	1.582(3)	1.586(4)	1.588(3)	1.585(3)	1.581(3)
C1—C8	1.495(5)	1.495(3)	1.490(5)	1.497(4)	1.493(4)	1.496(4)
C2—C3	1.452(5)	1.441(3)	1.450(4)	1.424(3)	1.421(3)	1.419(3)
C2—C8	1.675(5)	1.722(3)	1.741(5)	1.772(4)	1.798(4)	1.825(4)
C3—C4	1.337(5)	1.345(3)	1.348(5)	1.353(4)	1.353(4)	1.360(4)
C3—C7	3.031	3.023(3)	3.023(5)	3.024(4)	3.028(3)	3.029(3)
C4—C5	1.546(5)	1.537(3)	1.522(5)	1.526(4)	1.528(3)	1.524(3)
C4—C6	2.297(5)	2.244(3)	2.231(5)	2.199(4)	2.173(4)	2.145(4)
C5—C6	1.536(5)	1.532(3)	1.528(5)	1.523(4)	1.523(4)	1.525(4)
C6—C7	1.334(5)	1.344(3)	1.346(5)	1.353(4)	1.355(4)	1.363(4)
C7—C8	1.454(5)	1.440(3)	1.443(4)	1.432(3)	1.421(3)	1.410(3)
C2—C3 + C3—C4	2.789	2.786	2.798	2.777	2.774	2.779
C6—C7 + C7—C8	2.788	2.784	2.789	2.785	2.776	2.773
C2—C8 + C4—C6	3.972	3.966	3.972	3.971	3.971	3.970

Table 4–26 (cont'd). Selected Interatomic Distances (Å) in the Ring of Sb-8 at Various Temperatures

	181 K	**208 K**	**236 K**	**265 K**	**279 K**	**294 K**
C1—C2	1.514(4)	1.517(4)	1.516(4)	1.510(5)	1.515(5)	1.512(5)
C1—C5	1.585(3)	1.587(3)	1.587(3)	1.592(4)	1.581(4)	1.587(4)
C1—C8	1.497(4)	1.503(4)	1.499(4)	1.497(5)	1.503(5)	1.508(5)
C2—C3	1.405(3)	1.400(3)	1.392(3)	1.386(3)	1.388(4)	1.383(4)
C2—C8	1.875(4)	1.918(5)	1.949(5)	1.967(5)	1.978(5)	1.990(5)
C3—C4	1.366(4)	1.372(4)	1.374(4)	1.378(4)	1.379(5)	1.381(5)
C3—C7	3.024(4)	3.030(4)	3.026(4)	3.037(4)	3.032(4)	3.033(5)
C4—C5	1.519(4)	1.520(4)	1.520(4)	1.518(4)	1.519(4)	1.512(5)
C4—C6	2.098(4)	2.064(4)	2.034(5)	2.013(5)	2.002(5)	1.987(5)
C5—C6	1.515(4)	1.512(4)	1.508(4)	1.505(4)	1.502(5)	1.500(5)
C6—C7	1.363(4)	1.363(4)	1.376(4)	1.376(5)	1.379(5)	1.381(5)
C7—C8	1.403(3)	1.402(3)	1.389(4)	1.384(4)	1.388(4)	1.383(4)
C2—C3 + C3—C4	2.771	2.772	2.7660	2.764	2.767	2.764
C6—C7 + C7—C8	2.766	2.765	2.765	2.760	2.767	2.764
C2—C8 + C4—C6	3.973	3.982	3.983	3.980	3.980	3.977

Table 4–26 (cont'd). Selected Interatomic Distances (Å) in the Ring of Sb-8 at Various Temperatures

	295 K	**295 K**	**335 K**	**360 K**
C1—C2	1.517(3)	1.515(3)	1.510(7)	1.511(6)
C1—C5	1.577(3)	1.578(3)	1.585(6)	1.583(5)
C1—C8	1.499(3)	1.499(3)	1.502(7)	1.505(6)
C2—C3	1.389(2)	1.387(2)	1.399(5)	1.385(4)
C2—C8	1.990(4)	1.990(4)	2.001(7)	2.017(6)
C3—C4	1.378(3)	1.382(3)	1.373(7)	1.385(5)
C3—C7	3.035(3)	3.035(3)	3.040(6)	3.040(6)
C4—C5	1.522(3)	1.517(3)	1.501(6)	1.514(5)
C4—C6	1.996(4)	1.991(4)	1.973(7)	1.974(6)
C5—C6	1.505(3)	1.503(3)	1.510(7)	1.496(6)
C6—C7	1.381(3)	1.377(3)	1.378(7)	1.391(6)
C7—C8	1.389(3)	1.387(3)	1.384(6)	1.379(5)
C2—C3 + C3—C4	2.767	2.769	2.772	2.770
C6—C7 + C7—C8	2.770	2.764	2.762	2.770
C2—C8 + C4—C6	3.986	3.981	3.974	3.991

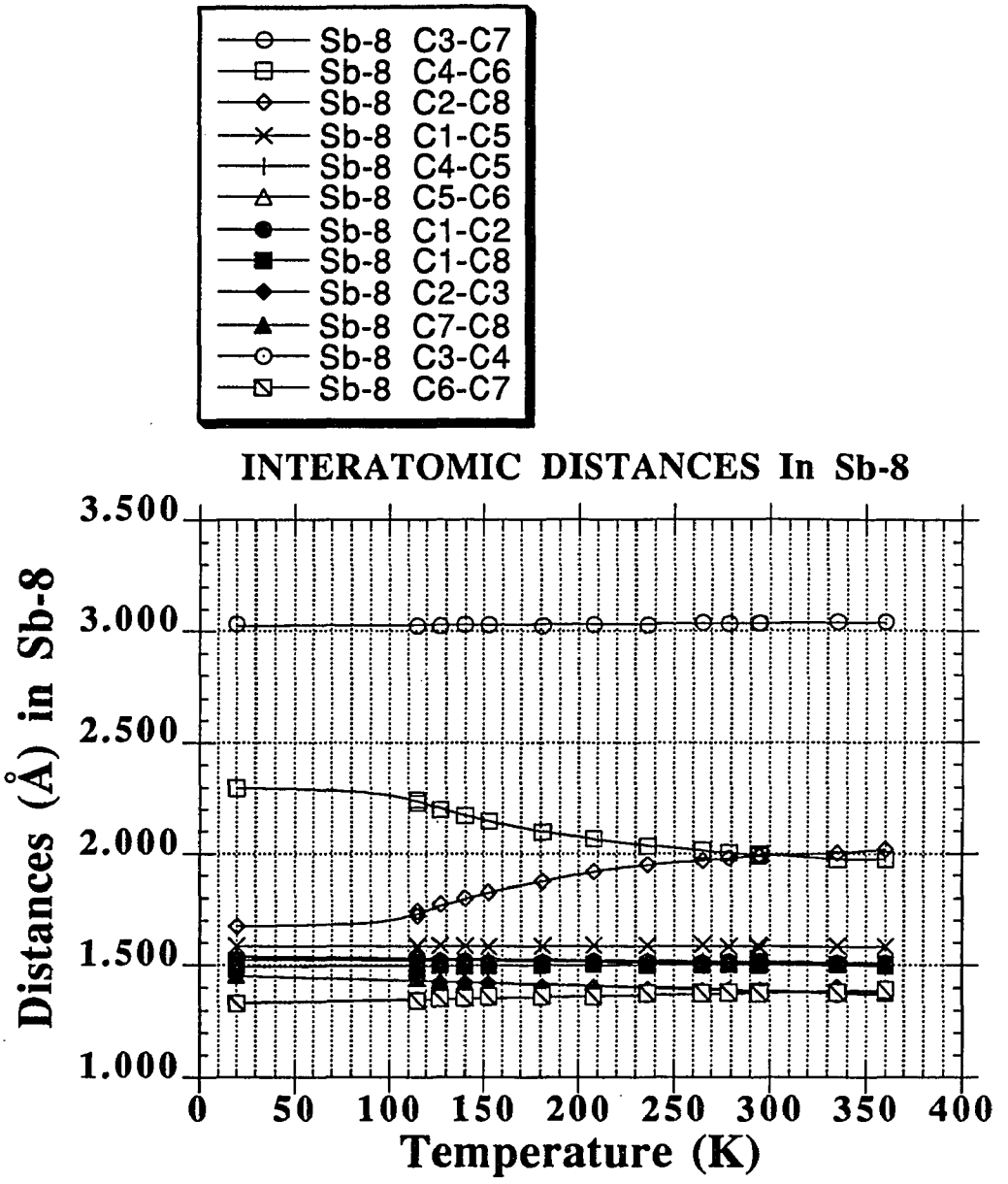


Figure 4–200. Plots of selected interatomic distances in the semibullvalene ring of Sb-8 versus temperature.

The interatomic distances C3—C7 and C1—C5 in Sb-8 are virtually unchanged throughout the temperature range from 20 to 360 K, as shown in Figure 4–201.

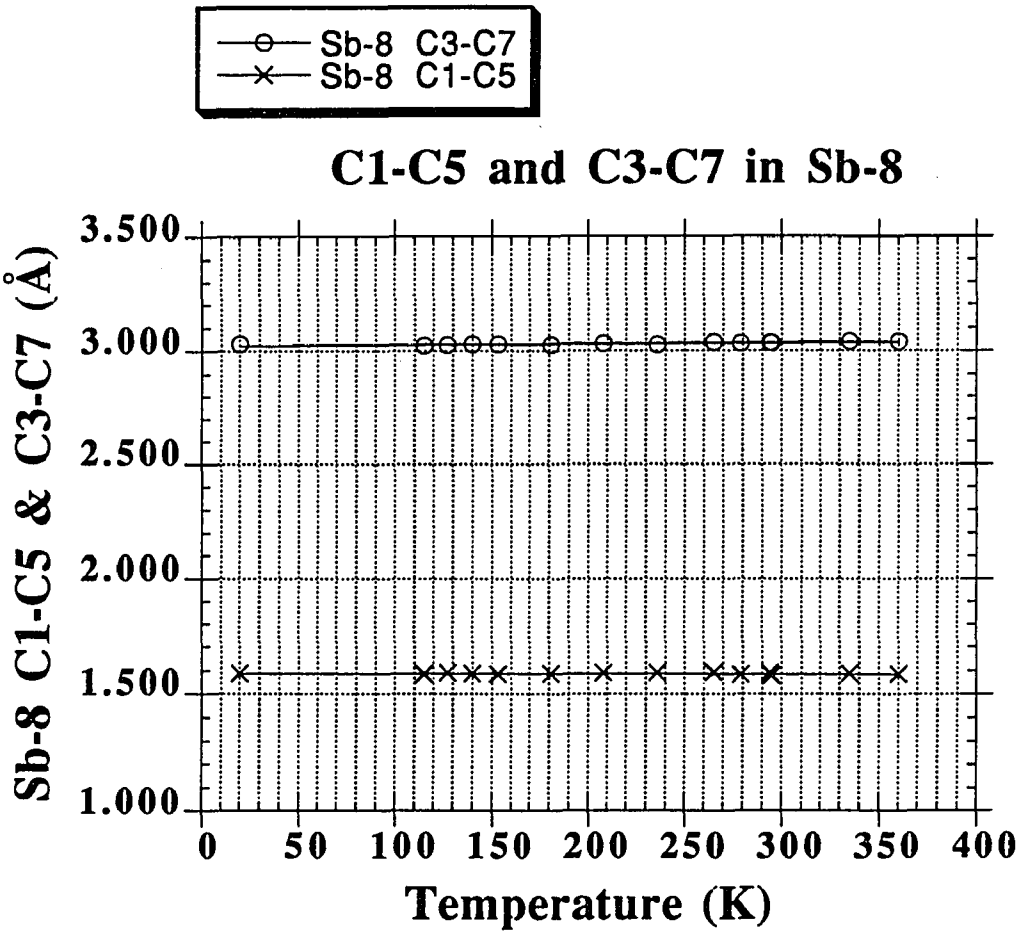


Figure 4–201. Plots of C1—C5 and C3—C7 distances in Sb-8 versus temperature.

Small changes occur in bond lengths from the bridgehead carbons C1 and C5 to their respective bonded atoms (C1—C2 and C1—C8, C5-C4 and C5—C6) as illustrated in Figures 4-202 and 4–203. The reasons for the minute contractions and elongations are obscure.

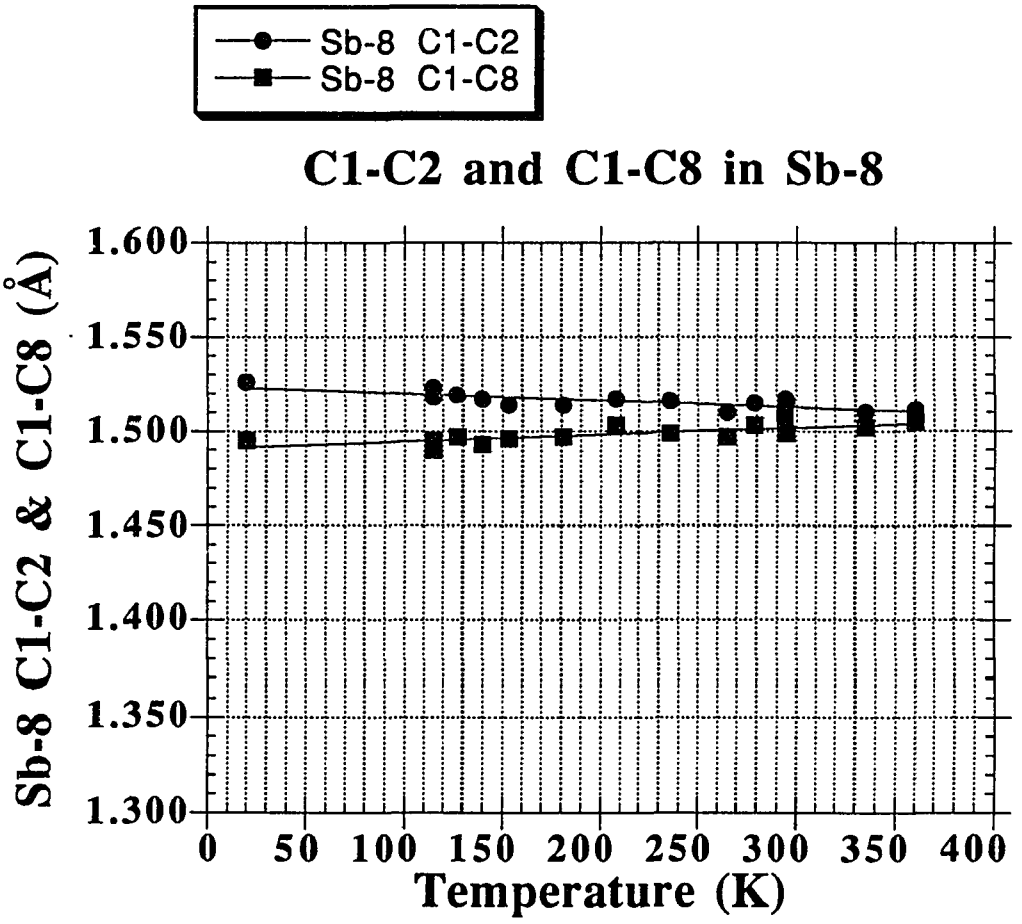


Figure 4–202. Plots of C1—C2 and C1—C8 distances in Sb-8 versus temperature.

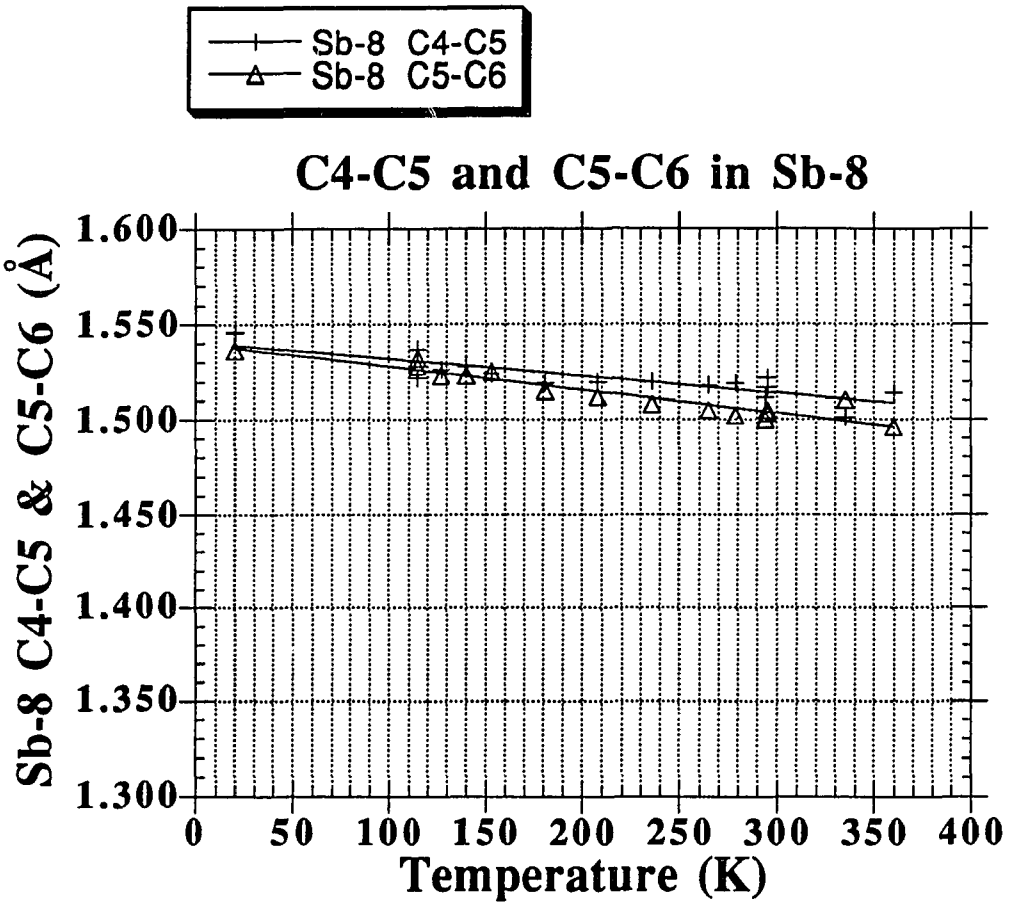


Figure 4–203. Plots of C4—C5 and C5—C6 distances in Sb-8 versus temperature.

For the first time, we see in Sb-8 that the single and double bonds in the semibullvalene ring of Sb-8 in Figures 4–204 and 206 converge to the same value of approximately 1.39 Å, which is almost equal to the benzene bond distance of 1.398 Å from neutron diffraction. Actually, bond distances of benzene from X-ray diffraction in Chapter 1 appear to be shorter when they are left uncorrected for thermal motion. Perhaps, structural parameters of Sb-8 should also corrected for thermal motion to improve the comparison with benzene itself! Also, it is clear from the graphs in Figures 4–204, 205, 206, and 207 that the single and double bonds converge almost symmetrically, that is, the single bonds become shorter by the same amount as the double bonds become longer.

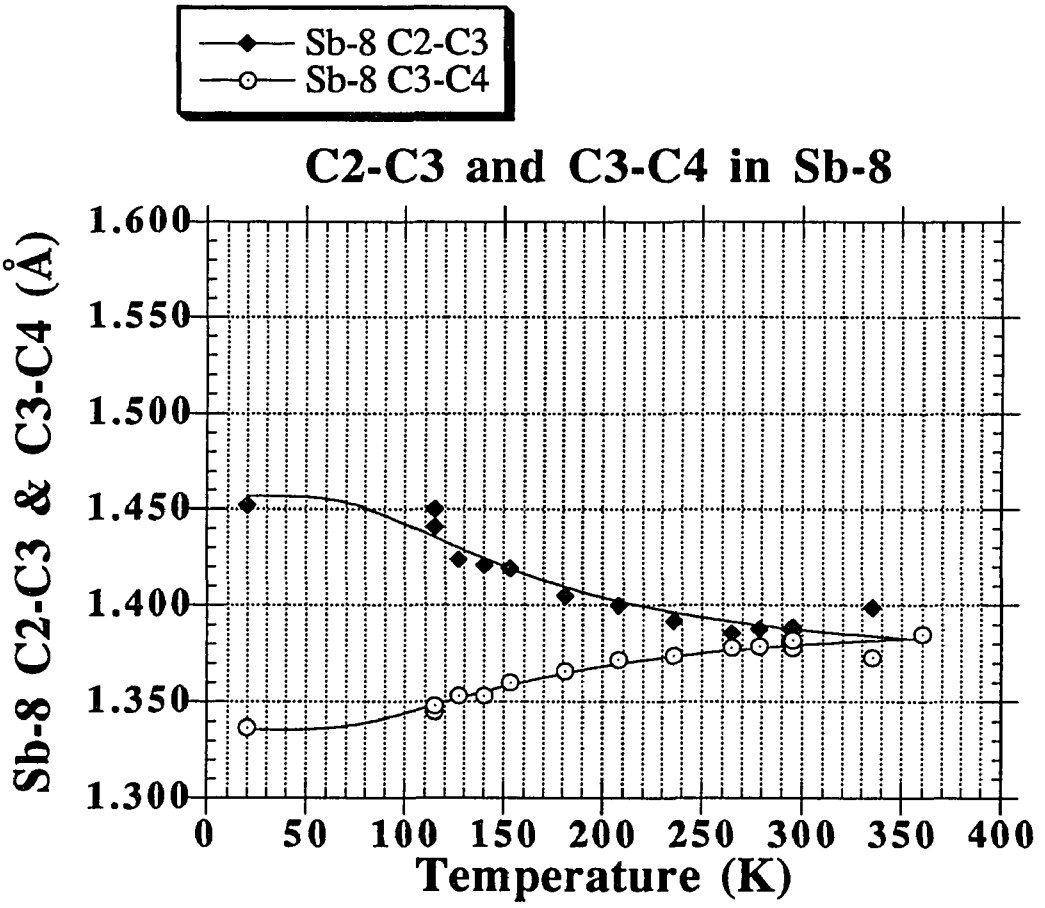


Figure 4–204. Plots of C2—C3 and C3—C4 distances in Sb-8 versus temperature.

Figure 4–205 shows clearly that the sum of the distances C2—C3 and C3—C4 remains constant as the temperature varies from 20 to 360 K:

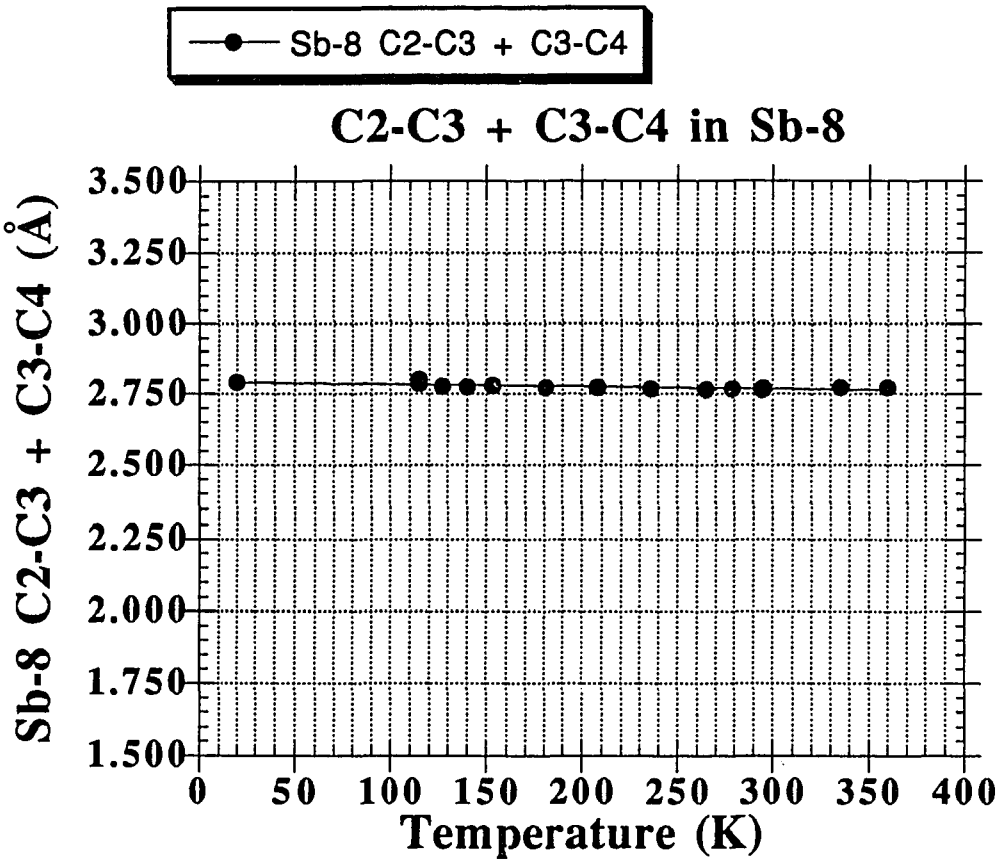


Figure 4–205. A plot of the sum of the distances C2—C3 and C3—C4 in Sb-8 versus temperature.

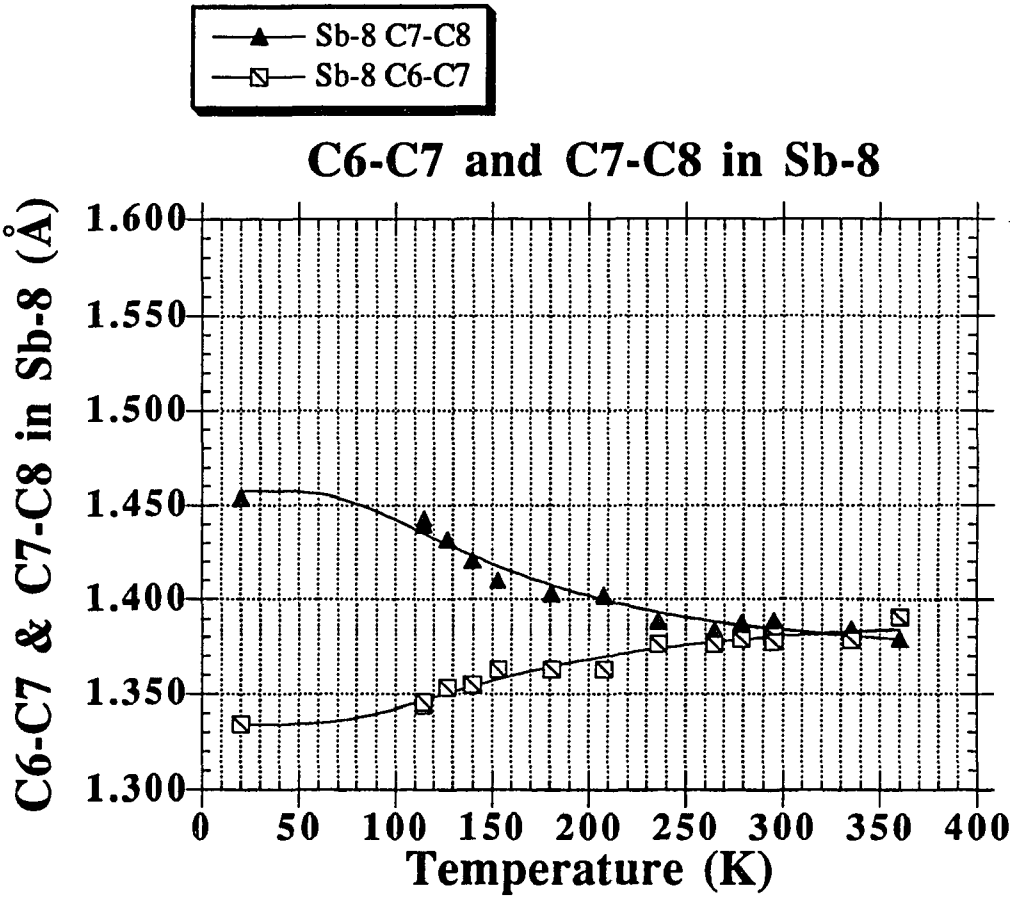


Figure 4–206. Plots of C6—C7 and 7—C8 distances in Sb-8 versus temperature.

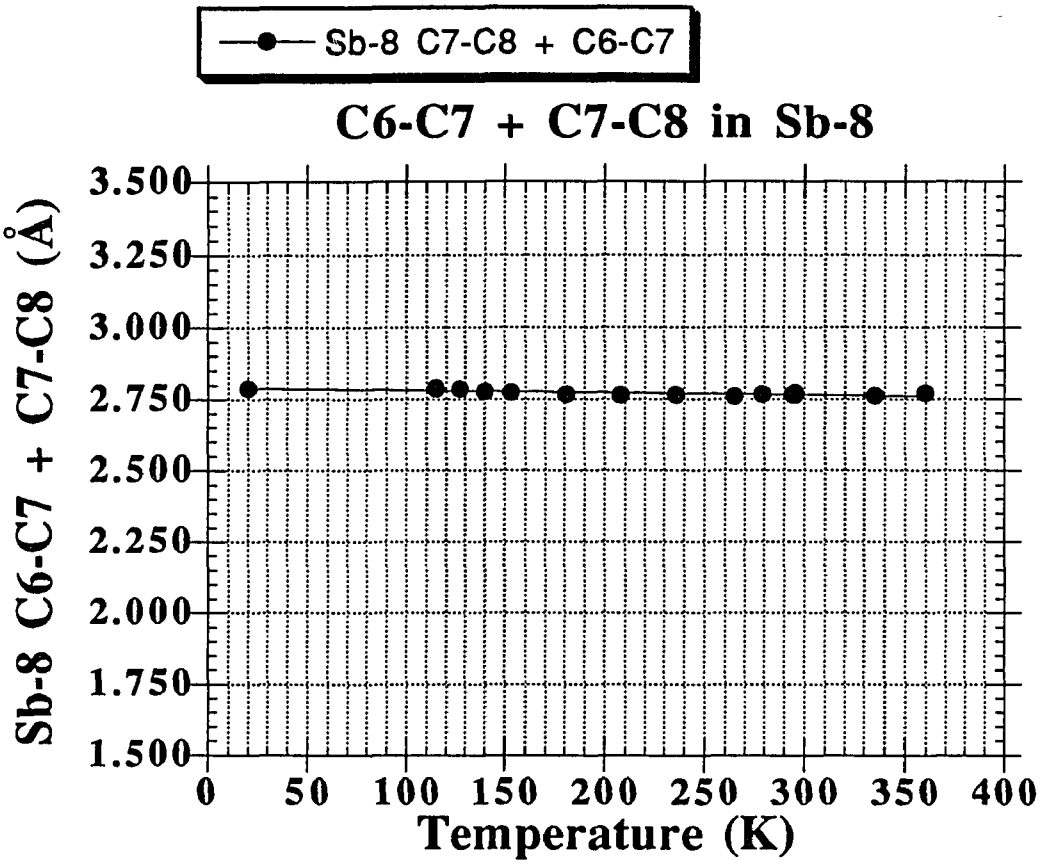


Figure 4–207. A plot of the sum of the distances C6—C7 and C7—C8 in Sb-8 versus temperature.

Figure 4–208 depicts the most dramatic changes which we have witnessed up to now in any of the previous candidates. At room temperature, C2—C8 and C4—C6 have really become equal by symmetrically converging to 1.99 Å! Above room temperature, however, an unexpected result flashes on as a mysterious crossover begins to creep in the C2—C8 and C4—C6 interatomic distances. Certainly, since the melting point of Sb-8 is about 170 °C, more data at higher temperatures can be collected to discover the extent of this crossover.

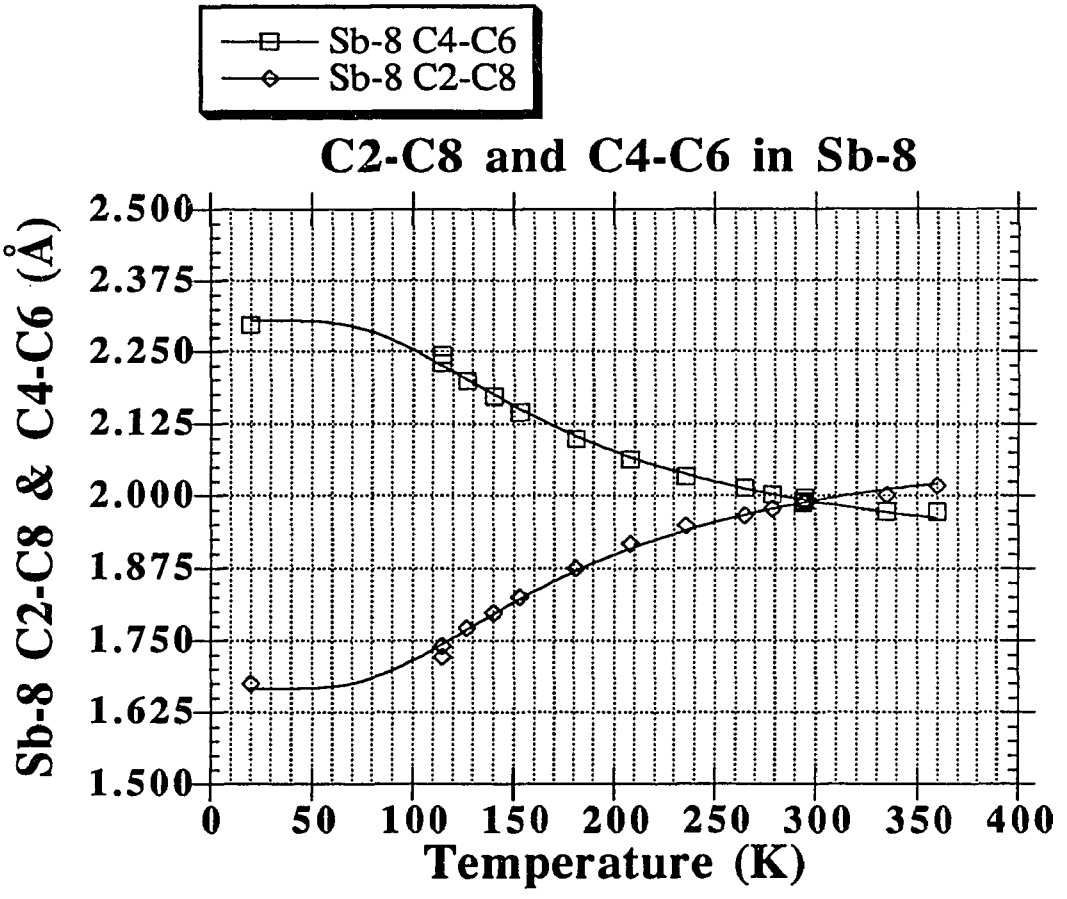


Figure 4–208. Plots of the distances C2—C8 and C4—C6 in Sb-8 versus temperature

Because the distances C2—C8 and C4—C6 approach each other symmetrically, their sum stays constant in the temperature range from 20 to 360 K (Figure 4–209).

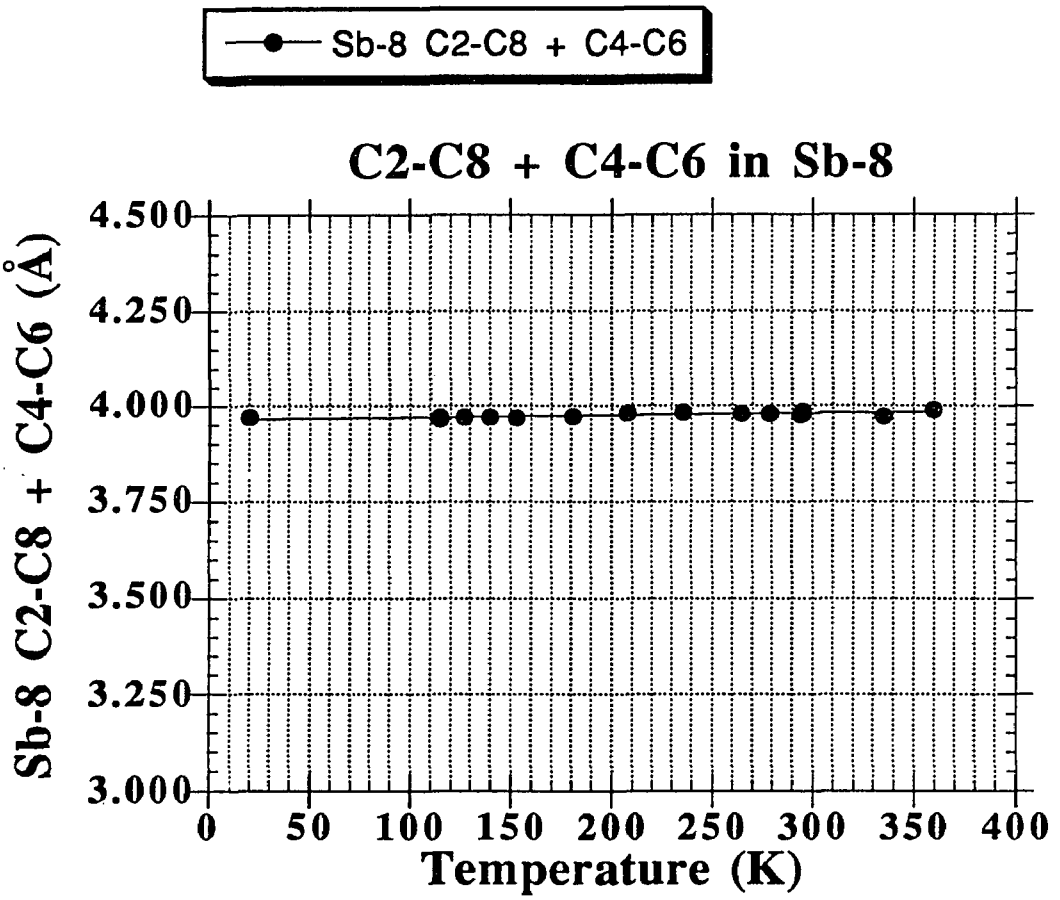


Figure 4–209. A plot of the sum of the distances C2—C8 and C4—C6 in Sb-8 versus temperature

The selected semibullvalene ring angles of Sb-8 in Table 4–27 with their associated graphs essentially confirm and reflect the changes which occur in the interatomic distances as the temperature is varied.

Table 4–27. Selected Angles (°) in the Semibullvalene Ring of Sb-8 at Various Temperatures

	20 K	**115 K**	**115 K**	**127 K**	**140 K**	**153 K**
C2—C1—C5	103.4(3)	103.6(1)	103.2(2)	102.9(1)	103.3(2)	103.6(2)
C2—C1—C8	67.3(2)	69.6(2)	70.7(3)	72.0(2)	73.3(2)	74.7(2)
C5—C1—C8	103.6(3)	103.6(1)	103.3(2)	103.0(2)	103.3(2)	103.5(2)
C1—C2—C3	108.8(3)	109.1(2)	109.5(3)	110.1(2)	110.0(2)	110.0(2)
C1—C2—C8	55.5(2)	54.4(1)	53.9(2)	53.5(2)	52.7(2)	52.2(2)
C3—C2—C8	117.5(3)	116.7(2)	116.0(2)	116.0(2)	115.5(2)	115.0(2)
C2—C3—C4	111.7(3)	111.4(1)	110.6(3)	111.2(3)	111.3(2)	111.2(2)
C3—C4—C5	111.3(3)	111.6(1)	112.0(3)	111.5(2)	111.6(2)	111.5(2)
C5—C4—C6	41.7(2)	42.9(2)	43.1(1)	43.8(1)	44.5(2)	45.3(1)
C1—C5—C4	102.7(3)	102.8(2)	103.3(2)	103.2(2)	103.0(2)	103.2(1)
C1—C5—C6	102.1(3)	102.6(1)	102.5(3)	103.0(2)	102.8(2)	102.9(2)
C4—C5—C6	96.3(3)	94.0(2)	94.0(3)	92.3(2)	90.8(1)	89.4(2)
C4—C6—C5	42.0(3)	43.1(1)	42.9(2)	43.9(1)	44.7(1)	45.3(1)
C5—C6—C7	111.5(3)	111.3(2)	111.6(3)	111.5(2)	111.5(2)	111.1(2)
C6—C7—C8	110.8(3)	110.7(2)	110.0(3)	110.3(2)	110.4(2)	110.7(2)
C1—C8—C2	57.2(2)	56.0(1)	55.4(2)	54.6(2)	54.0(2)	53.1(2)
C1—C8—C7	109.2(3)	109.9(2)	110.5(3)	110.7(2)	110.9(2)	111.0(2)
C2—C8—C7	118.1(3)	117.0(2)	116.7(2)	116.0(2)	115.7(2)	115.4(2)
$(\alpha+\beta)/2$[a]	81.8	81.8	82.3	82.2	82.1	82.1
C3—M[b]—C7	84.2	83.93	83.8	84.0	84.2	84.3

[a] α = C2—C1—C8, β = C4—C5—C6.
[b] M = midpoint between C1 and C5 bond.

Table 4–27 (cont'd). Selected Angles (°) in the Semibullvalene Ring of Sb-8 at Various Temperatures

	181 K	**208 K**	**236 K**	**265 K**	**279 K**	**294 K**
C2—C1—C5	103.4(2)	103.4(2)	103.3(2)	103.2(2)	103.3(2)	103.1(2)
C2—C1—C8	77.0(2)	78.8(2)	80.5(2)	81.7(2)	81.9(3)	82.4(3)
C5—C1—C8	103.4(2)	103.3(2)	103.4(2)	103.3(2)	103.2(2)	103.0(2)
C1—C2—C3	110.6(2)	110.8(2)	111.0(2)	111.6(3)	111.0(3)	111.5(3)
C1—C2—C8	51.1(2)	50.2(2)	49.4(2)	48.9(2)	48.8(2)	48.7(2)
C3—C2—C8	114.3(2)	113.4(2)	112.8(2)	113.0(2)	112.4(2)	112.3(2)
C2—C3—C4	111.0(2)	111.0(2)	111.2(3)	110.7(3)	111.2(3)	110.8(2)
C3—C4—C5	111.7(2)	111.6(2)	111.4(2)	111.7(2)	111.0(2)	111.4(3)
C5—C4—C6	46.2(1)	46.9(1)	47.5(2)	48.0(2)	48.1(2)	48.5(2)
C1—C5—C4	103.1(2)	103.1(2)	103.2(2)	102.8(2)	103.4(3)	103.2(3)
C1—C5—C6	102.9(2)	102.8(2)	103.0(2)	102.7(2)	103.1(3)	102.9(3)
C4—C5—C6	87.5(1)	85.8(2)	84.4(3)	83.5(3)	83.0(2)	82.5(2)
C4—C6—C5	46.3(1)	47.3(2)	48.0(2)	48.5(2)	48.9(2)	49.0(2)
C5—C6—C7	111.6(2)	112.2(2)	111.6(2)	111.9(2)	111.9(3)	112.3(3)
C6—C7—C8	110.7(2)	110.4(3)	110.5(3)	110.4(3)	110.1(3)	109.9(3)
C1—C8—C2	51.9(2)	50.9(2)	50.1(2)	49.4(2)	49.3(2)	48.9(2)
C1—C8—C7	111.1(2)	111.2(2)	111.4(2)	111.6(3)	111.6(3)	111.8(3)
C2—C8—C7	114.0(2)	113.4(2)	112.8(2)	112.4(2)	112.2(2)	112.0(2)
$(\alpha+\beta)/2$[a]	82.3	82.3	82.4	82.6	82.4	82.4
C3—M[b]—C7	84.2	84.2	84.3	84.6	84.4	84.4

[a] α = C2—C1—C8, β = C4—C5—C6.
[b] M = midpoint between C1 and C5 bond.

Table 4–27 (cont'd). Selected Angles (°) in the Semibullvalene Ring of Sb-8 at Various Temperatures

	295 K	295 K	335 K	360 K
C2—C1—C5	103.8(1)	103.4(1)	102.9(3)	103.3(3)
C2—C1—C8	82.6(2)	82.6(2)	83.3(4)	83.9(3)
C5—C1—C8	103.5(1)	103.4(1)	103.7(3)	103.2(3)
C1—C2—C3	110.7(2)	111.3(2)	111.3(4)	111.4(3)
C1—C2—C8	48.3(1)	48.3(1)	48.2(3)	47.9(2)
C3—C2—C8	111.8(2)	112.2(2)	112.2(3)	112.0(3)
C2—C3—C4	111.2(2)	110.6(2)	110.1(4)	110.7(3)
C3—C4—C5	111.2(2)	111.4(1)	112.2(4)	111.3(3)
C5—C4—C6	48.4(1)	48.5(1)	49.3(3)	48.6(2)
C1—C5—C4	103.1(2)	103.3(2)	103.4(3)	103.3(3)
C1—C5—C6	103.0(2)	102.9(2)	102.2(4)	103.3(3)
C4—C5—C6	82.5(2)	82.5(2)	81.9(3)	81.9(3)
C4—C6—C5	49.1(1)	49.1(1)	48.9(3)	49.4(2)
C5—C6—C7	112.1(2)	112.2(2)	112.5(4)	111.7(3)
C6—C7—C8	109.8(2)	109.7(2)	109.8(4)	110.1(4)
C1—C8—C2	49.1(1)	49.0(1)	48.5(3)	48.2(2)
C1—C8—C7	111.7(2)	111.8(2)	111.7(4)	111.6(3)
C2—C8—C7	112.4(2)	112.1(2)	111.6(3)	111.5(3)
$(\alpha+\beta)/2$[a]	82.6	82.6	82.6	82.9
C3—M[b]—C7	84.4	84.4	84.5	84.7

[a] α = C2—C1—C8, β = C4—C5—C6.
[b] M = midpoint between C1 and C5 bond.

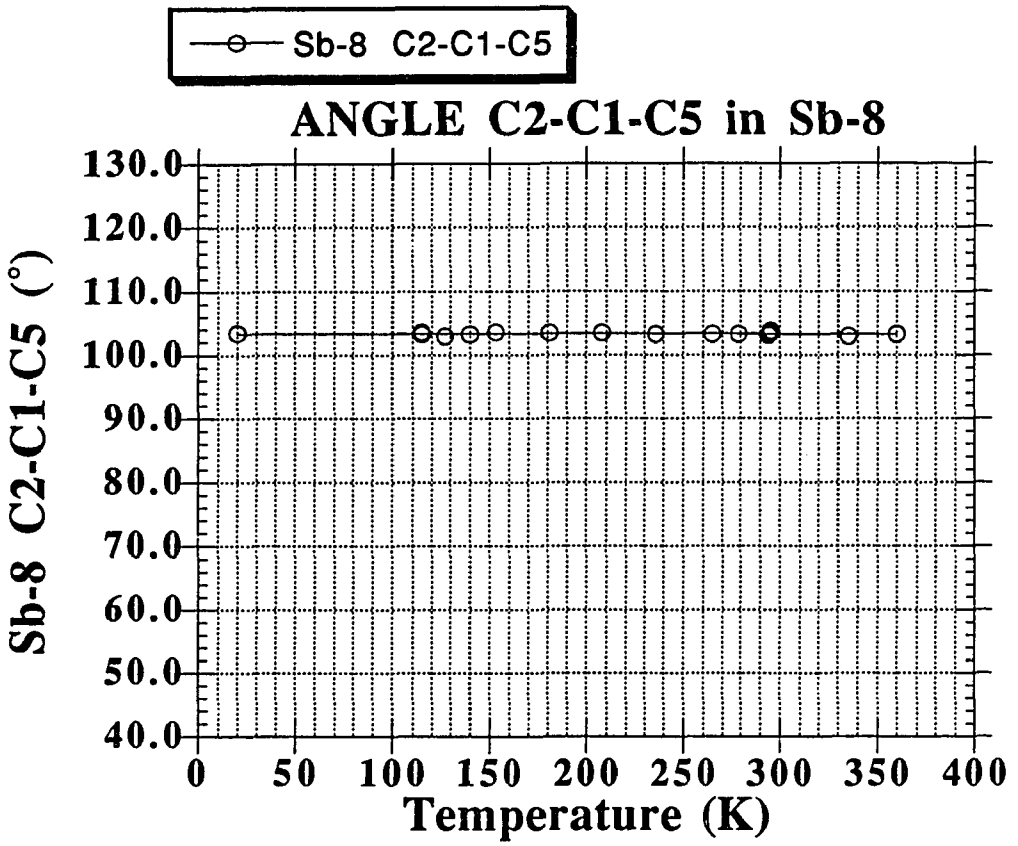


Figure 4–210. A plot of the angle C2—C1—C5 in Sb-8 versus temperature.

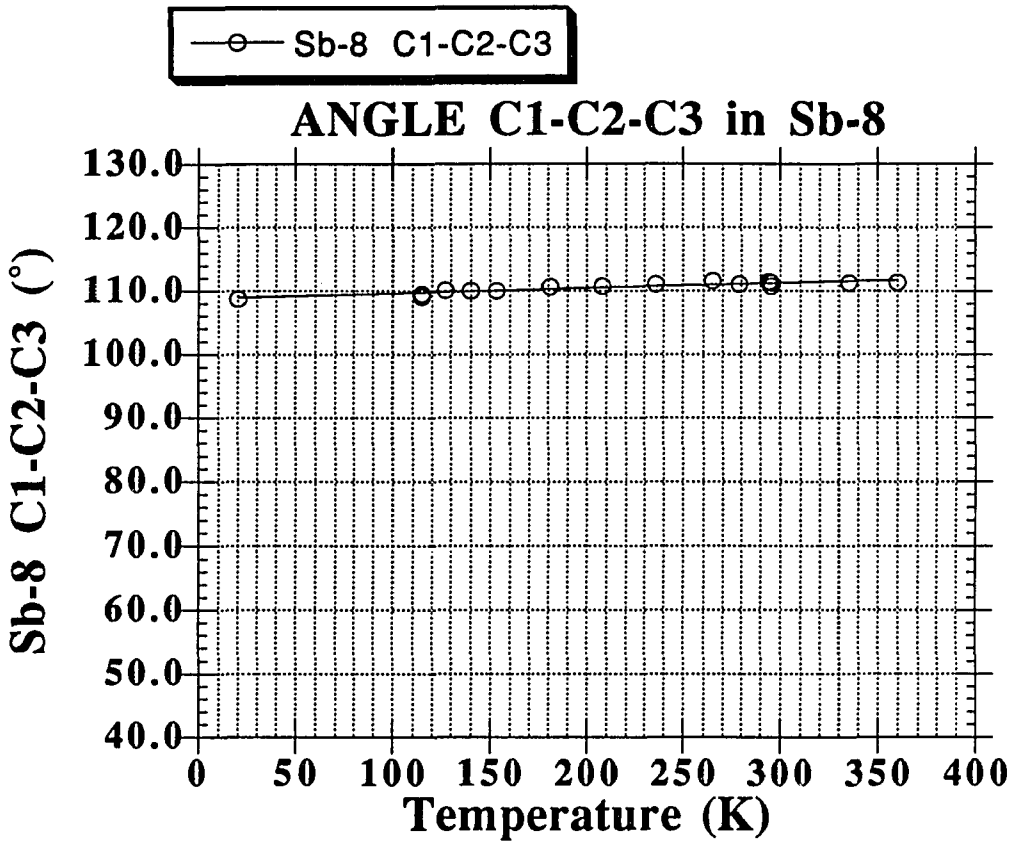


Figure 4–211. A plot of the angle C1—C2—C3 in Sb-8 versus temperature.

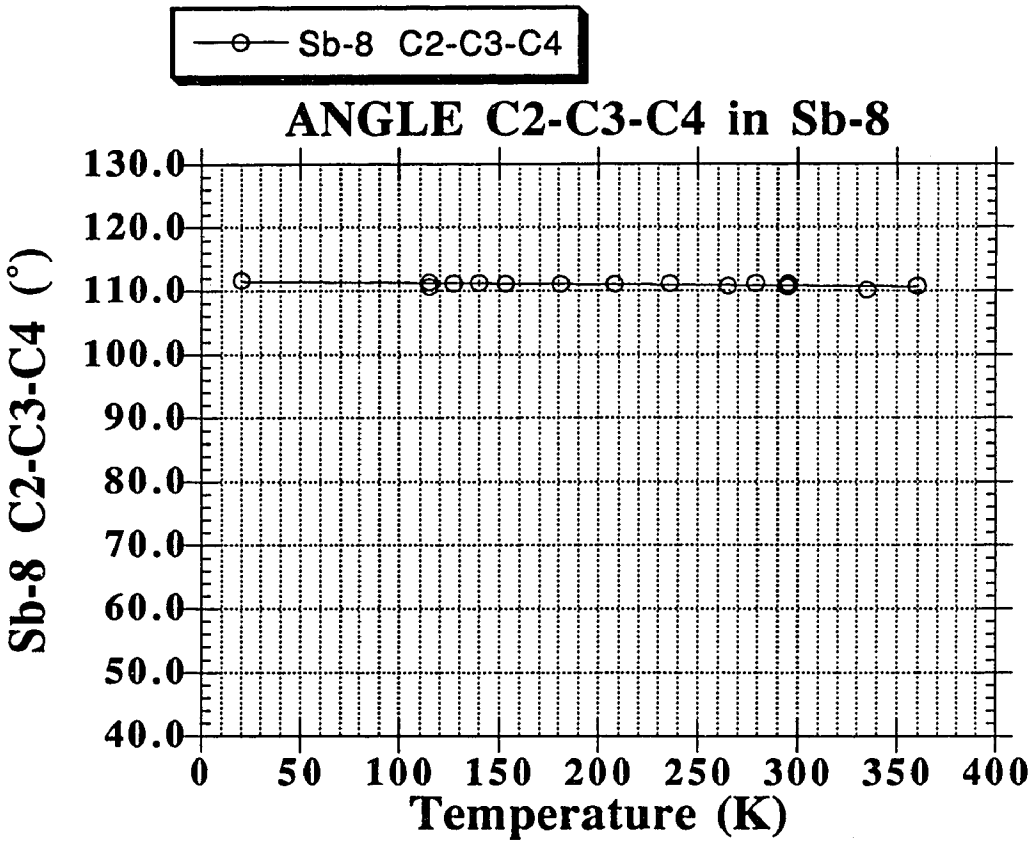


Figure 4–212. A plot of the angle C2—C3—C4 in Sb-8 versus temperature.

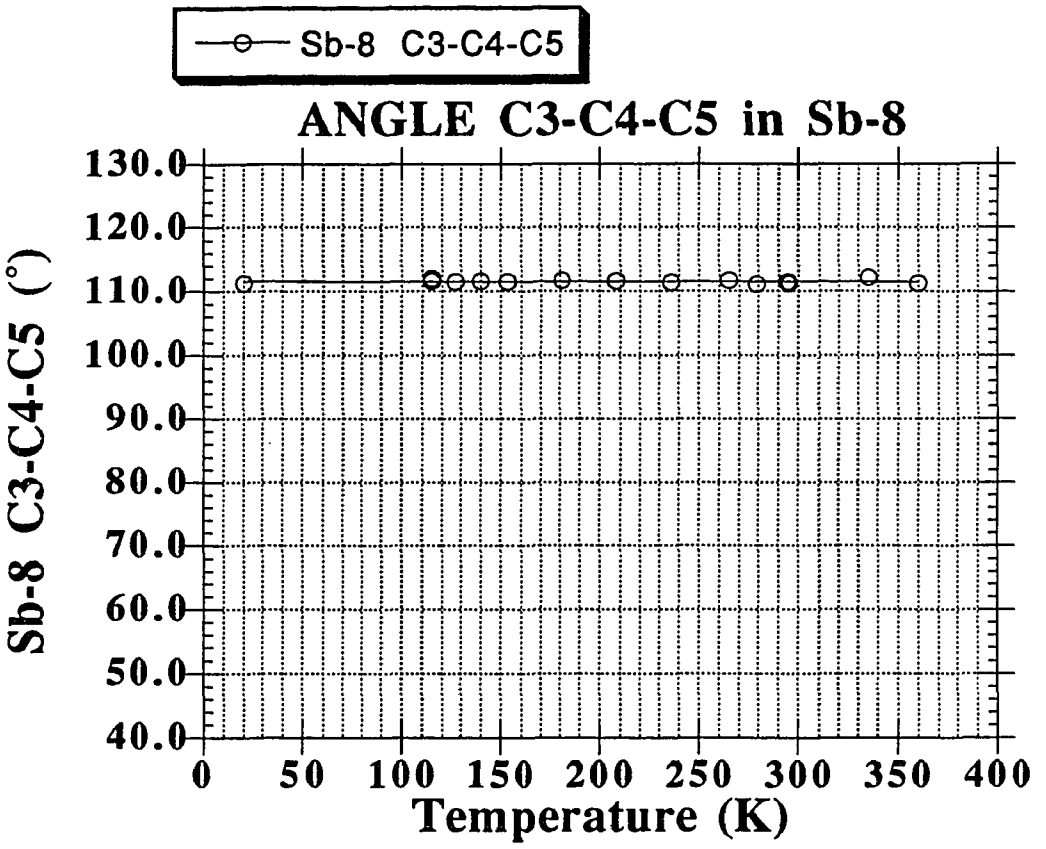


Figure 4–213. A plot of the angle C3—C4—C5 in Sb-8 versus temperature.

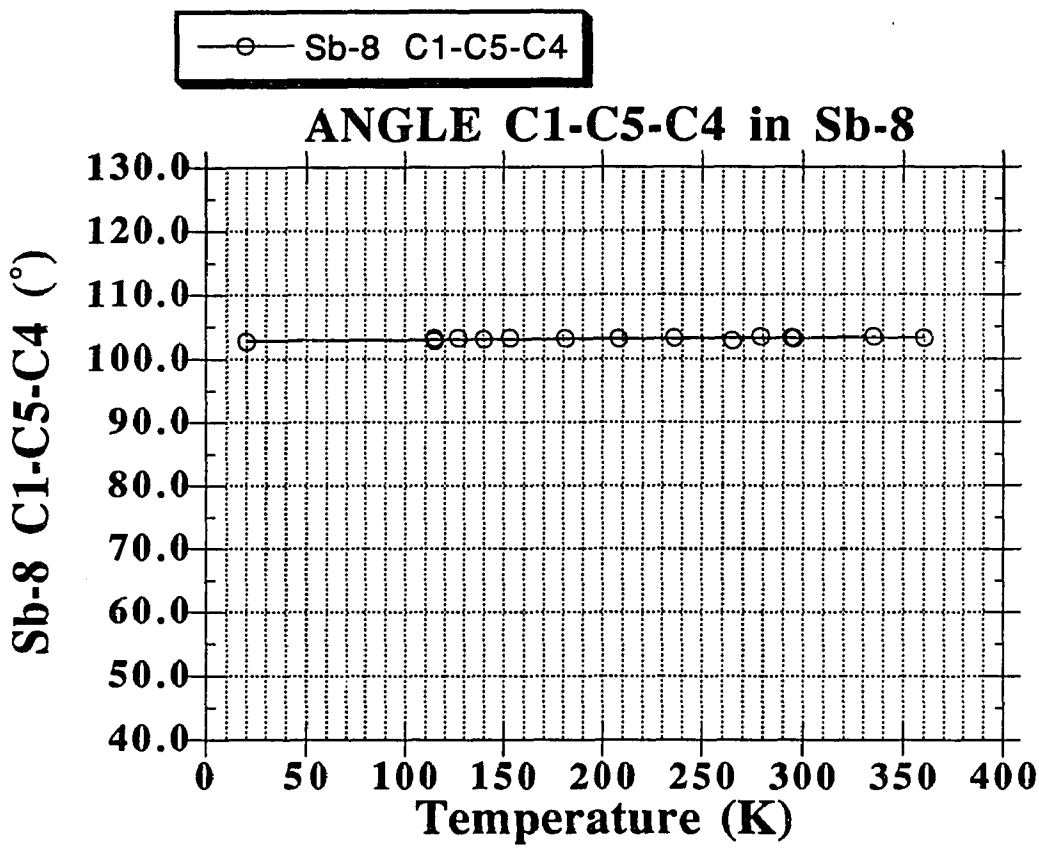


Figure 4–214. A plot of the angle C1—C5—C4 in Sb-8 versus temperature.

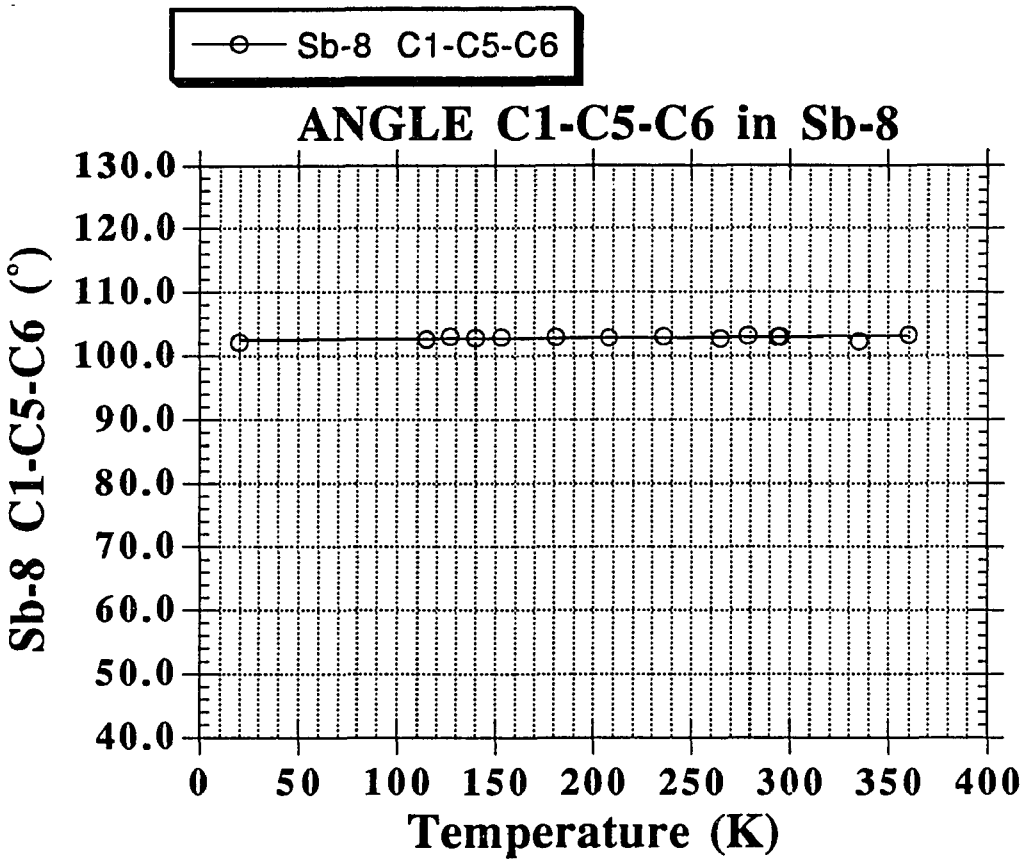


Figure 4–215. A plot of the angle C1—C5—C6 in Sb-8 versus temperature.

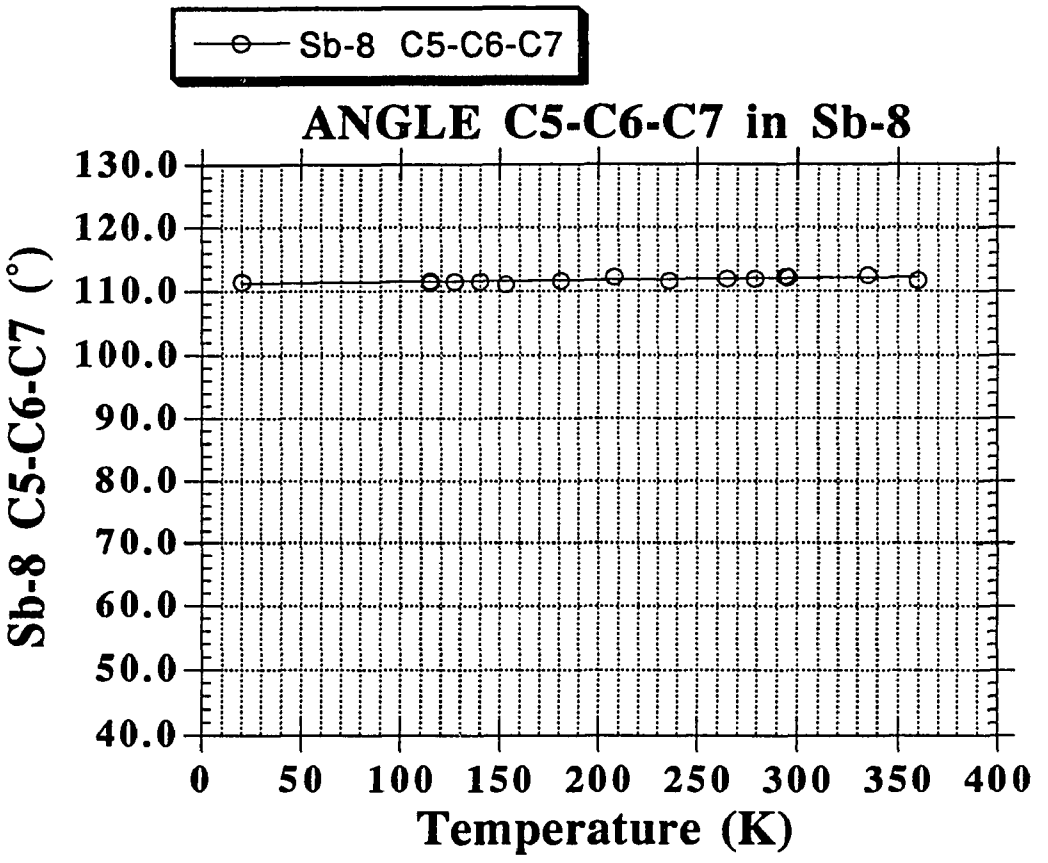


Figure 4–216. A plot of the angle C5—C6—C7 in Sb-8 versus temperature.

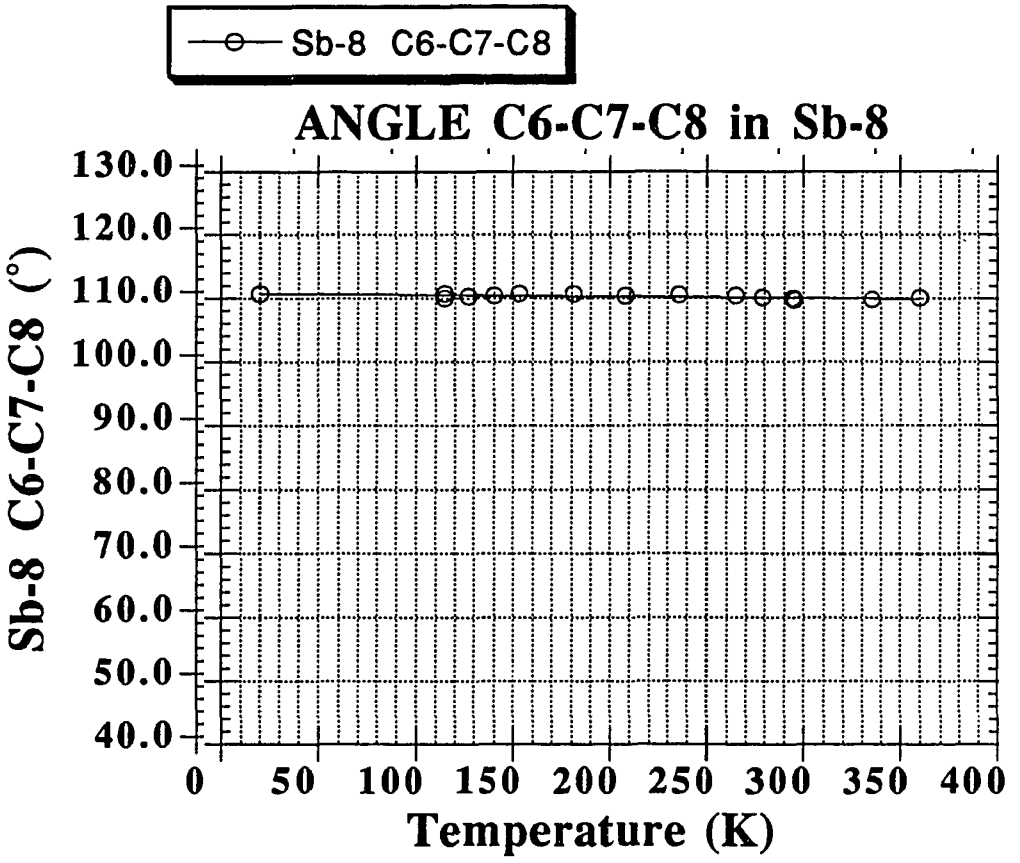


Figure 4–217. A plot of the angle C6—C7—C8 in Sb-8 versus temperature.

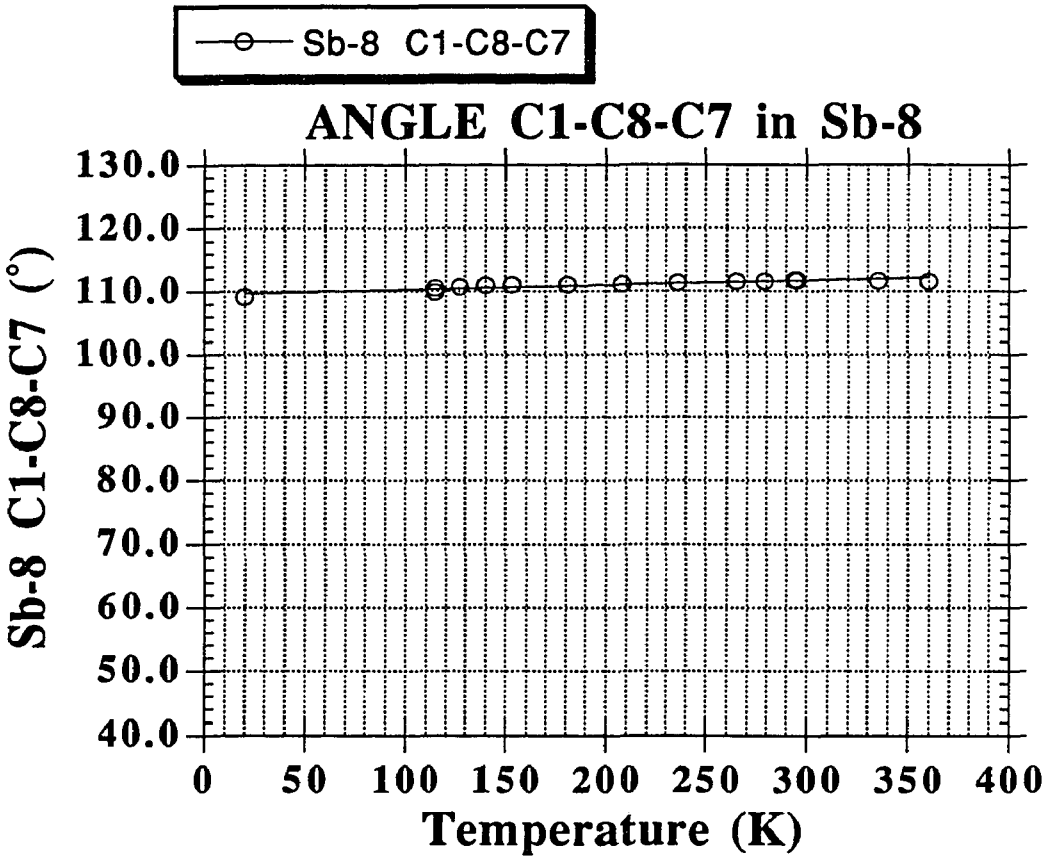


Figure 4–218. A plot of the angle C1—C8—C7 in Sb-8 versus temperature.

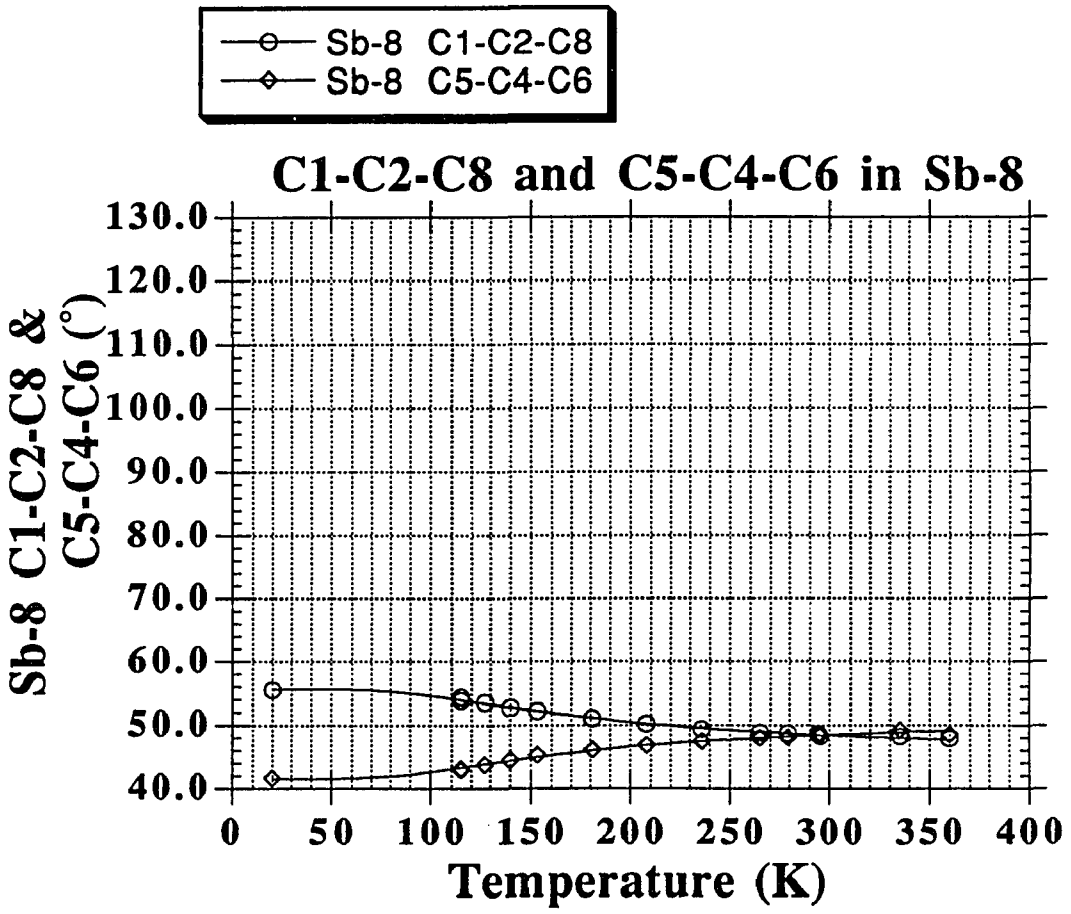


Figure 4–219. Plots of the angles C1—C2—C8 and C5—C4—C6 in Sb-8 versus temperature.

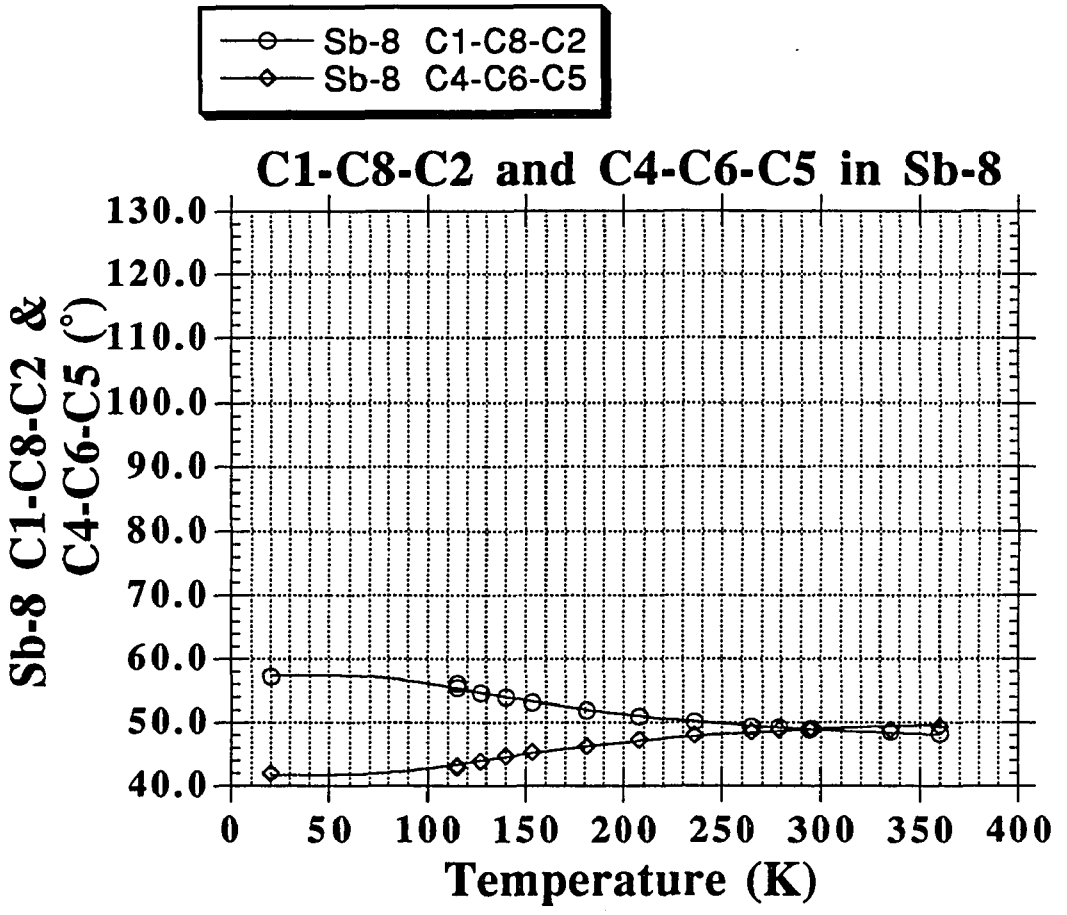


Figure 4–220. Plots of the angles C1—C8—C2 and C4—C6—C5 in Sb-8 versus temperature.

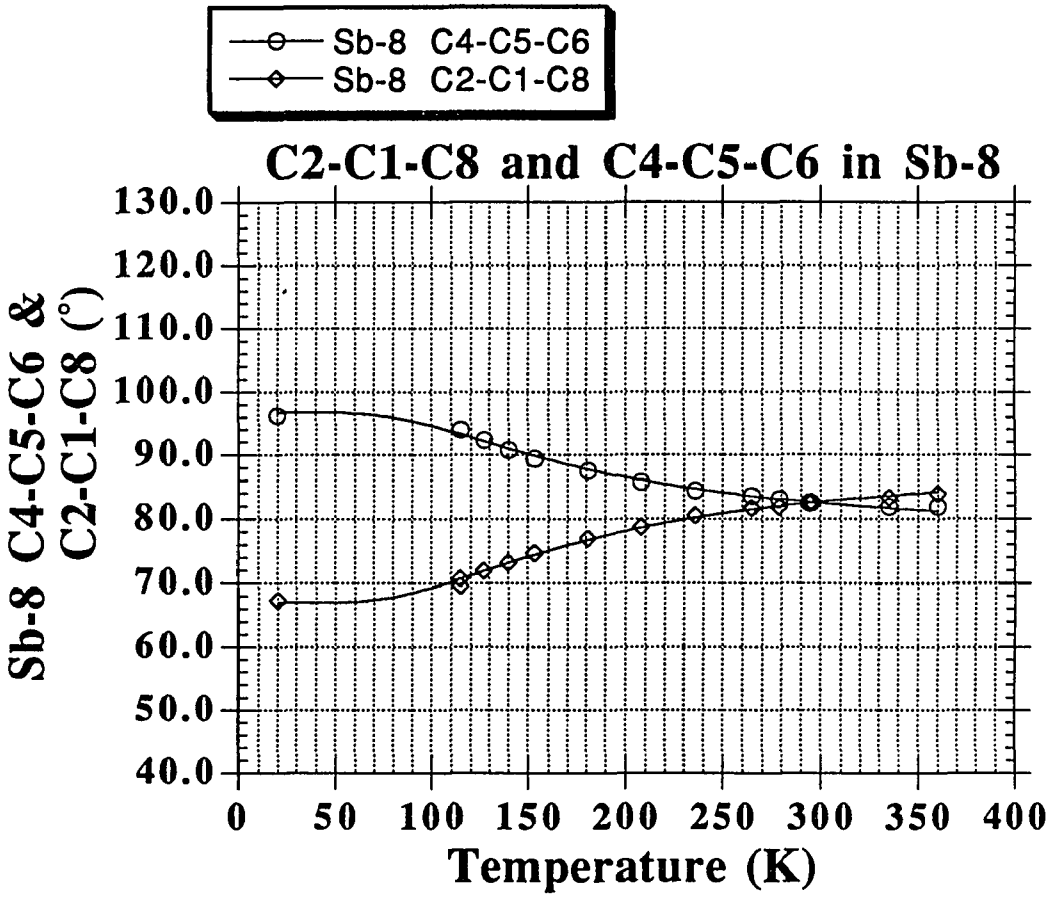


Figure 4–221. Plots of the angles C2—C1—C8 and C4—C5—C6 in Sb-8 versus temperature.

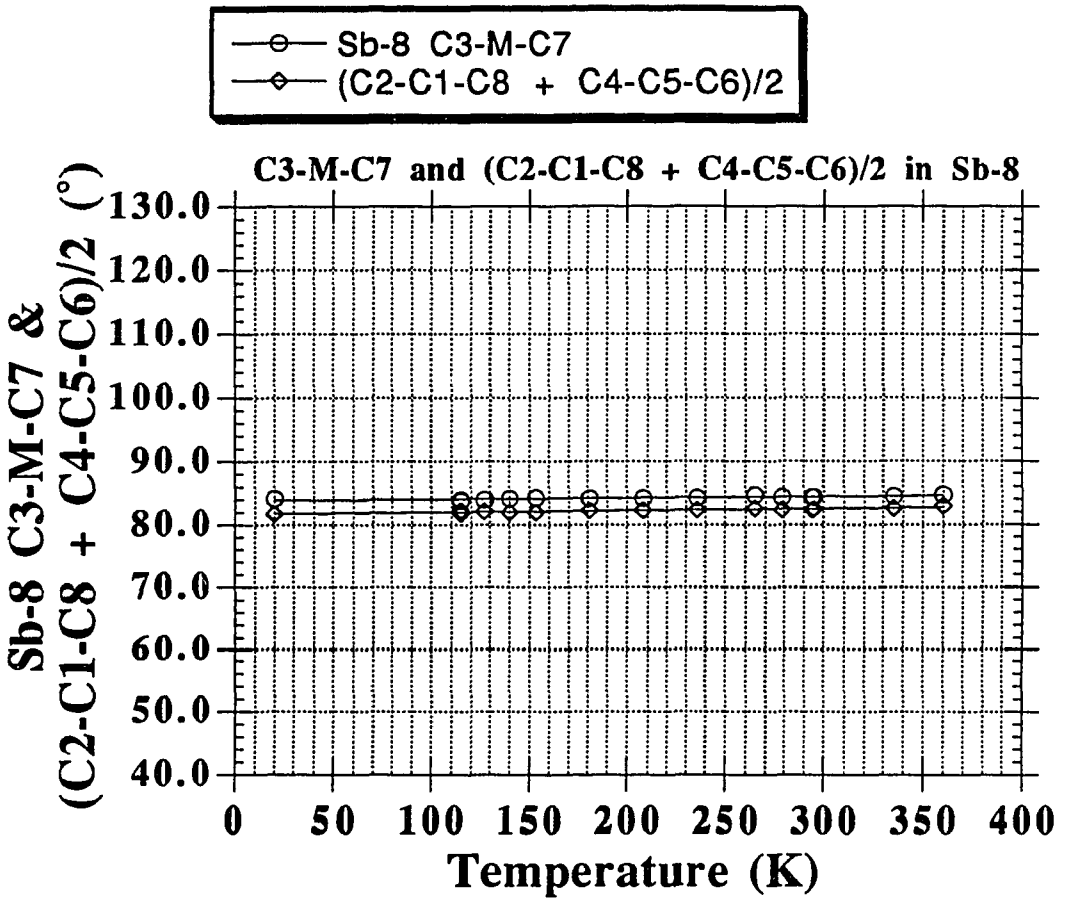


Figure 4–222. Plots of the angle C3—M—C7 (M = midpoint between C1 and C5) and the average angle of C2—C1—C8 and C4—C5—C6 in Sb-8 versus temperature.

The maximum root-mean-square displacements in Table 4–20 and the *ORTEP* drawings of Sb-8 at the end of this section reveal that, especially at high temperatures, the atoms C2, C4, C6, C8 vibrate in a plane parallel to the cyclopropyl ring. This direction of vibration for these atoms is consistent with the Cope rearrangement in action.

Table 4–28. Selected Root-Mean-Square Amplitudes (Å) of Thermal Vibrations in the Ring of Sb-8 at Various Temperatures

		Min.	Int'med	Max.
20 K	C1	0.080	0.123	0.156
	C2	0.066	0.136	0.160
	C3	0.067	0.118	0.164
	C4	0.084	0.113	0.161
	C5	0.065	0.135	0.152
	C6	0.057	0.131	0.161
	C7	0.075	0.121	0.164
	C8	0.032	0.135	0.158
115 K	C1	0.107	0.120	0.132
	C2	0.111	0.130	0.162
	C3	0.103	0.119	0.135
	C4	0.106	0.127	0.144
	C5	0.108	0.123	0.128
	C6	0.132	0.146	0.152
	C7	0.108	0.125	0.147
	C8	0.126	0.130	0.145
115 K	C1	0.118	0.124	0.167
	C2	0.118	0.160	0.178
	C3	0.110	0.128	0.161
	C4	0.123	0.137	0.156
	C5	0.121	0.122	0.167
	C6	0.137	0.152	0.181
	C7	0.126	0.145	0.156
	C8	0.122	0.140	0.195
127 K	C1	0.116	0.135	0.145
	C2	0.122	0.150	0.194
	C3	0.114	0.131	0.134
	C4	0.119	0.131	0.168
	C5	0.120	0.131	0.149
	C6	0.140	0.149	0.186
	C7	0.109	0.139	0.147
	C8	0.135	0.151	0.176

Table 4–28 (cont'd). Selected Root-Mean-Square Amplitudes (Å) of Thermal Vibrations in the Ring of Sb-8 at Various Temperatures

		Min.	Int'med	Max.
140 K	C1	0.122	0.142	0.142
	C2	0.122	0.150	0.209
	C3	0.124	0.130	0.144
	C4	0.125	0.131	0.193
	C5	0.118	0.137	0.157
	C6	0.148	0.159	0.201
	C7	0.117	0.149	0.158
	C8	0.134	0.162	0.184
153 K	C1	0.125	0.146	0.159
	C2	0.130	0.146	0.224
	C3	0.134	0.138	0.150
	C4	0.124	0.149	0.196
	C5	0.116	0.146	0.159
	C6	0.154	0.169	0.209
	C7	0.122	0.156	0.167
	C8	0.146	0.155	0.192
181 K	C1	0.133	0.160	0.164
	C2	0.139	0.147	0.248
	C3	0.137	0.148	0.159
	C4	0.134	0.149	0.223
	C5	0.120	0.157	0.170
	C6	0.159	0.176	0.229
	C7	0.132	0.159	0.186
	C8	0.154	0.162	0.206
208 K	C1	0.131	0.170	0.182
	C2	0.138	0.161	0.264
	C3	0.148	0.160	0.164
	C4	0.142	0.158	0.234
	C5	0.132	0.166	0.184
	C6	0.172	0.183	0.242
	C7	0.146	0.178	0.189
	C8	0.165	0.173	0.219
236 K	C1	0.149	0.184	0.187
	C2	0.154	0.170	0.269
	C3	0.159	0.171	0.182
	C4	0.153	0.171	0.244
	C5	0.130	0.177	0.201
	C6	0.182	0.197	0.247
	C7	0.154	0.185	0.207
	C8	0.180	0.184	0.224

Table 4–28 (cont'd). Selected Root-Mean-Square Amplitudes (Å) of Thermal Vibrations in the Ring of Sb-8 at Various Temperatures

		Min.	Int'med	Max.
265 K	C1	0.153	0.195	0.207
	C2	0.163	0.175	0.284
	C3	0.168	0.177	0.193
	C4	0.158	0.178	0.260
	C5	0.143	0.196	0.208
	C6	0.184	0.213	0.257
	C7	0.170	0.195	0.216
	C8	0.189	0.194	0.236
279 K	C1	0.166	0.200	0.202
	C2	0.164	0.184	0.286
	C3	0.169	0.187	0.195
	C4	0.163	0.186	0.264
	C5	0.152	0.196	0.213
	C6	0.191	0.214	0.266
	C7	0.174	0.201	0.227
	C8	0.192	0.200	0.236
294 K	C1	0.160	0.209	0.212
	C2	0.169	0.185	0.290
	C3	0.162	0.194	0.204
	C4	0.162	0.191	0.275
	C5	0.155	0.206	0.220
	C6	0.199	0.218	0.271
	C7	0.177	0.207	0.230
	C8	0.193	0.205	0.247
295 K	C1	0.174	0.211	0.220
	C2	0.174	0.197	0.300
	C3	0.173	0.199	0.217
	C4	0.172	0.195	0.281
	C5	0.164	0.205	0.233
	C6	0.205	0.227	0.278
	C7	0.189	0.219	0.232
	C8	0.213	0.213	0.252
295 K	C1	0.177	0.203	0.209
	C2	0.164	0.196	0.294
	C3	0.166	0.193	0.211
	C4	0.170	0.188	0.278
	C5	0.163	0.201	0.223
	C6	0.203	0.225	0.276
	C7	0.197	0.212	0.225
	C8	0.200	0.210	0.253

Table 4–28 (cont'd). Selected Root-Mean-Square Amplitudes (Å) of Thermal Vibrations in the Ring of Sb-8 at Various Temperatures

		Min.	Int'med	Max.
335 K	C1	0.175	0.232	0.252
	C2	0.184	0.201	0.309
	C3	0.192	0.205	0.234
	C4	0.187	0.214	0.291
	C5	0.207	0.217	0.244
	C6	0.206	0.269	0.274
	C7	0.205	0.220	0.275
	C8	0.199	0.222	0.278
360 K	C1	0.201	0.231	0.239
	C2	0.197	0.222	0.306
	C3	0.192	0.221	0.230
	C4	0.193	0.207	0.301
	C5	0.191	0.222	0.250
	C6	0.235	0.250	0.275
	C7	0.211	0.234	0.266
	C8	0.218	0.241	0.267

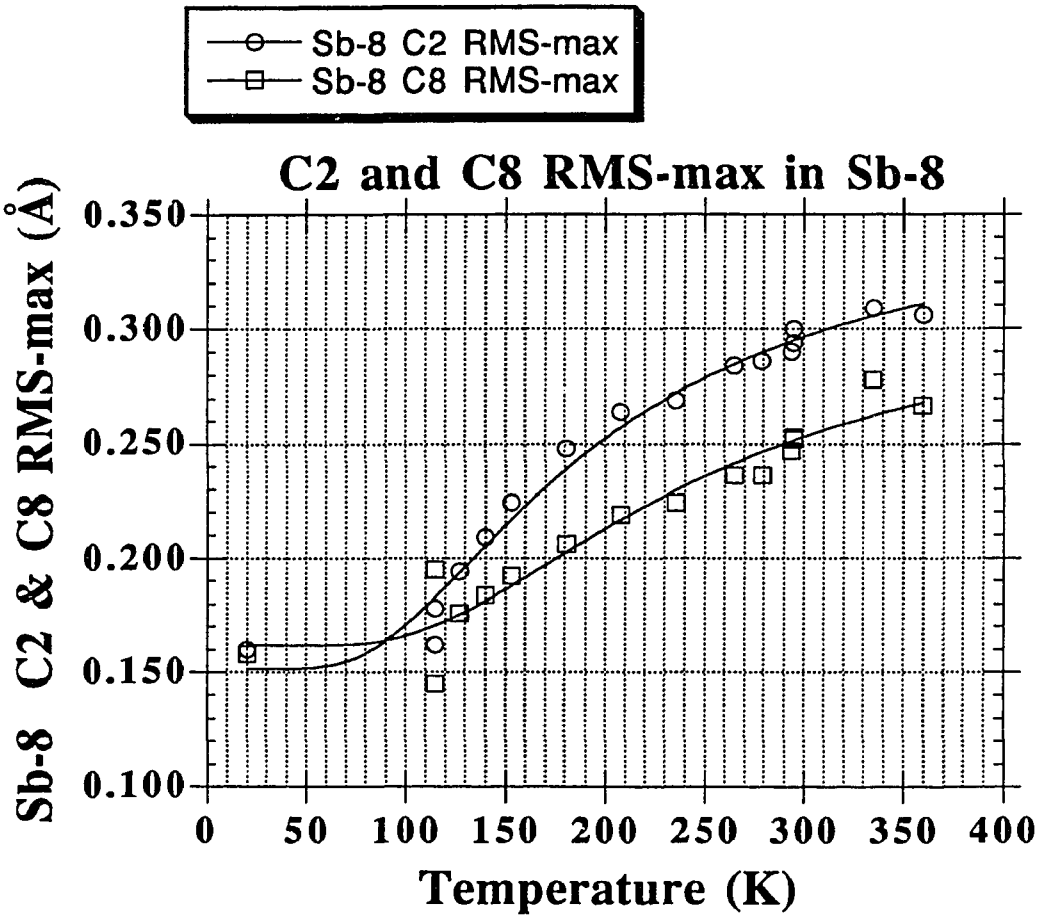


Figure 4–223. Plots of C2 RMS-max and C8 RMS-max in Sb-8 versus temperature.

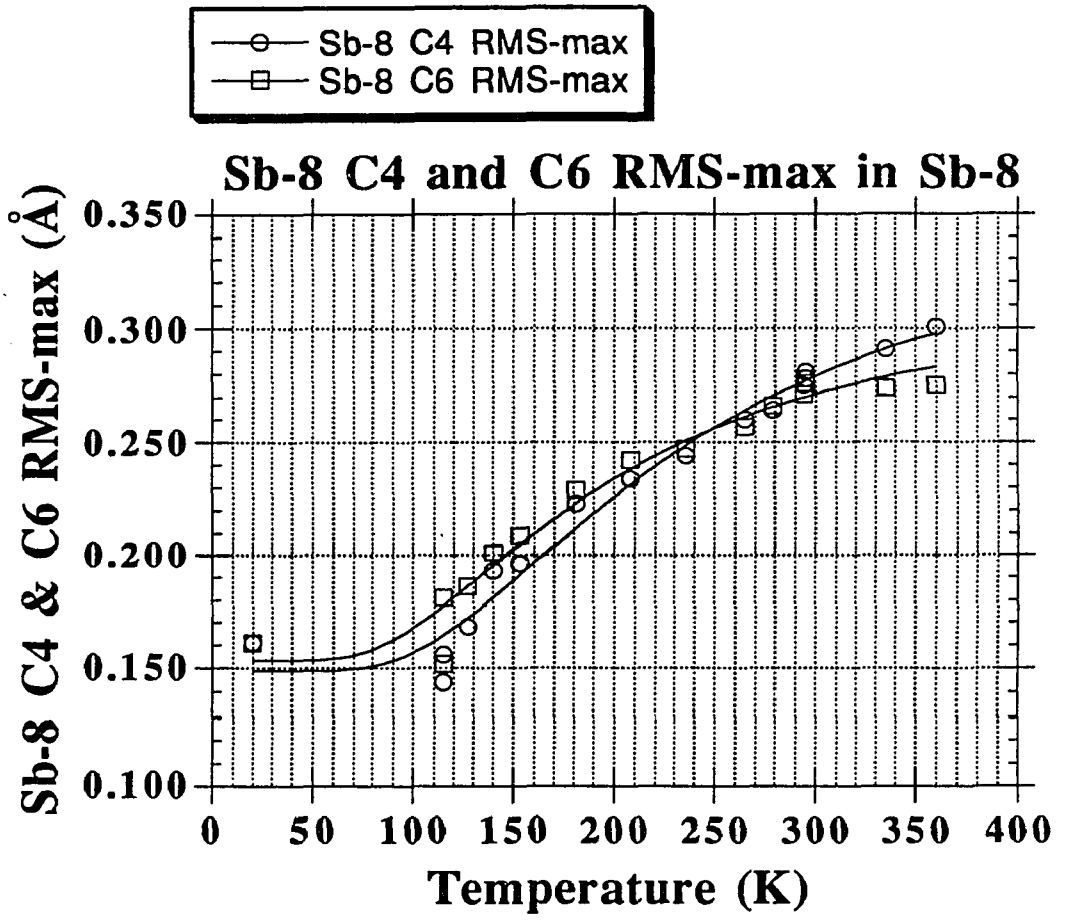
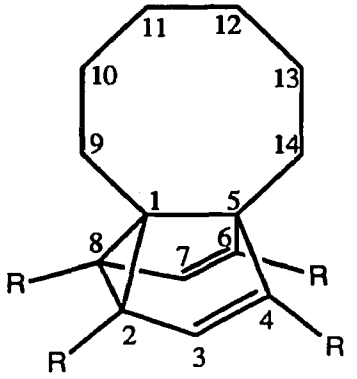


Figure 4–224. Plots of C4 RMS-max and C6 RMS-max in Sb-8 versus temperature.

The two methylenes C11 and C12 are disordered in the crystal. The cyclooctane ring adopts two conformations as C11 and C12 flip-flop.



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

The *ORTEP* drawings illustrate the two conformations of the cyclooctane ring. in the major and minor conformers. As the temperature increases, the population of the major conformer decreases from 90% to 30%, while that of the minor conformer increases by the same amount. In other words, The occupancies of C11 and C12 in the major conformer decrease from approximately 0.90 at 20 K to 0.7 at 360 K; and those of the minor conformer increase from 0.1 to 0.3.

Solution and solid-state NMR spectra of Sb-8 are included at the end of this section. These spectra indicate that Sb-8 undergoes the Cope rearrangement in solution as well as in the solid state. The CP-MAS 13C NMR spectrum, however, reveals that the structure of Sb-8 is frozen out at –182 °C.

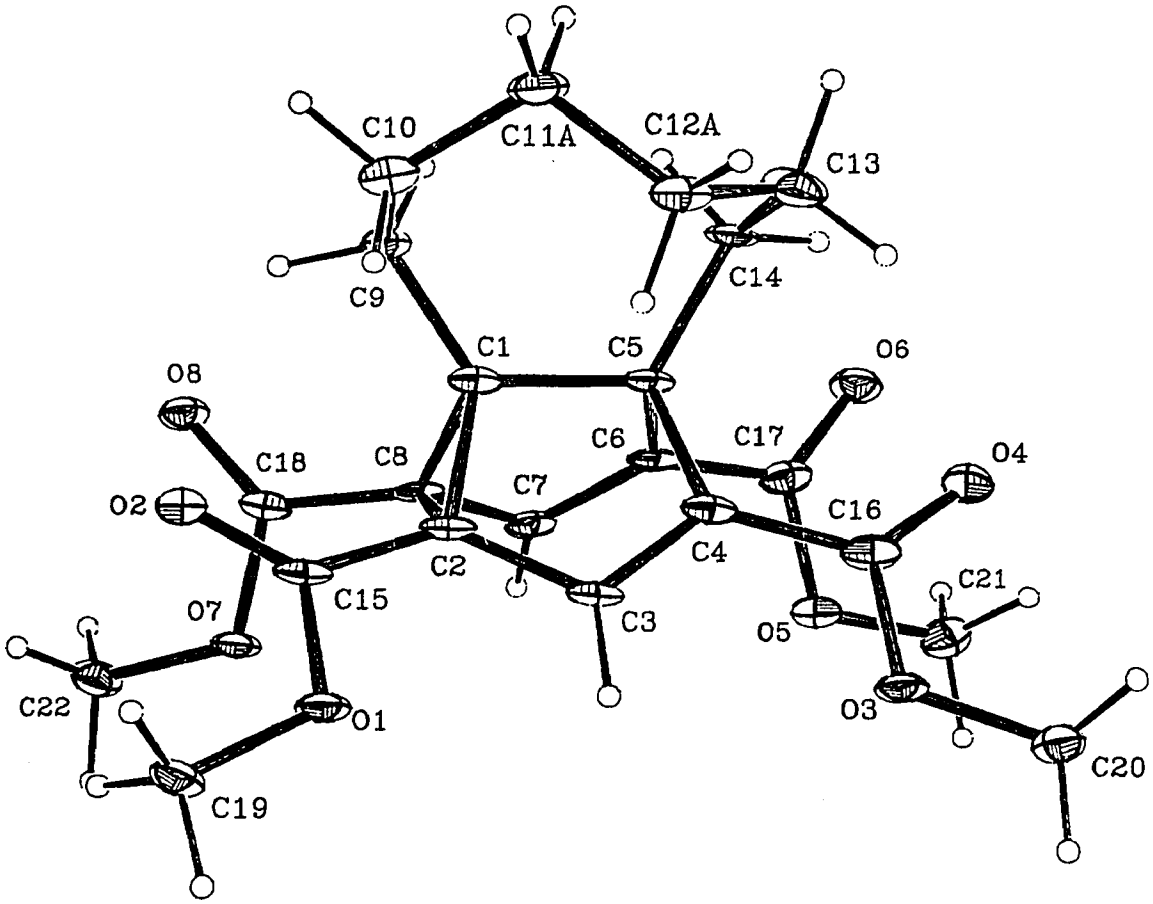


Figure 4–225. *ORTEP* drawing of Sb-8 (major conformer) at **20 K** with 50% thermal ellipsoids.

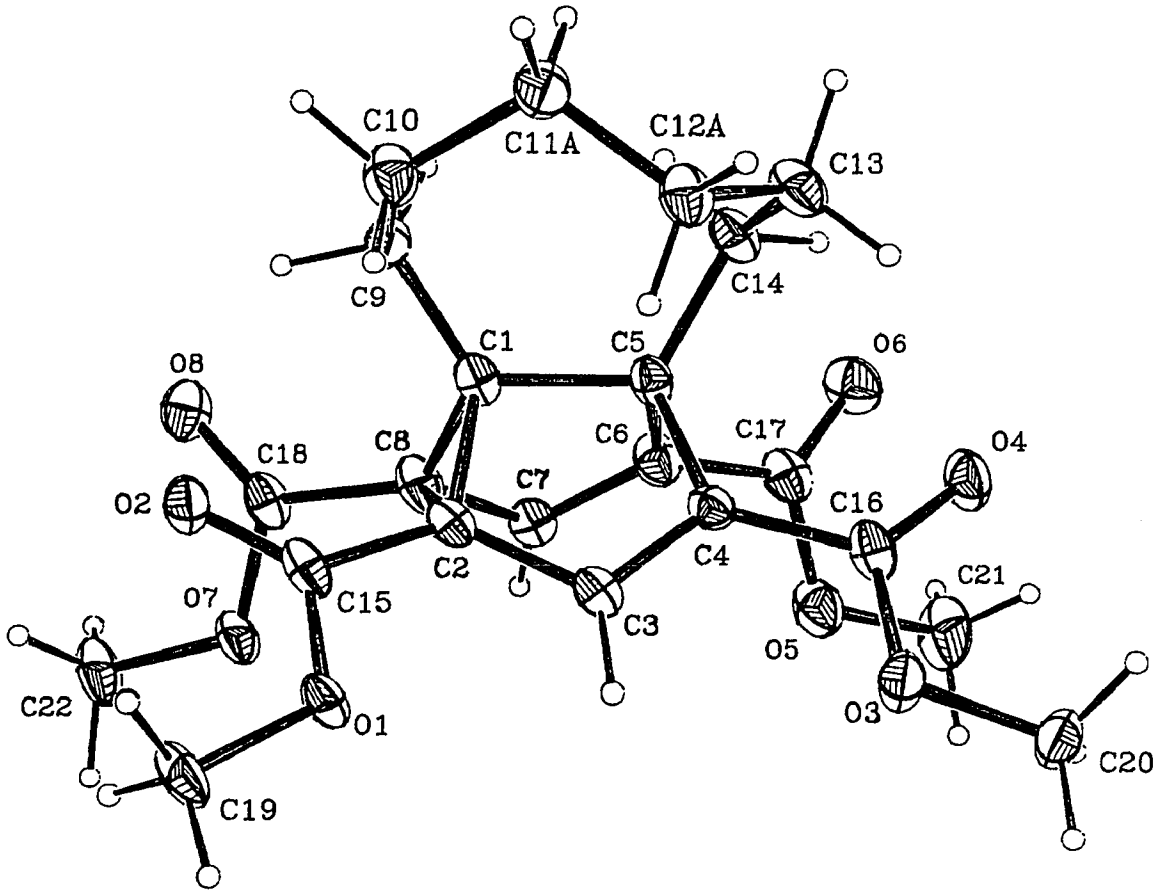


Figure 4–226. *ORTEP* drawing of Sb-8 (major conformer) at **115 K** with 50% thermal ellipsoids.

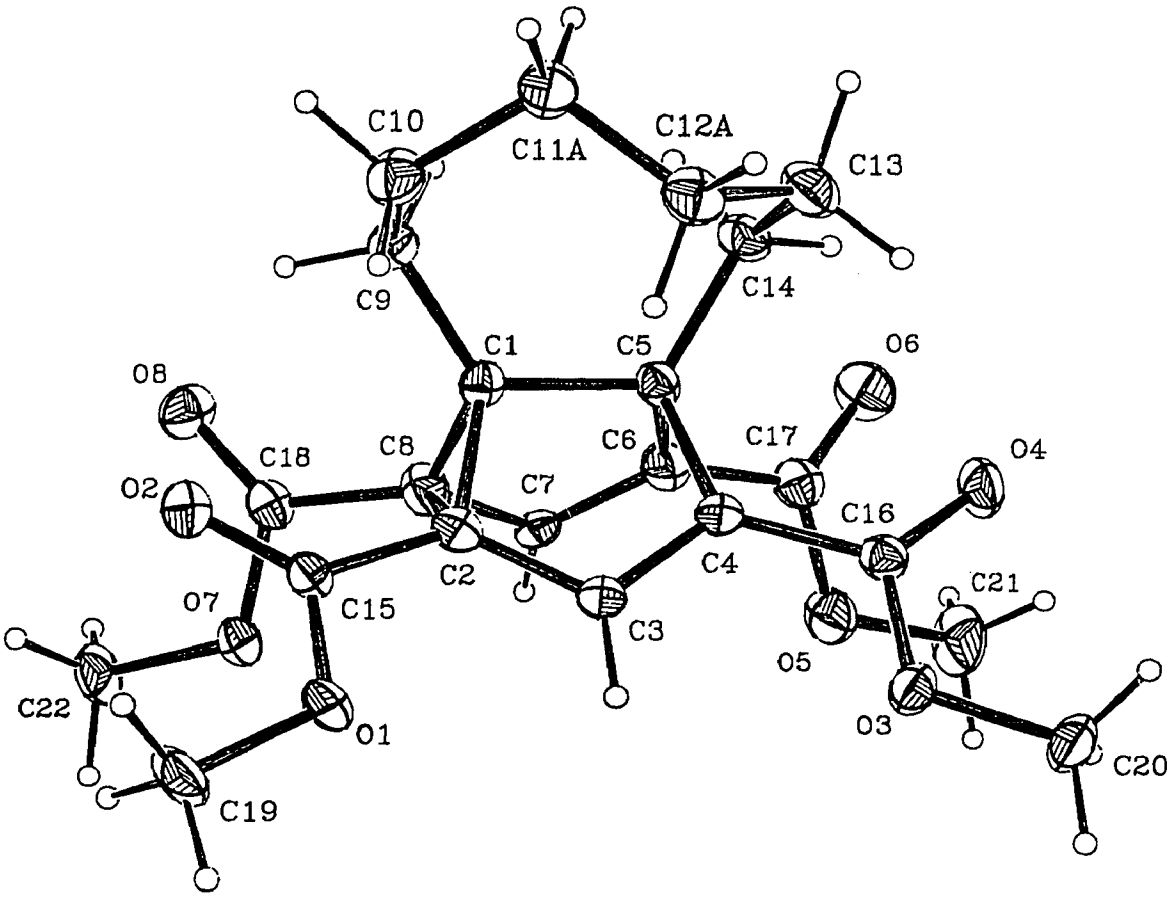


Figure 4–227. *ORTEP* drawing of Sb-8 (major conformer) at **127 K** with 50% thermal ellipsoids.

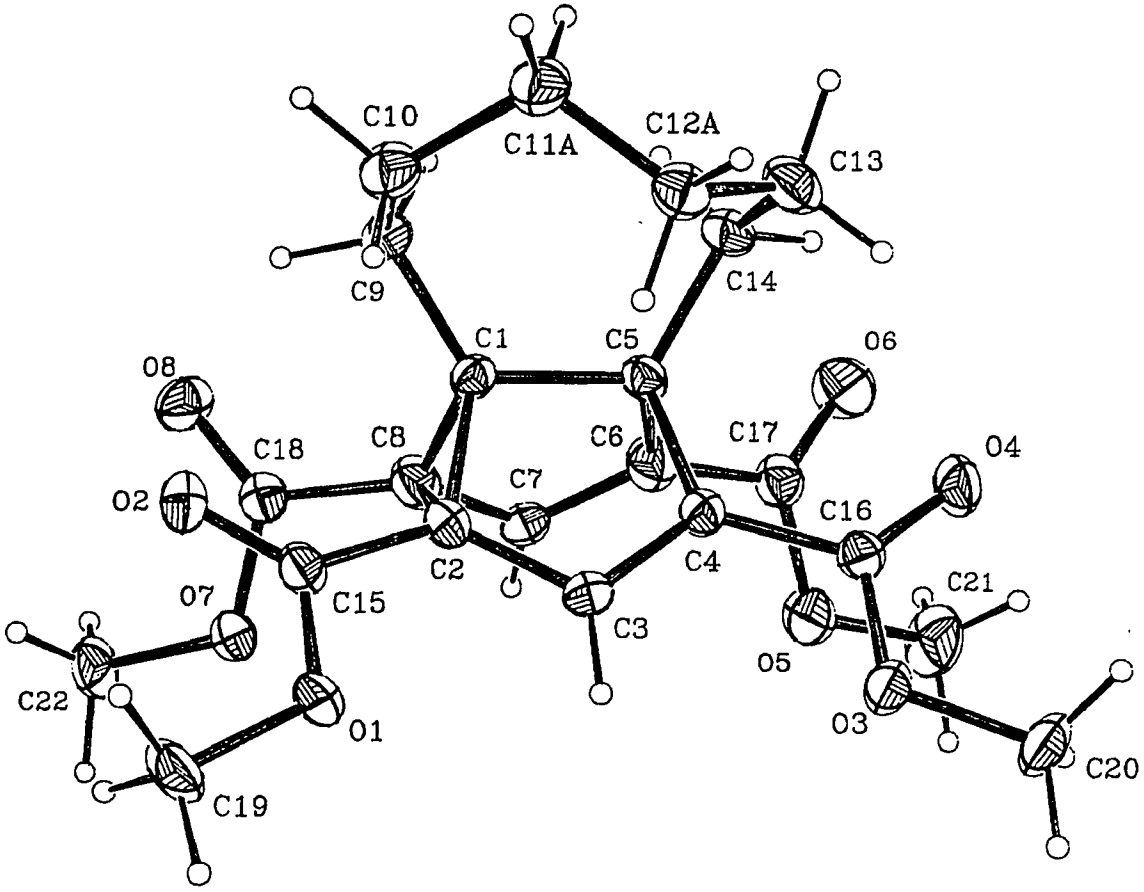


Figure 4–228. *ORTEP* drawing of Sb-8 (major conformer) at **140 K** with 50% thermal ellipsoids.

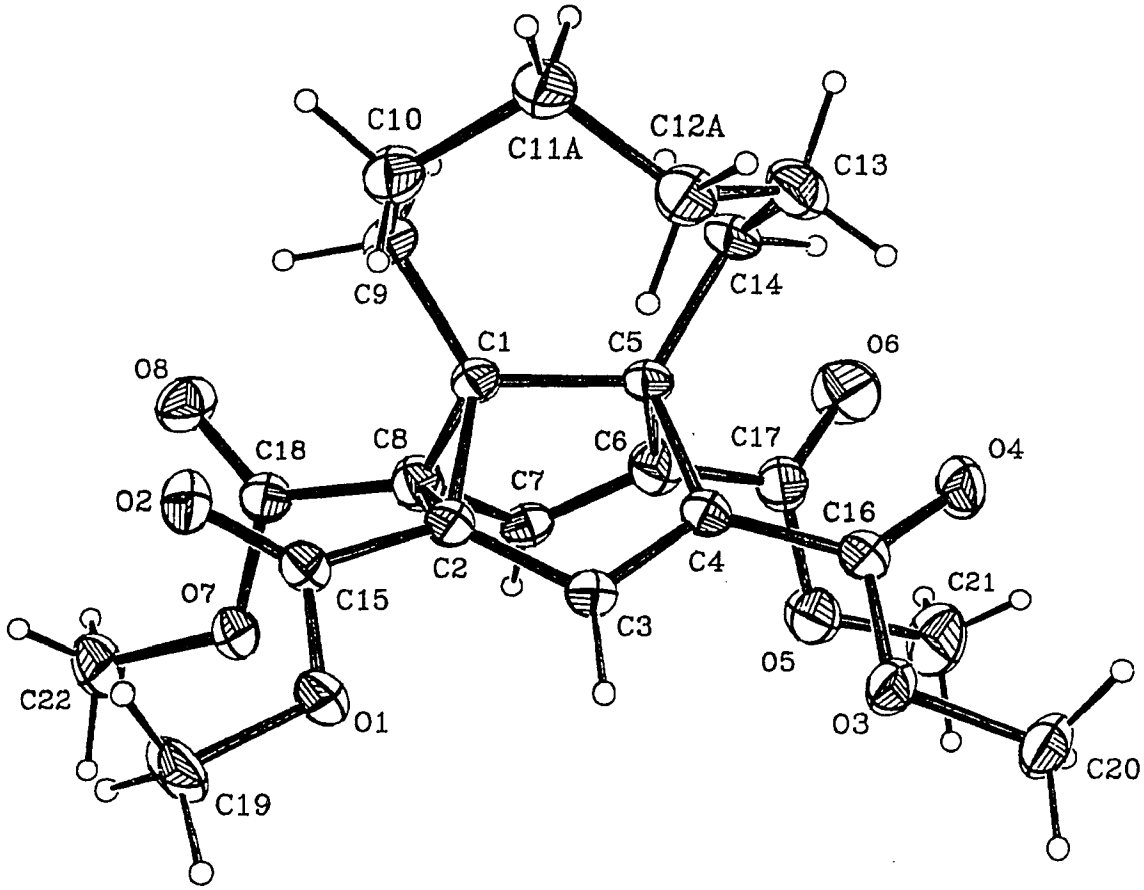


Figure 4–229. *ORTEP* drawing of Sb-8 (major conformer) at **153 K** with 50% thermal ellipsoids.

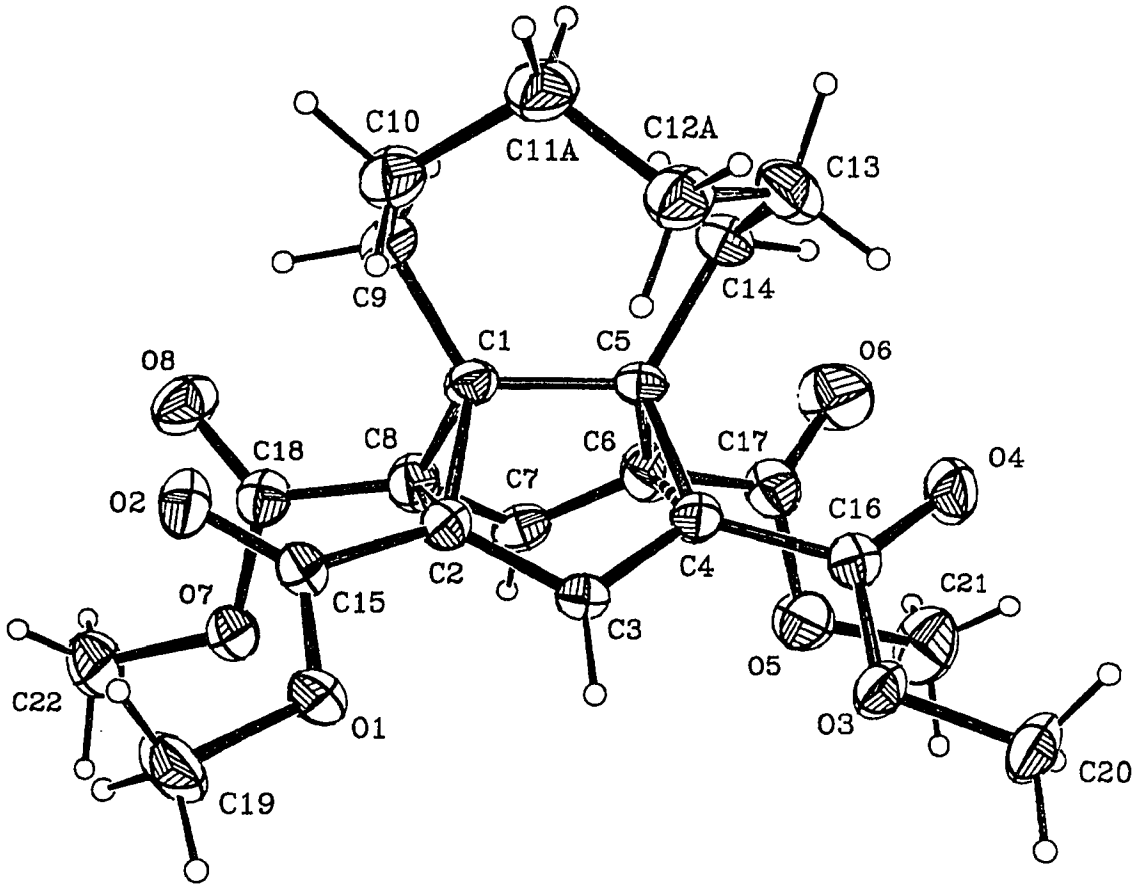


Figure 4–230. *ORTEP* drawing of Sb-8 (major conformer) at **181 K** with 50% thermal ellipsoids.

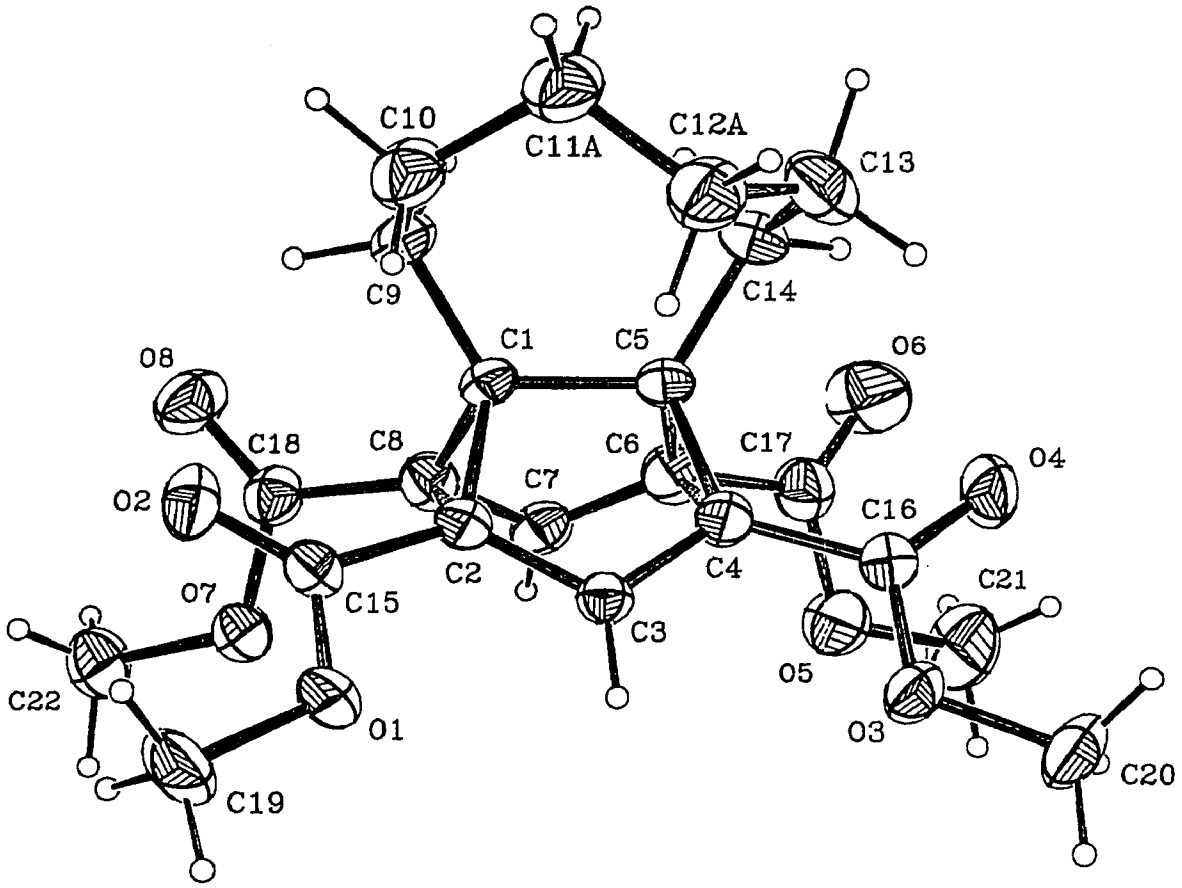


Figure 4–231. *ORTEP* drawing of Sb-8 (major conformer) at **208 K** with 50% thermal ellipsoids.

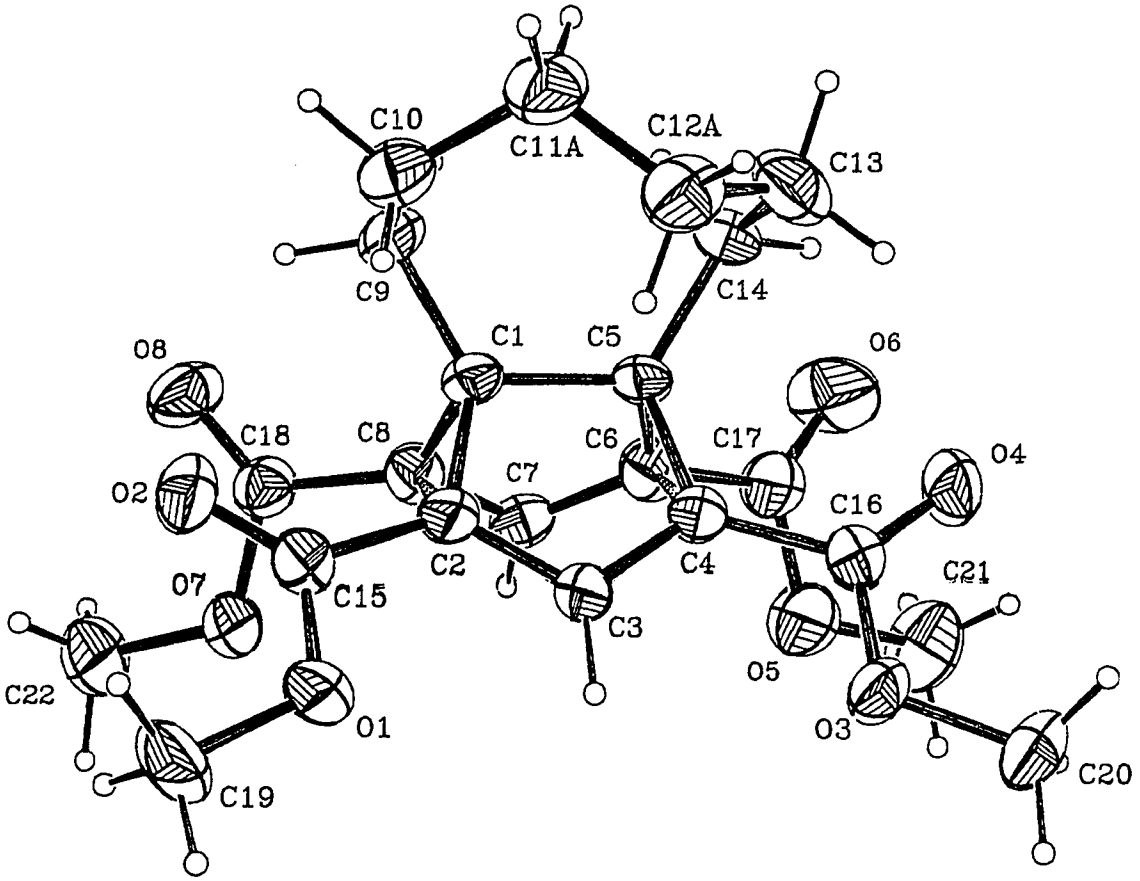


Figure 4–232. *ORTEP* drawing of Sb-8 (major conformer) at **236 K** with 50% thermal ellipsoids.

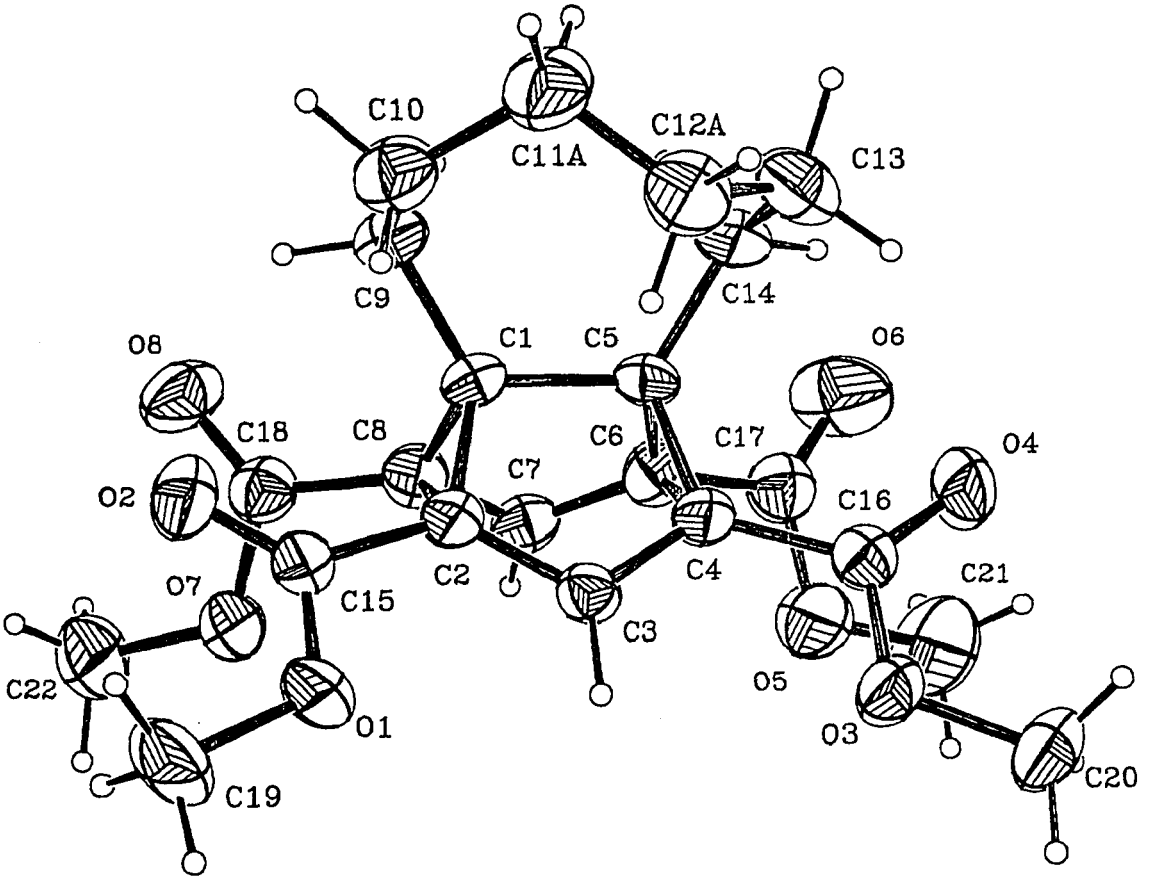


Figure 4–233. *ORTEP* drawing of Sb-8 (major conformer) at **265 K** with 50% thermal ellipsoids.

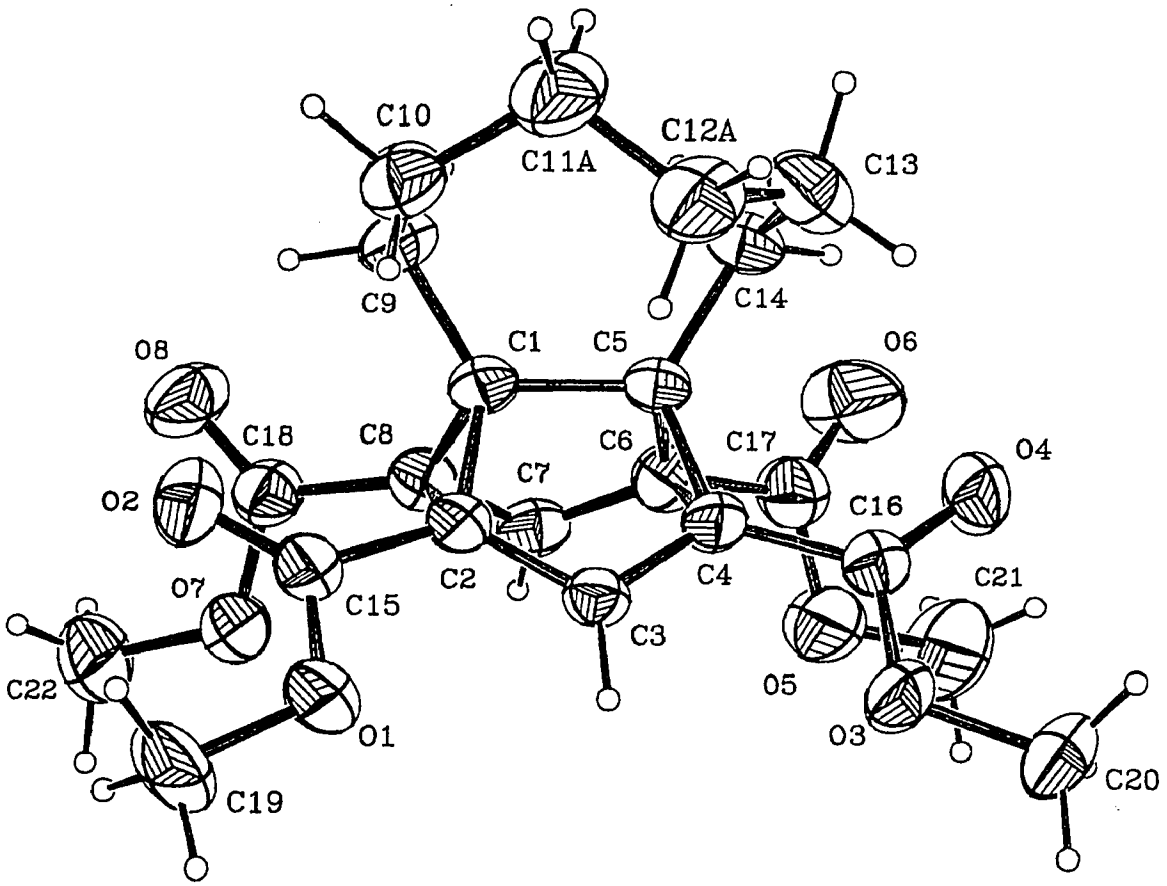


Figure 4–234. *ORTEP* drawing of Sb-8 (major conformer) at **279 K** with 50% thermal ellipsoids.

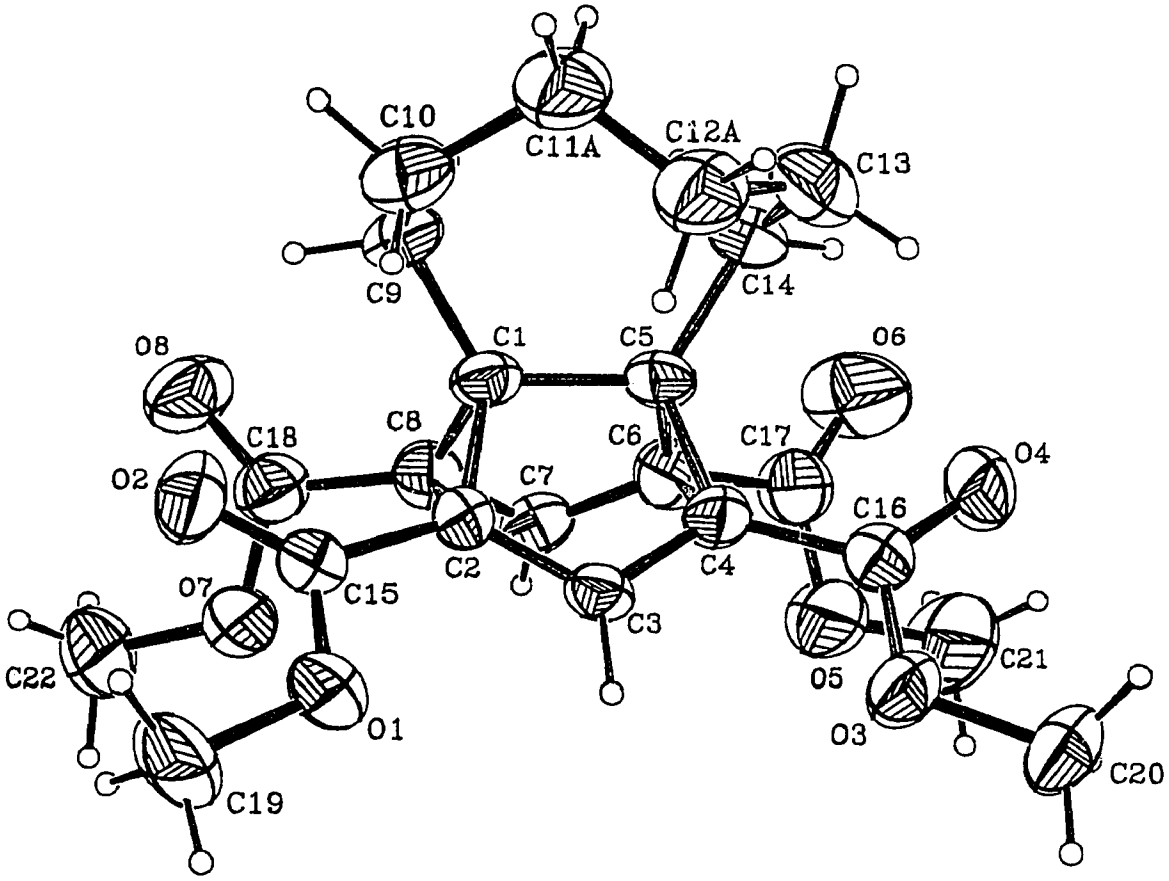


Figure 4–235. *ORTEP* drawing of Sb-8 (major conformer) at **294 K** with 50% thermal ellipsoids.

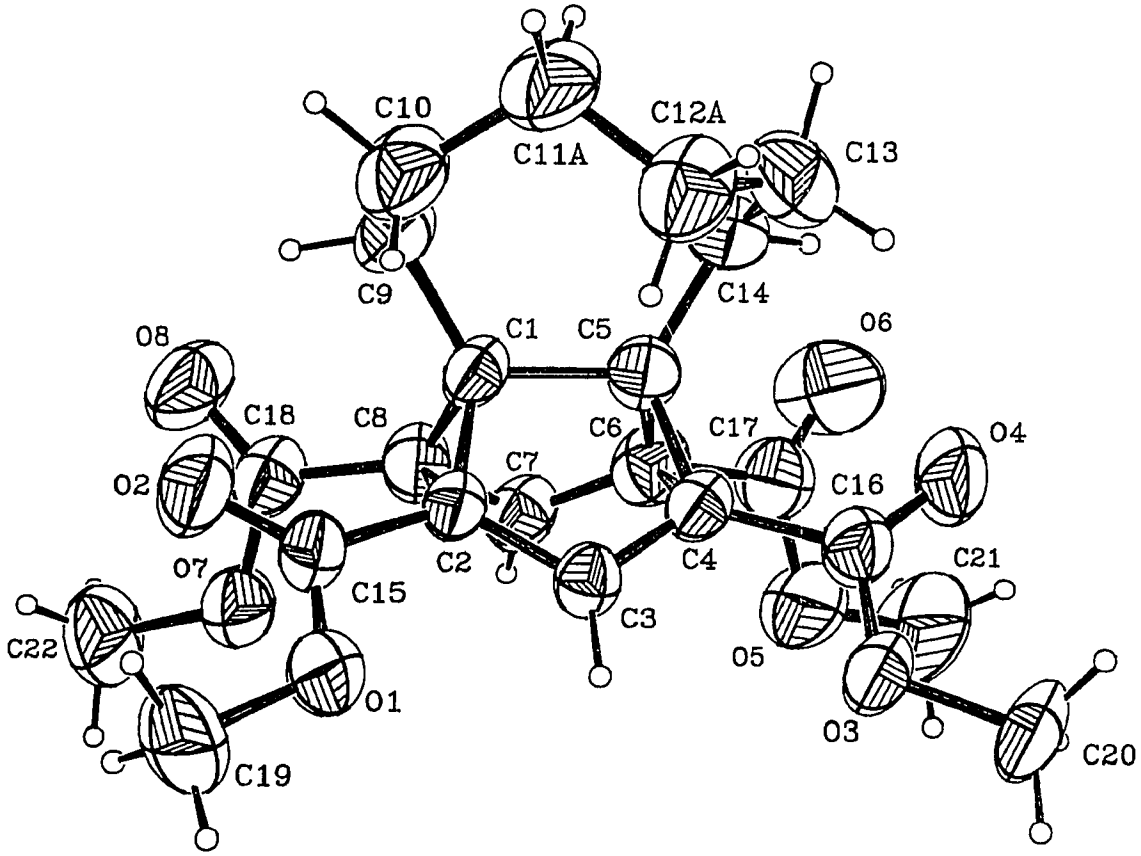


Figure 4–236. *ORTEP* drawing of Sb-8 (major conformer) at **335 K** with 50% thermal ellipsoids.

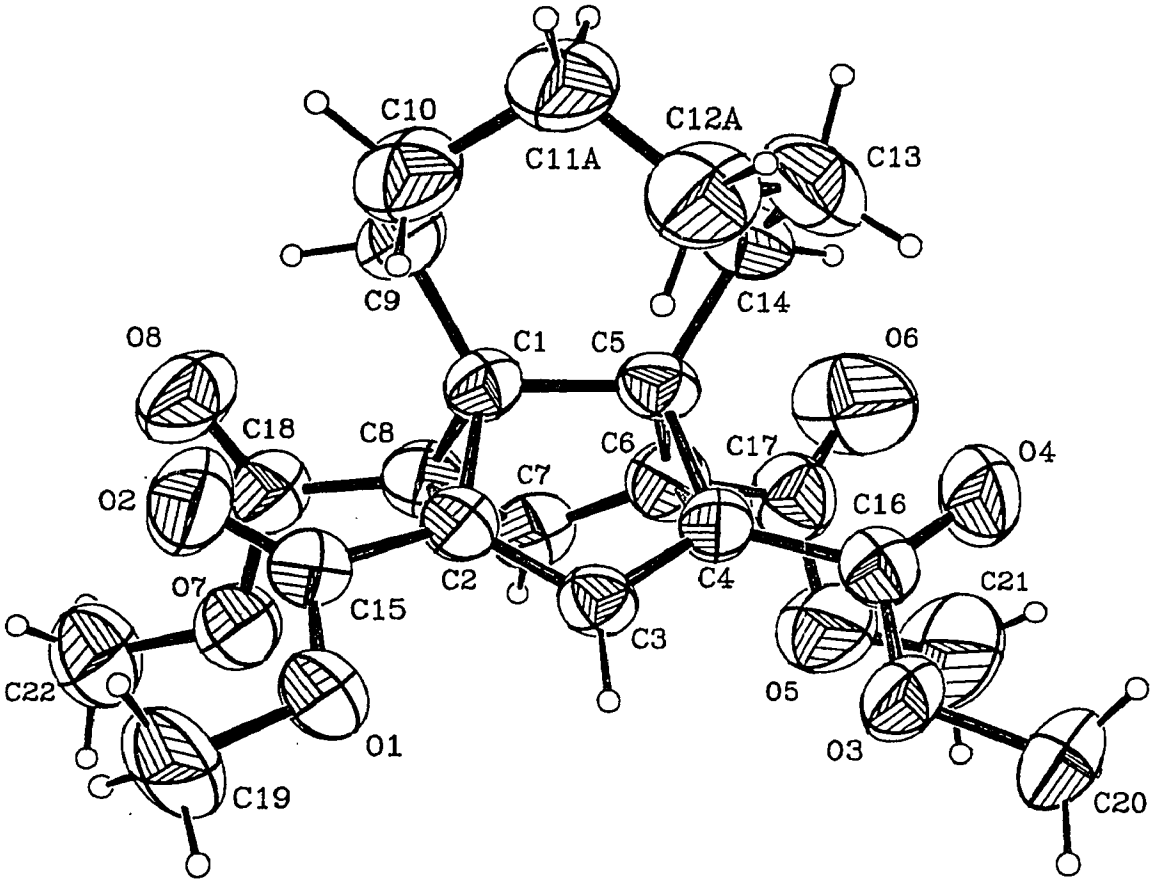


Figure 4–237. *ORTEP* drawing of Sb-8 (major conformer) at **360 K** with 50% thermal ellipsoids.

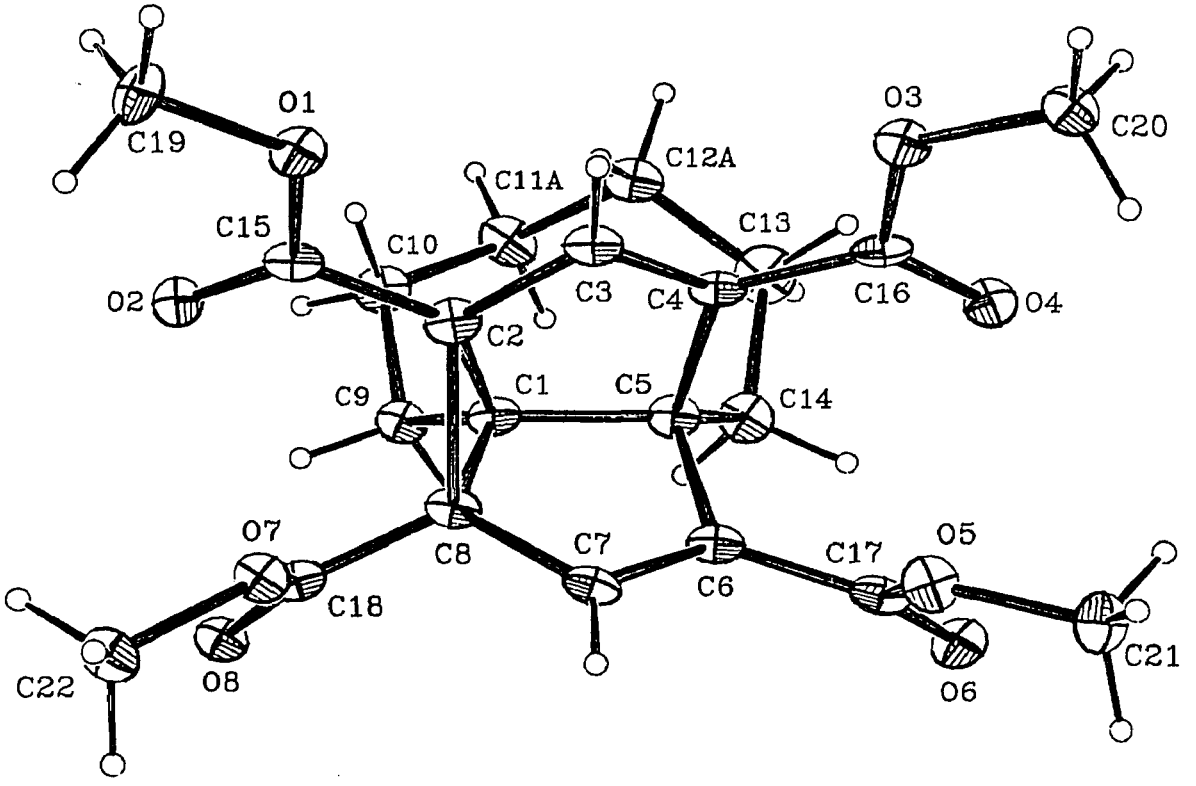


Figure 4–238. *ORTEP* drawing of Sb-8 (major conformer) at **20 K** with 50% thermal ellipsoids.

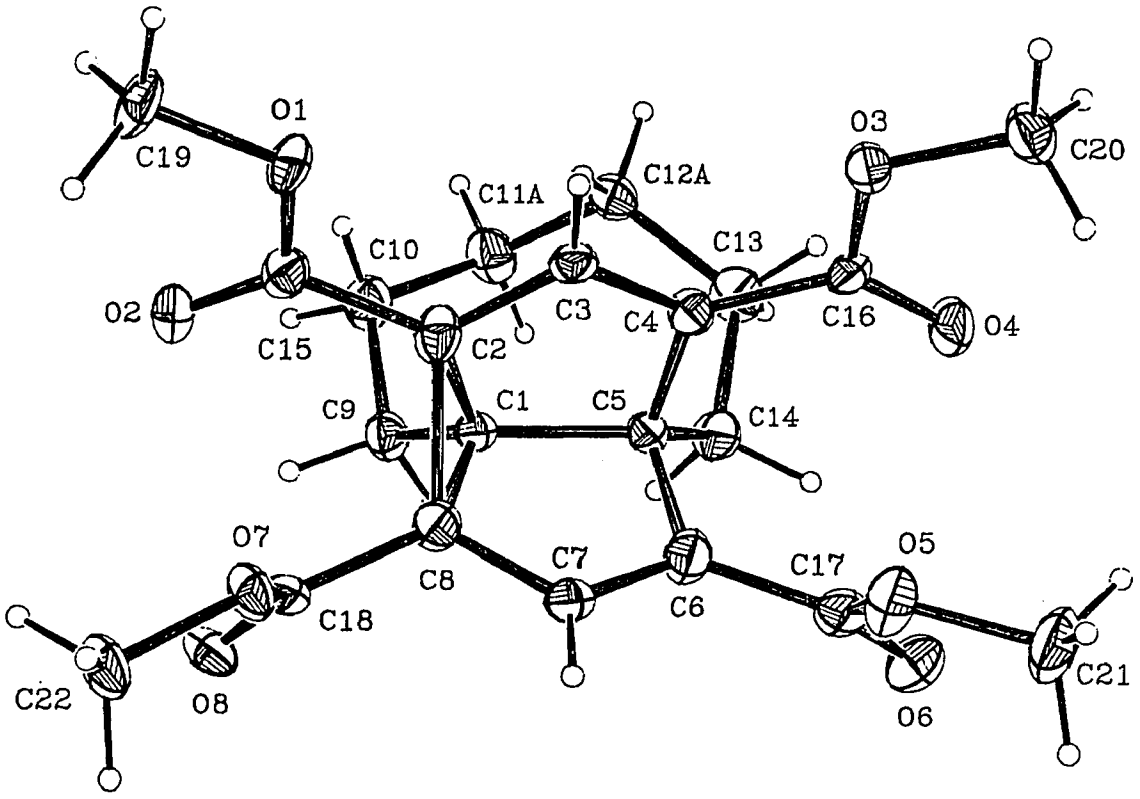


Figure 4–239. *ORTEP* drawing of Sb-8 (major conformer) at **115 K** with 50% thermal ellipsoids.

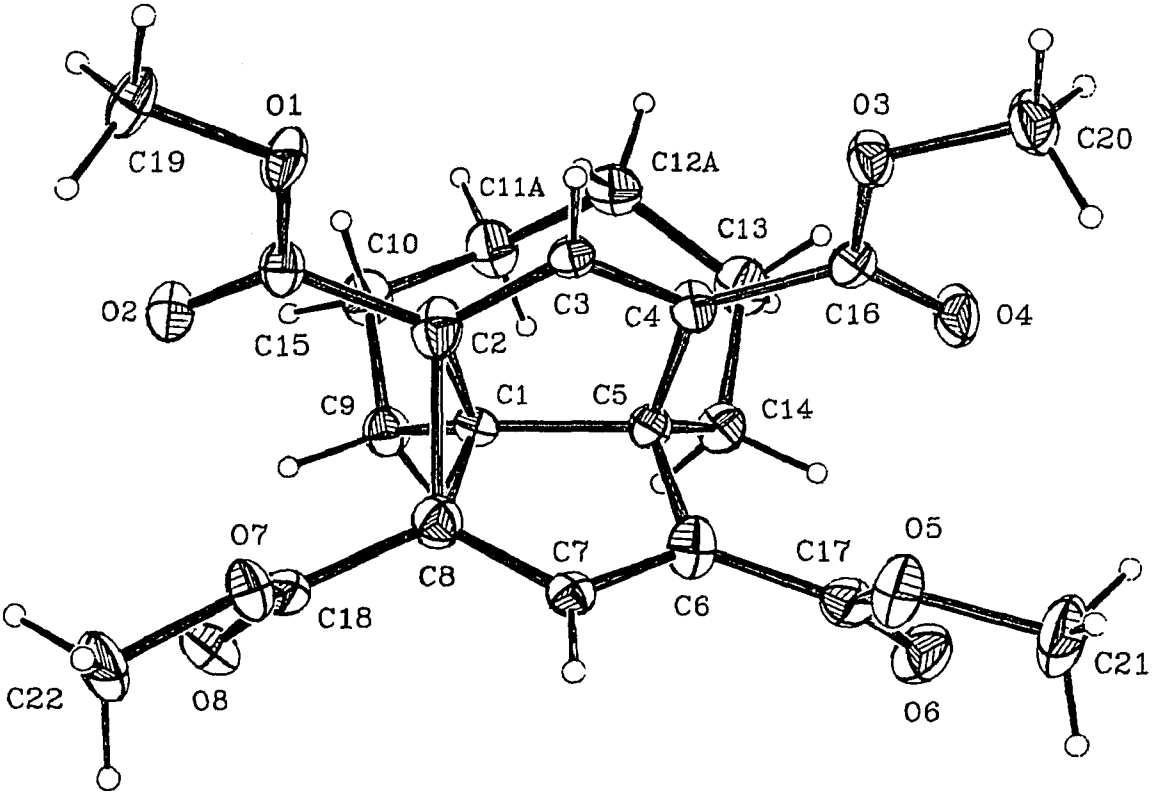


Figure 4–240. *ORTEP* drawing of Sb-8 (major conformer) at **127 K** with 50% thermal ellipsoids.

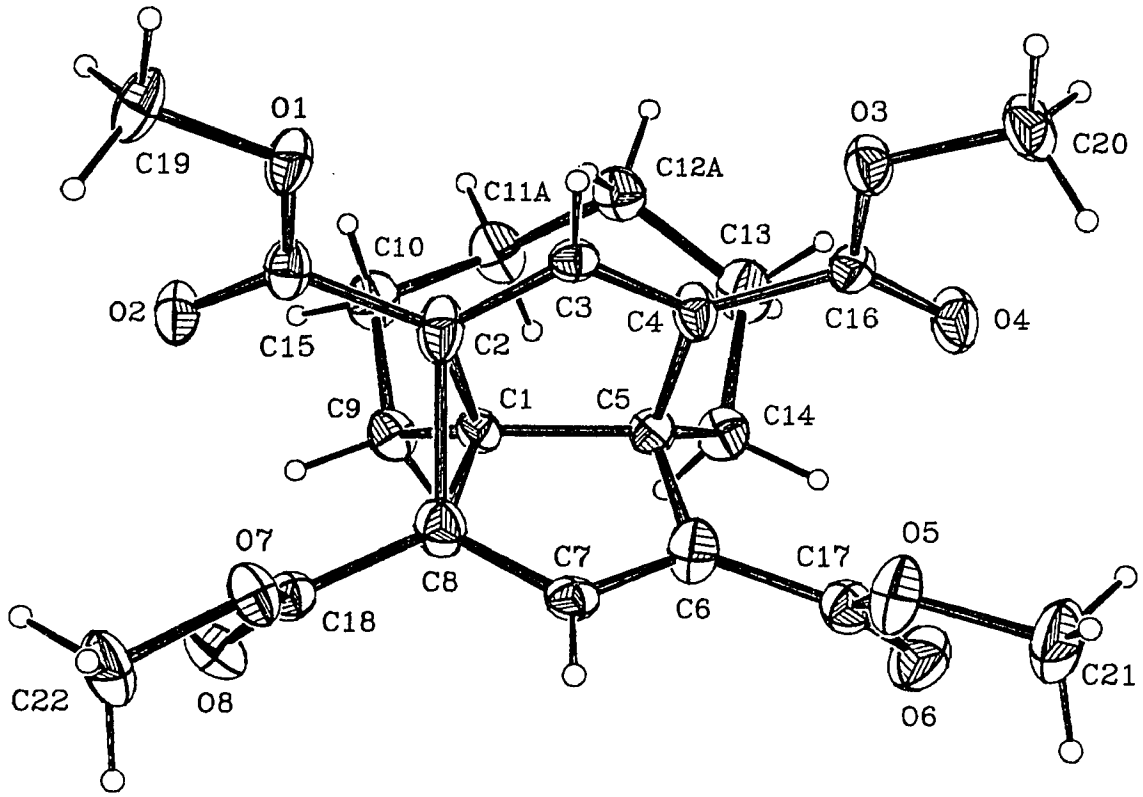


Figure 4–241. *ORTEP* drawing of Sb-8 (major conformer) at **140 K** with 50% thermal ellipsoids.

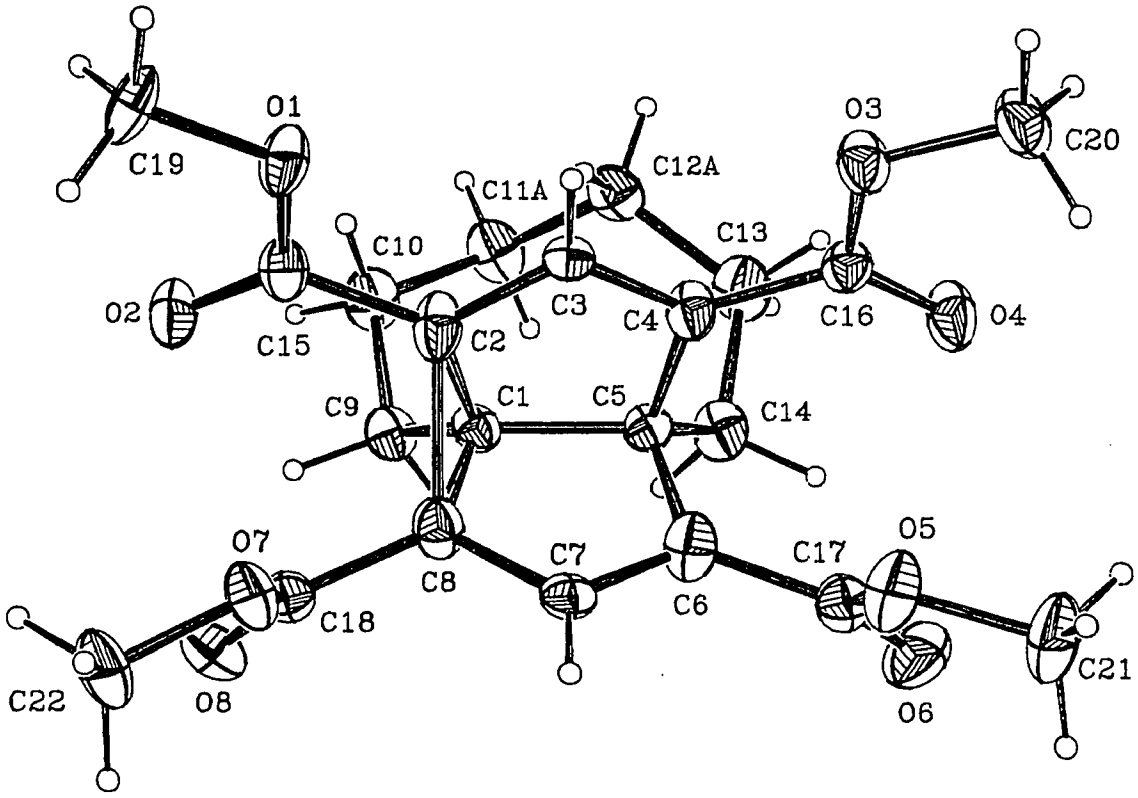


Figure 4–242. *ORTEP* drawing of Sb-8 (major conformer) at **153 K** with 50% thermal ellipsoids.

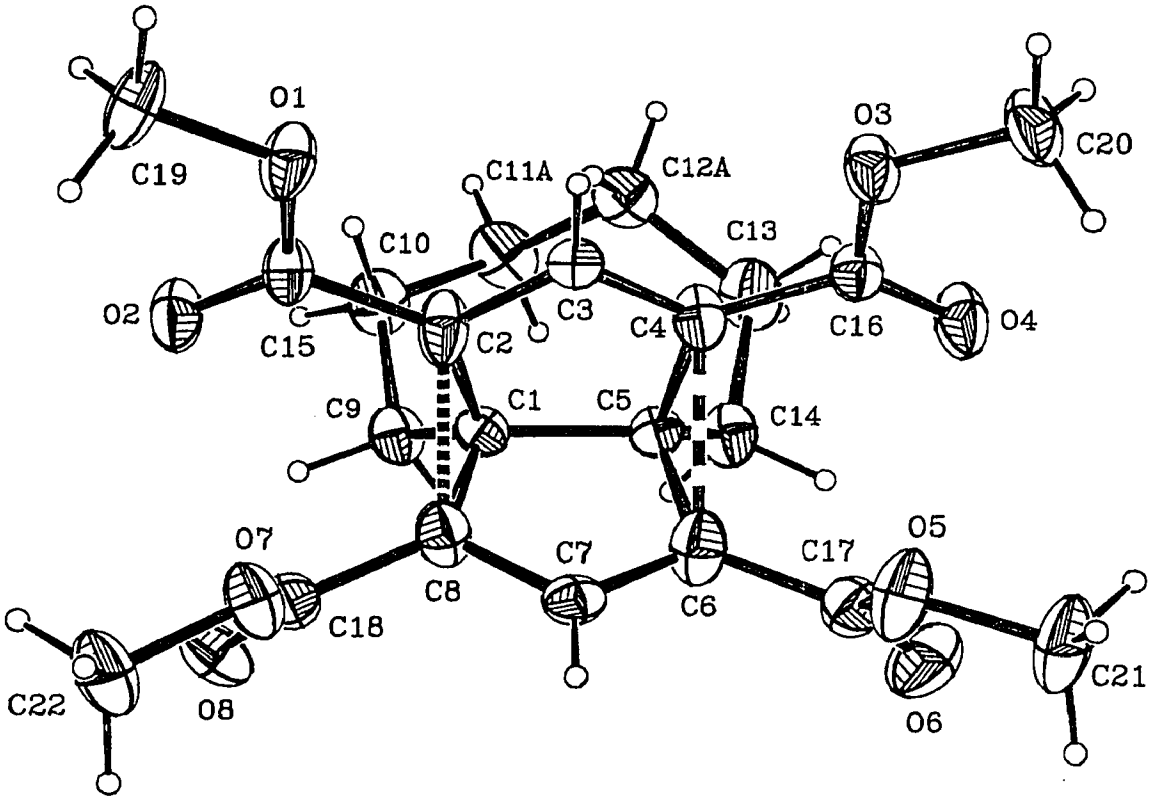


Figure 4–243. *ORTEP* drawing of Sb-8 (major conformer) at **181 K** with 50% thermal ellipsoids.

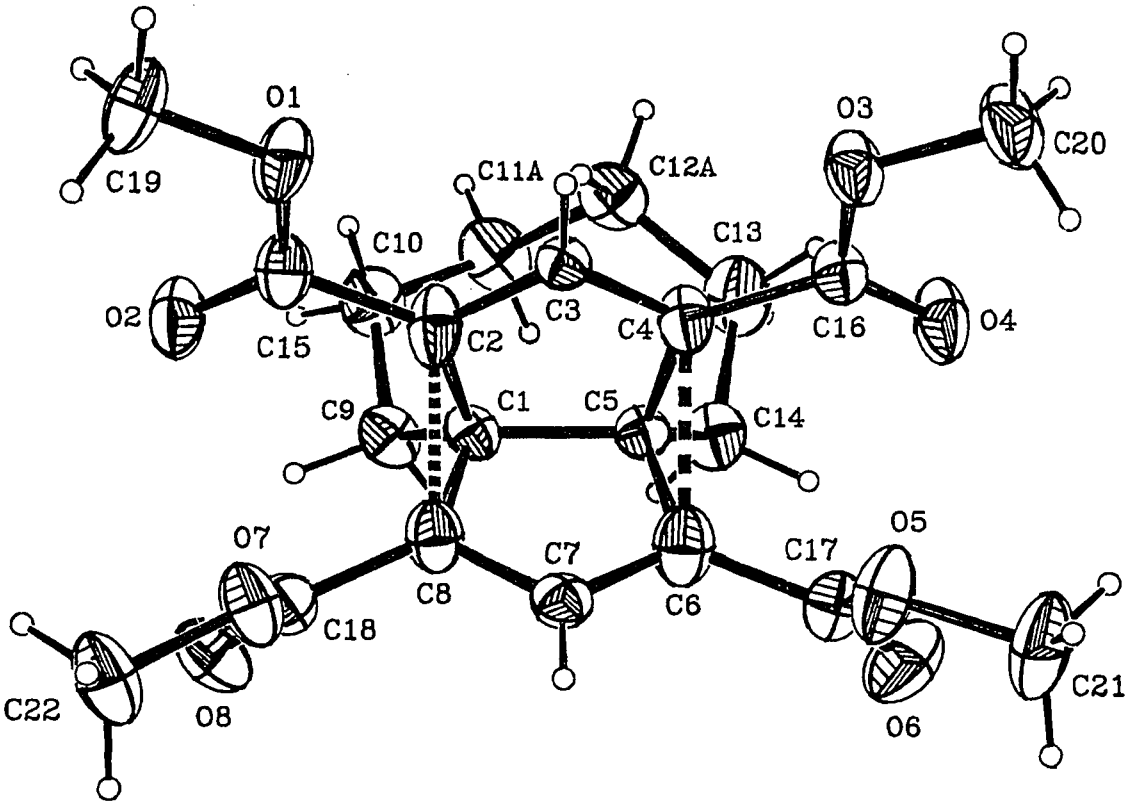


Figure 4–244. *ORTEP* drawing of Sb-8 (major conformer) at **208 K** with 50% thermal ellipsoids.

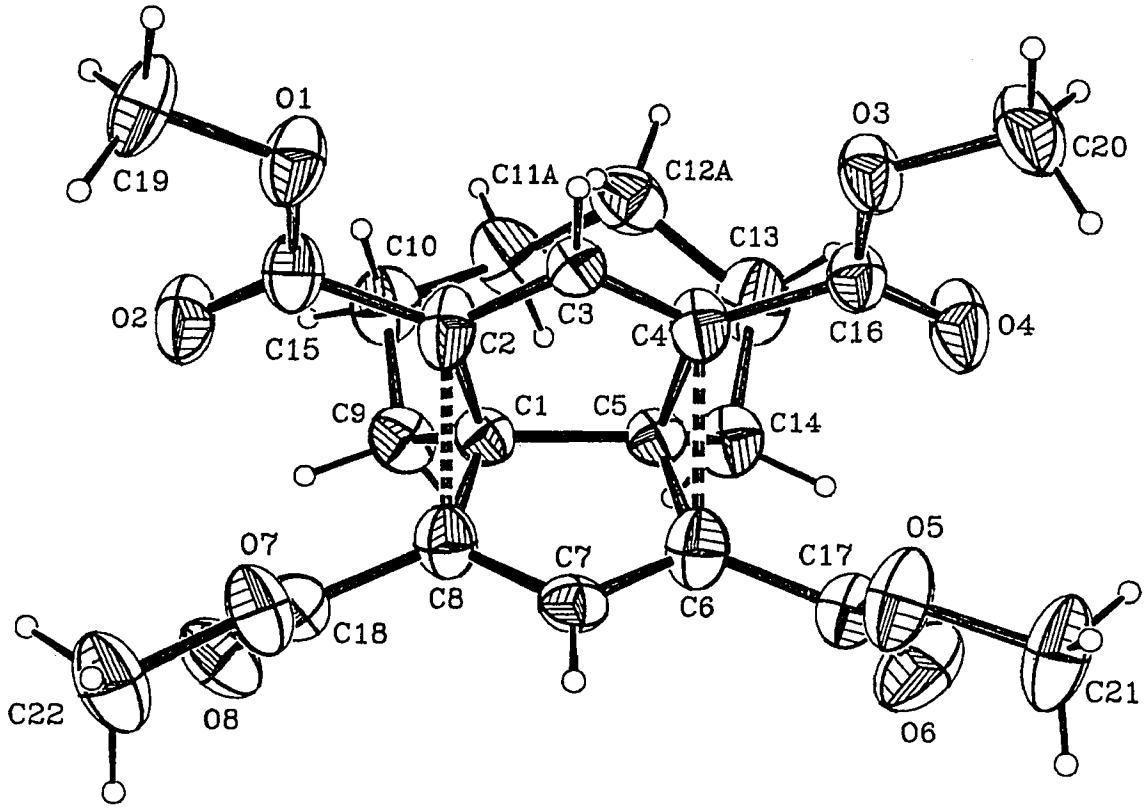


Figure 4–245. *ORTEP* drawing of Sb-8 (major conformer) at **236 K** with 50% thermal ellipsoids.

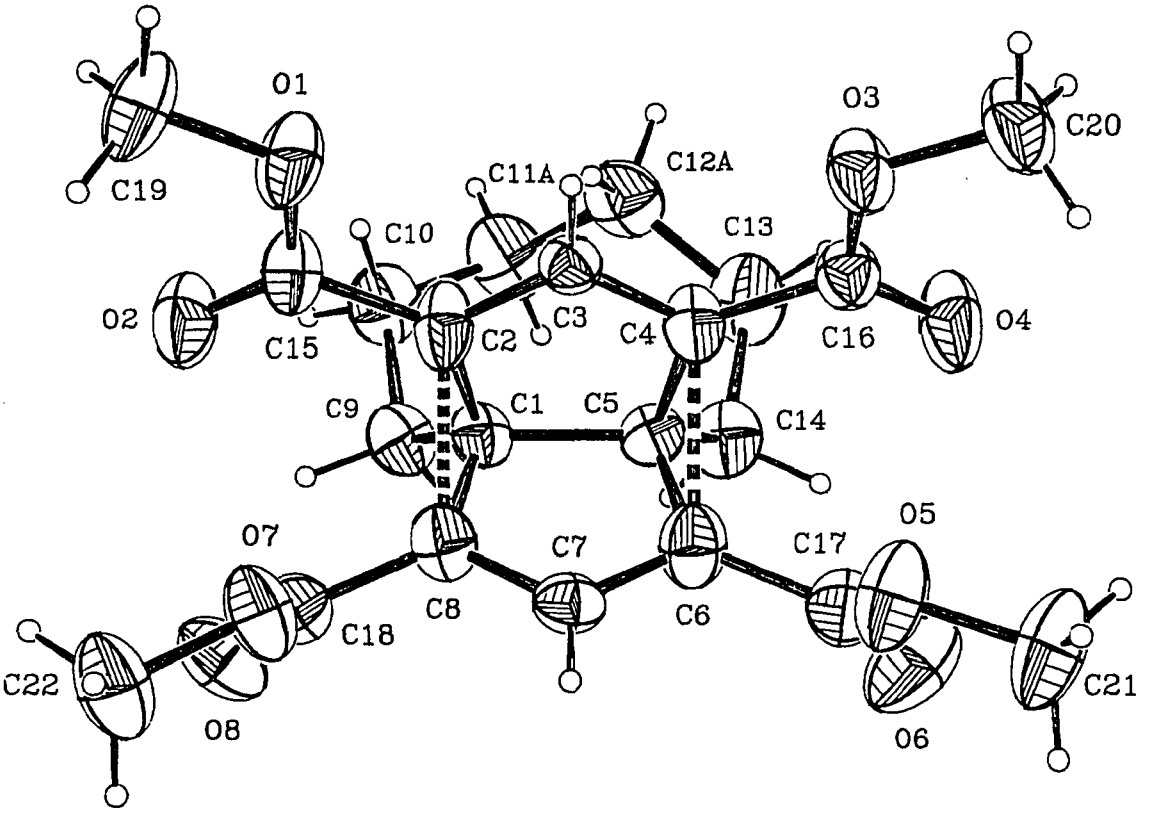


Figure 4–246. *ORTEP* drawing of Sb-8 (major conformer) at **265 K** with 50% thermal ellipsoids.

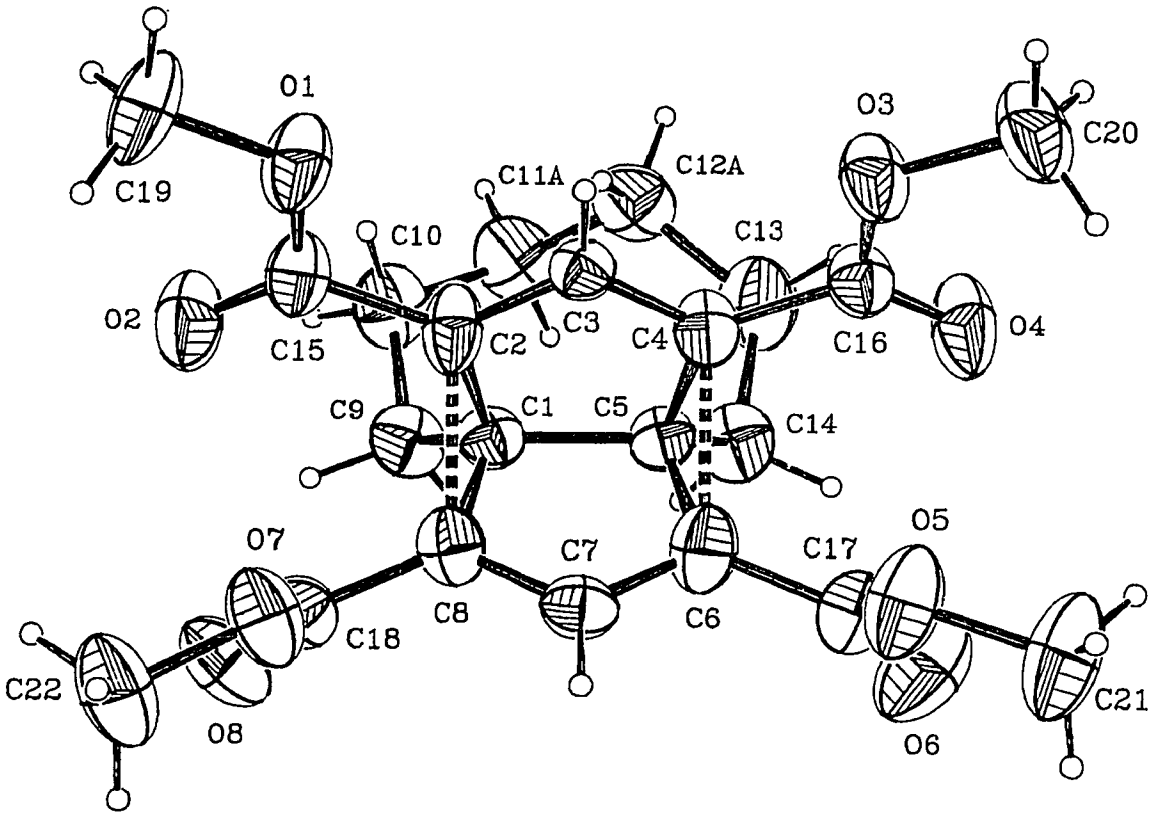


Figure 4–247. *ORTEP* drawing of Sb-8 (major conformer) at **279 K** with 50% thermal ellipsoids.

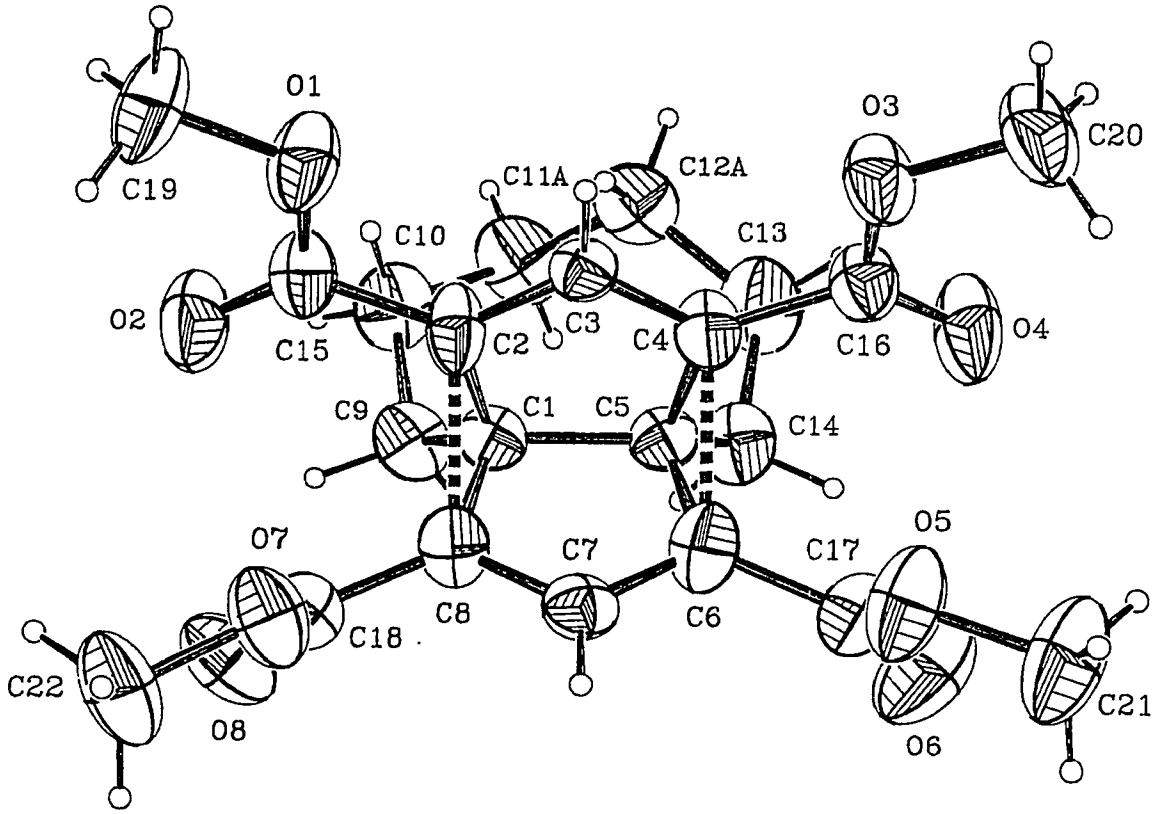


Figure 4–248. *ORTEP* drawing of Sb-8 (major conformer) at **294 K** with 50% thermal ellipsoids.

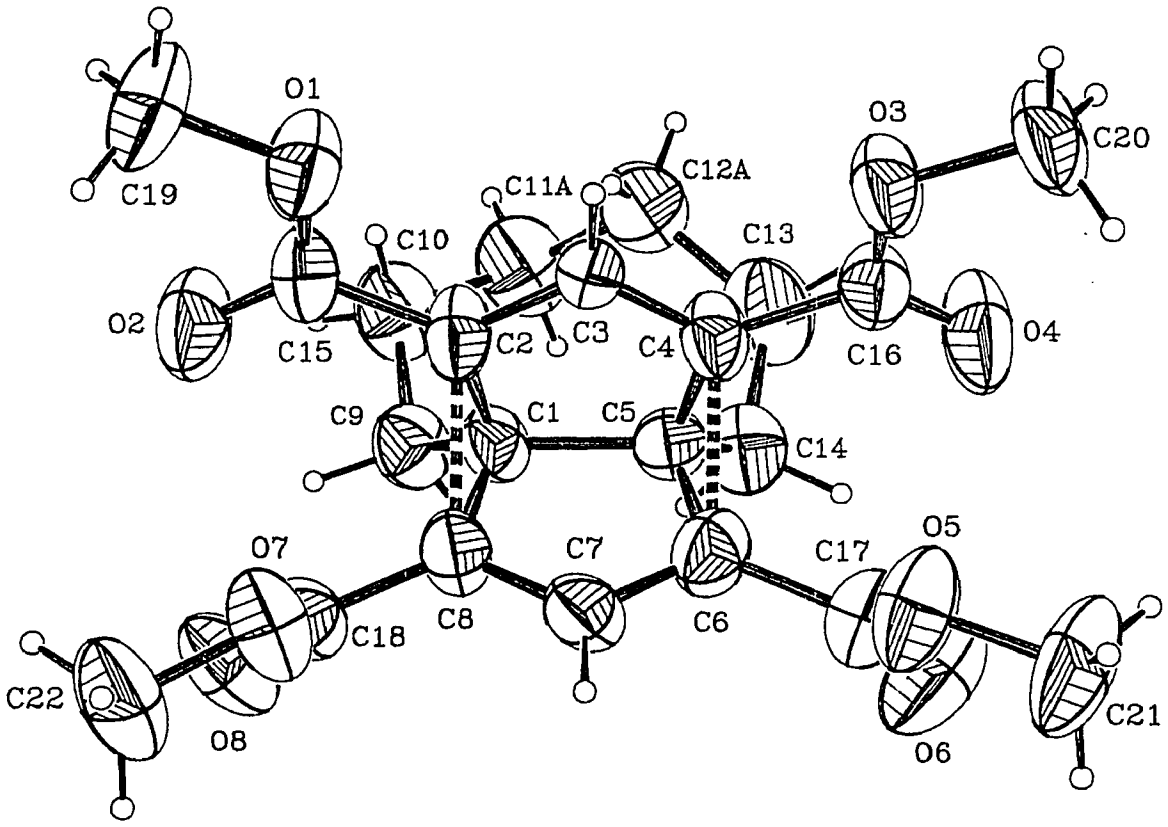


Figure 4–249. *ORTEP* drawing of Sb-8 (major conformer) at **335 K** with 50% thermal ellipsoids.

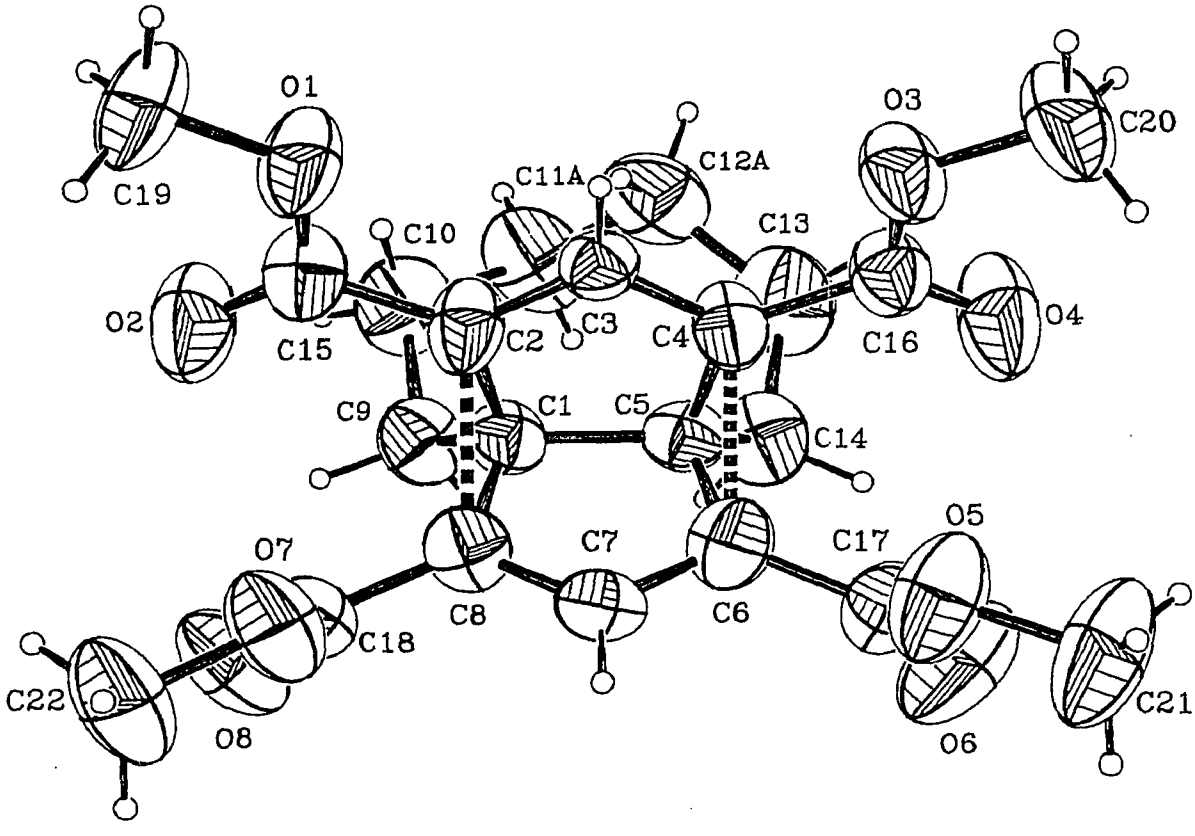


Figure 4–250. *ORTEP* drawing of Sb-8 (major conformer) at **360 K** with 50% thermal ellipsoids.

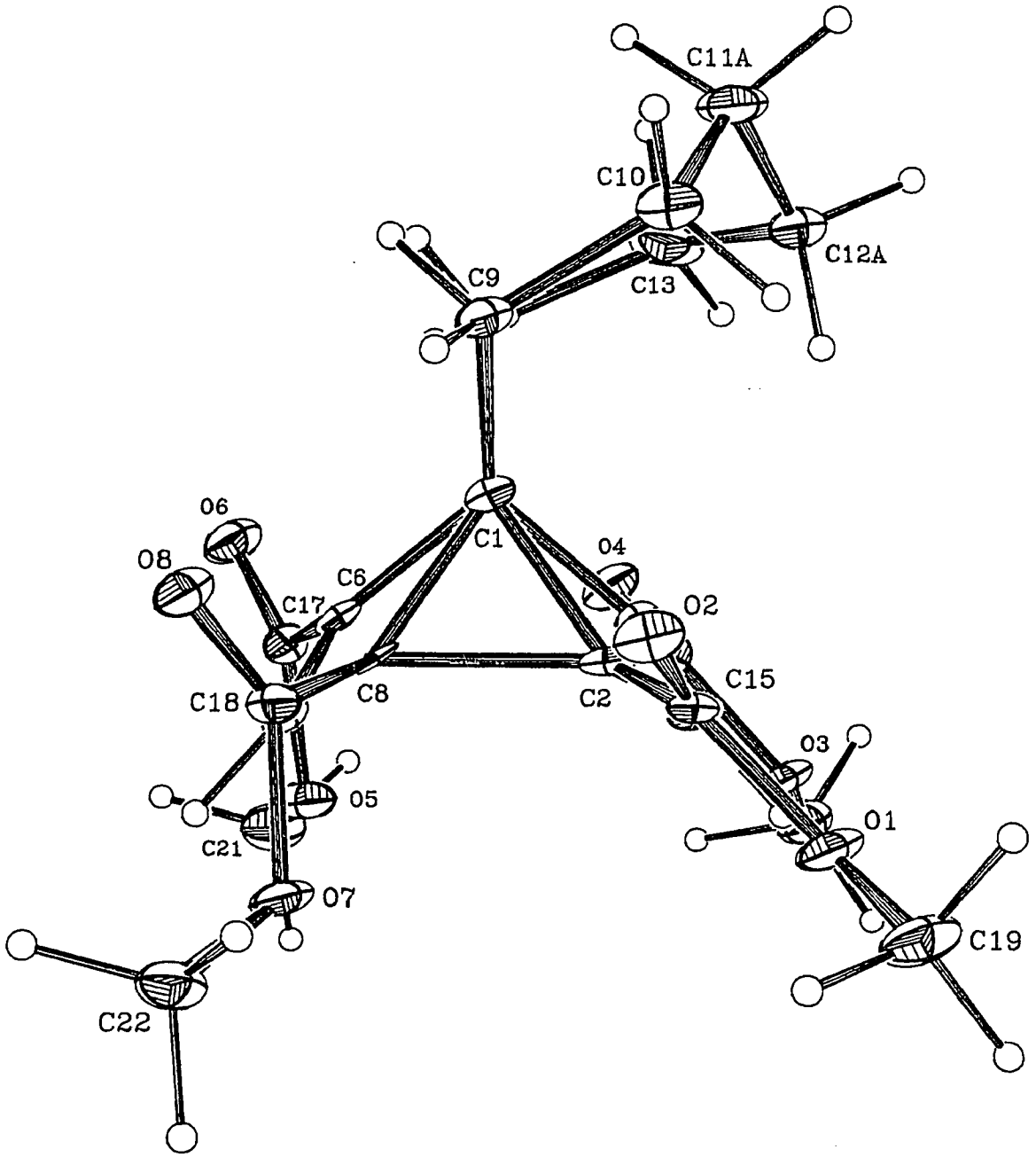


Figure 4–251. *ORTEP* drawing of Sb-8 (major conformer) at **20 K** with 50% thermal ellipsoids.

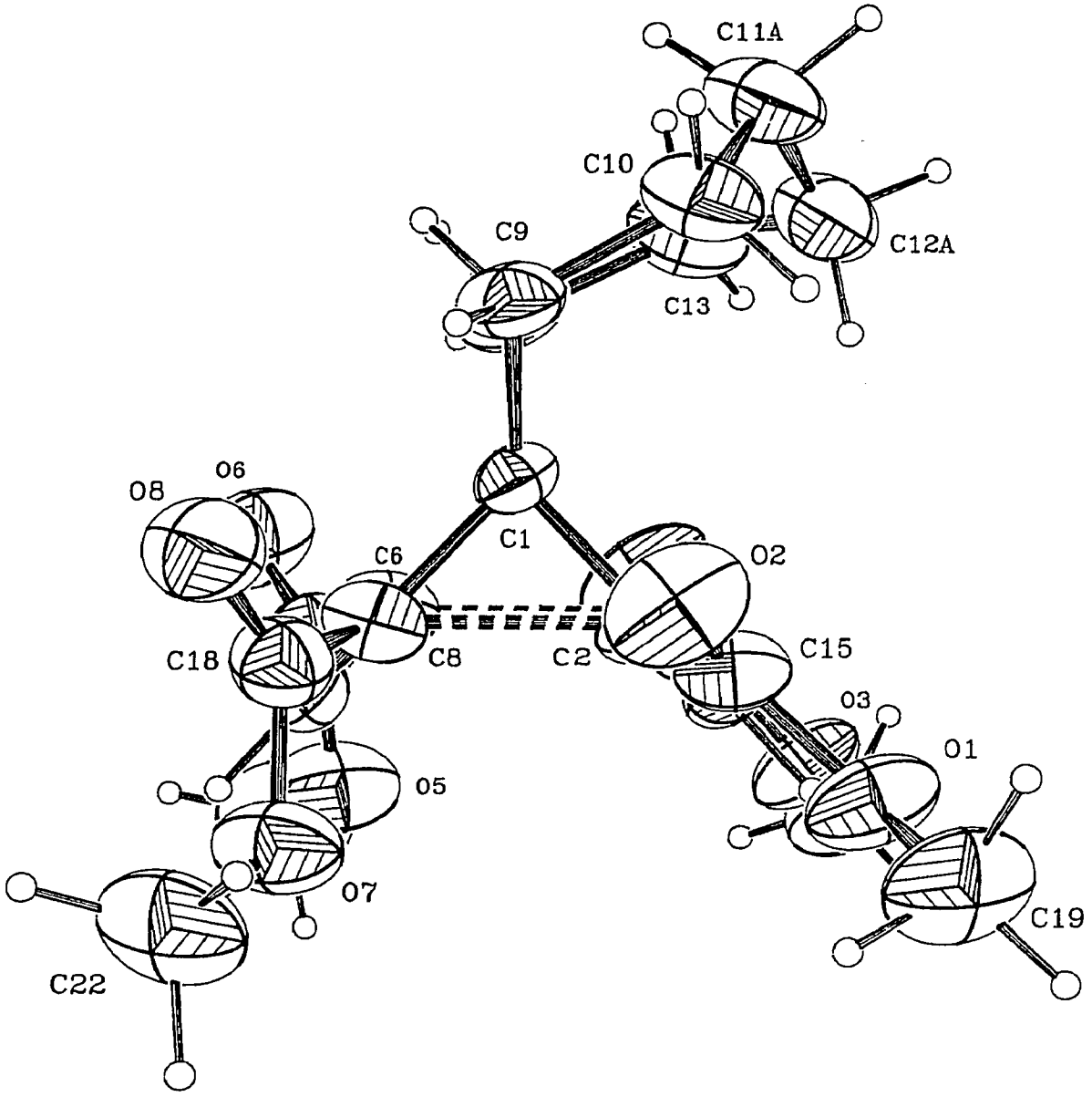


Figure 4–252. *ORTEP* drawing of Sb-8 (major conformer) at **294 K** with 50% thermal ellipsoids.

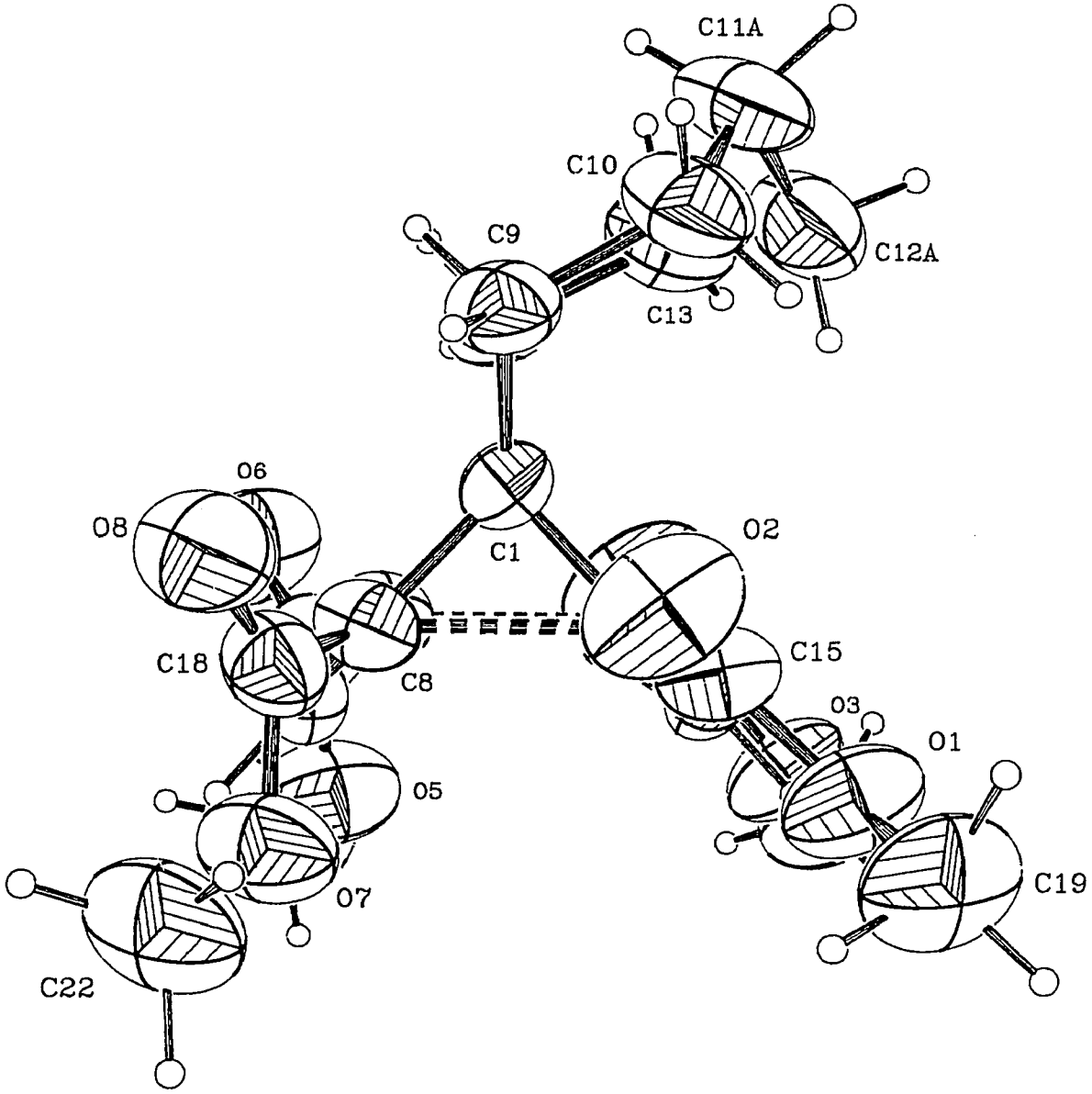


Figure 4–253. *ORTEP* drawing of Sb-8 (major conformer) at **360 K** with 50% thermal ellipsoids.

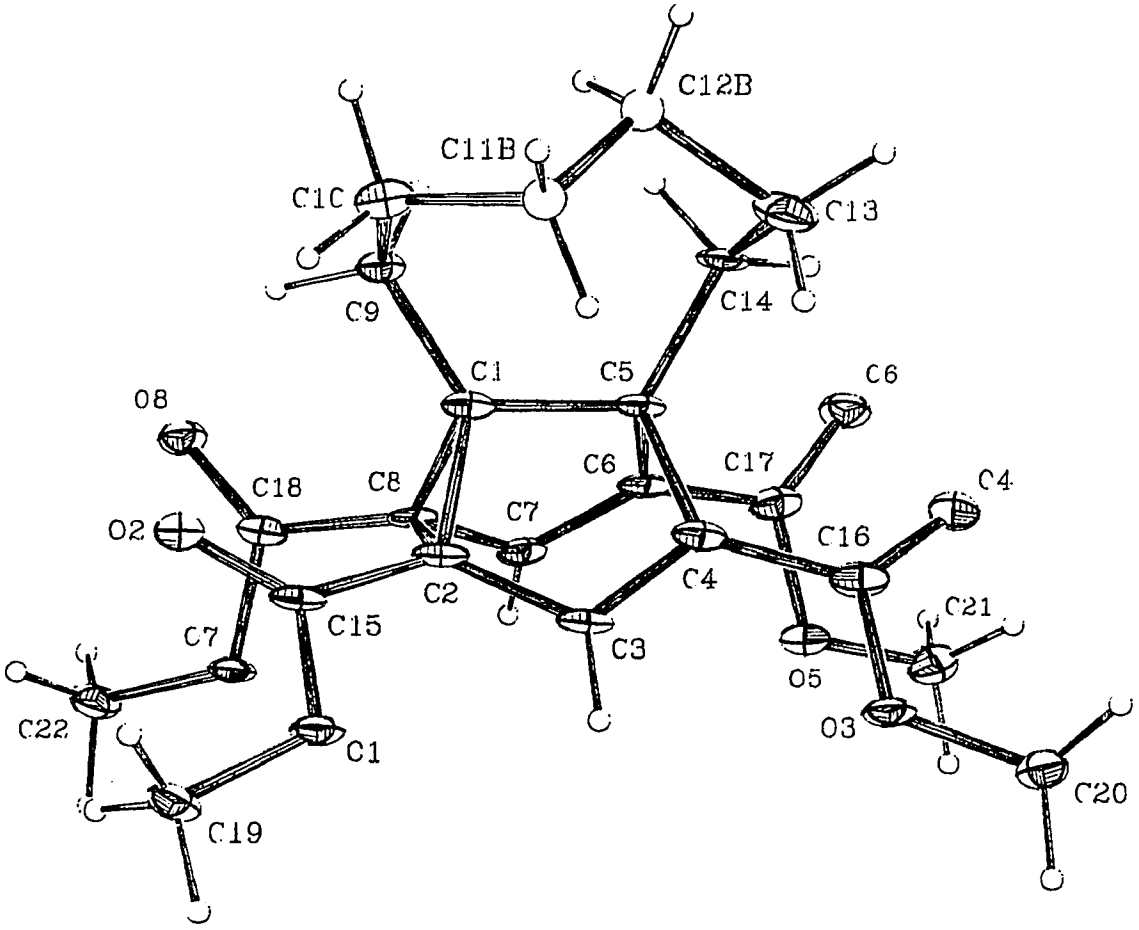


Figure 4–254. *ORTEP* drawing of Sb-8 (minor conformer) at **20 K** with 50% thermal ellipsoids.

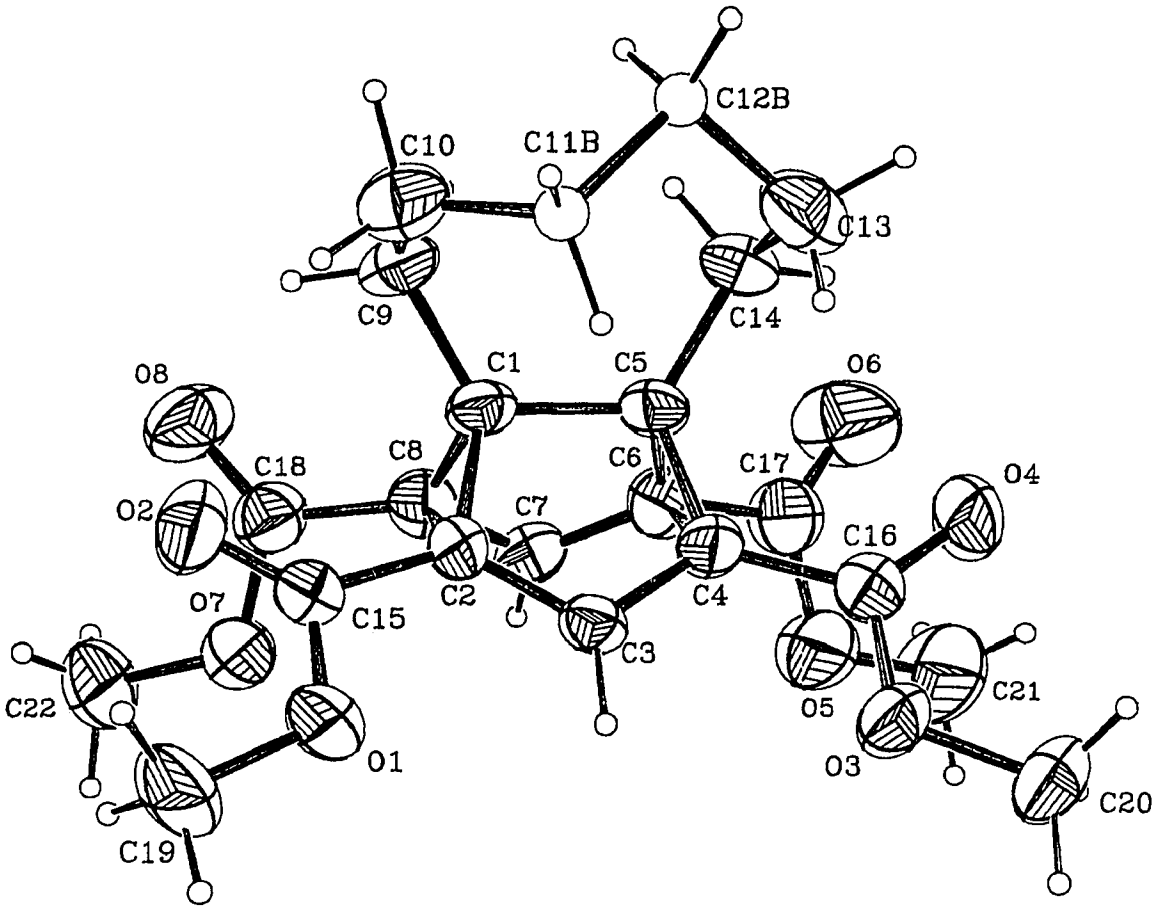


Figure 4–255. *ORTEP* drawing of Sb-8 (minor conformer) at **294 K** with 50% thermal ellipsoids.

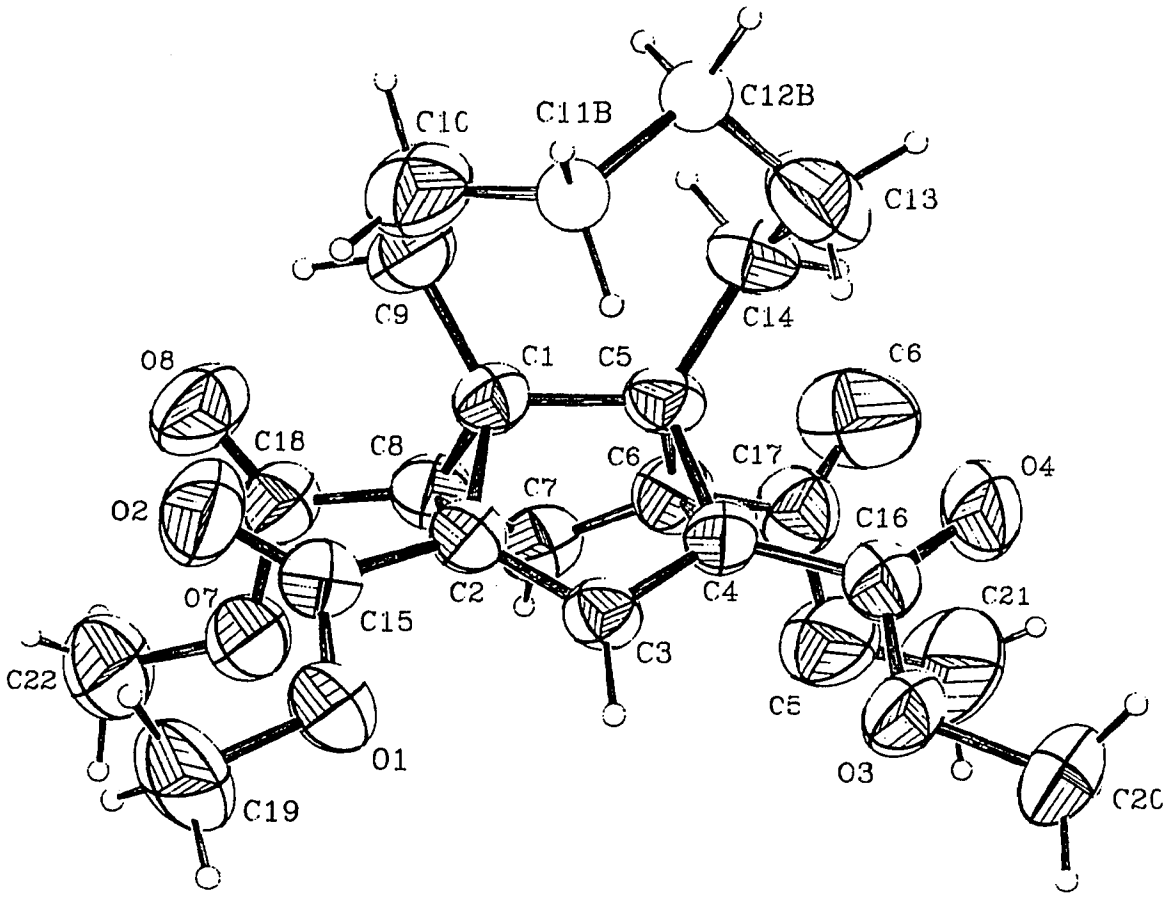


Figure 4–256. *ORTEP* drawing of Sb-8 (minor conformer) at **360 K** with 50% thermal ellipsoids.

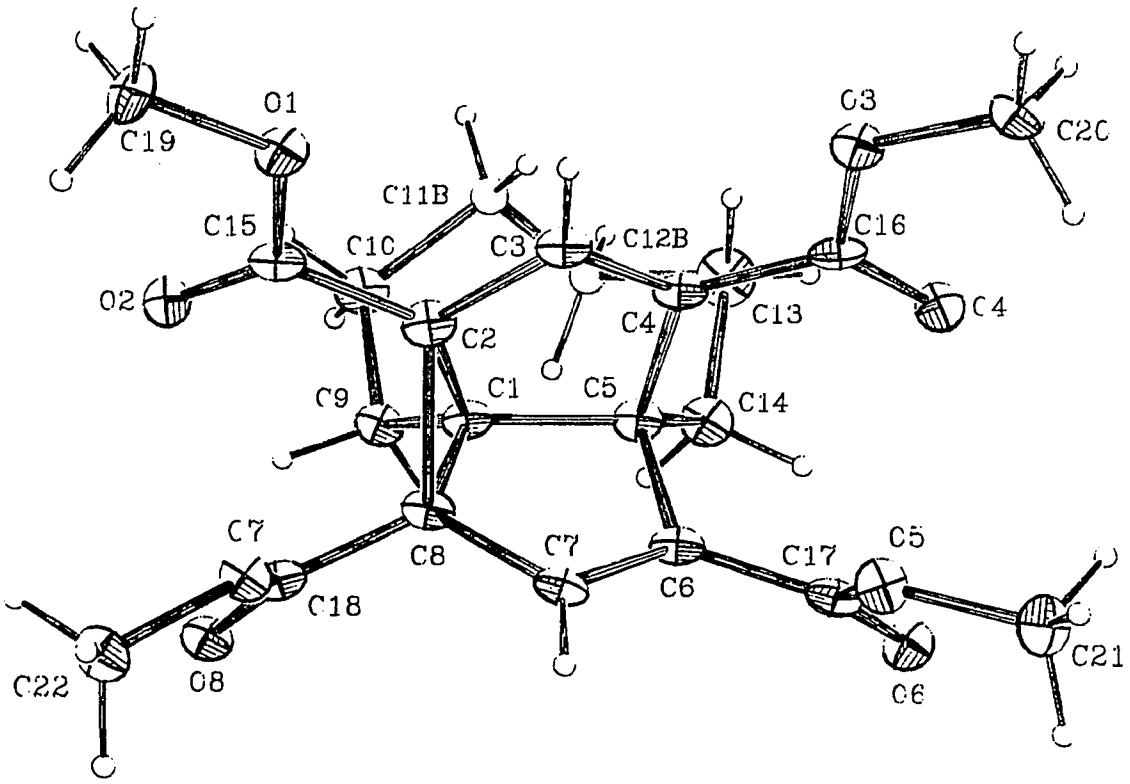


Figure 4–257. *ORTEP* drawing of Sb-8 (minor conformer) at **20 K** with 50% thermal ellipsoids.

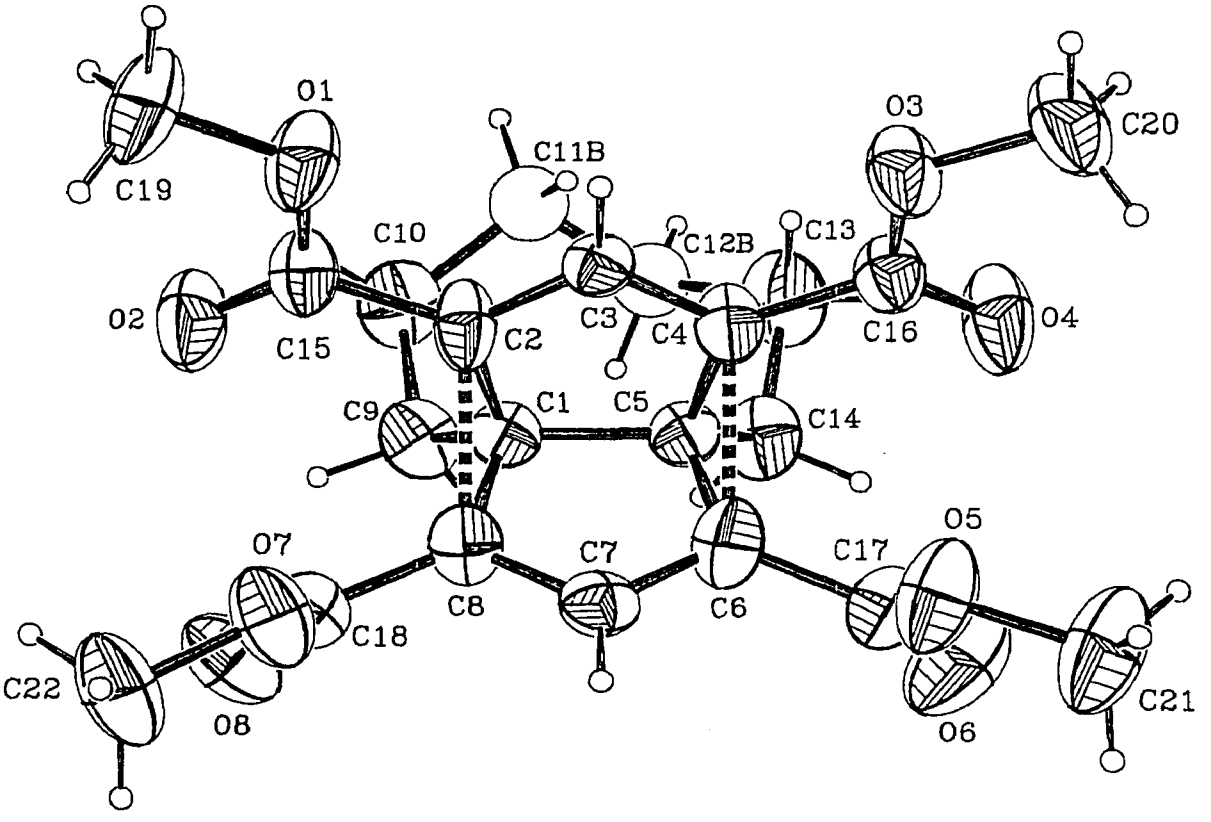


Figure 4–258. *ORTEP* drawing of Sb-8 (minor conformer) at **294 K** with 50% thermal ellipsoids.

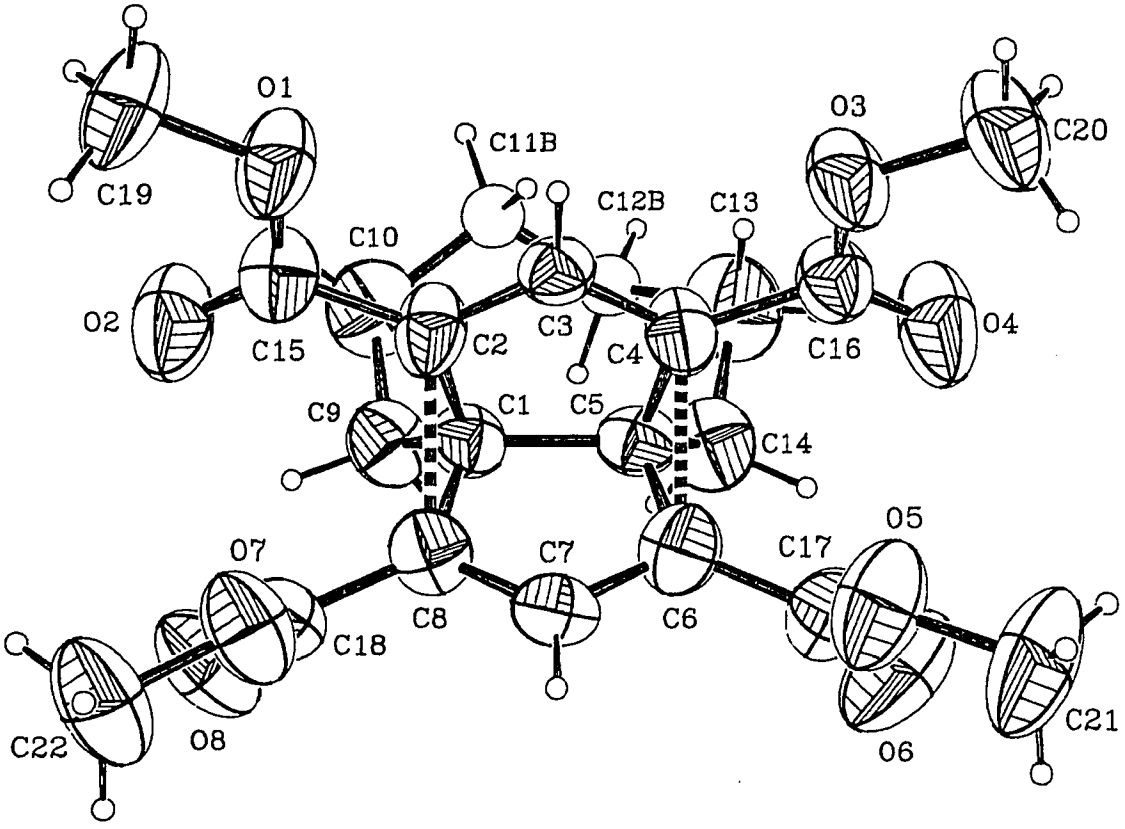


Figure 4–259. *ORTEP* drawing of Sb-8 (minor conformer) at **360 K** with 50% thermal ellipsoids.

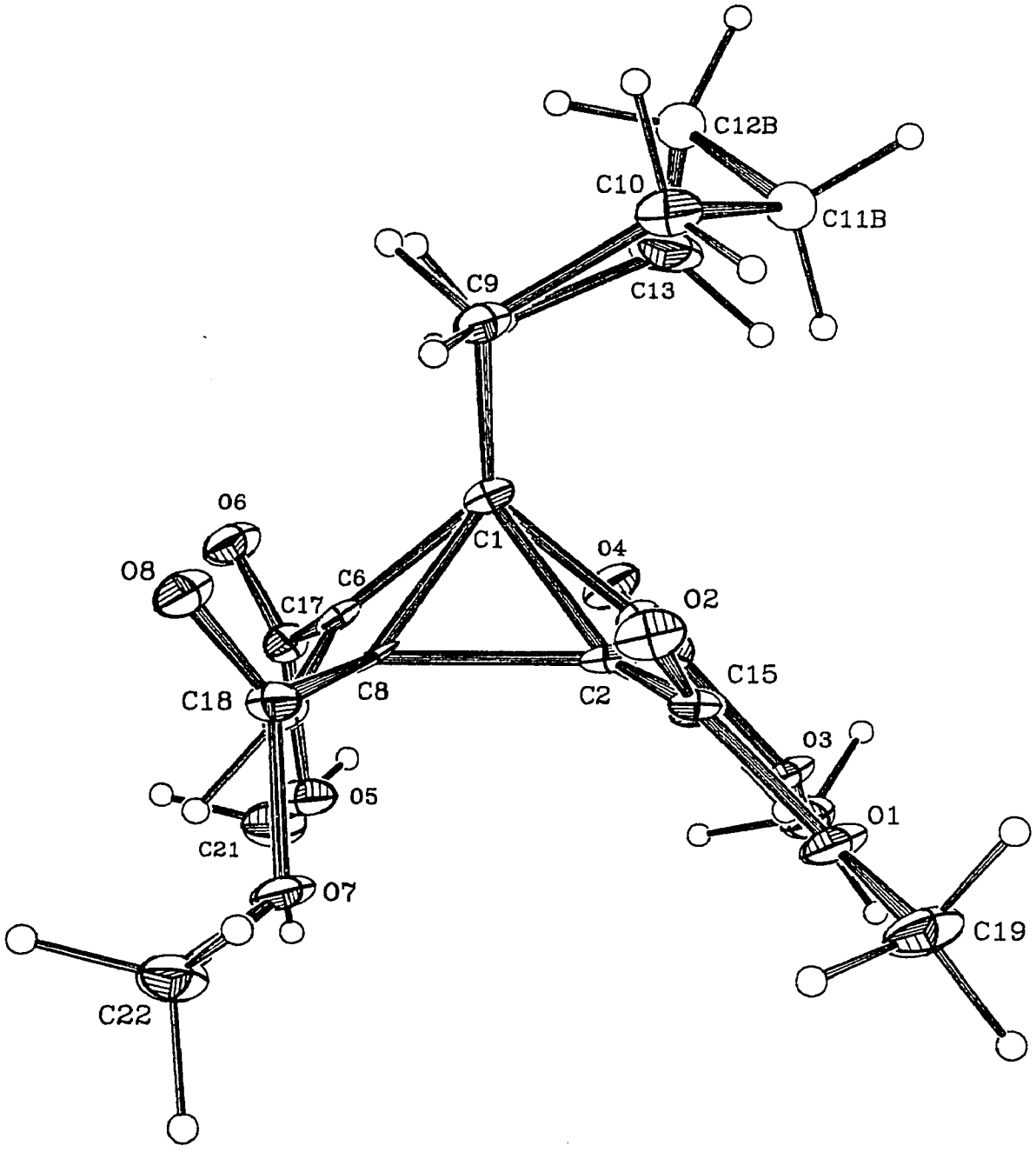


Figure 4–260. *ORTEP* drawing of Sb-8 (minor conformer) at **20 K** with 50% thermal ellipsoids.

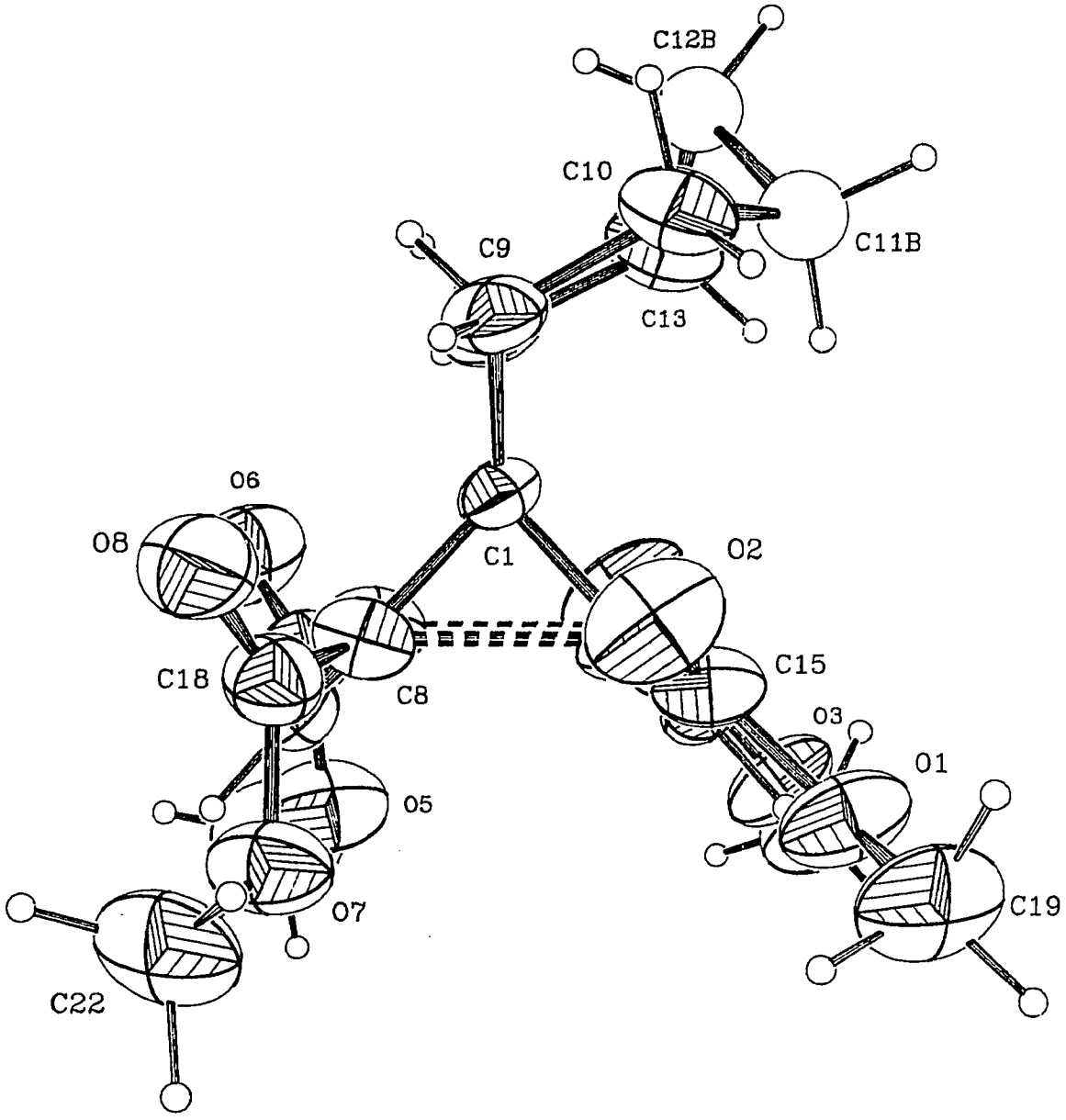


Figure 4-261. *ORTEP* drawing of Sb-8 (minor conformer) at **294 K** with 50% thermal ellipsoids.

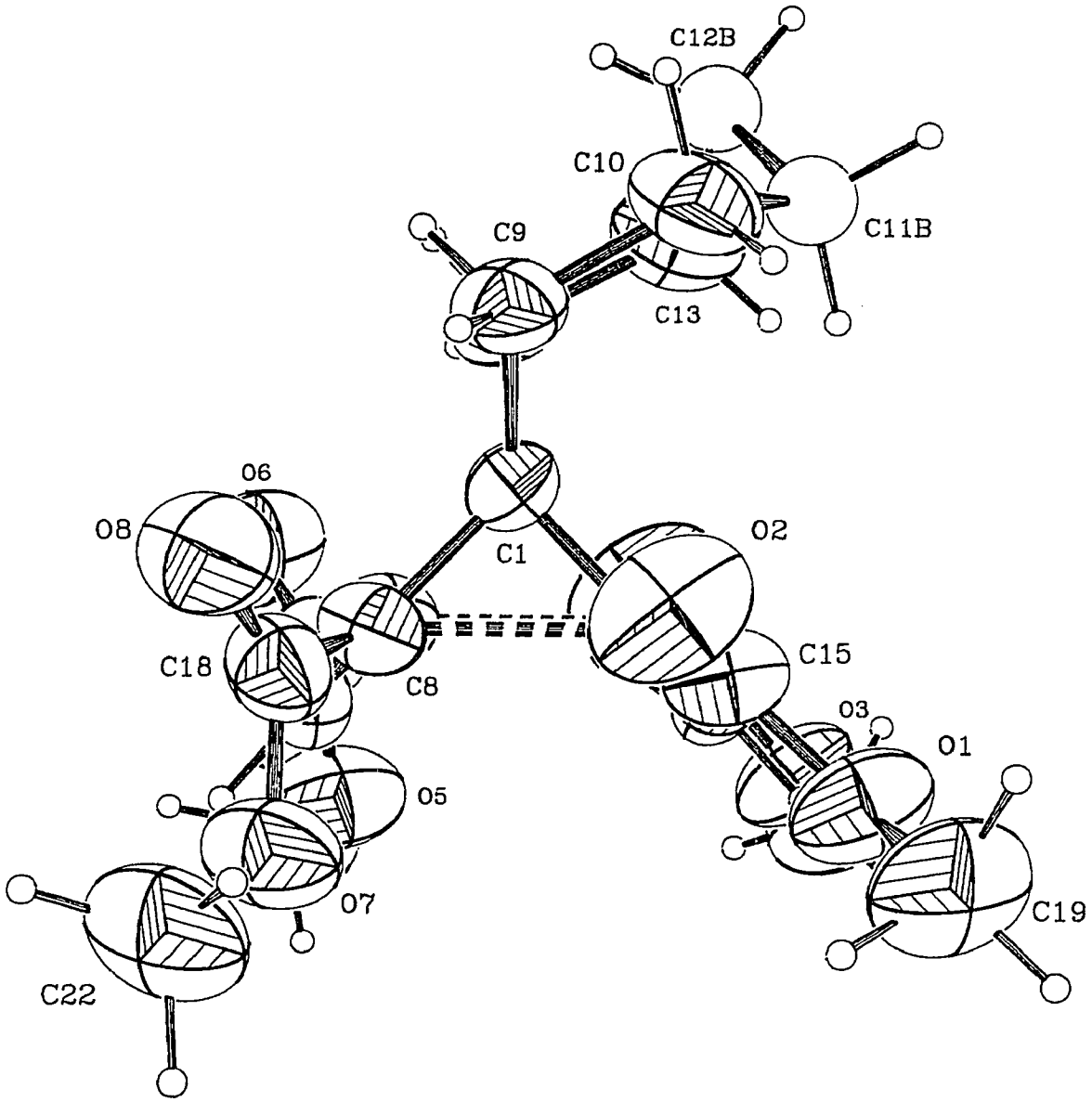


Figure 4–262. *ORTEP* drawing of Sb-8 (minor conformer) at **360 K** with 50% thermal ellipsoids.

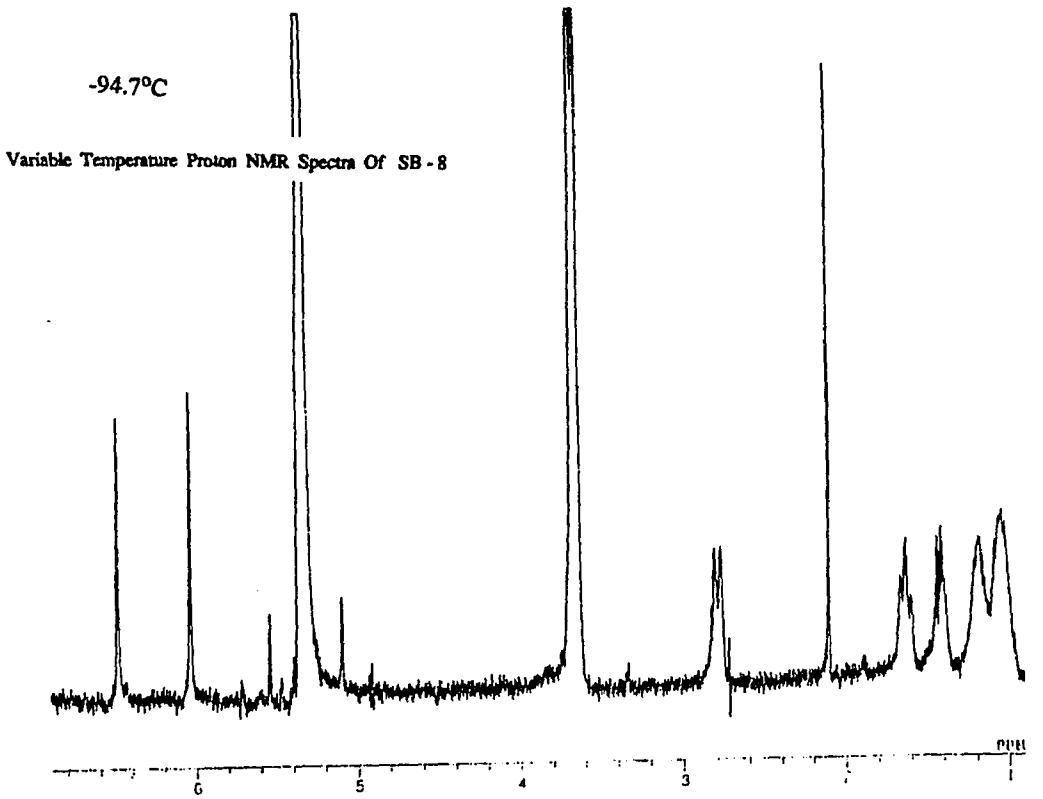


Figure 4–263. ^{1}H NMR spectrum of Sb-8 in acetone and CH_2Cl_2 at -95 °C.

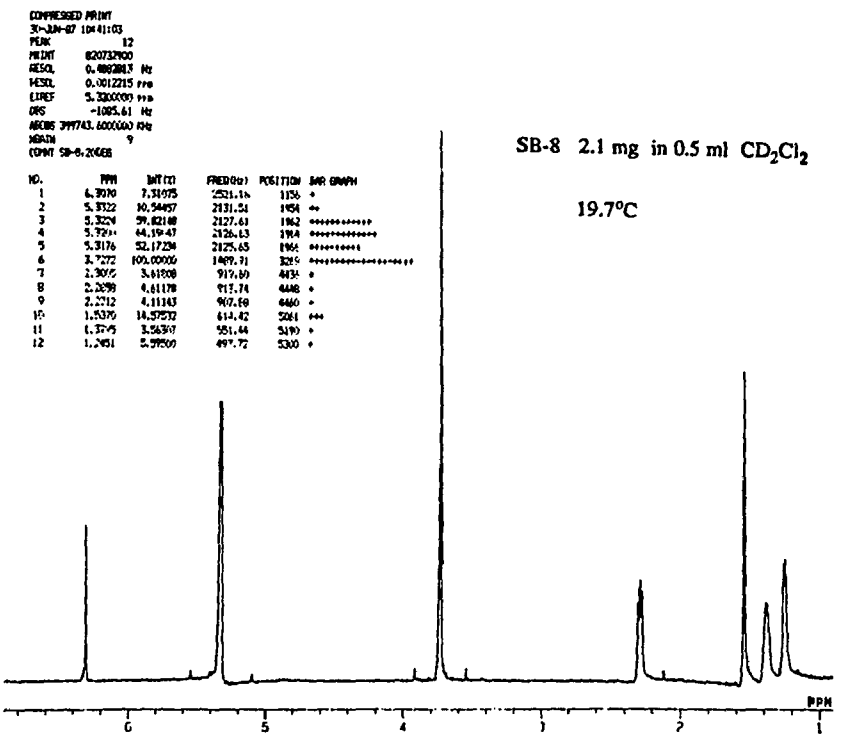


Figure 4–264. ^{1}H NMR spectrum of Sb-8 in water and CD_2Cl_2 at 20 °C.

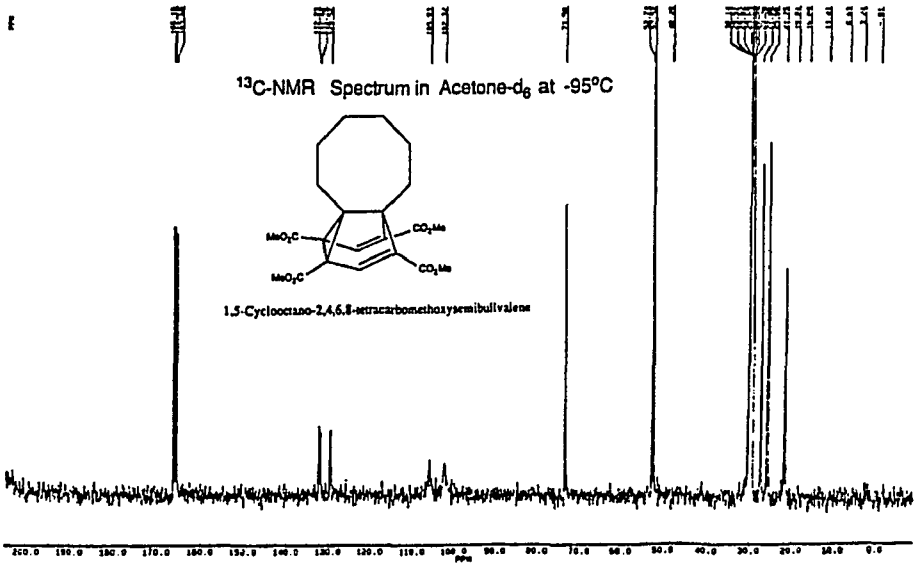


Figure 4–265. ^{13}C NMR spectrum of Sb-8 in acetone at -95 °C.

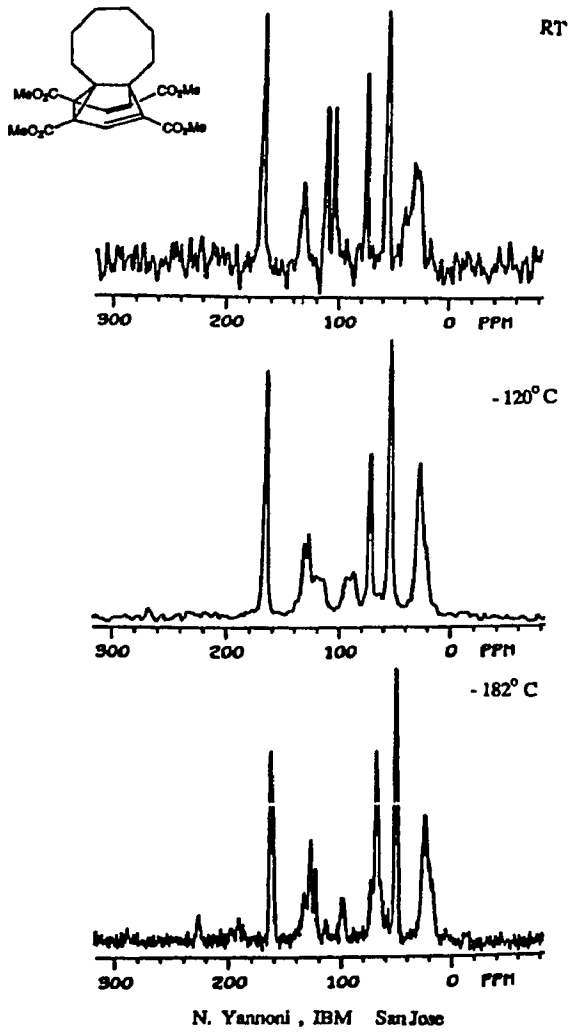


Figure 4–266. Variable temperature solid-state CP-MAS ^{13}C NMR spectra of Sb-8.

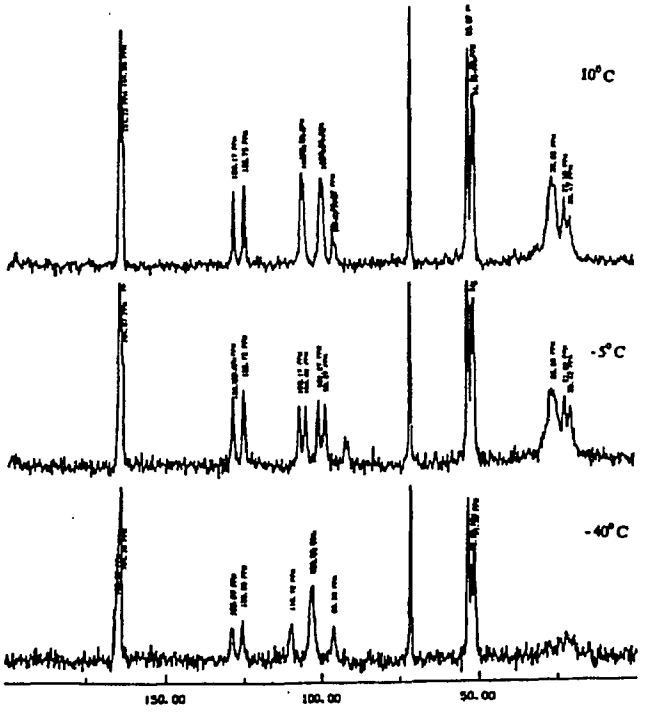


Figure 4–267. Variable temperature solid-state CP-MAS ^{13}C NMR spectra of Sb-8.

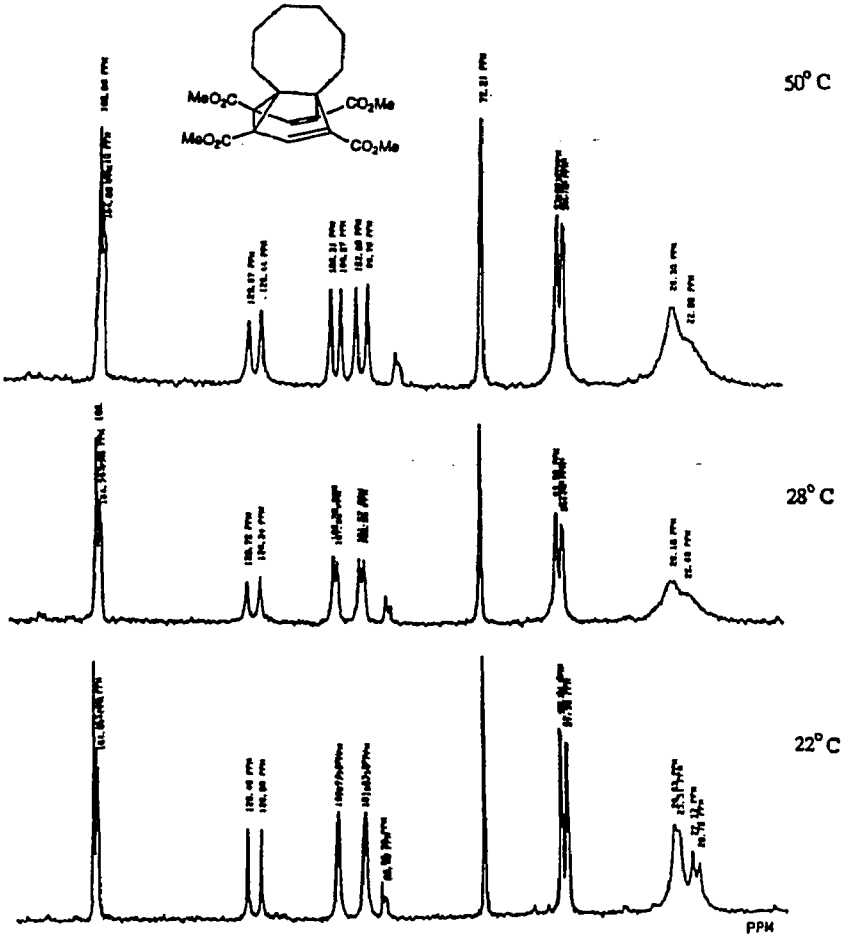


Figure 4–268. Variable temperature solid-state CP-MAS ^{13}C NMR spectra of Sb-8.

The two bands of the solid-line IR spectrum (4 scans) in Figure 4–269 coalesce into one band as the carbonyl groups are "warmed up" by the IR frequency of the 25 scans in Figure 4–269.

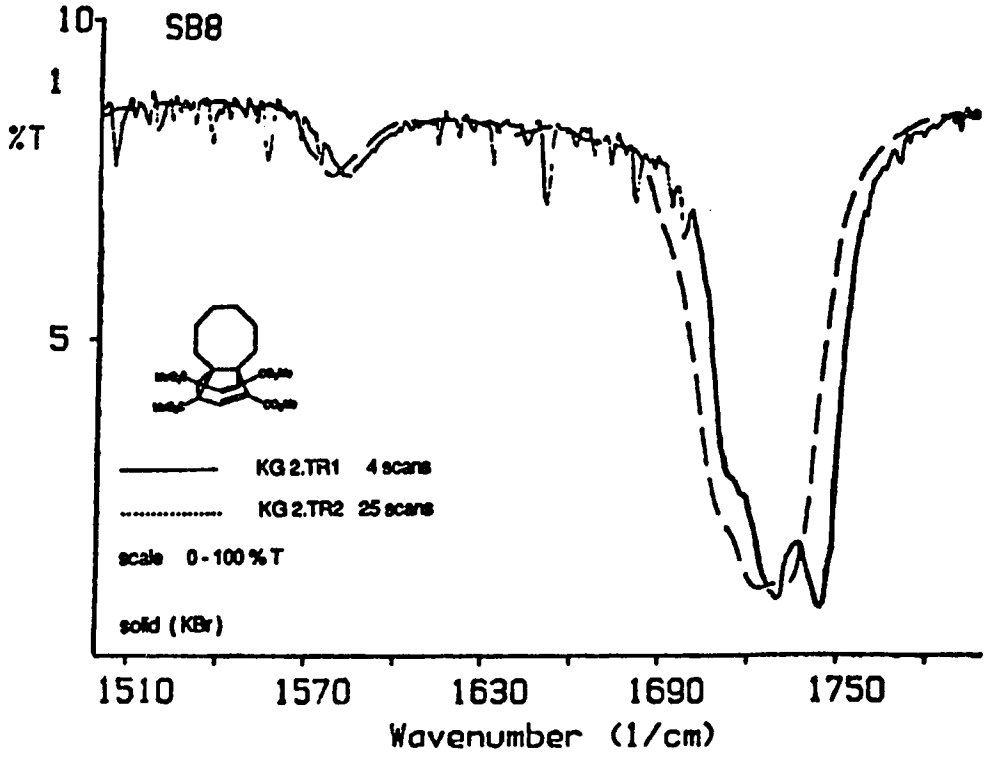


Figure 4–269. Solid-state FT-IR spectrum of Sb-8 at room temperature.

4.7 A VIEW FROM THE BRIDGE

To get a good assessment how the candidates rate against one another, we now present together, like a view from a bridge, corresponding structural features of these compounds.

The unit-cell volume of the candidates changes approximately linearly with temperature as shown in Figure 4–270.

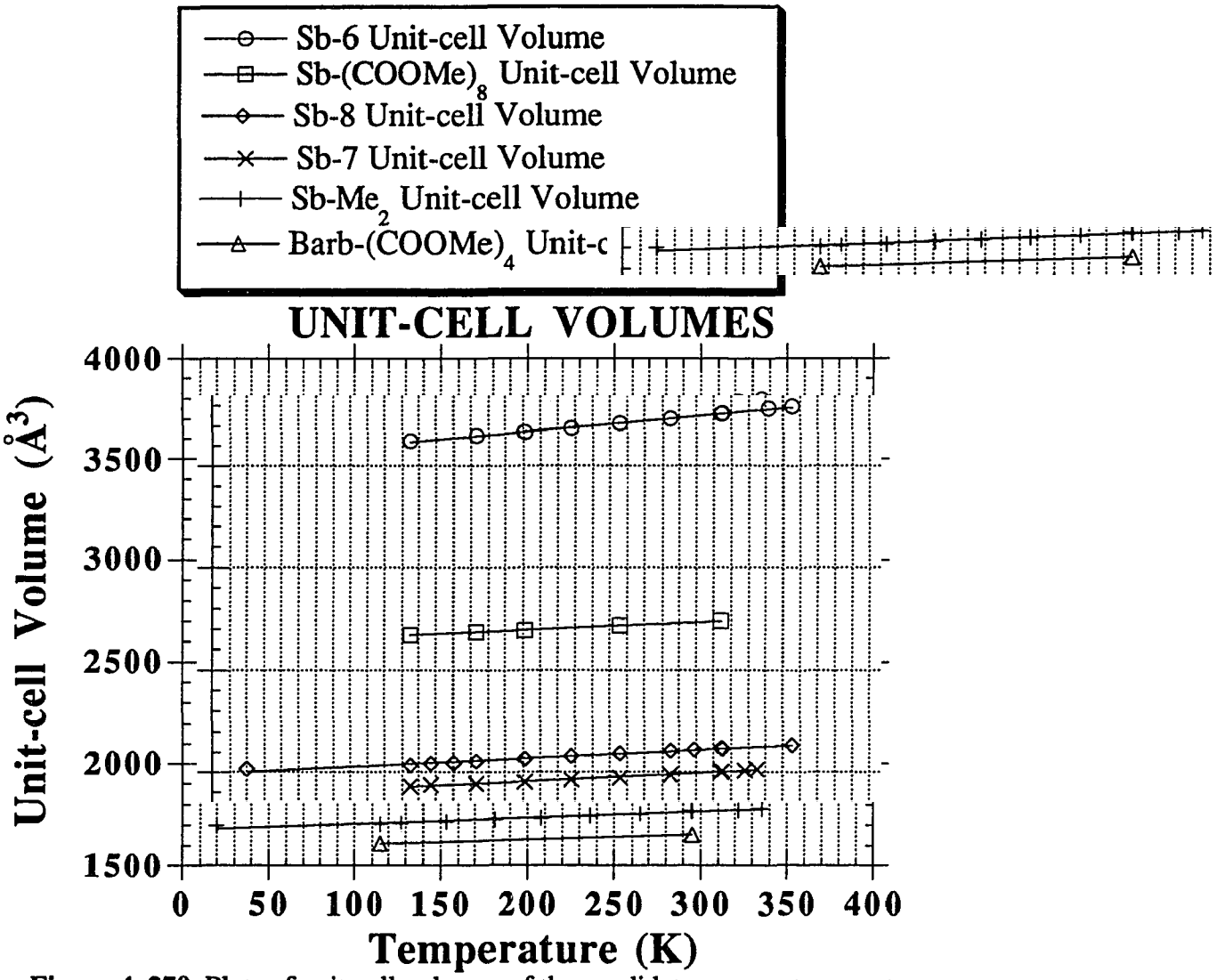


Figure 4–270. Plots of unit-cell volumes of the candidates versus temperature.

The rate at which the unit-cell volume changes with temperature for each candidate is nearly constant. The rates are listed in Table 4–29 and are plotted in Figure-4–271.

Table 4–29. The Rate of Change of Unit-cell Volume for Four Molecules in the Temperature Range from 20 to 360 K

Compound	Rate (Å^3/K))	Formula	Number of non-H's	Number of H's
Barb-(COOMe)$_4$	0.252	$C_{17}H_{18}O_8$	100	72
Sb-Me$_2$	0.354	$C_{18}H_{20}O_8$	104	80
Sb-(COOMe)$_8$	0.373	$C_{24}H_{24}O_{16}$	160	96
Sb-6	0.395[a]	$C_{20}H_{22}O_8$	112	88
Sb-7	0.408	$C_{21}H_{24}O_8$	116	96
Sb-8	0.463	$C_{22}H_{16}O_8$	120	104

[a] Since there are eight molecules of Sb-6 in the unit cell, this rate is for four molecules in half of the unit-cell.

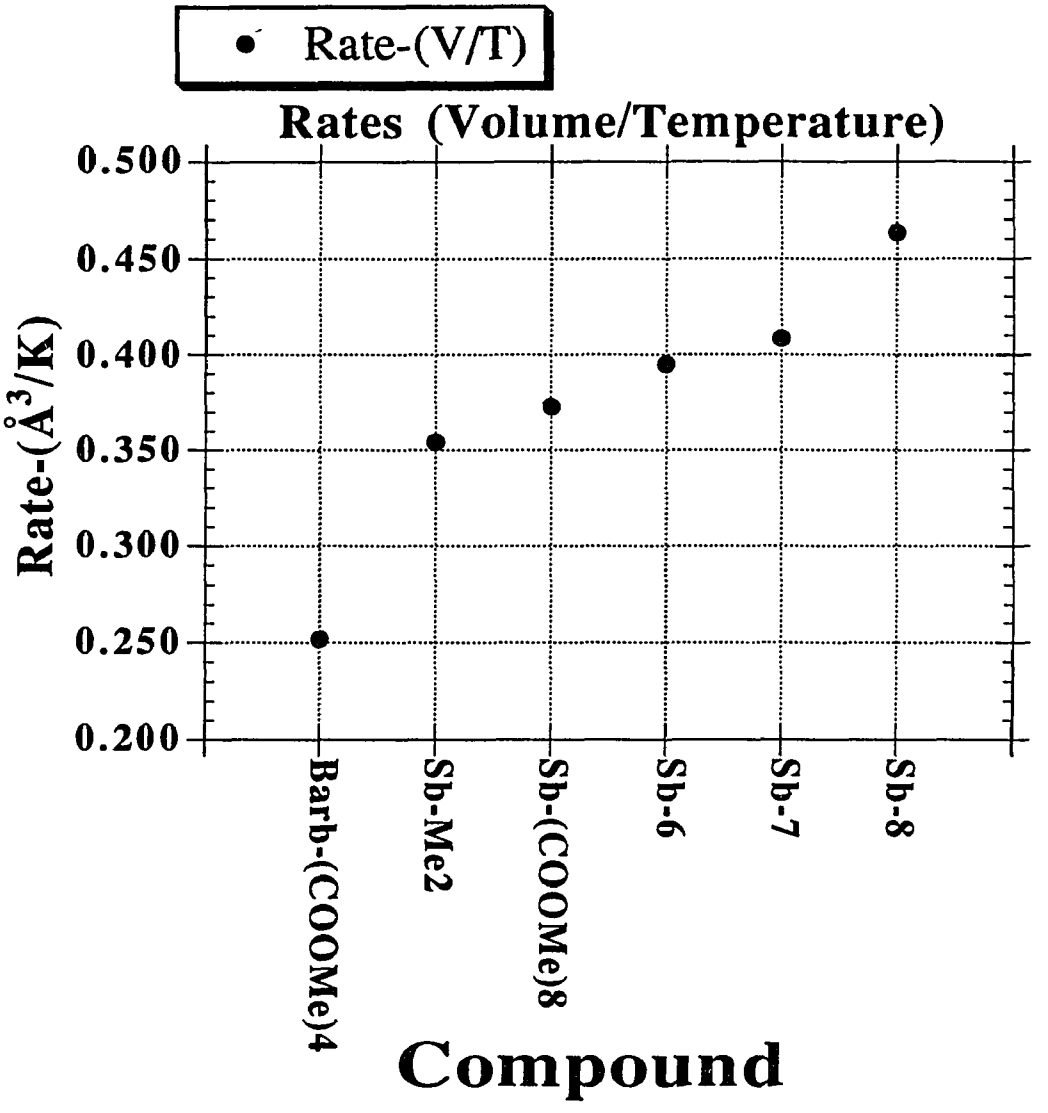


Figure 4–271. A plot of the rate (volume/temperature) of the candidates.

The densities are plotted in Figure 4–272. Barbaralane-$(COOMe)_4$ has the highest density and Sb-8 has the lowest. This may be due, in part, to the fact that there is more atomic motion in Sb-8 than in barbaralane-$(COOMe)_4$, as evident from the previous RMS's tables for each compound.

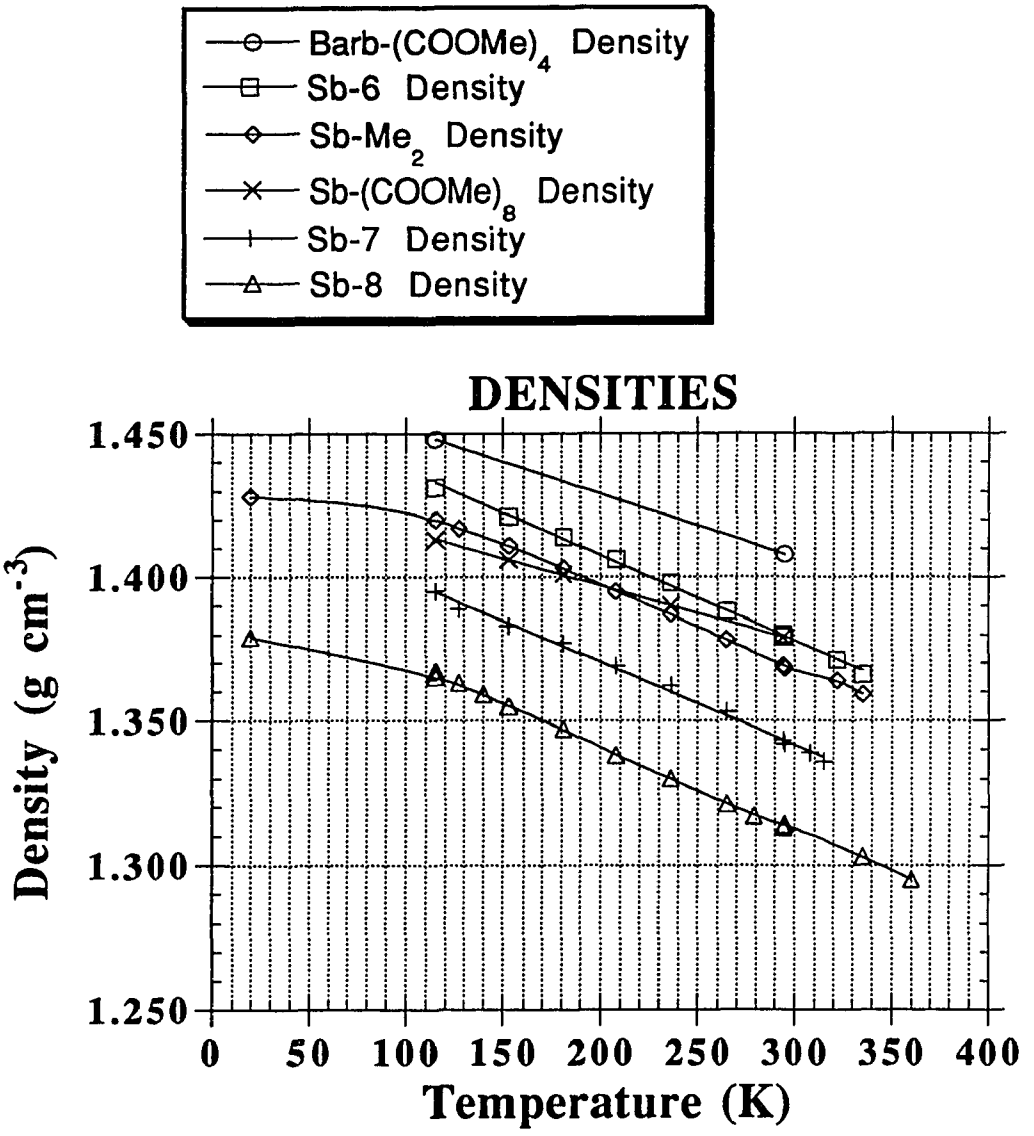


Figure 4–272. Plots of densities of the candidates versus temperature.

Next, we compare the interatomic distances at the base of semibullvalene ring system for each compound in the following graphs.

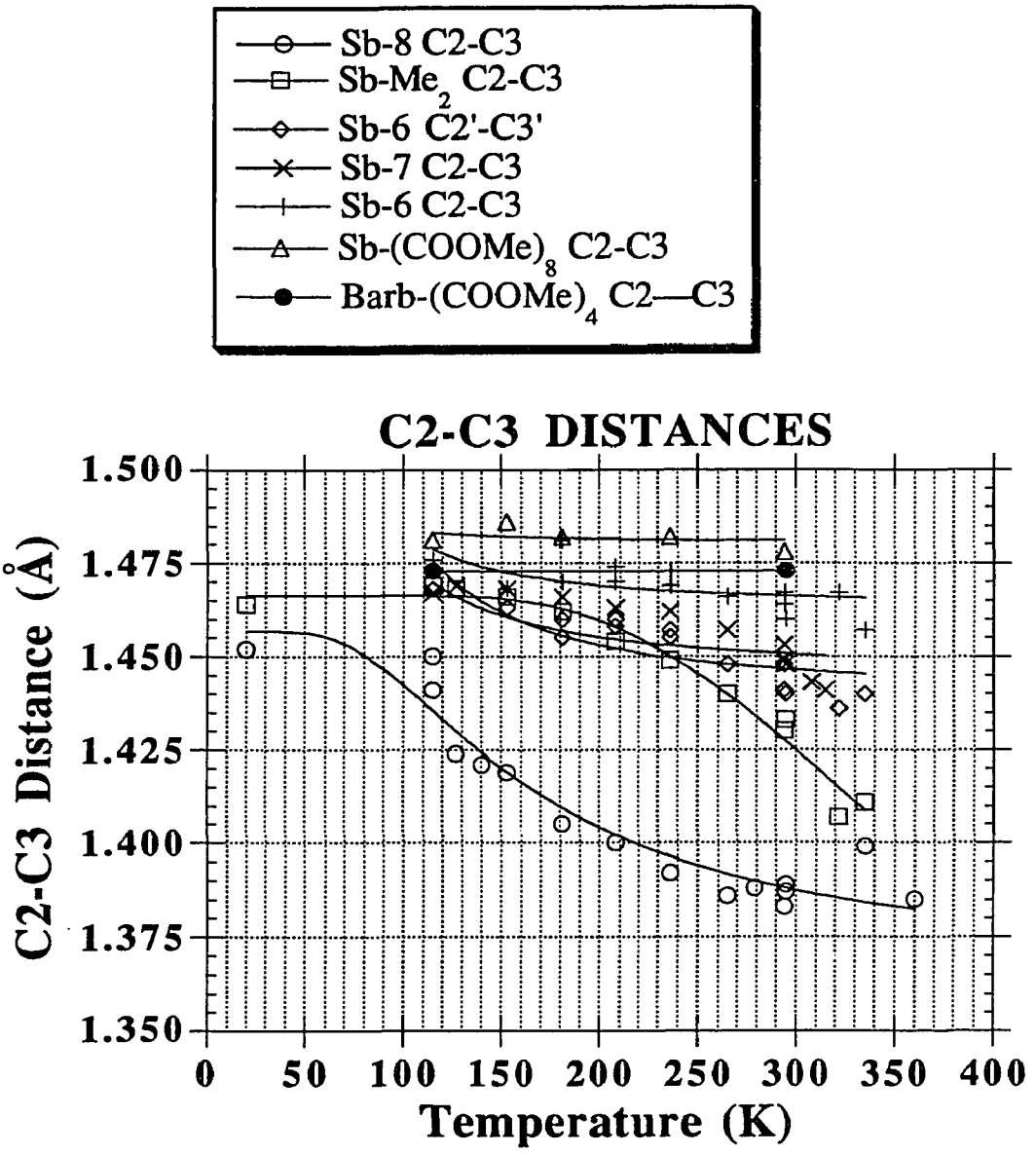


Figure 4–273. Plots of C2—C3 distances for the candidates versus temperature.

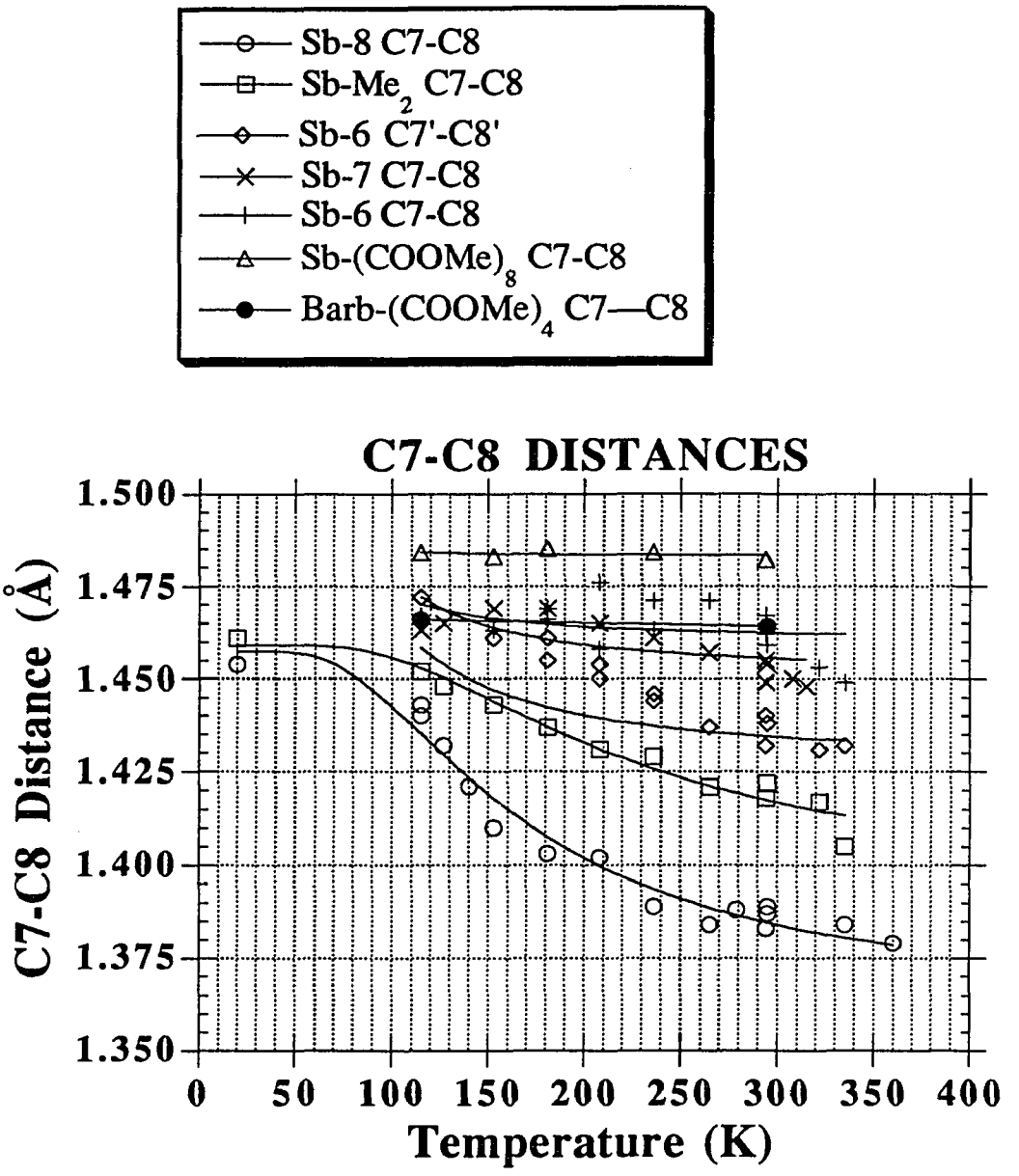


Figure 4–274. Plots of C7—C8 distances for the candidates versus temperature.

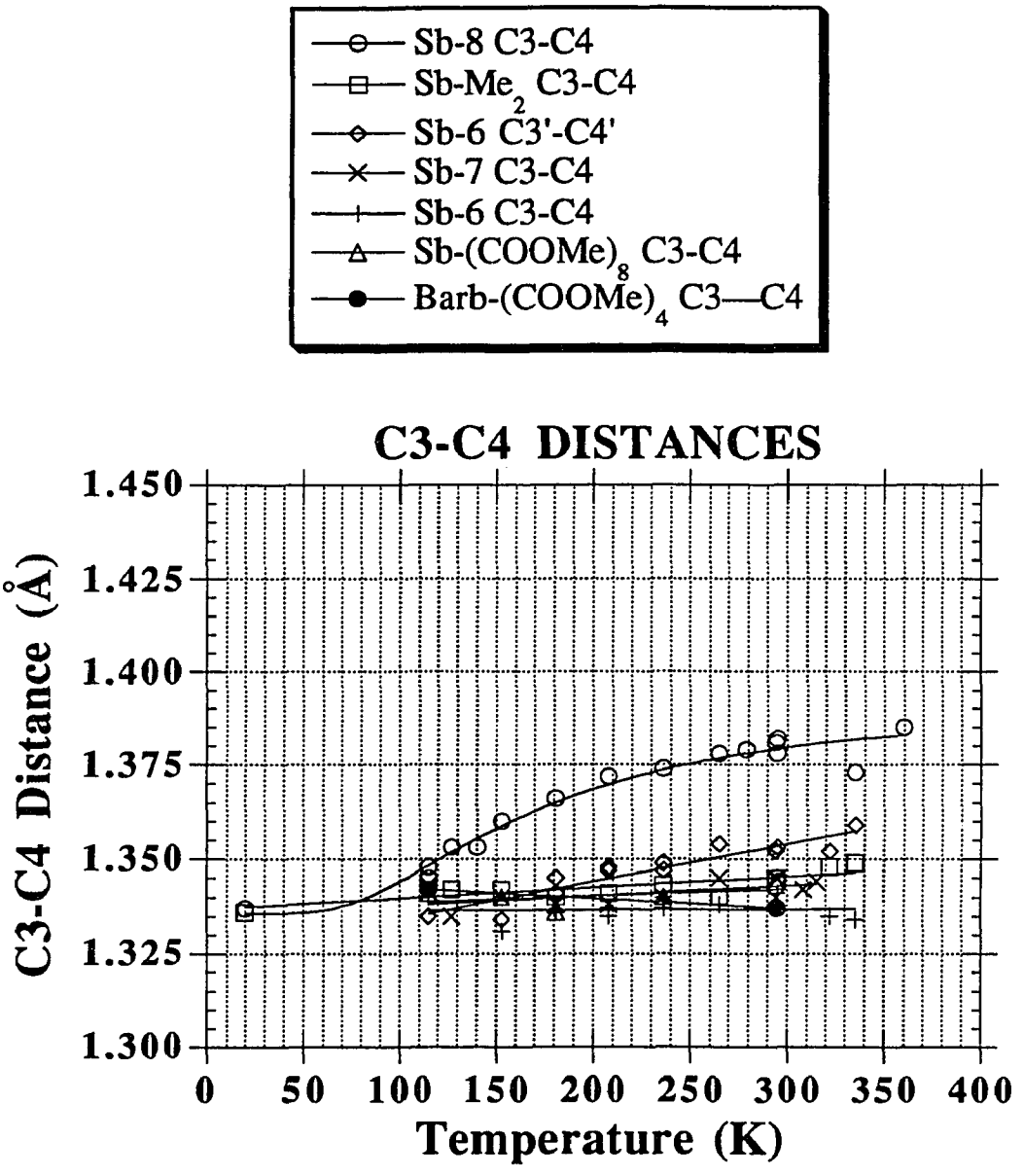


Figure 4–275. Plots of C3—C4 distances for the candidates versus temperature.

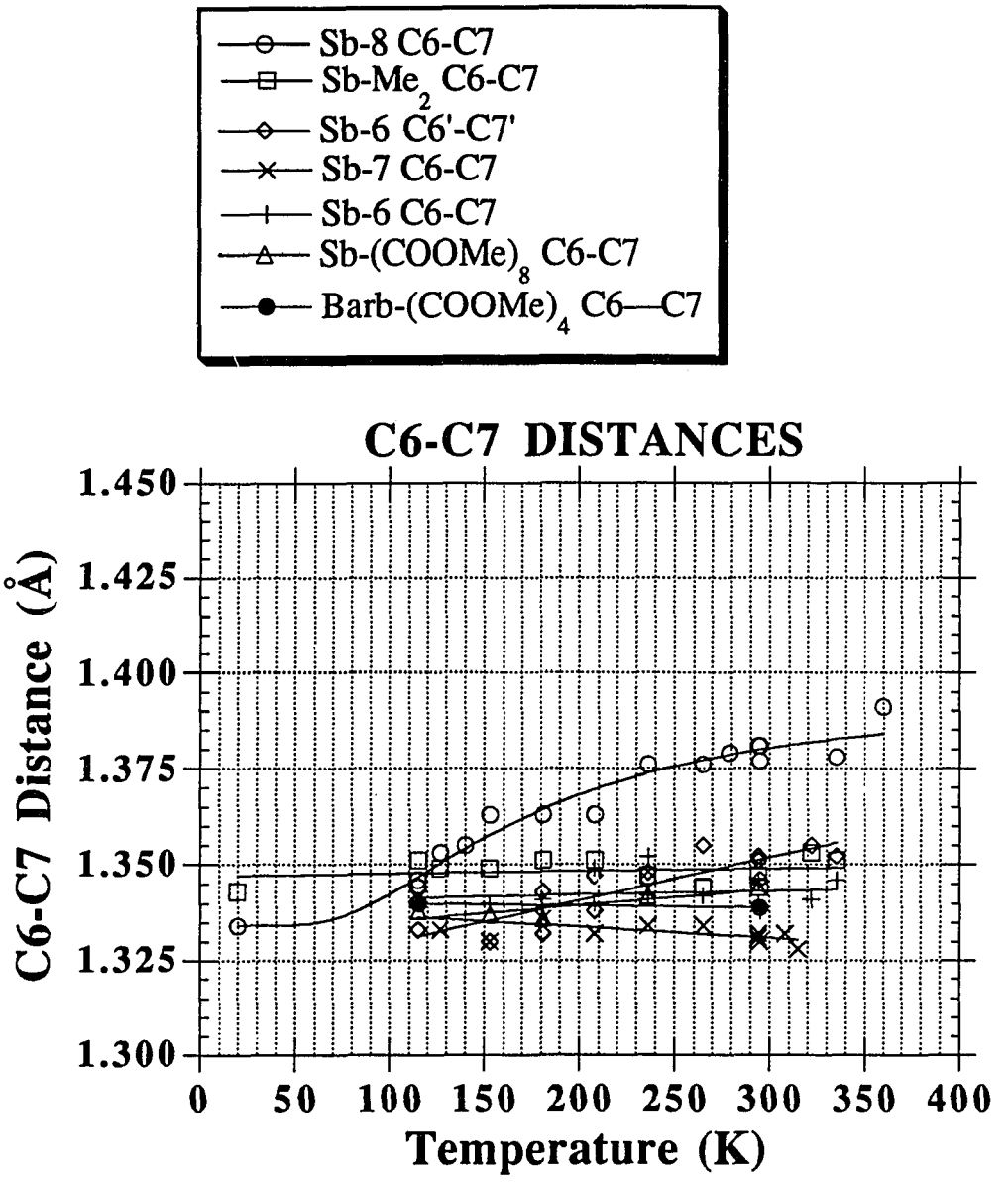


Figure 4–276. Plots of C6—C7 distances for the candidates versus temperature.

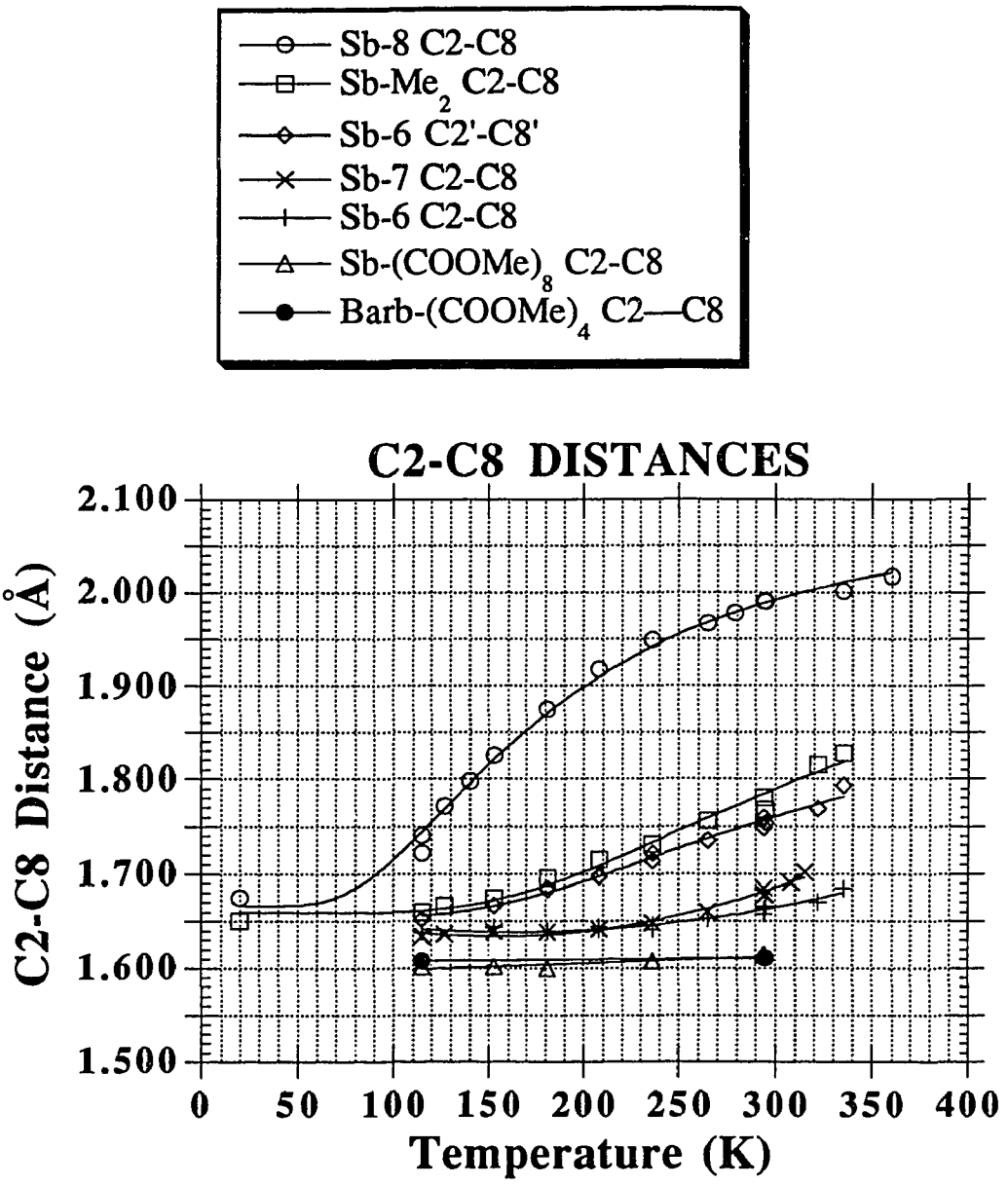


Figure 4–277. Plots of C2—C8 distances for the candidates versus temperature.

Since the RMS's of C4, C6, and C8 are similar to C2, we graph just those of C2 for each compound in Figure 4–278.

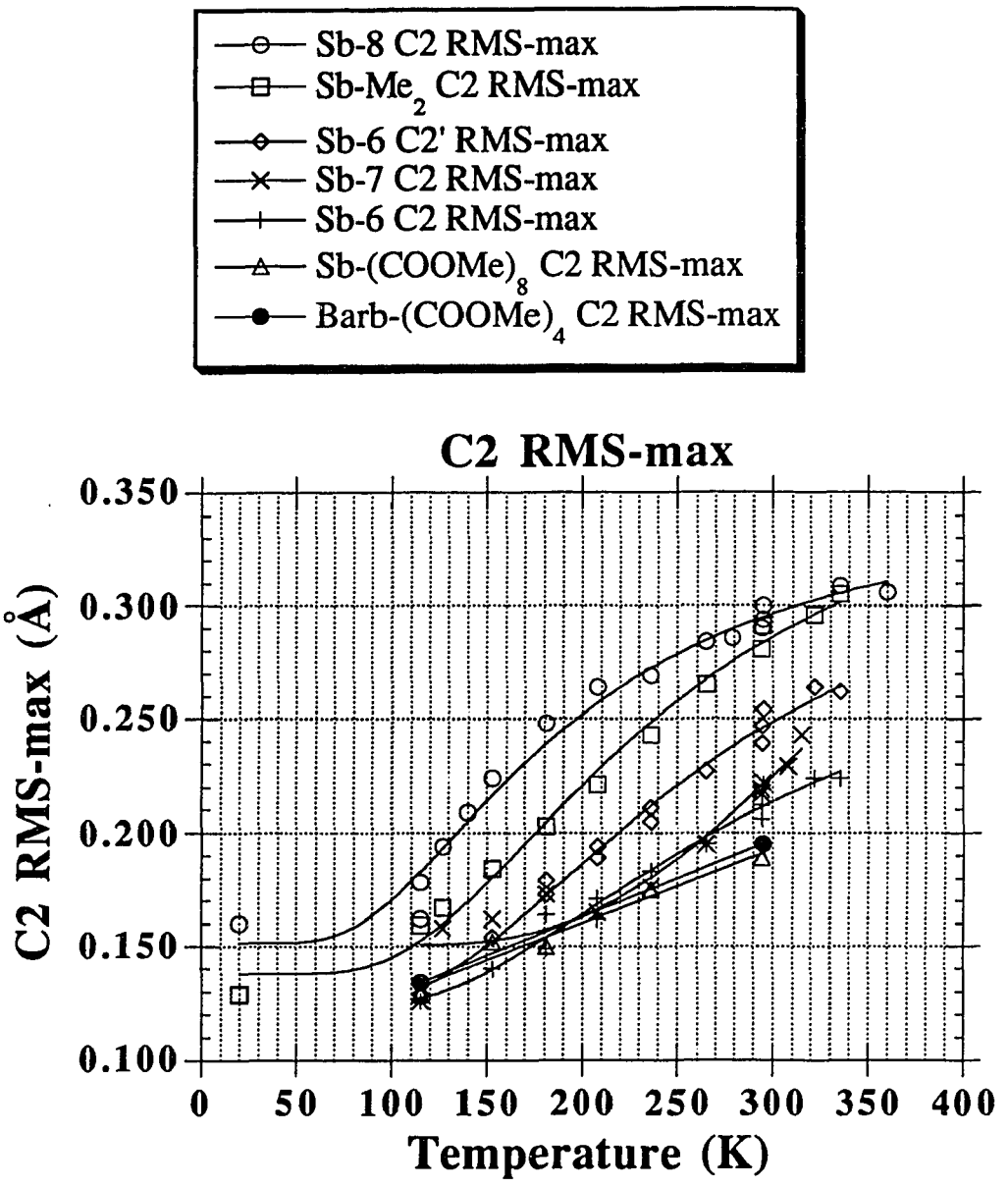


Figure 4–278. Plots of C2 maximum RMS distances for the candidates versus temperature.

The data clearly indicate that the six compounds, barbaralane-$(COOMe)_4$, Sb-$(COOMe)_8$, Sb-6, Sb-7, Sb-Me_2, and Sb-8, are molecules approaching the bishomoaromatic transition state with increasing temperature, that is, **they become more and more like benzene.** Sb-8, in indeed, exhibits at room temperature the symmetrical delocalized structure expected for a neutral bishomoaromatic structure. Thus, for the first time, we have characterized a neutral bishomobenzene molecule of the type which Hoffmann and Dewar had predicted more than twenty years ago.

Since Sb-Me_2 and Sb-8 appear to be the most dynamic of these six compounds, we will explore in the next chapter thermodynamics properties associated with these two special compounds.

REFERENCES

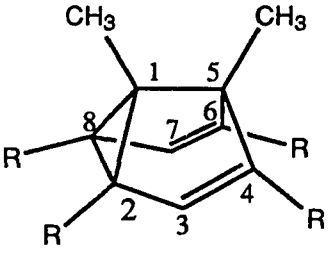
[1] J. C. Kauer, H. E. Simmons, *J. Org. Chem.*, **33**, 2720 (1968).

CHAPTER 5

THE CONTINUING TALE OF THE DYNAMIC DUO

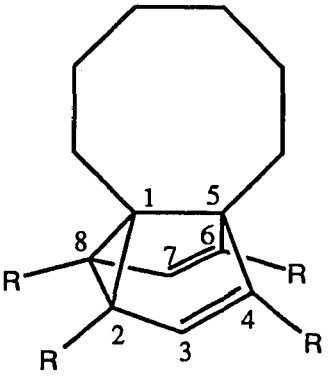
5.1 SB-Me$_2$ AND SB-8 IN THE LIMELIGHT

Of the six candidates, Sb-Me$_2$ and Sb-8 are the most dynamic.



R = $COOCH_3$

Sb-Me$_2$



R = $COOCH_3$

Sb-8

The interatomic distances C2—C8 and C4—C6 in Sb-Me$_2$ and Sb-8 change more than other ring distances in the temperature range from 20 to 360 K as shown in Figures 5–1 and 2.

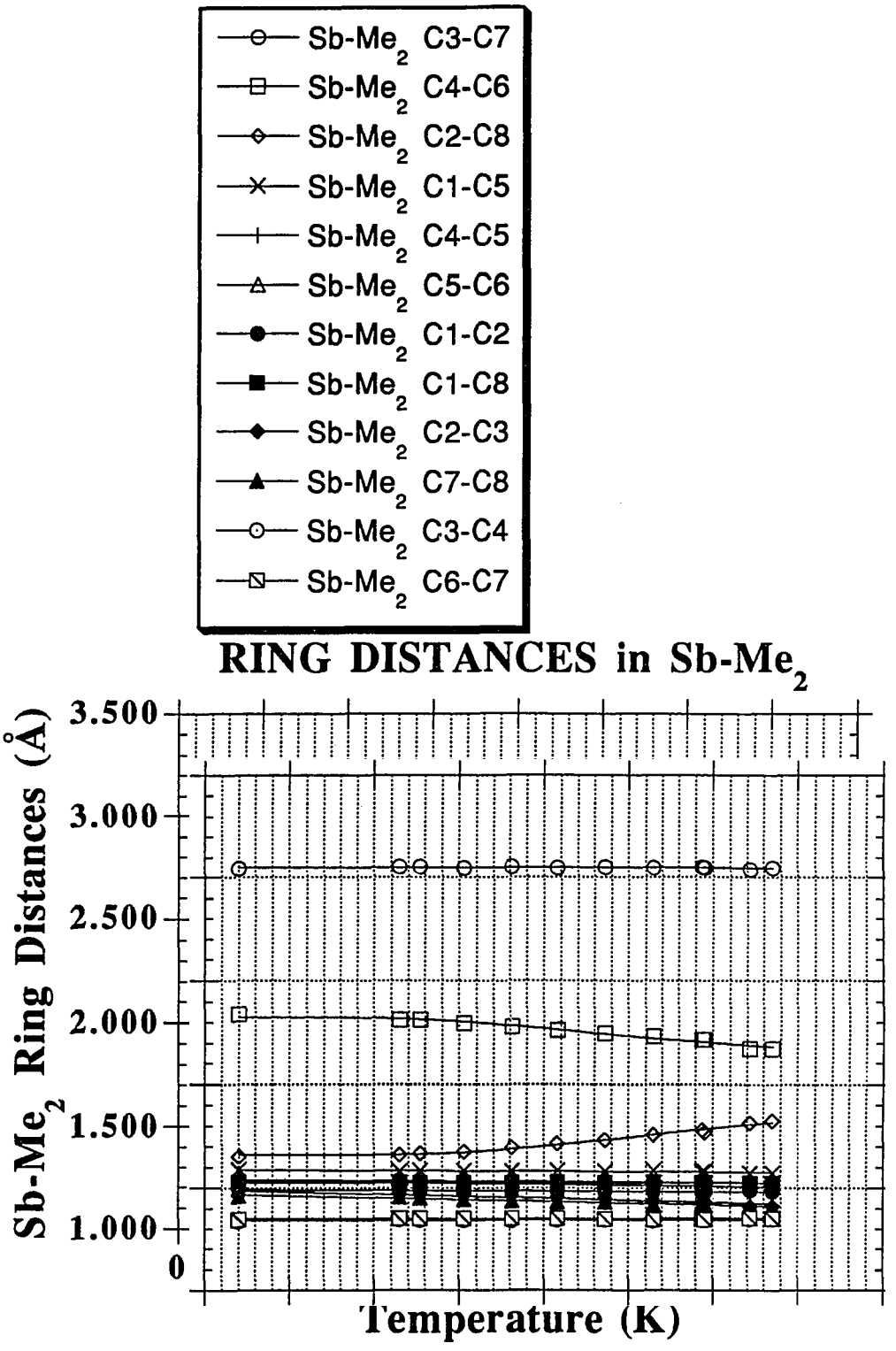


Figure 5–1. Plots of selected interatomic distances in the ring of $Sb\text{-}Me_2$ versus temperature.

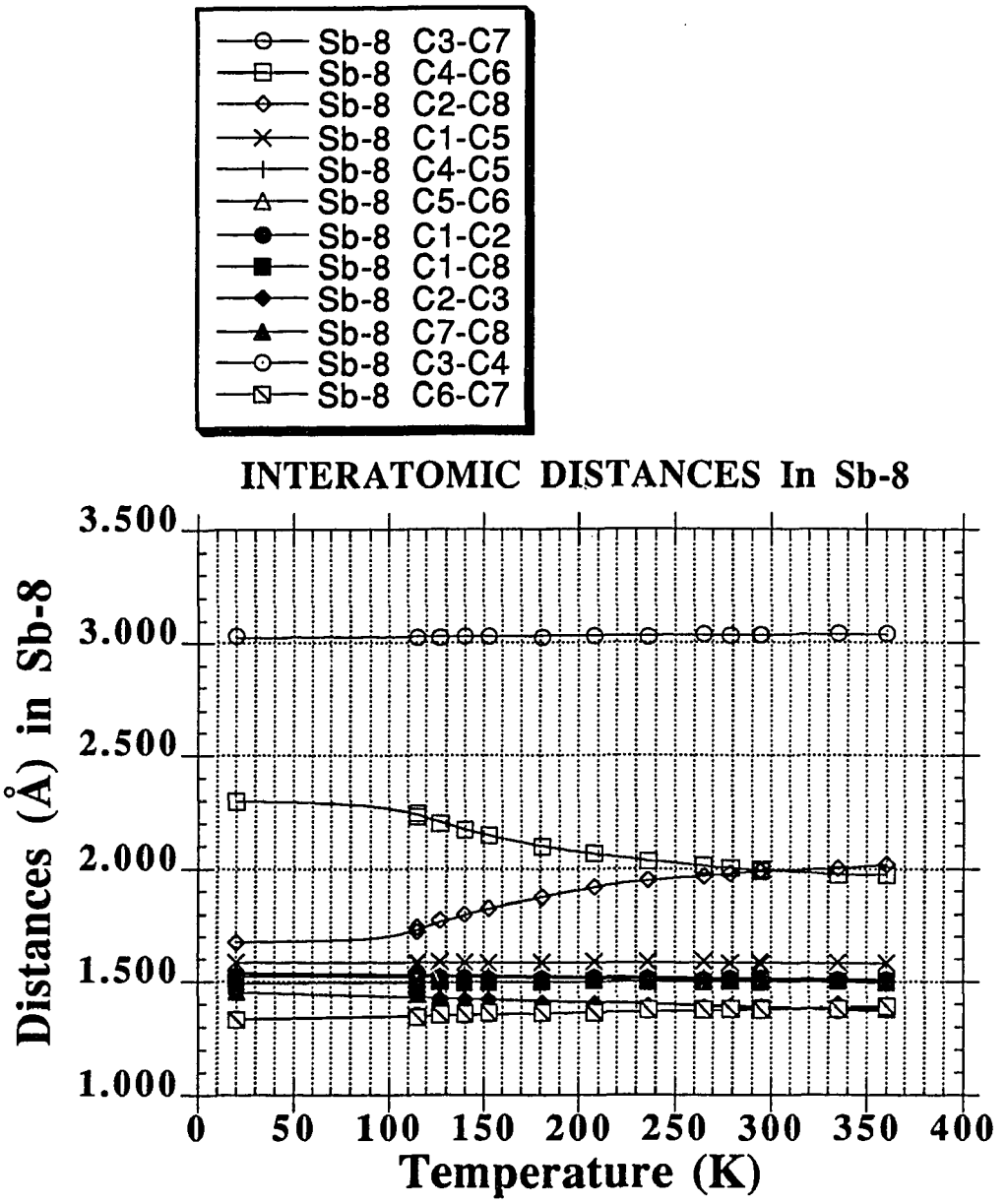


Figure 5–2. Plots of selected interatomic distances in the ring of Sb-8 versus temperature.

These unusual distances from the X-ray analyses are in fact average values probably resulting from nonequivalent valence tautomers (a low-energy tautomer, **A**, and

a high-energy tautomer, **B**) undergoing fast nondegenerate Cope rearrangement. These two tautomers for Sb-Me_2 and Sb-8 are in Figure 5–3 and 4, respectively.

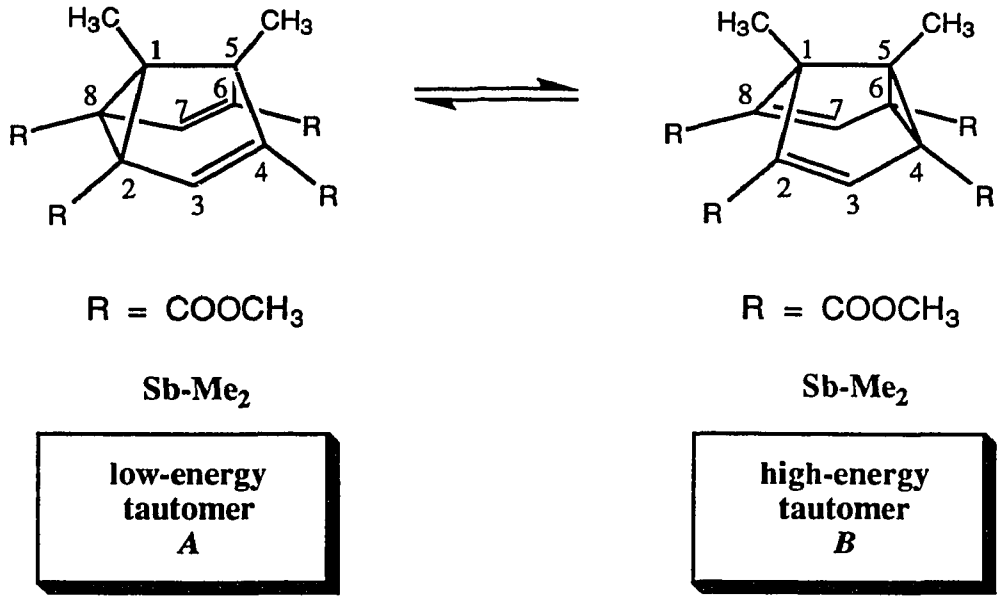


Figure 5–3. Low-energy and high-energy tautomers of Sb-Me_2.

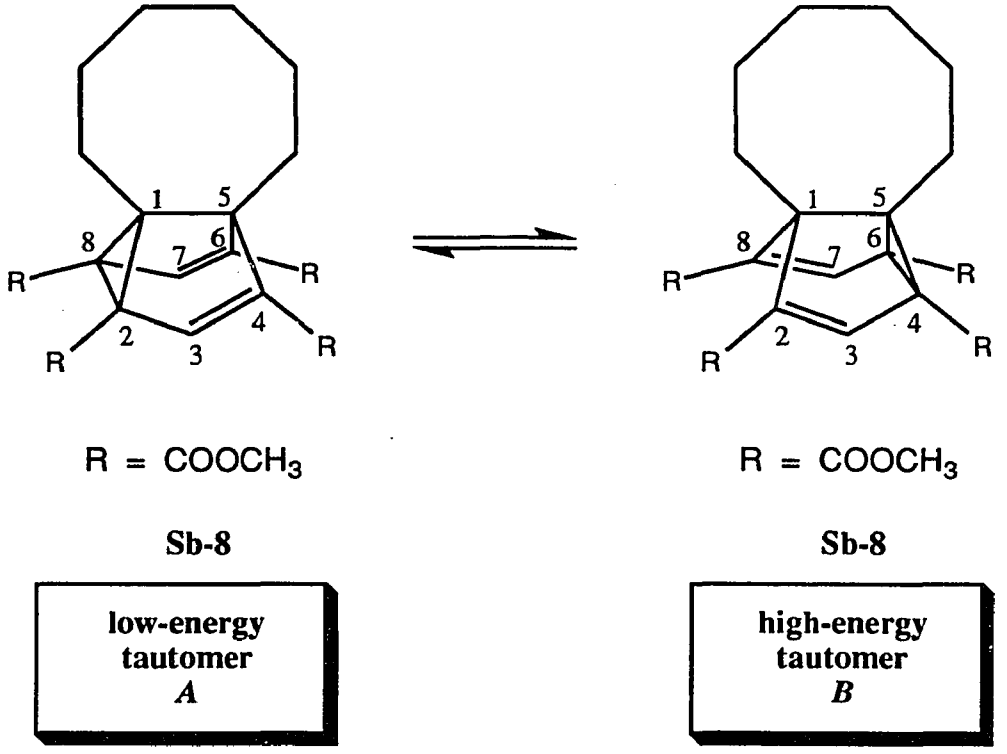


Figure 5–4. Low-energy and high-energy tautomers of Sb-8.

The population of tautomer ***A*** would be 100% at very low temperature

Following the lead by Quast and others,[1] the atomic distances, C2—C8 and C4—C6, obtained from the X-ray analyses may be used to estimate the ratio of the non-equivalent valence tautomers, ***A*** and ***B***, in the crystal, for the equilibrium:

$$\boldsymbol{A} \rightleftharpoons \boldsymbol{B}$$

From this ratio, we obtain the equilibrium constant, which in turn yields ΔG (not $\Delta G^{\ddagger}$) for the equilibrium. The equilibrium constant K for this process is:

$$K = \frac{[B]}{[A]} = \frac{n_A/V}{n_B/V} = \frac{n_B}{n_A} = \frac{\dfrac{n_B}{n_A + n_B}}{\dfrac{n_A}{n_A + n_B}} = \frac{x}{1-x}$$

where:

$[A]$ = concentration of tautomer ***A***
$[B]$ = concentration of tautomer ***B***
n_A = moles of tautomer ***A***
n_B = moles of tautomer ***B***
V = Volume
x = mole fraction of tautomer ***B***

The average distance $\langle C2 - C8 \rangle$ is related to the distance C2—C8 of tautomer ***A*** and to C2—C8 of tautomer ***B*** as

$$\langle C2 - C8 \rangle = (1-x)(C2 - C8)_A + x(C2 - C8)_B$$

But

$$(\boldsymbol{C2 - C8})_B \approx (\boldsymbol{C4 - C6})_A$$

Thus,

$$\langle C2 - C8 \rangle = (1-x)(C2 - C8)_A + x(C4 - C6)_A$$

Our immediate aim is to eliminate the mole fraction x from these two expressions:

$$K = \frac{x}{1-x}$$

$$\langle C2 - C8 \rangle = (1-x)(C2 - C8)_A + x(C4 - C6)_A$$

We begin by inverting the equilibrium constant formula to express x in terms of K, that is,

$$\begin{aligned} K &= \frac{x}{1-x} \\ K(1-x) &= x \\ K - Kx &= x \\ K &= x + Kx \\ K &= x(1+K) \\ x &= \frac{K}{1+K} \end{aligned}$$

Thus,

$$1 - x = \frac{1}{1+K}$$

We can now easily eliminate x from

$$\langle C2 - C8 \rangle = (1-x)(C2 - C8)_A + x(C4 - C6)_A$$

to obtain

$$\langle C2 - C8 \rangle = \left(\frac{1}{1+K}\right)(C2 - C8)_A + \left(\frac{K}{1+K}\right)(C4 - C6)_A$$

We continue to solve for K as follows:

$$\langle C2 - C8\rangle = \left(\frac{1}{1+K}\right)(C2 - C8)_A + \left(\frac{K}{1+K}\right)(C4 - C6)_A$$

$$(1+K)\langle C2 - C8\rangle = (C2 - C8)_A + K(C4 - C6)_A$$

$$\langle C2 - C8\rangle + K\langle C2 - C8\rangle = (C2 - C8)_A + K(C4 - C6)_A$$

$$\langle C2 - C8\rangle - (C2 - C8)_A = K(C4 - C6)_A - K\langle C2 - C8\rangle$$

$$\langle C2 - C8\rangle - (C2 - C8)_A = K[(C4 - C6)_A - \langle C2 - C8\rangle]$$

or

$$K = \frac{\langle C2 - C8\rangle - (C2 - C8)_A}{(C4 - C6)_A - \langle C2 - C8\rangle}$$

But the sum of the distances C2—C8 and C4—C6 does not vary with temperature in both X-ray structures of Sb-Me_2 and Sb-8 as shown in Figures 5–5 and 6. It is noteworthy to mention that while C2—C8 and C4—C6 change dramatically with temperature in Sb-8 and Sb-Me_2, the interatomic distance C3—C7 in both compounds remains stubbornly invariant to temperature, as pointed out in Chapter 4.

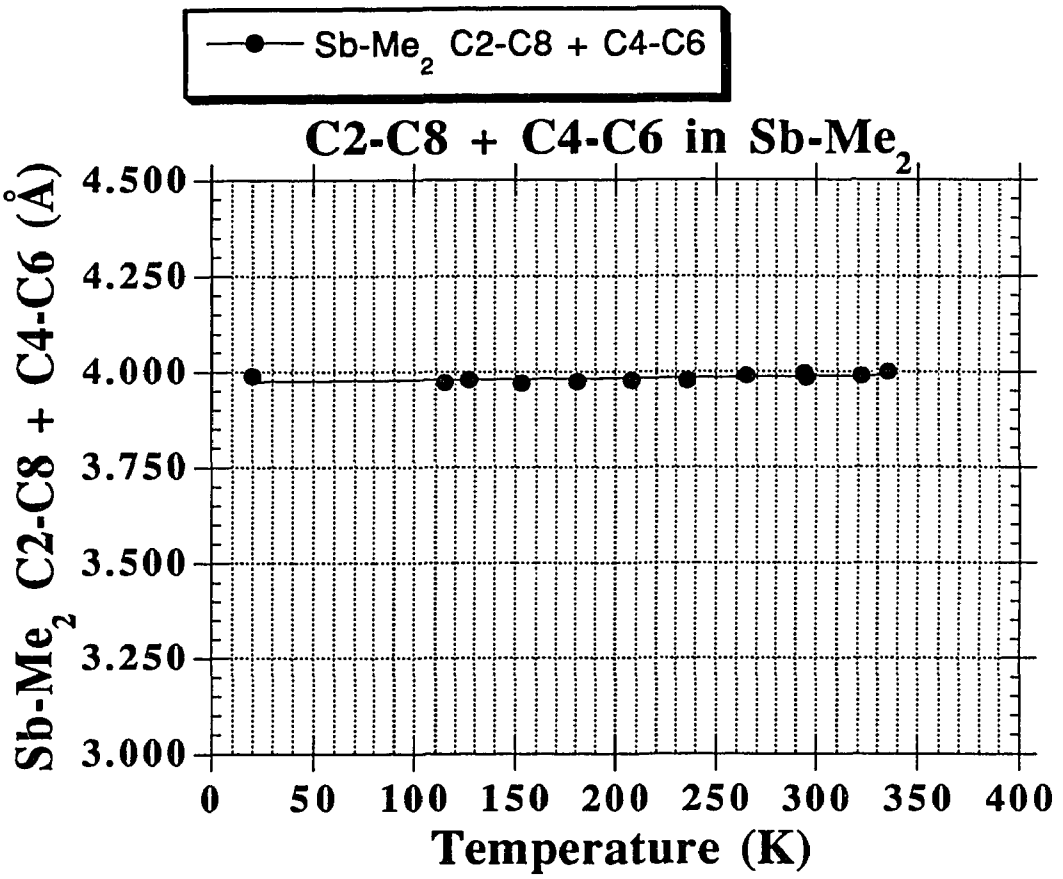


Figure 5–5. A plot of the sum of the distances C2—C8 and C4—C6 in $Sb\text{-}Me_2$ versus temperature.

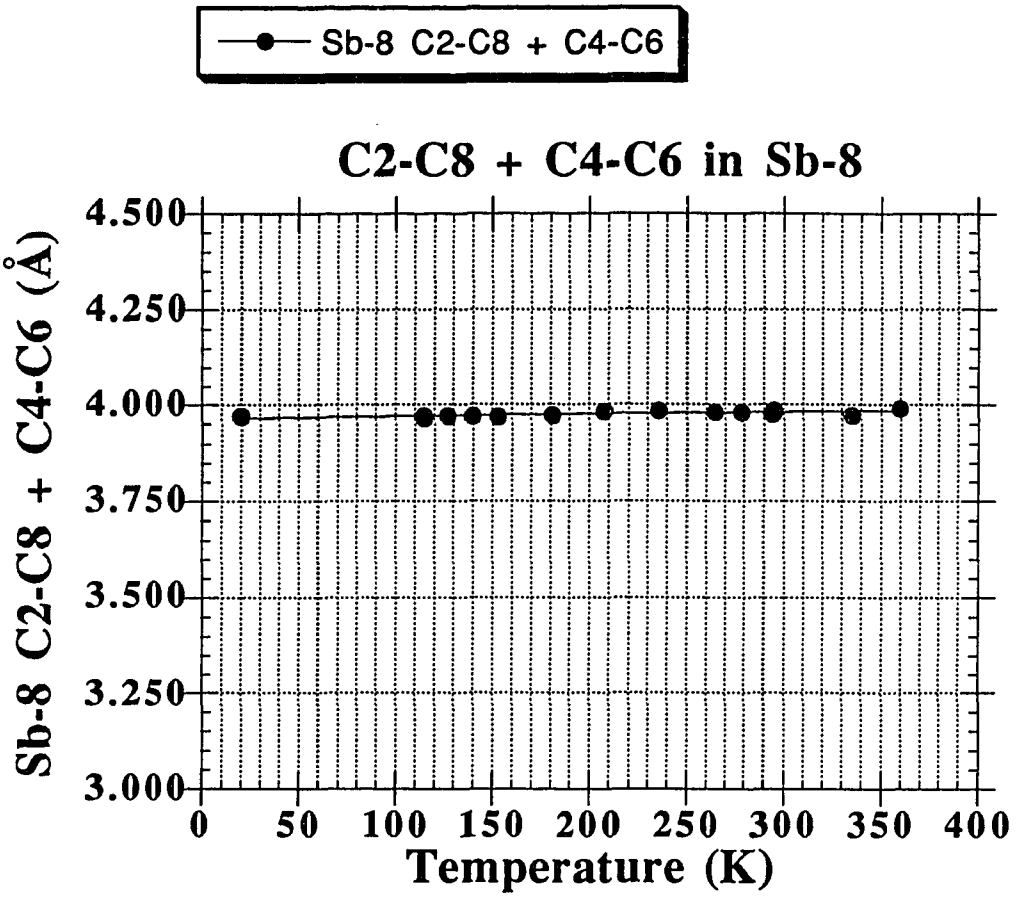


Figure 5–6. A plot of the sum of the distances C2—C8 and C4—C6 in Sb-8 versus temperature

Since the sum of the distances C2—C8 and C4—C6 is constant in both X-ray structures of Sb-Me_2 and Sb-8, it reasonable to state that

$$(C2-C8)_A + (C4-C6)_A = \langle C2-C8\rangle + \langle C4-C6\rangle$$

or

$$(C4-C6)_A - \langle C2-C8\rangle = \langle C4-C6\rangle - (C2-C8)_A$$

Therefore,

$$K = \frac{\langle C2-C8\rangle - (C2-C8)_A}{\langle C4-C6\rangle - (C2-C8)_A}$$

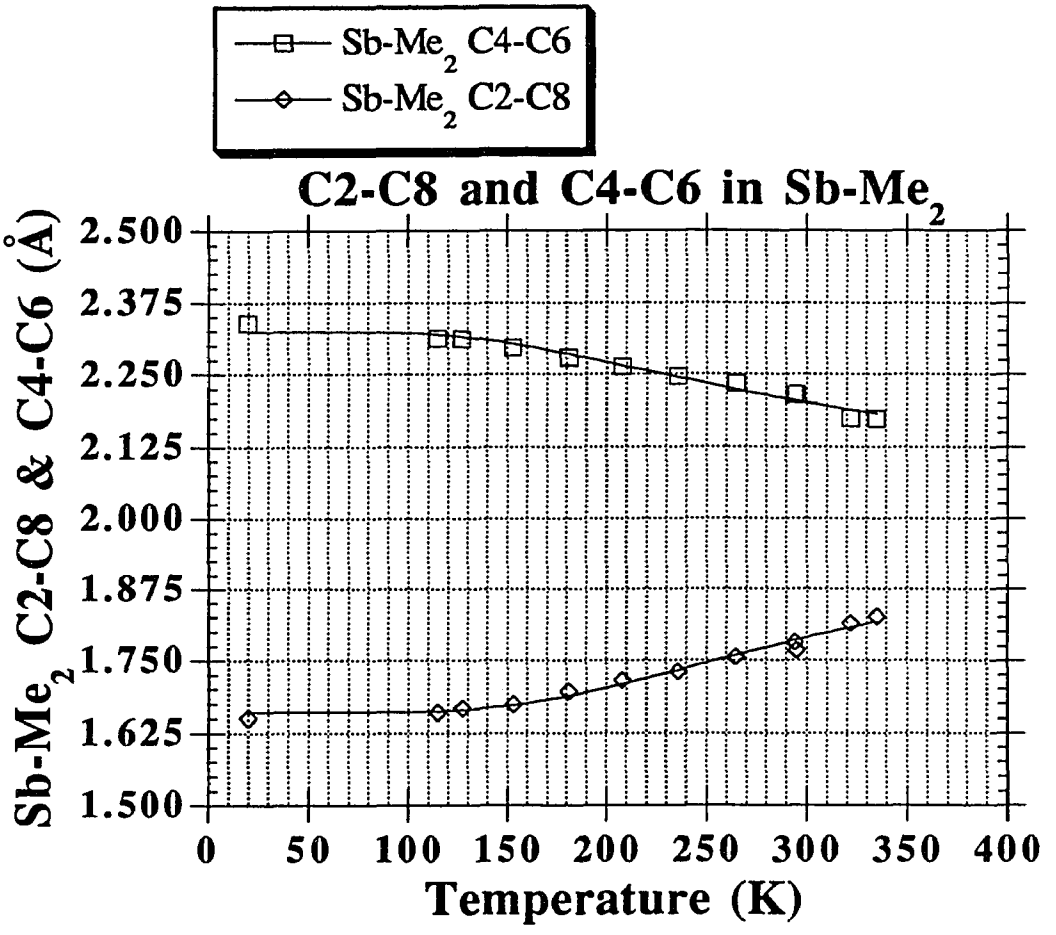


Figure 5–7. Plots of C2—C8 and C4—C6 distances in $Sb\text{-}Me_2$ versus temperature.

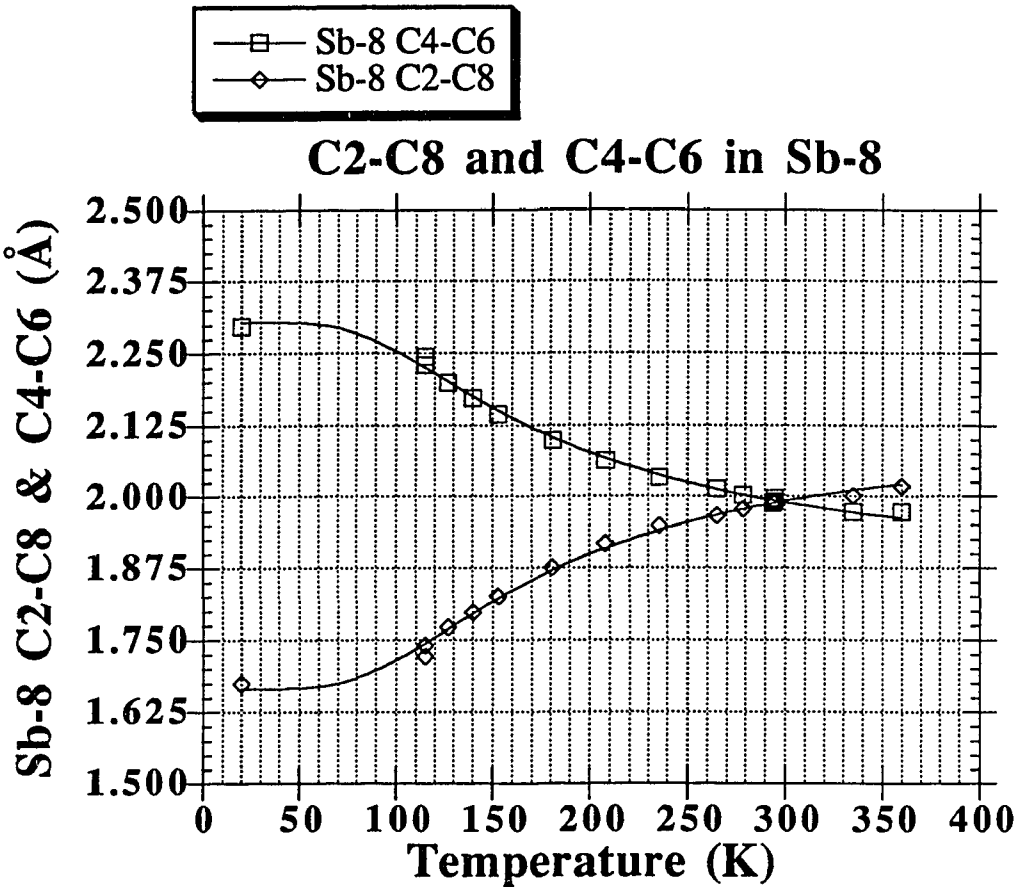


Figure 5–8. Plots of the distances C2—C8 and C4—C6 in Sb-8 versus temperature

The distances $(C2 — C8)_A$ used in the expression

$$K = \frac{\langle C2 — C8\rangle - (C2 — C8)_A}{\langle C4 — C6\rangle - (C2 — C8)_A}$$

for Sb-Me_2 is 1.650 Å and that for Sb-8 is 1.666 Å. These two parameters are the y-intercepts in the plots of Figures 5–7 and 5-8. We now can also calculate ΔG for the same equilibrium process using the familiar thermodynamic expression, which relates ΔG and K, that is,

$$\Delta G = -RT \ln K$$

Tables 5–1 and 5–2 summarize the calculate values of K and ΔG for Sb-Me_2 and Sb-8

Table 5–1. Calculated Values of the Equilibrium Constant K and ΔG for Sb-Me_2

Temperature (K)	C2—C8 (Å)	C4—C6 (Å)	C2—C8 + C4—C6	K	ΔG (kcal/mole)
20	1.651	2.339	3.990	0.0015	0.2597
115	1.660	2.313	3.973	0.0151	0.9584
127	1.667	2.312	3.979	0.0257	0.9241
153	1.674	2.296	3.970	0.0372	1.0010
181	1.696	2.279	3.975	0.0731	0.9407
208	1.715	2.263	3.978	0.1060	0.9274
236	1.731	2.247	3.978	0.1357	0.9367
265	1.756	2.234	3.990	0.1815	0.8985
294	1.781	2.215	3.996	0.2319	0.8539
295	1.768	2.216	3.984	0.2085	0.9191
322	1.815	2.174	3.989	0.3149	0.7393
335	1.827	2.173	4.000	0.3384	0.7212

Table 5–2. Calculated Values of the Equilibrium Constant K and ΔG for Sb-8

Temperature (K)	C2—C8 (Å)	C4—C6 (Å)	C2—C8 + C4—C6	K	ΔG (kcal/mole)
20	1.675	2.297	3.972	0.0143	0.1689
115	1.722	2.244	3.966	0.0969	0.5334
115	1.741	2.231	3.972	0.1327	0.4614
127	1.772	2.199	3.971	0.1989	0.4076
140	1.798	2.173	3.971	0.2604	0.3743
153	1.825	2.145	3.970	0.3319	0.3353
181	1.875	2.098	3.973	0.4838	0.2611
208	1.918	2.064	3.982	0.6332	0.1889
236	1.949	2.034	3.983	0.7690	0.1232
265	1.967	2.013	3.980	0.8674	0.0749
279	1.978	2.002	3.980	0.9286	0.0411
294	1.990	1.987	3.977	1.0093	-0.0054
295	1.990	1.996	3.986	0.9818	0.0108
295	1.990	1.991	3.981	0.9969	0.0018
335	2.001	1.973	3.974	1.0912	-0.0581
360	2.017	1.974	3.991	1.1396	-0.0935

From the data listed in Tables 5–1 and 5–2, we construct the following plots:

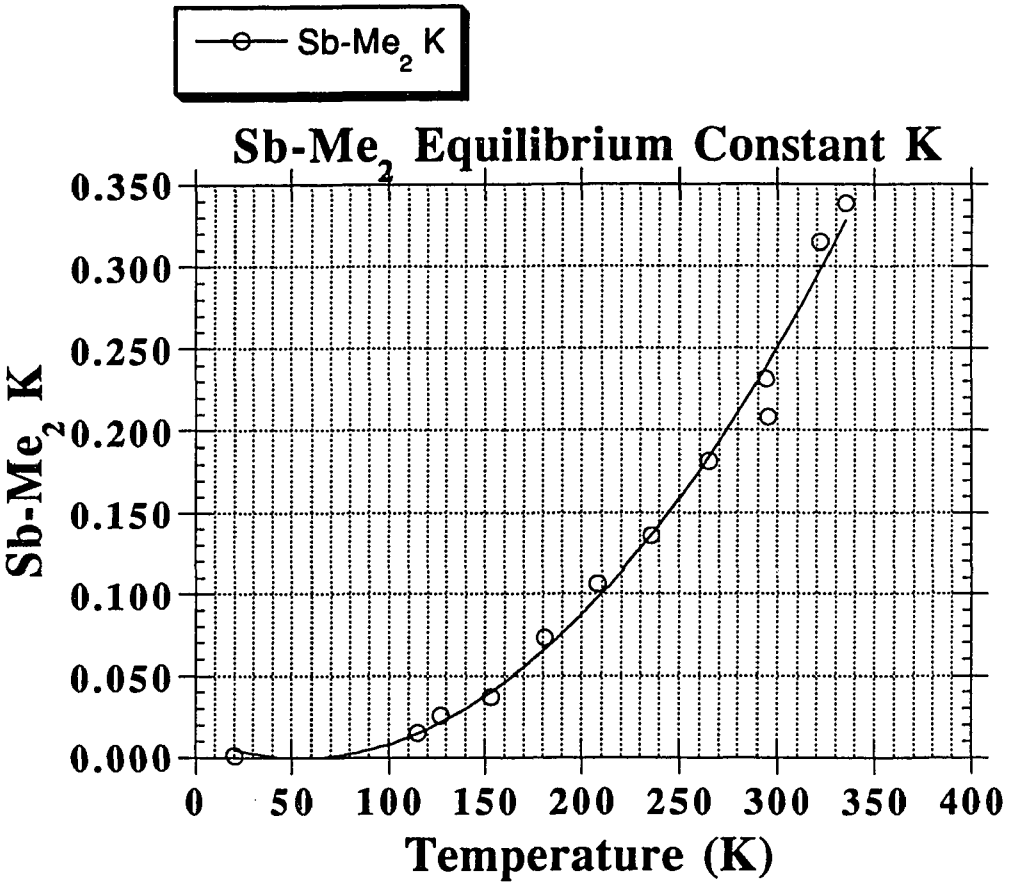


Figure 5–9. A plot of equilibrium constant *K* for $Sb\text{-}Me_2$ versus temperature

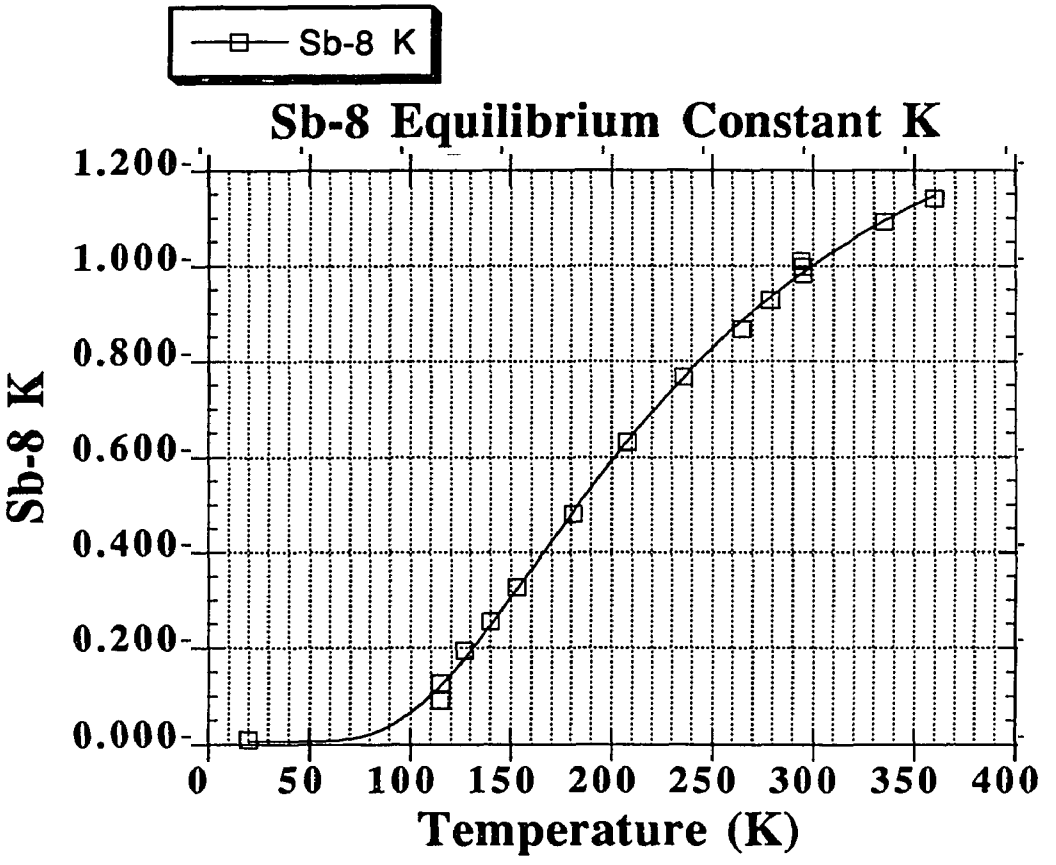


Figure 5–10. A plot of equilibrium constant *K* for Sb-8 versus temperature

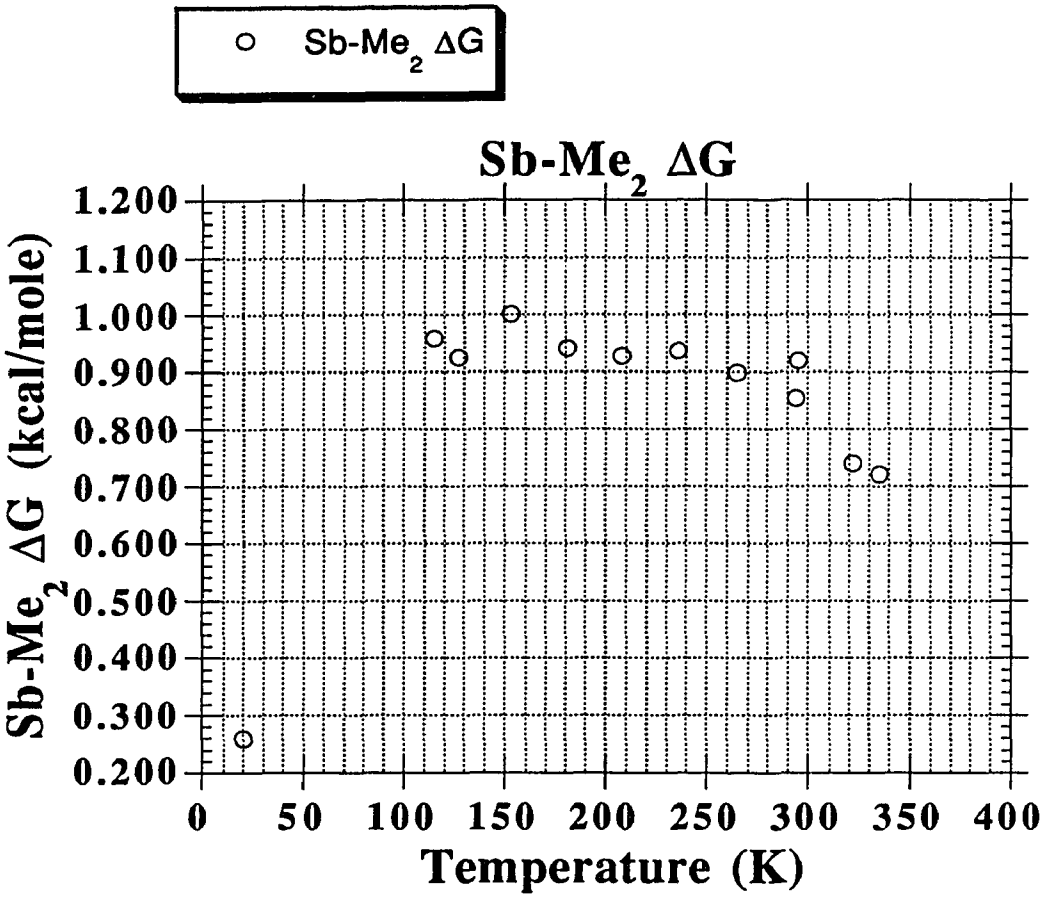


Figure 5–11. A plot of ΔG for $Sb\text{-}Me_2$ versus temperature.

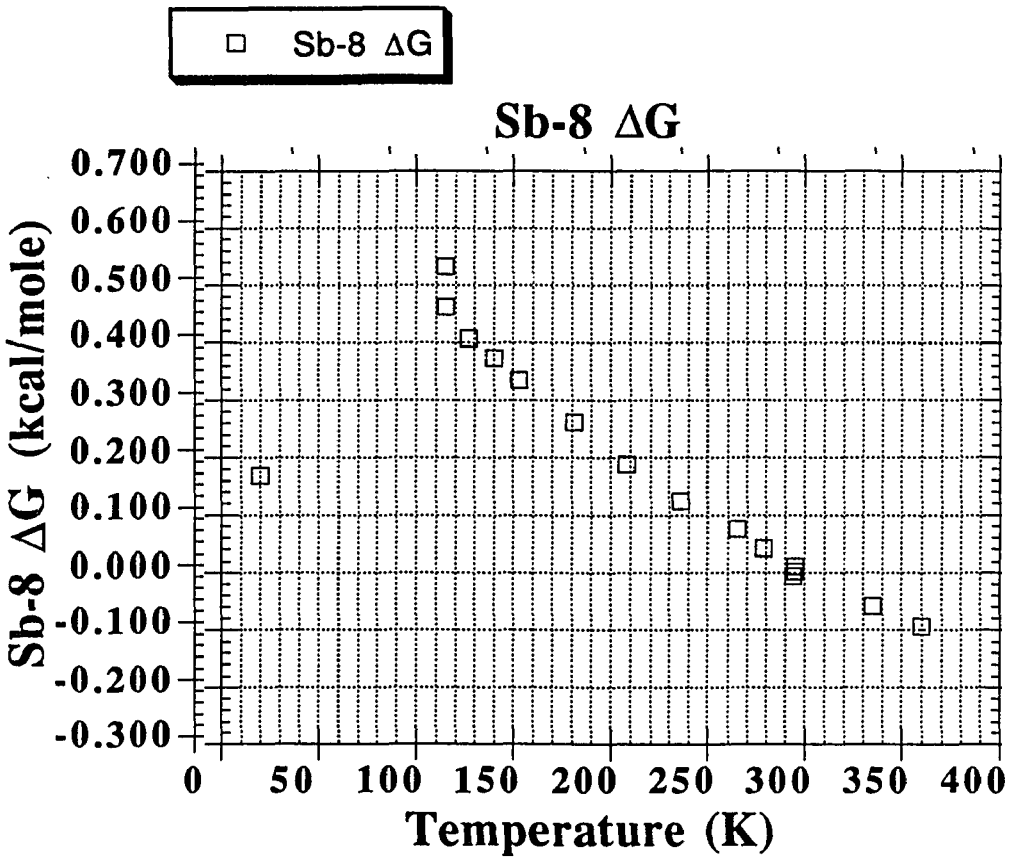


Figure 5–12. A plot of ΔG for Sb-8 versus temperature.

Since the distance C2—C8 does not change appreciably in the temperature range from 20 to approximately 100 K, we omit the point at 20 K in the last two plots and to fit the remaining data to a straight line (Figures 5–13 and 14). The reason for fitting the data to a straight line will soon become apparent.

ΔG = b + mT	
b	1.0966
m	-0.00088579
R	0.78968

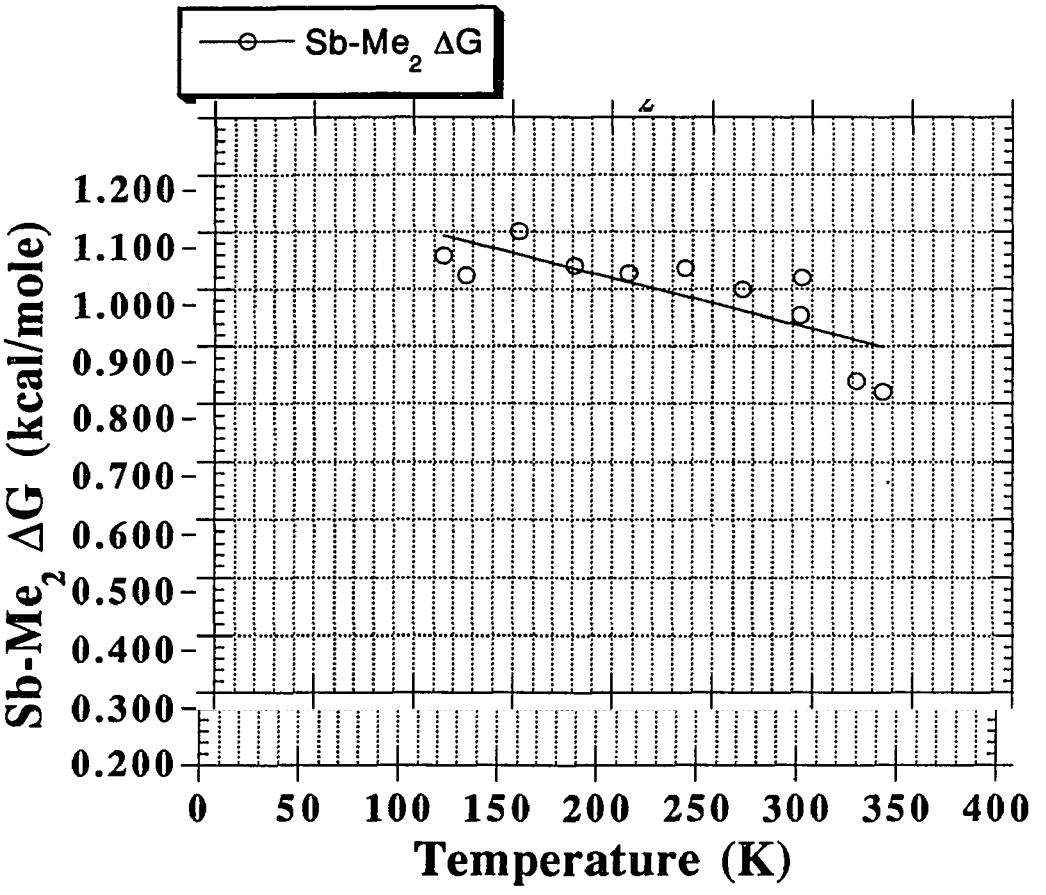


Figure 5–13. A plot of ΔG for Sb-Me_2 versus temperature. The data point at 20 K has been omitted.

ΔG = b + mT	
b	0.72315
m	-0.0024104
R	0.98693

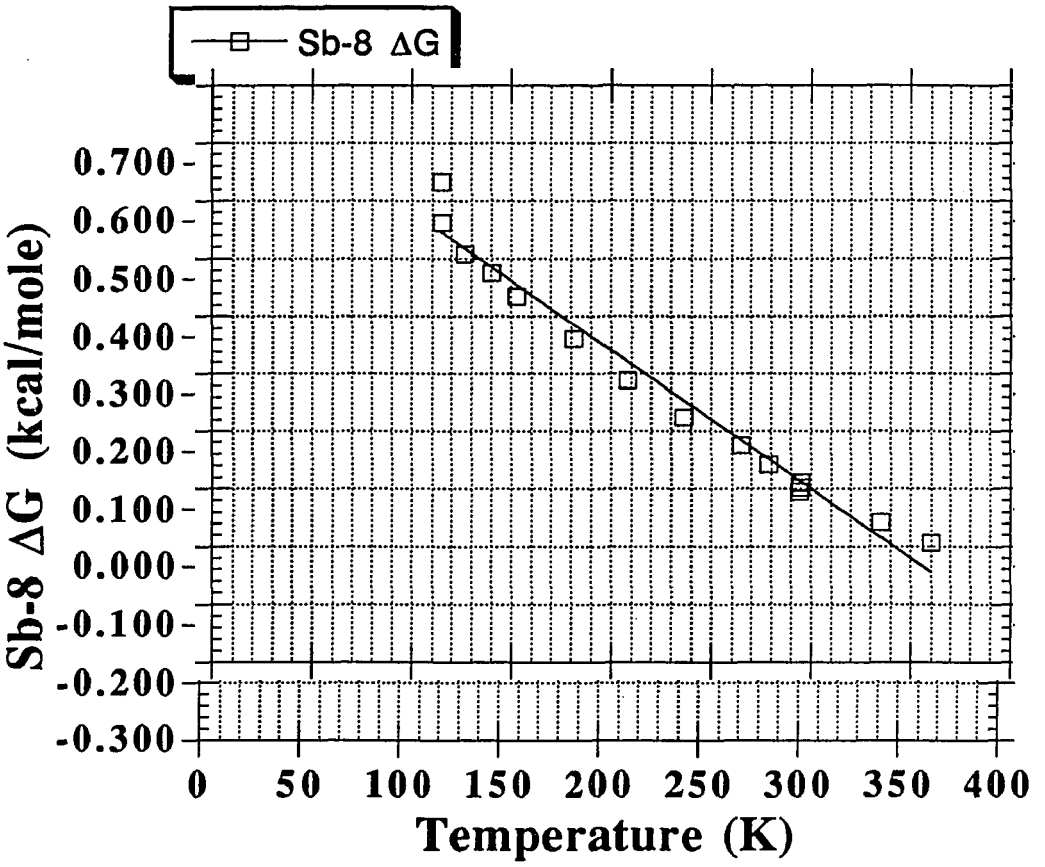


Figure 5–14. A plot of ΔG for Sb-8 versus temperature. The data point at 20 K has been omitted.

With the aid of the familiar thermodynamic expression

$$\Delta G = \Delta H - T\Delta S$$

we can now easily interpret the intercept b as ΔH and the slope m as $-\Delta S$, that is

$$\Delta H = b$$
$$\Delta S = -m$$

The following table summarizes the results.

Table 5–3. Thermodynamic Results for Sb-Me_2 and Sb-8

	$\Delta G^{\ddagger}$ (kcal mole^{-1})	ΔH (kcal mole^{-1})	ΔS (kcal mole^{-1}K^{-1})
Sb-Me_2	3.8[a]	1.10	0.00089
Sb-8		0.72	0.0024

[a] Calculated from line-shape analysis of ^{13}C NMR data.

From the diagram in Figure 5–15, we easily see that ΔH is a lower bound to the enthalpy of activation, $\Delta H^{\ddagger}$, for the forward process.

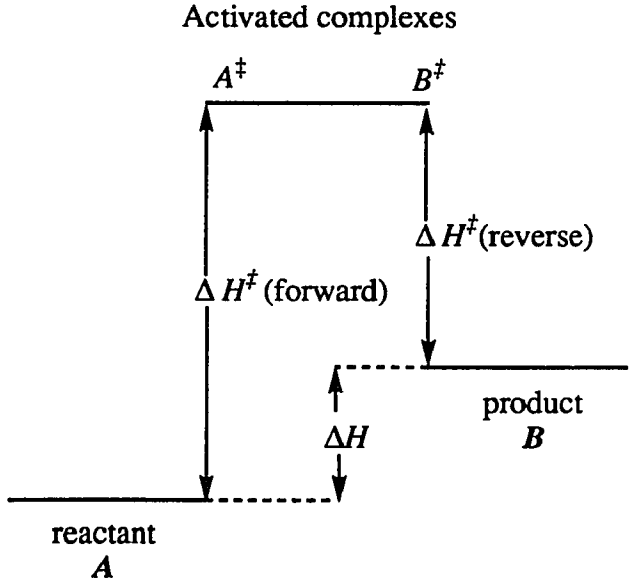


Figure 5–15. Energy diagram for the process $A \rightleftharpoons B$.

We conclude that the $\Delta H^{\ddagger}$ for the Cope rearrangement of Sb-Me_2 and Sb-8 must be greater than 1.10 and 0.72 kcal/mole, respectively. Also, we could expect that the $\Delta H^{\ddagger}$ of Sb-8 could be, at least, 0.39 kcal/mole lower than that of Sb-Me, that is, 0.39 = 0.1.10 – 0.72. It is worthwhile to mention that, as we have seen all along, activation energies (E_a, $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$) have a weak dependence on temperature and do not differ markedly from each other.

These numbers, 1.10 and 0.72 kcal/mole, are reasonable when compared to the ΔG of 0.8 kcal/mole for the nondegenerate Cope rearrangement of semibullvalene as calculated by Macho, Miller, and Yannoni from ^{13}C NMR data.[2] In Chapter 3, we pointed out that the degenerate Cope rearrangement of semibullvalene in solution becomes nondegenerate in the dynamic phase of the solid state. For clarity, we repeat a portion of Chapter 3. Macho, Miller, and Yannoni have not only observed the lifting of the degeneracy in the mirror-image rearrangement of semibullvalene caused by solid-state effect but also have conclusively demonstrated a dramatic solid-state suppression of the rate of rearrangement in semibullvalene from the ^{13}C NMR spectra shown in Figures 5–16 and 5–17.

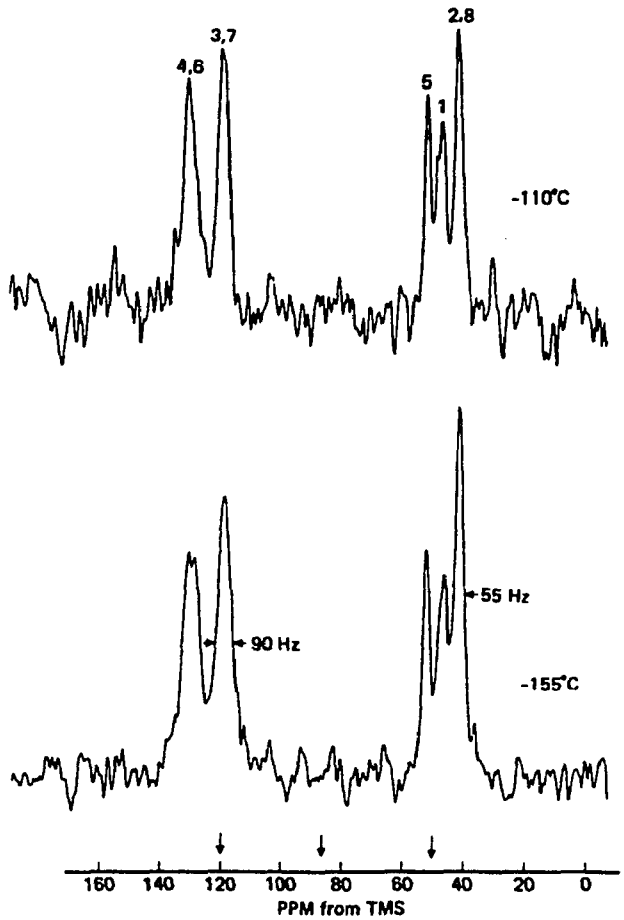


Figure 5–16. CP-MAS ^{13}C NMR Spectra of solid semibullvalene at –155 °C and at –110 °C, showing suppression of the degenerate Cope rearrangement. The arrows show the position of the averaged chemical shifts found in solution.[3]

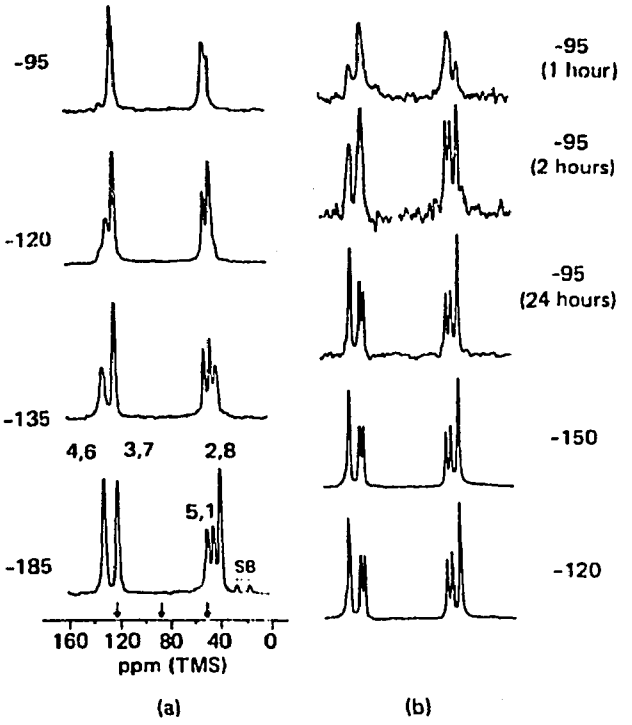


Figure 5–17. (a) CP-MAS ^{13}C NMR spectra of semibullvalene cooled into the solid state showing reversible dynamical behavior. The arrows mark the positions of the three resonances for the average spectrum obtained in solution. The peaks marked SB are the upfield spinning sidebands of the vinylic carbon resonances. (b) Spectra of the same sample during annealing at –95 °C. After annealing for several hours, the spectra no longer change with temperature cycling.

They have calculated the rate constants, k_1 and k_2, for the nondegenerate Cope rearrangement at –132 °C to be 486 and 8514 s^{-1}, respectively. The $\Delta G^{\ddagger}$ for the slow process at this temperature is 6.3 kcal $mole^{-1}$. The free-energy profile is shown in Figure 5–18.

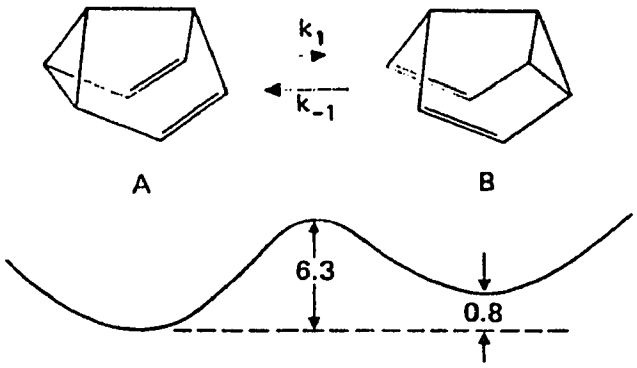


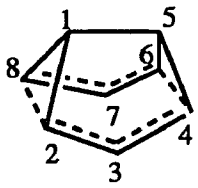
Figure 5–18. Free-energy profile (kcal/mole) for the nondegenerate Cope rearrangement of semibullvalene obtained from line-shape analysis of the previous CP-MAS ^{13}C spectra.

Macho, Miller, and Yannoni have demonstrated that solid-state morphology can have significant influences on the Cope rearrangement of semibullvalene. This solid-state effect manifests itself as a perturbation of the equilibrium and as a rate retardation; the free energy of activation for the higher barrier, 6.3 kcal mole^{-1} at –132 °C, for the rearrangement of semibullvalene in the solid state, however, is remarkably comparable to the solution value of 5.5 kcal mole^{-1} at –143 °C.

5.2 IN SUMMARY

We have undertaken a systematic, variable-temperature single-crystal X-ray study of substituted barbaralanes and semibullvalenes, which have a low activation energy for the Cope rearrangement. The single-crystal X-ray analyses were carried out in the temperature range from 20 to 360 K. The data clearly indicate that the six compounds, barbaralane-$(COOMe)_4$, Sb-$(COOMe)_8$, Sb-6, Sb-7, Sb-Me_2, and Sb-8, are molecules approaching the bishomoaromatic transition state in the solid state with increasing temperature, that is, **they become more and more like benzene.** In solution these six compounds undergo Cope rearrangement. In the solid state, however, no significant

structural alterations take place in barbaralane-$(COOMe)_4$ with temperature; gradual changes creep in Sb-$(COOMe)_8$; and spectacular transformations occur in Sb-8. These six compounds may be then classified in an order of increasing dynamic behavior in the solid state: barbaralane-$(COOMe)_4$ being the least dynamic or nearly static while Sb-8 is the most dynamic. The rest fell between these two extremes. Stepping over one candidate to the next, we saw in Chapter 4 that the trend toward the bishomoaromatic state intensified. The climax was reached when Sb-8 achieved at room temperature the long-sought, symmetric delocalized bishomoaromatic structure (except for the dissymmetry introduced by the 8-membered ring), where the single bonds in the semibullvalene ring system, C2—C3 and C7—C8, and double bonds, C3—C4 and C6—C7 were all equal, along with the interatomic distances, C2—C8 and C4—C6, that is,



Semibullvalene ring system in Sb-8 at room temperature

Thus, for the first time, we have characterized a symmetric neutral bishomobenzene molecule of the type which Hoffmann and Dewar had predicted more than twenty years ago. Even though Sb-8 at room temperature has the delocalized structure expected for a neutral bishomoaromatic compound, it is, nevertheless, static at temperatures approximately below 90 K. As we pointed out in Chapter 1, the bond distances in benzene from neutron diffraction data are not altered as the temperature is lowered to 92 K. And so, we conclude that Sb-8 has not crossed the barrier between valence tautomerism ($\Delta G^{\ddagger} > 0$) to resonance ($\Delta G^{\ddagger} < 0$) as in benzene. The significance of low-temperature work is then clear. It plays a central role and is indispensable in preventing

misconceptions, which may be construed from examining just room-temperature data when characterizing compounds which are claimed to exhibit benzene-like behavior.

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[1] H. Quast, J.-C. Carlsen, R. Janiak, E.-M. Peters, K. Peters, H. G. von Schnering, *Chem. Ber.* **125**, 995, (1992).

[2] V. Macho, R. D. Miller, C. S. Yannoni, *J. Am. Chem. Soc.*, **105**, 3735(1983).

[3] R. D. Miller, C. S. Yannoni, *J. Am. Chem. Soc.*, **102**, 7396(1980).

CHAPTER 6

DRIFTING AND DREAMING WITH INTERLUDES OF MATHEMATICAL ESCAPADES:

A Speculative Method For Calculating Energies Similar Or Perhaps Proportional To The Classical Activation Energies

The laws of nature are replete with analogies and similarities. The graphs of C2—C8 distances against temperature for Sb-Me_2 and Sb-8 resemble the curves of the heat capacities of crystalline monatomic solids as functions of temperature. The similarities become apparent by comparing Figures 6–1 and 2.

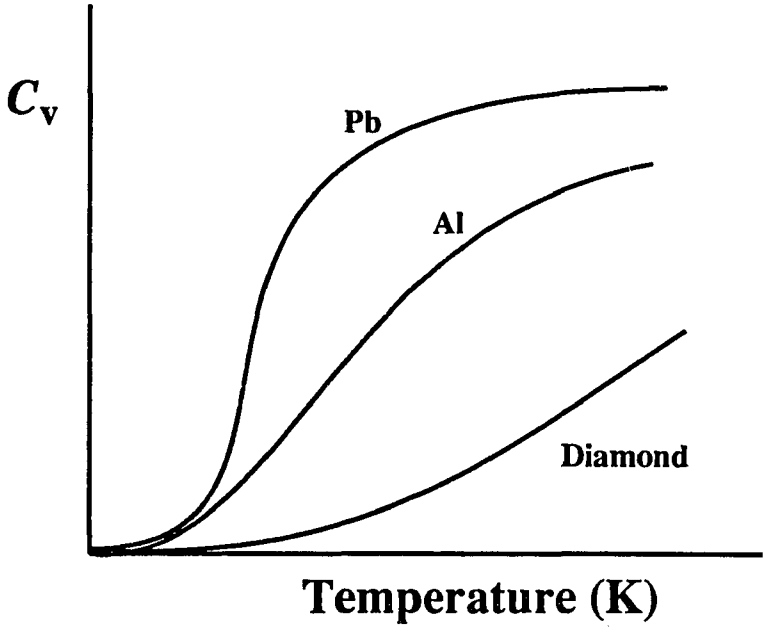


Figure 6–1. Atomic heat capacity, C_V, at constant volume versus temperature.

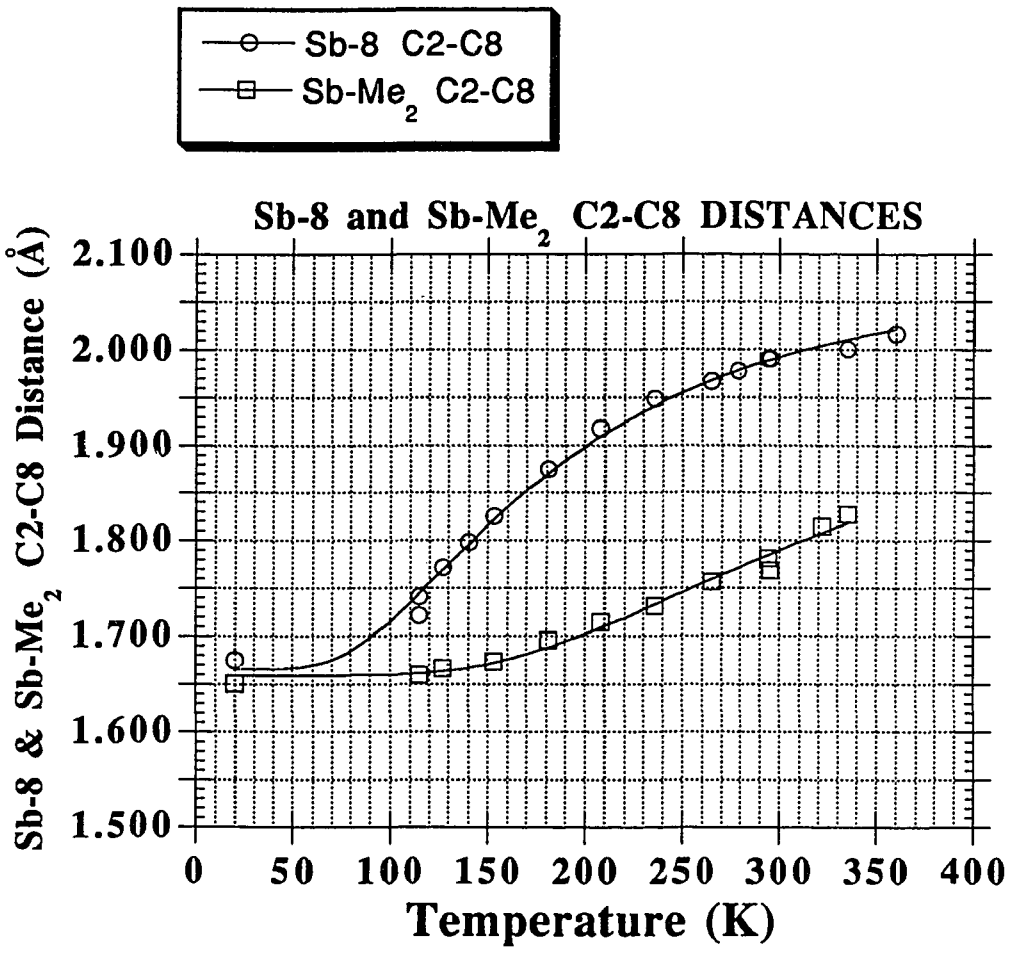


Figure 6–2. Plots of C2—C8 distances for Sb-Me_2 and Sb-8 versus temperature.

By exploiting these similarities, we can calculate, with the information at hand, energies which are similar or perhaps proportional to classical activation energies of Sb-Me_2 and Sb-8.

With the aid of quantum mechanics and statistical mechanics, Einstein derived a mathematical expression to almost match the behavior of the experimental atomic heat capacities at constant volume against temperature. Einstein's famous expression, which relates heat capacity and temperature, is

$$C_v = 3R\left(\frac{h\nu}{k_B T}\right)^2 \frac{e^{h\nu/k_B T}}{\left(e^{h\nu/k_B T}-1\right)^2}$$

where:

$C_v =$ molar heat capacity at constant volume
$h\nu =$ difference between adjacent energy levels of oscillator
$k_B =$ Boltzmann's constant
$R =$ gas constant
$T =$ temperature (K)

The general form of this Einstein equation is

$$F(T) = a\left(\frac{b}{T}\right)^2 \frac{e^{b/T}}{\left(e^{b/T}-1\right)^2} + c$$

where a, b, and c are constants. The parameter c is an additive constant and is zero for the curve $\{T, C_v\}$. The constant a is nothing more than a scale factor; and, in fact, it is the limit of $F(T)$ as the temperature increases without bounds, that is,

$$\lim_{T\to\infty} F(T) = a$$

One way to evaluate

$$\lim_{T\to\infty} F(T) = \lim_{T\to\infty} a\left(\frac{b}{T}\right)^2 \frac{e^{b/T}}{\left(e^{b/T}-1\right)^2}$$

is to notice that at high temperatures

$$e^{b/T} \approx 1 + \frac{b}{T}$$

This approximation is based on the Maclaurin's expansion (Taylor's expansion near zero) of e^x, which is

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$

where x is defined as

$$x \equiv \frac{b}{T}$$

When T is large, x is small; and so, the higher order terms in the expansion for e^x become vanishingly small. The infinite series then may be truncated and just the first two terms survive, that is,

$$e^x \approx 1+x$$

or

$$e^{b/T} \approx 1+\frac{b}{T}$$

Thus,

$$\begin{aligned}
\lim_{T\to\infty} F(T) &= \lim_{T\to\infty} a\left(\frac{b}{T}\right)^2 \frac{e^{b/T}}{\left(e^{b/T}-1\right)^2} \\
&= a\lim_{T\to\infty}\left(\frac{b}{T}\right)^2 \frac{e^{b/T}}{\left(e^{b/T}-1\right)^2} \\
&= a\lim_{T\to\infty}\left(\frac{b}{T}\right)^2 \frac{1+b/T}{\left(1+b/T-1\right)^2} \\
&= a\lim_{T\to\infty}\left(\frac{b}{T}\right)^2 \frac{1+b/T}{\left(1+b/T-1\right)^2} \\
&= a\lim_{T\to\infty}\left(\frac{b}{T}\right)^2 \frac{1+b/T}{\left(b/T\right)^2} \\
&= a\lim_{T\to\infty}(1+b/T) \\
&= a(1+0) \\
\lim_{T\to\infty} F(T) &= a
\end{aligned}$$

The constant b, on the other hand, controls the steepness of the curve $\{T, F(T)\}$.The smaller this constant b is the faster is the rise in the curve. The constant b represents an energy, ε_b, divided by Boltzmann's constant, k_B, that is,

$$b = \frac{\varepsilon_b}{k_B}$$

In molar units, b is the ratio of a molar energy, E_b, divided by the gas constant, R:

$$b = \frac{E_b}{R}$$

or

$$E_b = Rb$$

Our objective then is to fit the experimental data of C2—C8 distances versus temperature for both Sb-8 and Sb-Me2 with $\{T, F(T)\}$ and thereby determining the constants a, b, and c. Knowing the constant b, we can determine E_b. The nonlinear regression analyses of C2-C8 distances for Sb-Me_2 and Sb-8 in Table 6–1 yield the following results, shown in Figures 6–3 and 4.

Table 6–1. Interatomic C2—C8 Distances (Å) for Sb-Me_2 and Sb-8 from X-ray Diffraction

Temperature (K)	Sb-Me_2	Sb-8
20	1.651	1.675
115	1.660	1.722
115		1.741
127	1.667	1.772
140		1.798
153	1.674	1.825
181	1.696	1.875
208	1.715	1.918
236	1.731	1.949
265	1.756	1.967
279		1.978
294	1.781	1.990
295	1.768	1.990
295		
322	1.815	1.990
335	1.827	2.001
360		2.017

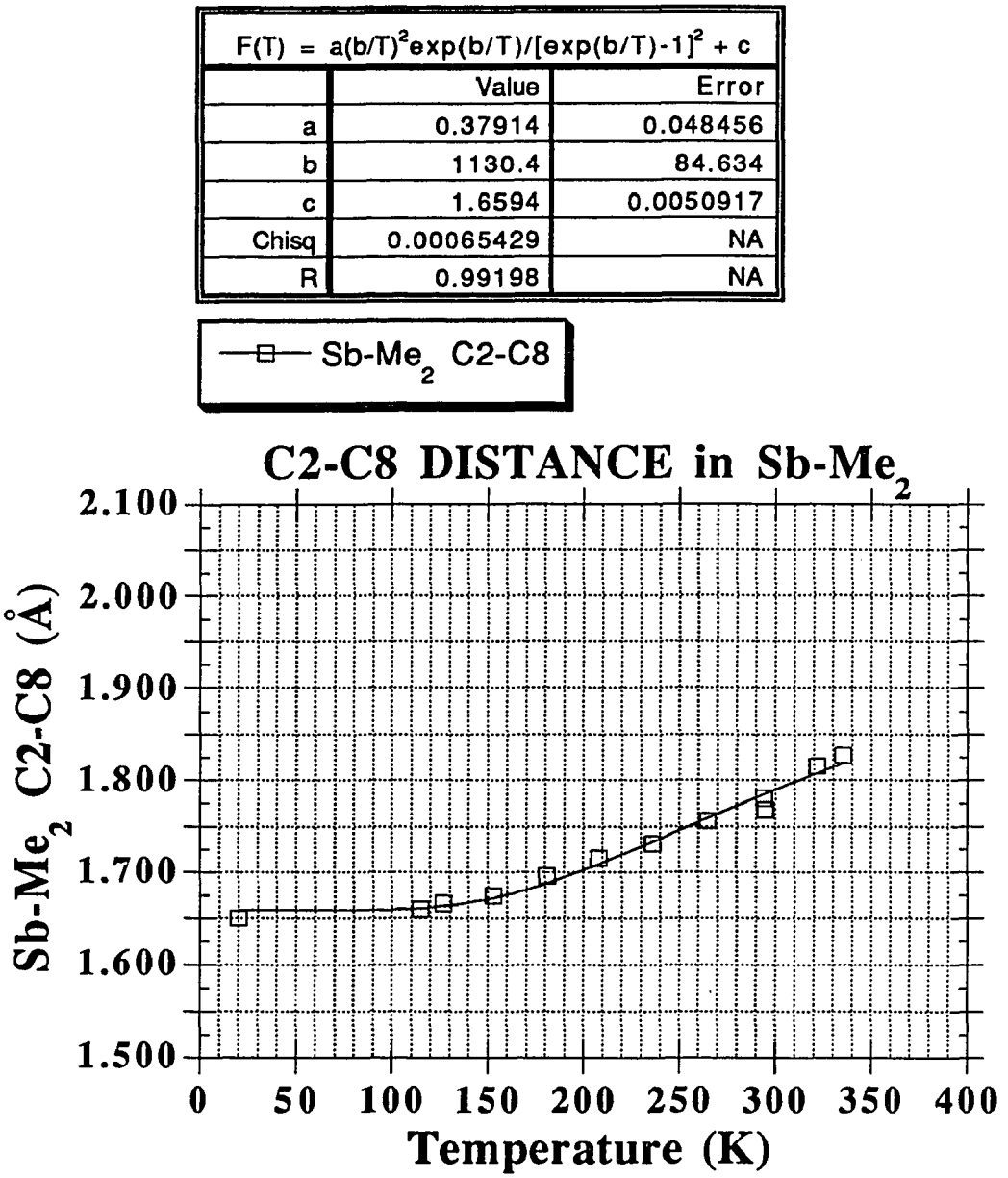


Figure 6–3. A plot of C2—C8 distances for Sb-Me_2 versus temperature. The results from the nonlinear regression analysis are shown in the box at the top (KaleidaGraph™, Abelbeck Software, Synergy Software, Reading, PA, Third Edition, 1993).

$F(T) = a(b/T)^2 \exp(b/T)/[\exp(b/T)-1]^2 + c$		
	Value	Error
a	0.43435	0.0080822
b	564.94	16.602
c	1.6663	0.0077403
Chisq	0.00089533	NA
R	0.99776	NA

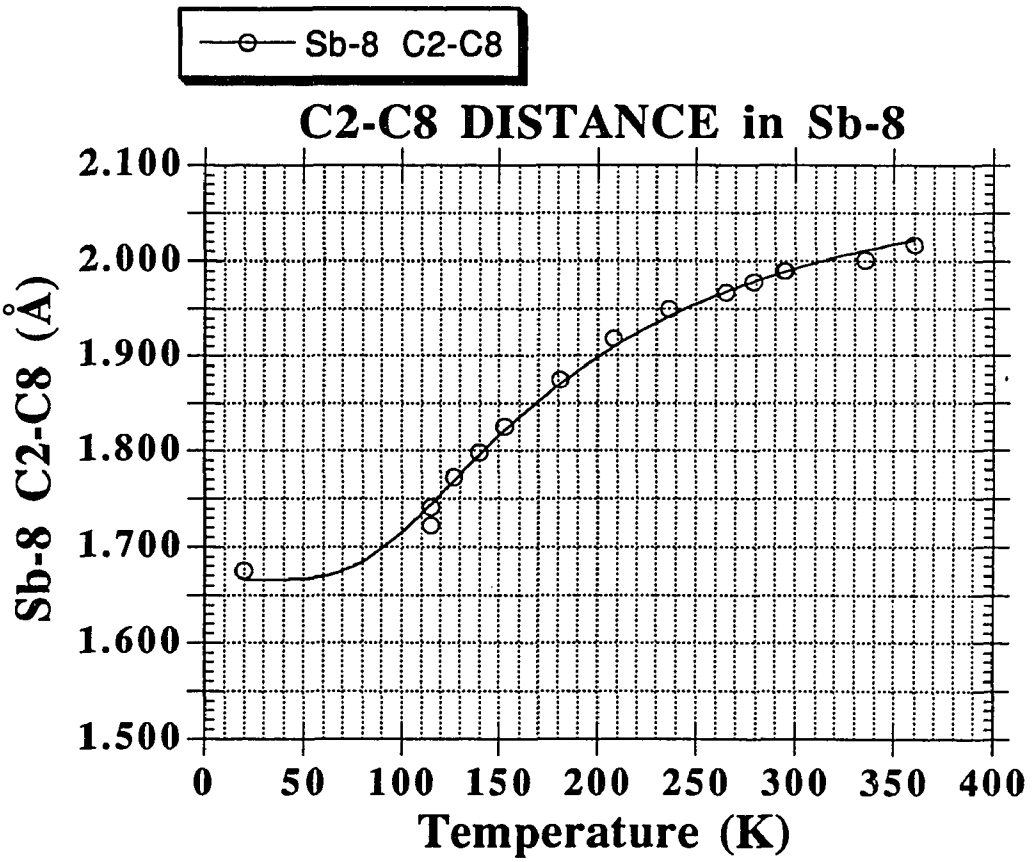


Figure 6–4. A plot of C2—C8 distances for Sb-8 versus temperature. The results from the nonlinear regression analysis are shown in the box at the top.

We can now calculate E_b for Sb-Me_2 and Sb-8 with the b values from the regression analyses, using the expression

$$E_b = Rb$$

For Sb-Me2,

$$E_b = (0.001987)(1130) \text{ kcal/mole} = 2.25 \text{ kcal/mlole}$$

and for Sb-8

$$E_b = (0.001987)(565) \text{ kcal/mole} = 1.12 \text{ kcal/mlole}$$

Activation energies for Sb-Me_2 and Sb-8 are summarized in Table 6–2.

Table 6–2. Activation Energies for Sb-Me_2 and Sb-8

	E_b (kcal/mole)	$\Delta G^{\ddagger}$ (kcal/mole)
Sb-Me_2	2.25	3.8[a]
Sb-8	1.12	

[a] From line-shape analysis of solid-state ^{13}C NMR data by K. Grohmann.

The ratio 2.25/1.12 is approximately 2.01.

Instead of choosing the C2—C8 distance to calculate E_b, we could have used the C3—C4 or C6—C7 distance to extract the b parameter. The changes in the distances C3—C4 and C6—C7 over the same temperature range, however, are less dramatic than in C2—C8 and are thus prone to more errors. Nevertheless, it is worthwhile to perform regression analyses on C3—C4 and C6—C7 distances to compare the magnitudes of b values obtained from these sources with that calculated from C2—C8 distance. This exercise will use C3—C4 and C6—C7 distances of only Sb-8 in Table 6–3.

Table 6–3. Interatomic C3—C4 and C6—C7 Distances (Å) for Sb-8

Temperature (K)	C3—C4	C6—C7
20	1.337	1.334
115	1.345	1.344
115	1.348	1.346
127	1.353	1.353
140	1.353	1.355
153	1.360	1.363
181	1.366	1.363
208	1.372	1.363
236	1.374	1.376
265	1.378	1.376
279	1.379	1.379
294	1.381	1.381
295	1.378	1.381
295	1.382	1.377
335	1.373	1.378
360	1.385	1.391

It is reassuring that the values of *b* from C3—C4 and C6—C7 distances of Sb-8 in Figures 6–5 and 6 are comparable to that from C2—C8 distance in Figure 6–4.

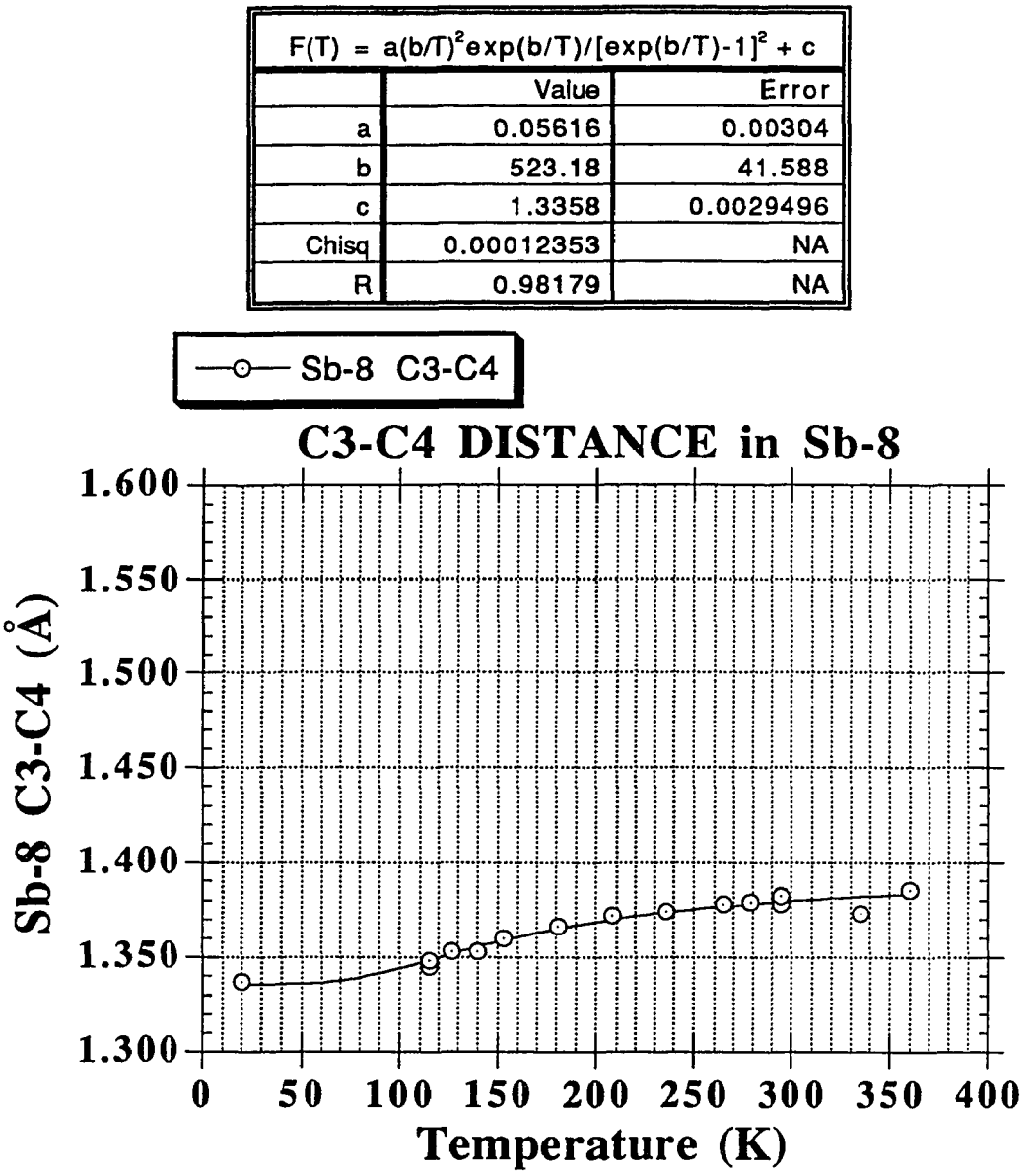


Figure 6–5. A plot of C3—C4 distances for Sb-8 versus temperature. The results from the nonlinear regression analysis are shown in the box at the top.

$F(T) = a(b/T)^2\exp(b/T)/[\exp(b/T)-1]^2 + c$		
	Value	Error
a	0.0598	0.0036175
b	535.68	48.723
c	1.3342	0.003506
Chisq	0.00017693	NA
R	0.97725	NA

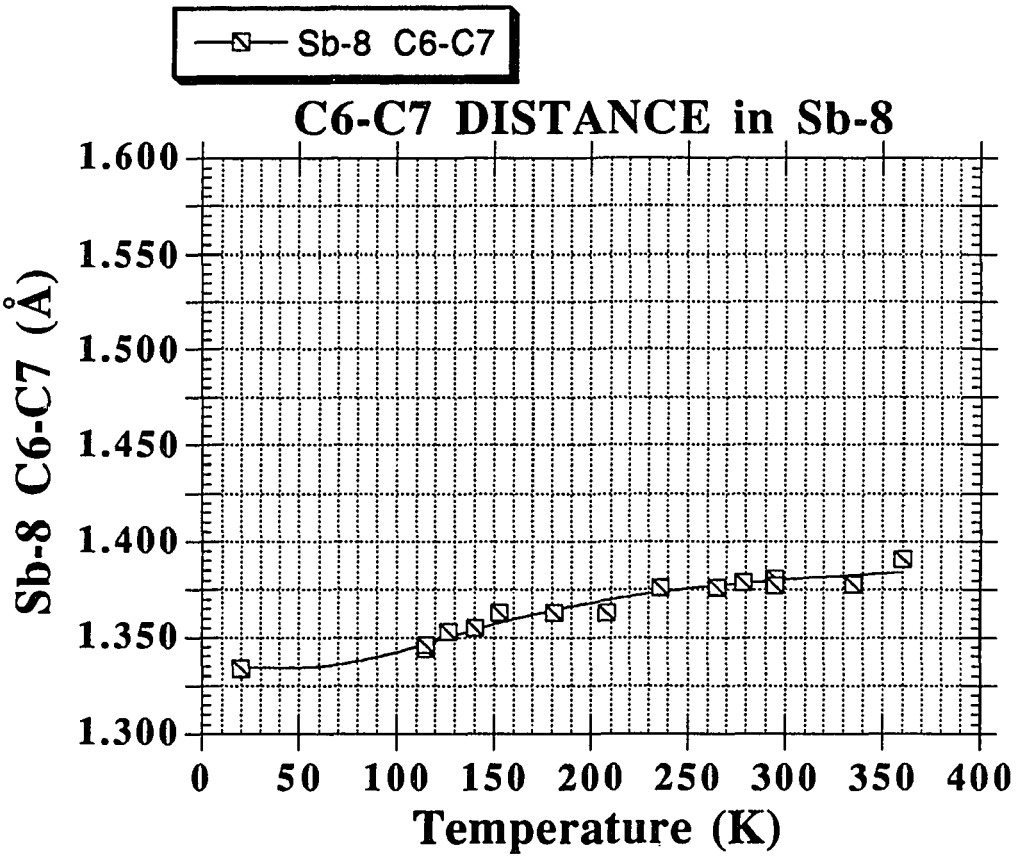


Figure 6–6. A plot of C6—C7 distances for Sb-8 versus temperature. The results from the nonlinear regression analysis are shown in the box at the top.

For comparison, we summarize the various b values and their associated E_b energies for Sb-8 in Table 6–4.

Table 6–4. Values of b and E_b from C2—C8, C3—C4, and C6—C7 Distances in Sb-8

	C2—C8	C3—C4	C6—C7
b	565	523	536
E_b	1.12	1.04	1.07

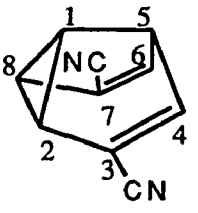
CHAPTER 7

MARCHING ONWARD AND FORWARD WITH MOLECULAR STIMULATIONS:

The Never-ending Saga of Research

If research answers a question, it generates more queries, which need further work to search out satisfactory answers. In other words, Research opens one door by answering a question, but it generates more questions and thus creates the need for more doors to be opened. Research opens up new vistas of new research and thus begets more research. Always there is more to do and there is never an end. Here are some suggestions for further work:

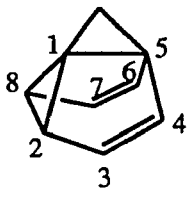
This work may have given the impression that a long C2—C8 bond in a semibullvalene derivative correlates with a low activation energy for its Cope rearrangement. Although this may seem plausible, compounds have surfaced in the literature, which have a long C2—C8 interatomic distance at room temperature, and yet have an activation energy higher than expected. Case in point is 3,7-dicyanosemibullvalene.[1,2]



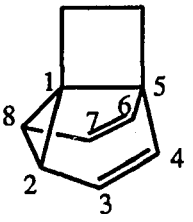
3,7-Dicyanosemibullvalene

It would be revealing to collect X-ray data of this compound at different temperatures to see how fast the graph of C2—C8 distance against temperature would rise. Chapter 6 indicated that a sharp rise implied a compound with low activation energy for the Cope rearrangement. This assumption needs to be scrutinized by analyzing key compounds, such as, 3,7-dicyanosemibullvalene.

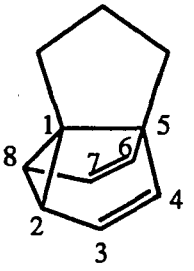
Another suggestion is to synthesize and characterize more annulated semibullvalenes with and without electron withdrawing substituents at positions 2,4,6,8. For example,



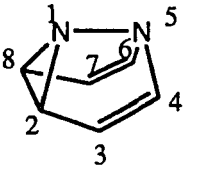
III



IV

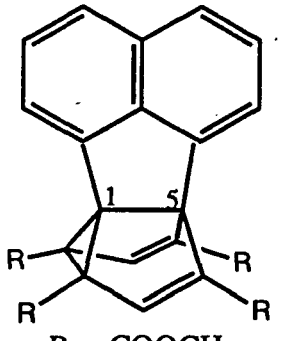


V



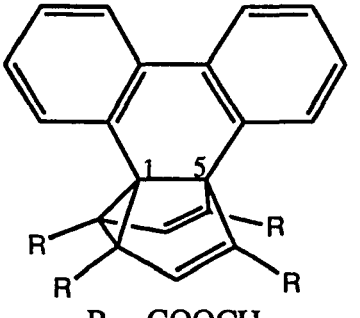
VI

The smaller rings on top of the semibullvalene ring induce more strain and thus favor the possibility of lowering the activation energy. The calculated energy for **III** is –9.1 kcal/mole and that for **VI** is –12.4 kcal/mole.[3] Other annulated compounds of a different breed are the ester derivatives of acenaphthosemibullvalene and phenanthro-semibullvalene:



R = $COOCH_3$

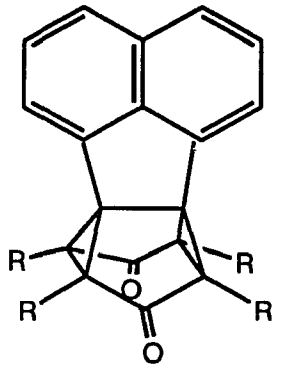
2,4,6,8-Tetracarbomethoxy-acenaphthosemibullvalene



R = $COOCH_3$

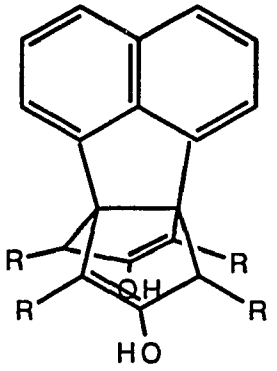
2,4,6,8-Tetracarbomethoxy-phenanthrosemibullvalene

These types of substituents at C1 and C5, unlike the saturated rings in Sb-6, Sb-7, and Sb-8, are planar and may lower the activation energy of the Cope rearrangement mostly through electronic effects rather than just introducing strain in the semibullvalene ring. Efforts to synthesize these compounds have not been successful up to now. Their precursors have already been synthesized and their crystals analyzed with single-crystal X-ray diffraction:



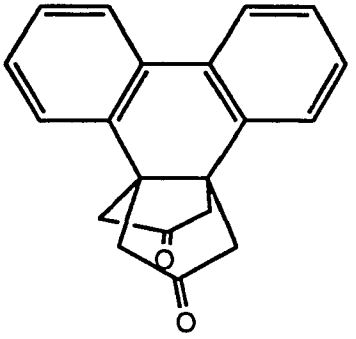
R = $COOCH_3$

Acenaphtho-tetracyclicester



R = $COOCH_3$

Acenaphtho-Weiss



Phenanthro-diketone

Plans for the future could also include:

- The carbomethoxy groups at positions 2, 4, 6, and 8 in the semibullvalene and barbaralane ring systems can be replaced with stronger electron acceptors, such as, CN and NO_2 to lower still further the activation energy of the Cope rearrangement. Not only do these groups have superior electronic advantages but also, in the case of cyano groups, have the favorable linear geometry needed to minimize crystal-packing effects over the bulky unsymmetrical carbomethoxy groups. In principle, crystal forces could lower as well as raise activation barriers in exchange processes since a molecule may be constrained to adopt a conformation which is mostly dictated by neighboring forces rather than by its own inherent electronic makeup. The calculated activation energy for 2,4,6,8-tetracyanosemibullvalene is –4.7 kcal/mole. To incorporate the cyano and nitro

groups in the semibullvalene and barbaralane rings is by no means a trivial synthetic escapade. On this route, many challenges lurk on.

- The crystal structure of the parent **semibullvalene** itself, which is a liquid at room temperature (m. p. approximately –90 °C), can posslibly be determined by the methods of Boese[4] (zone melting and programmed crystal growth) or Strousse (trapping semibullvalene by porphorins in the formation of clatharates).[5,6]

- Further work needs to do be done in extracting dynamic information from the thermal parameters of X-ray data.[7,8,9,10]

- By means of multiple regression analyses, the equilibrium constant *K* for Sb-Me_2 and Sb-8 can presumably be calculated by employing all the bond distances in the semibullvalene ring system instead of just using the C2—C8 distances as was done in Chapter 5.

- AM-1 calculations should be performed with the available X-ray data to obtain the energy of the ground state and transition state for both Sb-Me_2 and Sb-8 and hence derive their respective energy of activation for the Cope rearrangement.

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IN THE IMAGE AND LIKENESS OF BENZENE:

Variable-temperature X-ray Studies of Substituted Barbaralanes and Semibullvalenes

by

Louis J. Todaro

Volume II

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirement for the degree of Doctor of Philosophy, The City University of New York.

1993

CHAPTER 8

EXPERIMENTAL ROUNDUP:

A Collection of Blood, Sweat, and Tears

This chapter includes tables and *ORTEP*[1] drawings for all the compounds analyzed with single-crystal X-ray technique in this research. The intensity X-ray data in the temperature range of 115 to 360 K were measured on an Enraf-Nonius CAD4 diffractometer equipped with liquid-nitrogen device (graphite-monochromated, Cu $K\alpha$ radiation, ω-2θ scans). The intensity X-ray data at 20 K were measured on a Huber diffractometer equipped with a helium compressor (graphite-monochromated Mo $K\alpha$ radiation, ω-2θ scans) under the guidance and generous help of Drs. Charles. E. Strousse and Saeed I. Khan at UCLA Department of Chemistry and Biochemistry. The structures were solved by a multiple-solution procedure.[2] and were refined with Enraf-Nonius SDP programs[3], except the two structures at 20 K, which were refined by Dr. Charles. E. Strousse. The nonhydrogen atoms were refined anisotropically, except possibly for the isotropic refinement of disordered atoms in minor conformers or minor rotamers. The hydrogen atoms were included in the structure-factor calculations, but their parameters were not refined. Crystals at low temperatures were mounted with silicone grease. Those at high temperatures (above room temperature) were mounted either with silicone rubber or 3M high-temperature epoxy, as indicated in the experimental details of each crystal.

We now discuss some details of the calibration of the setpoint on the CAD-4 diffractometer used for data collection with controlled temperature. The CAD-4

diffractometer low-temperature controller maintains a temperature on the crystal by dialing a setpoint. A setpoint on the controller has a one-to-one correspondence with a certain temperature. The lowest setpoint is approximately 90 and the highest is 999. the setpoint of 100 corresponds to a measured temperature of 114.7 K and the setpoint 990 corresponds to a measured temperature of 359.6 K.

Table 8–1. Temperatures and Setpoints

Temperature[a] (°C)	Temperature[b] (K)	Temperature[c] (K)	Setpoint
-158.5	114.7	111.9	100
-152.2	121.0	118.9	125
-146.3	126.9	125.8	150
-139.9	133.3	132.8	175
-133.2	140.0	139.7	200
-126.3	146.9	146.7	225
-119.8	153.4	153.6	250
-113.2	160.0	160.6	275
-106.8	166.4	167.6	300
-99.3	173.9	174.5	325
-92.7	180.5	181.5	350
-85.8	187.4	188.4	375
-78.2	195.0	195.4	400
-71.6	201.6	202.3	425
-65.1	208.1	209.3	450
-57.5	215.7	216.3	475
-50.9	222.3	223.2	500
-44.0	229.2	230.2	525
-37.3	235.9	237.1	550
-29.8	243.4	244.1	575
-22.3	250.9	251.1	600
-15.1	258.1	258.0	625
-8.1	265.1	265.0	650
-0.9	272.3	271.9	675
5.9	279.1	278.9	700
13.1	286.3	285.8	725
20.3	293.5	292.8	750
34.5	307.7	306.7	800
48.7	321.9	320.6	850
62.2	335.4	334.5	900
75.9	349.1	348.5	950
86.4	359.6	359.6	990

[a] Measured with a Digi-Sense thermocouple thermometer (model no. 8528-20) from Cole-Palmer.
[b] Calculated with $T = 273.15 + C$.
[c] Calculated with $T = 84.065 + 0.27831S$ from the linear regression equation of setpoints and temperatures (K) in Figure 8–1.

$S = b_T + m_T T$	
b_T	-301.9
m_T	3.5924
R	0.99991

$T = b_S + m_S S$	
b_S	84.065
m_S	0.27831
R	0.99991

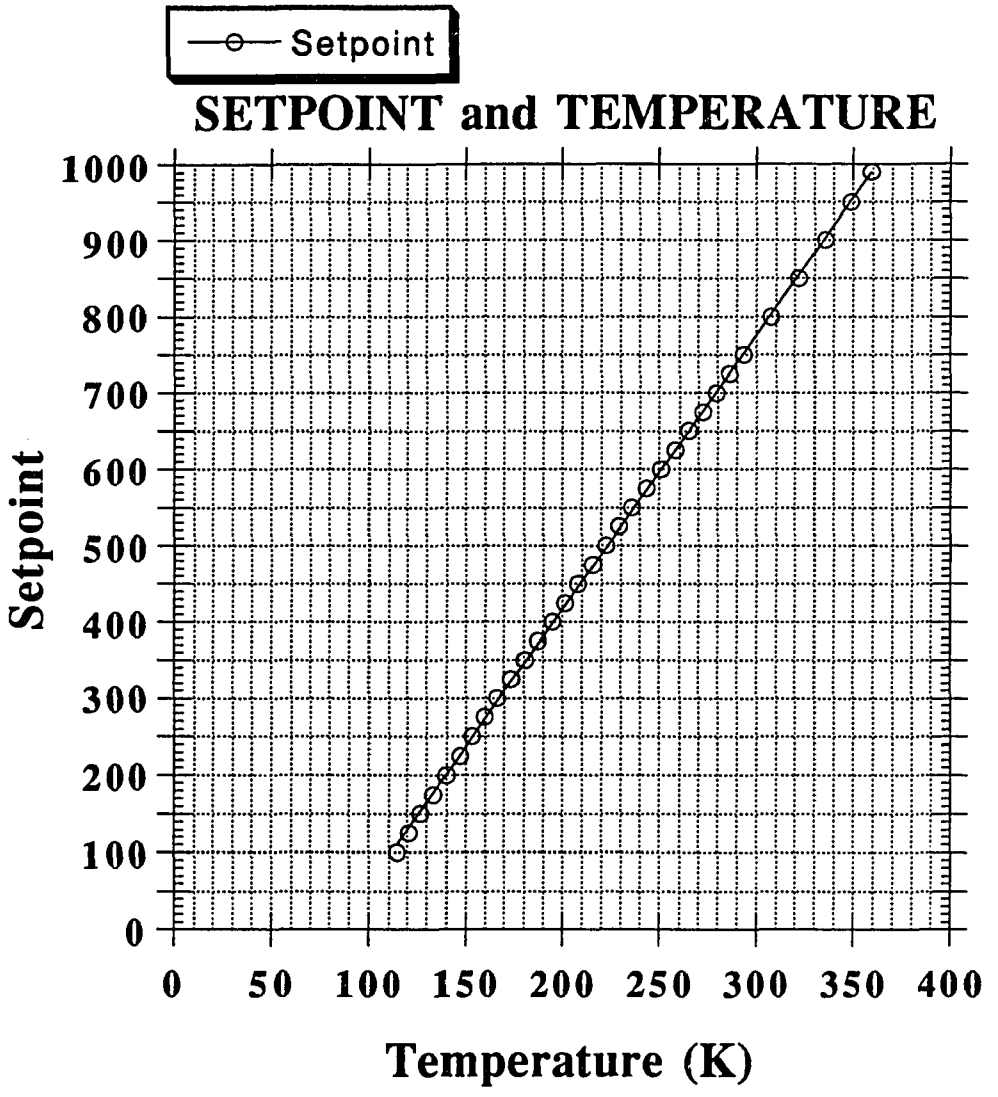
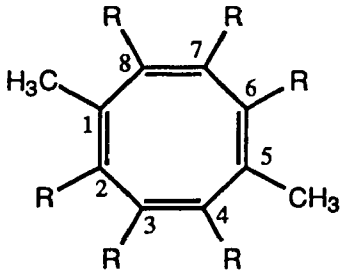


Figure 8–1. A plot of setpoint versus temperature. The results of the regression analyses of setpoints versus temperatures and vice versa are shown at the top.

8.1 1,5-DIMETHYL2,4,6,8-TETRACARBOMETHOXY CYCLOOCTATETRAENE



R = $COOCH_3$

1,5-Dimethyl-2,4,6,8-tetracarbomethoxycyclooctatetraene
[$Me_2(COOMe)_4COT$]

Table 8–2. X-ray Crystal Data for $Me_2(COOMe)_4COT$ at **295 K**

Formula	$C_{18}H_{20}O_8$
Formula weight	364.36
Melting point (°C)	108–109
Crystal size (mm)	0.17 x 0.34 x 0.45
Crystal system	monoclinic
Space group	*P*21/*c*
a (Å)	16.363(1)
b (Å)	15.733(1)
c (Å)	15.433(3)
β (°)	109.73(1)
Cell volume ($Å^3$)	3739.6
Z	8
d_{calc} (g cm^{-3})	1.294
μ(Cu $K\alpha$) (cm^{-1})	8.28
Maximum θ (°)	75
Unique reflections	7702
Observed reflections [$I > 3.0\sigma(I)$]	4973
Number of variables	469
R	0.049
R_w	0.063
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.24
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.22

Table 8.3. Final Atomic Parameters for $Me_2(COOMe)_4COT$ at **295 K**

Atom	x	y	z	B(Å^2)
O1	0.3676(1)	0.4626(1)	0.4586(1)	5.56(4)
O2	0.4510(1)	0.3656(1)	0.4257(1)	6.44(5)
O3	0.2235(1)	0.4449(1)	0.6636(1)	5.02(4)
O4	0.3176(1)	0.4371(2)	0.8062(1)	6.59(5)
O5	0.5854(1)	0.1920(2)	0.8257(1)	6.40(5)
O6	0.6118(1)	0.3193(2)	0.8938(1)	6.98(6)
O7	0.2932(1)	0.1301(1)	0.5132(1)	5.00(4)
O8	0.3167(1)	0.0847(1)	0.6565(1)	5.69(5)
C1	0.4130(1)	0.2555(2)	0.5598(1)	3.65(5)
C2	0.3905(1)	0.3380(2)	0.5443(1)	3.56(5)
C3	0.3379(1)	0.3798(2)	0.5923(1)	3.65(5)
C4	0.3634(1)	0.3937(2)	0.6827(1)	3.65(5)
C5	0.4532(1)	0.3760(2)	0.7481(1)	4.13(5)
C6	0.4812(1)	0.2960(2)	0.7647(1)	3.95(5)
C7	0.4255(1)	0.2234(2)	0.7220(1)	3.81(5)
C8	0.3911(1)	0.2072(2)	0.6317(1)	3.55(5)
C9	0.4592(2)	0.2039(2)	0.5079(2)	5.16(6)
C10	0.5026(2)	0.4546(2)	0.7925(2)	5.99(8)
C21	0.4076(2)	0.3877(2)	0.4702(1)	4.16(5)
C22	0.3773(2)	0.5155(2)	0.3853(2)	7.14(9)
C41	0.3010(2)	0.4281(2)	0.7250(2)	4.14(5)
C42	0.1551(2)	0.4665(2)	0.6993(2)	5.71(7)
C61	0.5666(2)	0.2731(2)	0.8351(2)	4.79(6)
C62	0.6608(2)	0.1571(3)	0.8962(2)	8.2(1)
C81	0.3319(1)	0.1336(2)	0.6046(1)	3.80(5)
C82	0.2343(2)	0.0597(2)	0.4791(2)	6.14(7)
O1'	0.9717(1)	0.4909(1)	1.1576(1)	5.59(4)
O2'	1.0753(1)	0.4717(1)	1.0979(2)	7.52(5)
O3'	0.8418(1)	0.7369(1)	1.1897(1)	4.78(4)
O4'	0.8464(1)	0.8412(1)	1.0943(1)	6.34(5)
O5'	1.1102(1)	0.9012(1)	0.9926(1)	6.26(5)
O6'	1.0399(2)	0.8081(2)	0.8877(1)	8.64(6)
O7'	1.2393(1)	0.8322(1)	1.2934(1)	6.00(5)
O8'	1.2482(2)	0.6960(1)	1.3335(1)	7.14(6)
C1'	1.1311(1)	0.6444(2)	1.1625(2)	3.76(5)
C2'	1.0535(1)	0.6099(1)	1.1518(1)	3.60(5)
C3'	0.9821(1)	0.6599(2)	1.1648(1)	3.59(5)
C4'	0.9437(1)	0.7256(1)	1.1125(1)	3.49(5)
C5'	0.9649(2)	0.7561(1)	1.0312(1)	3.66(5)
C6'	1.0425(2)	0.7920(1)	1.0430(1)	3.71(5)
C7'	1.1109(2)	0.8006(2)	1.1339(2)	3.78(5)
C8'	1.1480(1)	0.7358(2)	1.1882(2)	3.66(5)
C9'	1.2080(2)	0.5983(2)	1.1517(2)	5.48(7)
C10'	0.8930(2)	0.7467(2)	0.9406(2)	4.81(6)
C21'	1.0370(2)	0.5180(2)	1.1327(2)	4.15(5)
C22'	0.9499(2)	0.4013(2)	1.1416(3)	7.99(9)
C41'	0.8731(2)	0.7745(2)	1.1303(2)	4.11(5)
C42'	0.7714(2)	0.7805(2)	1.2070(2)	6.14(7)
C61'	1.0623(2)	0.8330(2)	0.9652(2)	4.55(6)
C62'	1.1339(2)	0.9488(2)	0.9245(2)	7.71(9)
C81'	1.2167(2)	0.7513(2)	1.2792(2)	4.46(6)
C82'	1.3080(3)	0.8508(3)	1.3791(3)	10.0(1)

Table 8.3 (cont.). Final Atomic Parameters for $Me_2(COOMe)_4COT$ at **295 K**

Atom	x	y	z	B(Å^2)
H3	0.278	0.399	0.554	4.4
H7	0.412	0.182	0.764	4.6
H9A	0.468	0.145	0.533	6.2
H9B	0.423	0.202	0.441	6.2
H9C	0.517	0.230	0.516	6.2
H10A	0.467	0.506	0.767	7.2
H10B	0.516	0.452	0.861	7.2
H10C	0.558	0.458	0.779	7.2
H22A	0.345	0.570	0.382	8.6
H22B	0.440	0.528	0.398	8.6
H22C	0.353	0.485	0.325	8.6
H42A	0.100	0.478	0.647	6.9
H42B	0.146	0.418	0.737	6.9
H42C	0.172	0.519	0.739	6.9
H62A	0.668	0.096	0.882	9.9
H62B	0.714	0.190	0.898	9.9
H62C	0.653	0.161	0.957	9.9
H82A	0.209	0.063	0.411	7.4
H82B	0.267	0.005	0.497	7.4
H82C	0.187	0.062	0.506	7.4
H3'	0.961	0.643	1.216	4.3
H7'	1.131	0.859	1.156	4.5
H9A'	1.258	0.639	1.163	6.6
H9B'	1.225	0.550	1.197	6.6
H9C'	1.192	0.575	1.088	6.6
H10A'	0.913	0.769	0.890	5.8
H10B'	0.877	0.685	0.929	5.8
H10C'	0.841	0.780	0.942	5.8
H22A'	0.900	0.388	1.163	9.6
H22B'	0.933	0.389	1.074	9.6
H22C'	1.001	0.366	1.177	9.6
H42A'	0.753	0.747	1.252	7.4
H42B'	0.791	0.838	1.233	7.4
H42C'	0.721	0.786	1.148	7.4
H62A'	1.170	0.999	0.954	9.3
H62B'	1.168	0.911	0.897	9.3
H62C'	1.080	0.969	0.875	9.3
H82A'	1.320	0.913	1.383	11.9
H82B'	1.290	0.833	1.432	11.9
H82C'	1.362	0.819	1.381	11.9

The parameters of the hydrogen atoms were not refined.

Table 8.4. Final Anisotropic Thermal Parameters (U's) for $Me_2(COOMe)_4COT$ at 295 K

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.097(1)	0.065(1)	0.0593(8)	0.006(1)	0.0403(7)	0.0176(8)
O2	0.101(1)	0.100(1)	0.0648(8)	0.011(1)	0.0552(6)	0.0169(9)
O3	0.0613(8)	0.078(1)	0.0580(8)	0.0088(9)	0.0284(6)	-0.0002(9)
O4	0.089(1)	0.120(2)	0.0491(8)	0.014(1)	0.0328(7)	-0.011(1)
O5	0.057(1)	0.110(2)	0.066(1)	0.015(1)	0.0081(9)	0.007(1)
O6	0.062(1)	0.123(2)	0.060(1)	-0.017(1)	-0.0058(9)	-0.001(1)
O7	0.074(1)	0.072(1)	0.0420(8)	-0.0195(9)	0.0166(7)	-0.0053(8)
O8	0.085(1)	0.071(1)	0.0540(9)	-0.018(1)	0.0154(8)	0.0130(9)
C1	0.0393(9)	0.066(1)	0.0345(9)	-0.002(1)	0.0136(7)	-0.001(1)
C2	0.044(1)	0.063(1)	0.0289(8)	-0.006(1)	0.0124(7)	0.0005(9)
C3	0.049(1)	0.050(1)	0.0398(9)	-0.004(1)	0.0160(8)	0.0016(9)
C4	0.052(1)	0.051(1)	0.0376(9)	-0.007(1)	0.0166(8)	-0.0026(9)
C5	0.052(1)	0.073(2)	0.0333(9)	-0.015(1)	0.0169(8)	-0.007(1)
C6	0.045(1)	0.072(1)	0.0328(9)	-0.007(1)	0.0130(7)	0.003(1)
C7	0.043(1)	0.062(1)	0.0389(9)	0.000(1)	0.0125(8)	0.007(1)
C8	0.044(1)	0.053(1)	0.0388(9)	0.004(1)	0.0147(8)	0.0032(9)
C9	0.062(1)	0.084(2)	0.059(1)	0.013(1)	0.0328(9)	0.004(1)
C10	0.074(2)	0.087(2)	0.060(1)	-0.028(1)	0.014(1)	-0.014(1)
C21	0.055(1)	0.070(2)	0.0325(9)	-0.010(1)	0.0147(8)	0.000(1)
C22	0.129(2)	0.082(2)	0.067(1)	-0.003(2)	0.042(1)	0.026(1)
C41	0.065(1)	0.049(1)	0.047(1)	-0.004(1)	0.0249(9)	-0.001(1)
C42	0.074(1)	0.067(2)	0.091(2)	0.011(1)	0.048(1)	0.005(1)
C61	0.045(1)	0.098(2)	0.038(1)	-0.007(1)	0.0125(8)	0.009(1)
C62	0.062(2)	0.142(3)	0.092(2)	0.028(2)	0.003(2)	0.032(2)
C81	0.049(1)	0.052(1)	0.043(1)	0.004(1)	0.0158(8)	0.004(1)
C82	0.091(2)	0.081(2)	0.059(1)	-0.034(2)	0.023(1)	-0.018(1)
O1'	0.0808(9)	0.0474(9)	0.100(1)	-0.0070(8)	0.0517(7)	-0.0039(9)
O2'	0.100(1)	0.061(1)	0.151(1)	-0.011(1)	0.0772(9)	-0.031(1)
O3'	0.0558(8)	0.072(1)	0.0580(8)	0.0207(8)	0.0250(6)	0.0136(8)
O4'	0.097(1)	0.063(1)	0.091(1)	0.0324(9)	0.0442(9)	0.0242(9)
O5'	0.116(1)	0.064(1)	0.0608(9)	-0.035(1)	0.0343(9)	-0.0020(9)
O6'	0.159(2)	0.122(2)	0.0454(9)	-0.071(1)	0.032(1)	-0.009(1)
O7'	0.076(1)	0.061(1)	0.059(1)	0.000(1)	-0.018(1)	-0.0033(9)
O8'	0.100(1)	0.073(1)	0.066(1)	0.010(1)	-0.014(1)	0.015(1)
C1'	0.050(1)	0.048(1)	0.044(1)	0.004(1)	0.0146(8)	0.001(1)
C2'	0.050(1)	0.045(1)	0.042(1)	0.006(1)	0.0159(8)	0.0026(9)
C3'	0.047(1)	0.047(1)	0.042(1)	0.004(1)	0.0151(8)	0.0018(9)
C4'	0.045(1)	0.045(1)	0.040(1)	0.002(1)	0.0109(8)	0.0027(9)
C5'	0.052(1)	0.043(1)	0.037(1)	0.003(1)	0.0074(9)	0.0062(9)
C6'	0.057(1)	0.043(1)	0.037(1)	-0.001(1)	0.0104(9)	0.0026(9)
C7'	0.051(1)	0.047(1)	0.041(1)	-0.001(1)	0.0105(9)	-0.001(1)
C8'	0.045(1)	0.050(1)	0.041(1)	0.001(1)	0.0110(8)	-0.000(1)
C9'	0.054(1)	0.069(2)	0.088(2)	0.008(1)	0.027(1)	-0.008(1)
C10'	0.057(1)	0.070(2)	0.045(1)	-0.002(1)	0.002(1)	0.003(1)
C21'	0.054(1)	0.047(1)	0.058(1)	0.005(1)	0.0213(9)	0.000(1)
C22'	0.125(2)	0.051(2)	0.155(2)	-0.022(2)	0.084(2)	-0.012(2)
C41'	0.053(1)	0.052(1)	0.048(1)	0.008(1)	0.0128(9)	0.005(1)
C42'	0.060(1)	0.107(2)	0.072(1)	0.034(1)	0.029(1)	0.014(2)
C61'	0.066(1)	0.058(1)	0.045(1)	-0.011(1)	0.013(1)	0.004(1)
C62'	0.137(2)	0.082(2)	0.086(2)	-0.037(2)	0.054(1)	0.013(1)
C81'	0.054(1)	0.057(1)	0.049(1)	0.007(1)	0.005(1)	0.003(1)
C82'	0.120(3)	0.095(3)	0.093(2)	-0.004(2)	-0.055(2)	-0.014(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8.5. Bond Distances (Å) for $Me_2(COOMe)_4COT$ at **295 K**

		Unprimed	Primed
O1	C21	1.330(3)	1.323(3)
O1	C22	1.455(4)	1.455(4)
O2	C21	1.194(3)	1.200(4)
O3	C41	1.328(3)	1.330(3)
O3	C42	1.445(4)	1.442(4)
O4	C41	1.198(3)	1.198(3)
O5	C61	1.332(4)	1.312(3)
O5	C62	1.450(4)	1.446(4)
O6	C61	1.202(3)	1.193(3)
O7	C81	1.337(2)	1.323(3)
O7	C82	1.445(3)	1.446(4)
O8	C81	1.196(3)	1.197(3)
C1	C2	1.348(3)	1.340(3)
C1	C8	1.486(3)	1.493(3)
C1	C9	1.510(4)	1.510(4)
C2	C3	1.468(4)	1.478(3)
C2	C21	1.487(3)	1.481(3)
C3	C4	1.334(3)	1.331(3)
C4	C5	1.502(3)	1.491(3)
C4	C41	1.487(4)	1.489(4)
C5	C6	1.334(4)	1.344(3)
C5	C10	1.509(4)	1.499(3)
C6	C7	1.471(3)	1.475(3)
C6	C61	1.496(3)	1.492(4)
C7	C8	1.339(3)	1.329(3)
C8	C81	1.476(3)	1.493(3)

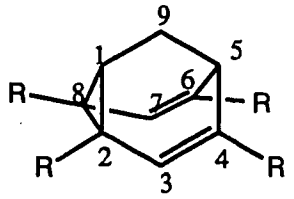
Table 8.6. Bond Angles (°) for $Me_2(COOMe)_4COT$ at **295 K**

			Unprimed	Primed
C21	O1	C22	115.7(2)	116.1(2)
C41	O3	C42	116.7(2)	115.7(2)
C61	O5	C62	116.7(2)	117.8(2)
C81	O7	C82	115.9(2)	115.7(2)
C2	C1	C8	120.3(2)	120.4(2)
C2	C1	C9	125.4(2)	125.6(2)
C8	C1	C9	114.3(2)	114.0(2)
C1	C2	C3	120.9(2)	121.9(2)
C1	C2	C21	122.1(2)	121.4(2)
C3	C2	C21	116.6(2)	116.6(2)
C2	C3	C4	124.9(2)	124.3(2)
C3	C4	C5	124.2(2)	124.4(2)
C3	C4	C41	120.0(2)	121.7(2)
C5	C4	C41	115.8(2)	113.9(2)
C4	C5	C6	119.9(2)	119.9(2)
C4	C5	C10	113.9(2)	114.8(2)
C6	C5	C10	126.1(2)	125.2(2)
C5	C6	C7	121.7(2)	123.1(2)
C5	C6	C61	122.8(2)	121.6(2)
C7	C6	C61	115.1(2)	115.1(2)
C6	C7	C8	126.3(2)	124.6(2)
C1	C8	C7	123.9(2)	124.5(2)
C1	C8	C81	119.3(2)	114.8(2)
C7	C8	C81	116.6(2)	120.5(2)
O1	C21	O2	122.7(2)	122.0(2)
O1	C21	C2	111.0(2)	111.6(2)
O2	C21	C2	126.3(2)	126.4(3)
O3	C41	O4	123.2(3)	122.9(3)
O3	C41	C4	113.0(2)	113.6(2)
O4	C41	C4	123.7(2)	123.5(3)
O5	C61	O6	123.8(2)	122.7(3)
O5	C61	C6	110.2(2)	111.2(2)
O6	C61	C6	126.0(3)	126.0(2)
O7	C81	O8	123.2(2)	123.6(2)
O7	C81	C8	111.3(2)	113.1(2)
O8	C81	C8	125.4(2)	123.3(2)

Table 8.7 of Root-Mean-Square Amplitudes of Thermal Vibration (Å) for $Me_2(COOMe)_4COT$ at **295 K**

	Unprimed			Primed		
Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O1	0.196	0.269	0.317	0.213	0.241	0.330
O2	0.186	0.300	0.347	0.219	0.263	0.410
O3	0.213	0.253	0.286	0.204	0.226	0.298
O4	0.195	0.292	0.357	0.205	0.274	0.352
O5	0.219	0.285	0.337	0.208	0.245	0.367
O6	0.200	0.308	0.361	0.207	0.260	0.467
O7	0.203	0.235	0.306	0.190	0.247	0.362
O8	0.211	0.250	0.330	0.202	0.284	0.387
C1	0.183	0.198	0.257	0.210	0.213	0.231
C2	0.168	0.206	0.254	0.200	0.206	0.233
C3	0.196	0.215	0.233	0.204	0.210	0.225
C4	0.191	0.211	0.241	0.195	0.215	0.220
C5	0.177	0.210	0.285	0.180	0.217	0.244
C6	0.179	0.208	0.273	0.190	0.208	0.248
C7	0.192	0.209	0.253	0.201	0.217	0.238
C8	0.195	0.207	0.233	0.200	0.219	0.226
C9	0.201	0.254	0.302	0.214	0.266	0.303
C10	0.212	0.270	0.331	0.195	0.259	0.279
C21	0.178	0.224	0.276	0.211	0.234	0.243
C22	0.200	0.319	0.360	0.211	0.292	0.417
C41	0.205	0.220	0.258	0.202	0.231	0.249
C42	0.218	0.261	0.319	0.202	0.260	0.354
C61	0.190	0.211	0.318	0.208	0.225	0.281
C62	0.208	0.335	0.397	0.201	0.311	0.395
C81	0.204	0.217	0.235	0.200	0.241	0.268
C82	0.212	0.261	0.347	0.189	0.311	0.496

8.2 2,4,6,8-TETRACARBOMETHOXYBARBARALANE



R = $COOCH_3$

2,4,6,8-Tetracarbomethoxybarbaralane
[Barbaralane-$(COOMe)_4$]

Table 8–8. X-ray Crystal Data for Barbaralane-$(COOMe)_4$ at **115 K**

Formula	$C_{17}H_{18}O_8$
Formula weight	350.33
Melting point (°C)	99–100
Crystal size (mm)	0.10 x 0.36 x 0.50
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	7.757(1)
b (Å)	16.101(5)
c (Å)	12.866(3)
β (°)	90.08(1)
Cell volume (Å^3)	1606.9(7)
Z	4
d_{calc} (g cm^{-3})	1.448
μ(Cu $K\alpha$) (cm^{-1})	9.4
Maximum θ (°)	75
Unique reflections	3314
Observed reflections [$I > 3.0\sigma(I)$]	2888
Number of variables	226
R	0.044
R_w	0.059
$(\Delta\rho)_{max}$ (e Å^{-3})	0.36
$(\Delta\rho)_{min}$ (e Å^{-3})	–0.31

Table 8-9. Final Atomic Parameters for Barbaralane-$(COOMe)_4$ at **115 K**

Atom	x	y	z	B(Å^2)
O1	0.2381(1)	0.42302(7)	0.87604(8)	1.52(2)
O2	0.4513(1)	0.32827(7)	0.88163(9)	1.60(2)
O3	-0.0038(1)	0.24728(8)	0.44488(9)	1.86(2)
O4	-0.1145(2)	0.24272(8)	0.60609(9)	1.98(2)
O5	0.1136(1)	0.40917(7)	0.33044(8)	1.53(2)
O6	0.1275(2)	0.54062(7)	0.38981(9)	1.62(2)
O7	0.4244(1)	0.59365(6)	0.70614(9)	1.52(2)
O8	0.5674(1)	0.49908(7)	0.80172(9)	1.56(2)
C1	0.4908(2)	0.37085(9)	0.6492(1)	1.07(2)
C2	0.3343(2)	0.37083(9)	0.7167(1)	1.08(2)
C3	0.1790(2)	0.32734(9)	0.6793(1)	1.15(2)
C4	0.1586(2)	0.30841(9)	0.5784(1)	1.10(2)
C5	0.2908(2)	0.33928(9)	0.5005(1)	1.10(2)
C6	0.2545(2)	0.43116(9)	0.4898(1)	1.08(2)
C7	0.3006(2)	0.48292(9)	0.5665(1)	1.10(2)
C8	0.3968(2)	0.45342(9)	0.6574(1)	1.07(2)
C9	0.4734(2)	0.32723(9)	0.5462(1)	1.13(2)
C14	0.3534(2)	0.37121(9)	0.8331(1)	1.19(2)
C15	-0.0014(2)	0.26401(9)	0.5470(1)	1.34(2)
C16	0.1591(2)	0.46726(9)	0.4003(1)	1.16(2)
C17	0.4734(2)	0.51616(9)	0.7298(1)	1.15(2)
C18	0.2492(2)	0.4306(1)	0.9876(1)	2.19(3)
C19	-0.1564(2)	0.2053(1)	0.4073(2)	2.62(3)
C20	0.0225(2)	0.4403(1)	0.2406(1)	1.78(3)
C21	0.4833(2)	0.6572(1)	0.7774(1)	1.92(3)
H1	0.605	0.367	0.685	1.3
H3	0.087	0.312	0.730	1.4
H5	0.284	0.309	0.433	1.3
H7	0.269	0.543	0.562	1.3
H9A	0.495	0.267	0.556	1.3
H9B	0.560	0.350	0.497	1.3
H18A	0.159	0.470	1.013	2.6
H18B	0.230	0.375	1.020	2.6
H18C	0.366	0.452	1.007	2.6
H19A	-0.146	0.196	0.331	3.1
H19B	-0.169	0.151	0.444	3.1
H19C	-0.260	0.240	0.421	3.1
H20A	-0.006	0.393	0.193	2.1
H20B	-0.086	0.468	0.263	2.1
H20C	0.097	0.481	0.203	2.1
H21A	0.441	0.713	0.753	2.3
H21B	0.438	0.645	0.848	2.3
H21C	0.612	0.658	0.779	2.3

The parameters of the hydrogen atoms were not refined.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos\gamma)*B(1,2) + ac(\cos\beta)*B(1,3) + bc(\cos\alpha)*B(2,3)]$

Table 8-10. Final Anisotropic Thermal Parameters (U's) for Barbaralane-$(COOMe)_4$ at **115 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0245(5)	0.0202(5)	0.0132(4)	0.0049(4)	-0.0009(4)	-0.0014(4)
O2	0.0232(5)	0.0174(5)	0.0202(5)	0.0016(4)	-0.0046(4)	0.0045(4)
O3	0.0186(5)	0.0300(6)	0.0221(5)	-0.0048(5)	-0.0025(4)	-0.0091(5)
O4	0.0232(5)	0.0272(6)	0.0249(5)	-0.0105(5)	-0.0008(5)	0.0024(5)
O5	0.0263(5)	0.0166(5)	0.0153(5)	0.0014(4)	-0.0065(4)	-0.0009(4)
O6	0.0260(5)	0.0135(5)	0.0220(5)	0.0037(4)	-0.0041(4)	0.0032(4)
O7	0.0281(5)	0.0078(4)	0.0217(5)	-0.0008(4)	-0.0058(4)	-0.0029(4)
O8	0.0241(5)	0.0158(5)	0.0193(5)	-0.0017(4)	-0.0067(4)	-0.0005(4)
C1	0.0157(6)	0.0091(6)	0.0157(6)	0.0010(5)	-0.0009(5)	0.0002(5)
C2	0.0174(6)	0.0089(6)	0.0148(6)	-0.0001(5)	-0.0012(5)	0.0007(5)
C3	0.0165(6)	0.0090(6)	0.0182(6)	-0.0000(5)	-0.0006(5)	0.0015(5)
C4	0.0159(6)	0.0080(6)	0.0180(6)	0.0005(5)	-0.0017(5)	0.0012(5)
C5	0.0172(6)	0.0095(6)	0.0151(6)	0.0001(5)	-0.0015(5)	-0.0002(5)
C6	0.0149(6)	0.0104(6)	0.0157(6)	0.0003(5)	-0.0009(5)	0.0017(5)
C7	0.0163(6)	0.0105(6)	0.0151(6)	-0.0001(5)	-0.0003(5)	0.0022(5)
C8	0.0176(6)	0.0083(6)	0.0147(6)	-0.0005(5)	-0.0012(5)	0.0003(5)
C9	0.0158(6)	0.0109(6)	0.0161(6)	0.0017(5)	0.0001(5)	-0.0011(5)
C14	0.0168(6)	0.0115(6)	0.0170(6)	-0.0024(5)	-0.0009(5)	0.0012(5)
C15	0.0191(6)	0.0107(6)	0.0210(7)	0.0003(5)	-0.0029(5)	0.0005(6)
C16	0.0155(6)	0.0138(6)	0.0146(6)	0.0004(5)	0.0000(5)	-0.0001(5)
C17	0.0178(6)	0.0098(6)	0.0161(6)	-0.0010(5)	0.0003(5)	-0.0002(5)
C18	0.0400(9)	0.0307(8)	0.0123(6)	0.0043(8)	-0.0005(6)	-0.0033(6)
C19	0.0203(7)	0.046(1)	0.0331(8)	-0.0081(7)	-0.0035(7)	-0.0171(8)
C20	0.0247(7)	0.0271(8)	0.0159(7)	0.0018(7)	-0.0060(6)	0.0017(6)
C21	0.0361(8)	0.0104(6)	0.0264(8)	-0.0025(6)	-0.0060(7)	-0.0069(6)

The form of the anisotropic displacement parameter is:
$\exp(-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)])$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-11. Interatomic Distances (Å) for Barbaralane-$(COOMe)_4$ at **115 K**

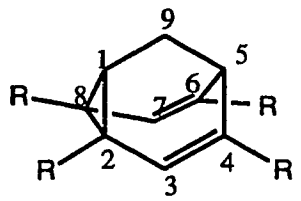
O1	C14	1.342(2)	C1	C9	1.505(2)
O1	C18	1.443(2)	C2	C3	1.473(2)
O2	C14	1.201(2)	C2	C8	1.608(2)
O3	C15	1.342(2)	C2	C14	1.505(2)
O3	C19	1.445(2)	C3	C4	1.342(2)
O4	C15	1.211(2)	C3	C7	3.046(2)
O5	C16	1.344(2)	C4	C5	1.519(2)
O5	C20	1.444(2)	C4	C6	2.400(2)
O6	C16	1.214(2)	C4	C15	1.487(2)
O7	C17	1.339(2)	C5	C6	1.512(2)
O7	C21	1.448(2)	C5	C9	1.545(2)
O8	C17	1.209(2)	C6	C7	1.340(2)
C1	C2	1.494(2)	C6	C16	1.486(2)
C1	C5	2.513(2)	C7	C8	1.466(2)
C1	C8	1.520(2)	C8	C17	1.497(2)

Table 8-12. Angles (°) for Barbaralane-$(COOMe)_4$ at **115 K**

C14	O1	C18	115.0(1)	C7	C6	C16	117.3(1)
C15	O3	C19	115.6(1)	C6	C7	C8	121.4(1)
C16	O5	C20	115.0(1)	C1	C8	C2	57.0(1)
C17	O7	C21	115.2(1)	C1	C8	C7	118.1(1)
C2	C1	C8	64.5(1)	C1	C8	C17	116.3(1)
C2	C1	C9	116.1(1)	C2	C8	C7	119.6(1)
C8	C1	C9	115.3(1)	C2	C8	C17	112.5(1)
C1	C2	C3	118.3(1)	C7	C8	C17	118.6(1)
C1	C2	C8	58.5(1)	C1	C9	C5	110.9(1)
C1	C2	C14	120.0(1)	O1	C14	O2	124.4(1)
C3	C2	C8	119.0(1)	O1	C14	C2	110.3(1)
C3	C2	C14	114.0(1)	O2	C14	C2	125.2(1)
C8	C2	C14	116.1(1)	O3	C15	O4	123.3(1)
C2	C3	C4	121.3(1)	O3	C15	C4	111.9(1)
C3	C4	C5	119.0(1)	O4	C15	C4	124.8(1)
C3	C4	C15	117.9(1)	O5	C16	O6	123.4(1)
C5	C4	C15	122.8(1)	O5	C16	C6	112.1(1)
C4	C5	C6	104.7(1)	O6	C16	C6	124.5(1)
C4	C5	C9	109.1(1)	O7	C17	O8	123.8(1)
C6	C5	C9	109.1(1)	O7	C17	C8	112.0(1)
C5	C6	C7	119.5(1)	O8	C17	C8	124.1(1)
C5	C6	C16	123.1(1)				

Table 8-13. Root-Mean-Square Amplitudes of Thermal Vibration for Barbaralane-$(COOMe)_4$ at **115 K**

Atom	Min.	Int'med.	Max.
O1	0.114	0.130	0.167
O2	0.112	0.147	0.164
O3	0.111	0.148	0.191
O4	0.120	0.156	0.191
O5	0.111	0.128	0.172
O6	0.104	0.148	0.170
O7	0.084	0.138	0.178
O8	0.117	0.129	0.170
C1	0.095	0.122	0.129
C2	0.094	0.120	0.134
C3	0.093	0.128	0.136
C4	0.089	0.123	0.138
C5	0.097	0.120	0.134
C6	0.100	0.121	0.129
C7	0.098	0.126	0.128
C8	0.091	0.119	0.134
C9	0.101	0.127	0.129
C14	0.102	0.127	0.137
C15	0.103	0.131	0.152
C16	0.117	0.121	0.125
C17	0.098	0.127	0.134
C18	0.108	0.172	0.205
C19	0.114	0.167	0.242
C20	0.112	0.164	0.169
C21	0.084	0.164	0.198



R = $COOCH_3$

2,4,6,8-tetracarbomethoxybarbaralane
[barbaralane-$(COOMe)_4$]

Table 8–14. X-ray Crystal Data for Barbaralane-$(COOMe)_4$ at **295 K**[a]

Formula	$C_{17}H_{18}O_8$
Formula weight	350.33
Melting point (°C)	99–100
Crystal size (mm)	0.10 x 0.36 x 0.50
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	7.854(1)
b (Å)	16.206(2)
c (Å)	12.982(2)
β (°)	90.64(1)
Cell volume (Å^3)	1652.3(7)
Z	4
d_{calc} (g cm^{-3})	1.408
μ(Cu $K\alpha$) (cm^{-1})	9.2
Maximum θ (°)	75
Unique reflections	3401
Observed reflections [$I > 3.0\sigma(I)$]	2735
Number of variables	226
R	0.046
R_w	0.059
$(\Delta\rho)_{max}$ (e Å^{-3})	0.21
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.24

[a] The temperature 295 K refers to room temperature.

Table 8-15. Final Atomic Parameters for Barbaralane-$(COOMe)_4$ at **295 K**

Atom	x	y	z	B(Å^2)
O1	0.2411(2)	0.42427(9)	0.87540(9)	3.80(3)
O2	0.4506(2)	0.33047(9)	0.8817(1)	4.21(3)
O3	-0.0046(2)	0.2492(1)	0.4500(1)	4.52(3)
O4	-0.1120(2)	0.2466(1)	0.6082(1)	5.00(3)
O5	0.1152(2)	0.40867(9)	0.3340(1)	3.91(3)
O6	0.1288(2)	0.53870(8)	0.3919(1)	4.26(3)
O7	0.4229(2)	0.59253(7)	0.7060(1)	3.84(3)
O8	0.5680(2)	0.49999(8)	0.8004(1)	3.97(3)
C1	0.4874(2)	0.3714(1)	0.6518(1)	2.55(3)
C2	0.3338(2)	0.37204(9)	0.7181(1)	2.50(3)
C3	0.1794(2)	0.3294(1)	0.6809(1)	2.64(3)
C4	0.1582(2)	0.31033(9)	0.5814(1)	2.59(3)
C5	0.2884(2)	0.33974(9)	0.5044(1)	2.52(3)
C6	0.2538(2)	0.43096(9)	0.4924(1)	2.38(3)
C7	0.3008(2)	0.48260(9)	0.5681(1)	2.48(3)
C8	0.3961(2)	0.45376(9)	0.6587(1)	2.41(3)
C9	0.4687(2)	0.3276(1)	0.5497(1)	2.65(3)
C14	0.3539(2)	0.3728(1)	0.8337(1)	2.90(3)
C15	-0.0002(2)	0.2662(1)	0.5503(1)	3.15(3)
C16	0.1600(2)	0.4664(1)	0.4027(1)	2.79(3)
C17	0.4731(2)	0.5162(1)	0.7297(1)	2.79(3)
C18	0.2500(4)	0.4321(2)	0.9862(2)	5.68(6)
C19	-0.1559(3)	0.2082(2)	0.4114(2)	6.38(6)
C20	0.0244(3)	0.4381(2)	0.2439(2)	4.80(5)
C21	0.4819(4)	0.6570(1)	0.7749(2)	5.04(5)
H1	0.600	0.367	0.688	3.0
H3	0.089	0.314	0.731	3.1
H5	0.281	0.309	0.438	3.0
H7	0.270	0.542	0.563	2.9
H9A	0.490	0.267	0.560	3.1
H9B	0.554	0.350	0.501	3.1
H18A	0.161	0.472	1.010	6.8
H18B	0.230	0.377	1.018	6.8
H18C	0.365	0.453	1.007	6.8
H19A	-0.145	0.199	0.335	7.6
H19B	-0.170	0.154	0.447	7.6
H19C	-0.258	0.244	0.424	7.6
H20A	-0.003	0.391	0.198	5.7
H20B	-0.083	0.466	0.265	5.7
H20C	0.097	0.479	0.206	5.7
H21A	0.437	0.712	0.750	6.0
H21B	0.440	0.646	0.846	6.0
H21C	0.609	0.658	0.776	6.0

The parameters of the hydrogen atoms were not refined.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos\gamma)*B(1,2) + ac(\cos\beta)*B(1,3) + bc(\cos\alpha)*B(2,3)]$

Table 8-16. Final Anisotropic Thermal Parameters (U's) for Barbaralane-$(COOMe)_4$ at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0575(7)	0.0600(8)	0.0270(5)	0.0118(6)	-0.0005(5)	-0.0035(6)
O2	0.0630(8)	0.0540(7)	0.0428(6)	0.0109(6)	-0.0119(6)	0.0133(6)
O3	0.0440(6)	0.0793(9)	0.0484(7)	-0.0151(7)	-0.0040(6)	-0.0179(7)
O4	0.0538(7)	0.0804(9)	0.0557(8)	-0.0298(7)	0.0027(7)	0.0038(8)
O5	0.0634(7)	0.0522(7)	0.0325(6)	0.0037(6)	-0.0145(5)	-0.0019(6)
O6	0.0691(8)	0.0421(6)	0.0502(7)	0.0120(6)	-0.0107(7)	0.0090(6)
O7	0.0693(8)	0.0277(5)	0.0488(7)	-0.0018(6)	-0.0148(6)	-0.0074(5)
O8	0.0618(7)	0.0441(6)	0.0446(6)	-0.0060(6)	-0.0189(6)	-0.0028(6)
C1	0.0326(7)	0.0298(7)	0.0345(7)	0.0025(6)	-0.0027(6)	0.0018(6)
C2	0.0376(7)	0.0276(7)	0.0297(7)	0.0002(6)	-0.0018(6)	0.0025(6)
C3	0.0376(7)	0.0278(7)	0.0349(7)	-0.0020(6)	0.0003(6)	0.0041(6)
C4	0.0357(7)	0.0254(6)	0.0371(7)	-0.0011(6)	-0.0020(6)	0.0019(6)
C5	0.0379(7)	0.0270(7)	0.0307(7)	0.0010(6)	-0.0007(6)	-0.0009(6)
C6	0.0325(7)	0.0294(7)	0.0284(6)	0.0009(6)	0.0003(6)	0.0027(6)
C7	0.0367(7)	0.0268(7)	0.0308(7)	0.0004(6)	0.0006(6)	0.0031(6)
C8	0.0356(7)	0.0268(6)	0.0291(6)	-0.0019(6)	-0.0016(6)	-0.0001(6)
C9	0.0354(7)	0.0301(7)	0.0353(7)	0.0043(6)	0.0020(6)	-0.0007(6)
C14	0.0429(8)	0.0348(7)	0.0326(7)	-0.0027(7)	-0.0042(7)	0.0049(6)
C15	0.0395(8)	0.0343(8)	0.0456(9)	-0.0033(7)	-0.0050(7)	-0.0006(7)
C16	0.0361(7)	0.0390(8)	0.0309(7)	0.0025(6)	0.0007(6)	0.0040(6)
C17	0.0401(8)	0.0319(7)	0.0340(7)	-0.0048(6)	0.0003(6)	-0.0007(6)
C18	0.097(2)	0.093(2)	0.0256(8)	0.010(1)	0.001(1)	-0.008(1)
C19	0.048(1)	0.122(2)	0.072(1)	-0.023(1)	-0.009(1)	-0.038(1)
C20	0.061(1)	0.085(2)	0.0364(9)	0.006(1)	-0.0164(8)	0.004(1)
C21	0.091(1)	0.0329(9)	0.067(1)	-0.007(1)	-0.019(1)	-0.0178(9)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-17. Interatomic Distances (Å) for Barbaralane-$(COOMe)_4$ at **295 K**

O1	C14	1.336(2)	C1	C9	1.509(2)
O1	C18	1.445(2)	C2	C3	1.473(2)
O2	C14	1.194(2)	C2	C8	1.611(2)
O3	C15	1.331(2)	C2	C14	1.507(2)
O3	C19	1.446(3)	C3	C4	1.337(2)
O4	C15	1.204(2)	C3	C7	3.042(2)
O5	C16	1.337(2)	C4	C5	1.515(2)
O5	C20	1.444(3)	C4	C6	2.36(2)
O6	C16	1.205(2)	C4	C15	1.487(2)
O7	C17	1.333(2)	C5	C6	1.511(2)
O7	C21	1.448(3)	C5	C9	1.539(2)
O8	C17	1.205(2)	C6	C7	1.339(2)
C1	C2	1.490(2)	C6	C16	1.487(2)
C1	C5	2.509(2)	C7	C8	1.464(2)
C1	C8	1.518(2)	C8	C17	1.492(2)

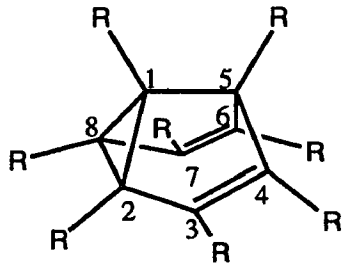
Table 8-18. Angles (°) for Barbaralane-$(COOMe)_4$ at **295 K**

C14	O1	C18	115.7(2)	C7	C6	C16	117.6(1)
C15	O3	C19	116.5(2)	C6	C7	C8	121.6(1)
C16	O5	C20	115.6(2)	C1	C8	C2	56.8(1)
C17	O7	C21	115.8(1)	C1	C8	C7	118.1(1)
C2	C1	C8	64.8(1)	C1	C8	C17	116.4(1)
C2	C1	C9	116.1(1)	C2	C8	C7	119.4(1)
C8	C1	C9	115.1(1)	C2	C8	C17	112.6(1)
C1	C2	C3	118.4(1)	C7	C8	C17	118.7(1)
C1	C2	C8	58.5(1)	C1	C9	C5	110.8(1)
C1	C2	C14	119.9(1)	O1	C14	O2	124.6(2)
C3	C2	C8	118.8(1)	O1	C14	C2	110.2(1)
C3	C2	C14	114.0(1)	O2	C14	C2	125.0(2)
C8	C2	C14	116.1(1)	O3	C15	O4	123.0(2)
C2	C3	C4	121.3(1)	O3	C15	C4	112.1(1)
C3	C4	C5	119.1(1)	O4	C15	C4	124.8(2)
C3	C4	C15	117.9(1)	O5	C16	O6	123.5(2)
C5	C4	C15	122.8(1)	O5	C16	C6	112.1(1)
C4	C5	C6	104.7(1)	O6	C16	C6	124.4(2)
C4	C5	C9	109.5(1)	O7	C17	O8	123.8(2)
C6	C5	C9	109.1(1)	O7	C17	C8	111.7(1)
C5	C6	C7	119.2(1)	O8	C17	C8	124.4(2)
C5	C6	C16	123.1(1)				

Table 8-19. Root-Mean-Square Amplitudes of Thermal Vibration for Barbaralane-$(COOMe)_4$ at **295 K**

Atom	Min.	Int'med.	Max.
O1	0.163	0.217	0.266
O2	0.163	0.250	0.266
O3	0.175	0.225	0.301
O4	0.184	0.237	0.316
O5	0.163	0.226	0.266
O6	0.172	0.236	0.276
O7	0.156	0.210	0.279
O8	0.173	0.214	0.274
C1	0.164	0.182	0.192
C2	0.161	0.176	0.195
C3	0.160	0.190	0.196
C4	0.158	0.184	0.198
C5	0.164	0.175	0.195
C6	0.162	0.177	0.181
C7	0.159	0.180	0.192
C8	0.162	0.169	0.191
C9	0.166	0.187	0.195
C14	0.169	0.188	0.215
C15	0.179	0.196	0.221
C16	0.171	0.187	0.204
C17	0.172	0.185	0.206
C18	0.157	0.293	0.325
C19	0.174	0.261	0.380
C20	0.165	0.263	0.293
C21	0.150	0.258	0.321

8.3 *OCTACARBOMETHOXYSEMIBULLVALENE*



R = $COOCH_3$

Octacarbomethoxysemibullvalene
[Sb-(COOMe)$_8$]

Table 8–20. X-ray Crystal Data for Sb-(COOMe)$_8$ at **115 K**

Formula	$C_{24}H_{24}O_{16}$
Formula weight	568.45
Melting point (°C)	162–163.2
Crystal size (mm)	0.10 x 0.29 x 0.35
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	10.442(3)
b (Å)	30.412(4)
c (Å)	9.407(1)
β (°)	116.53(1)
Cell volume (Å^3)	2672.5(17.8)
Z	4
d_{calc} (g cm^{-3})	1.413
μ(Cu $K\alpha$) (cm^{-1})	10.07
Maximum θ(°)	60.000
Unique reflections	3962
Observed reflections	3060
[$I > 3.0\sigma(I)$]	
Number of variables	361
R	0.035
R_w	0.043
$(\Delta\rho)_{max}$ (e Å^{-3})	0.24
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.27

Table 21. Final Atomic Parameters for Sb-$(COOMe)_8$ at 115 K

Atom	x	y	z	B(Å^2)
O1	0.6949(1)	0.38973(5)	0.8360(1)	1.47(3)
O2	0.9173(1)	0.36379(5)	0.9029(2)	1.67(3)
O3	0.9025(1)	0.48977(5)	0.5827(2)	1.42(3)
O4	0.9044(1)	0.46247(5)	0.8066(2)	1.59(3)
O5	0.6001(1)	0.50887(5)	0.3649(2)	1.58(3)
O6	0.6565(2)	0.46846(5)	0.2007(2)	1.85(3)
O7	0.3549(1)	0.44211(5)	0.2148(2)	1.52(3)
O8	0.3451(1)	0.36804(5)	0.1950(2)	1.64(3)
O9	0.6030(1)	0.30564(5)	0.6561(2)	1.58(3)
O10	0.4100(1)	0.35012(5)	0.5473(2)	1.51(3)
O11	0.4958(1)	0.28086(5)	0.3122(2)	1.60(3)
O12	0.5567(2)	0.31003(5)	0.1302(2)	1.99(3)
O13	0.9790(1)	0.35998(5)	0.3519(2)	1.28(3)
O14	0.8774(1)	0.29260(5)	0.3003(2)	1.80(3)
O15	1.0691(1)	0.33479(5)	0.6917(2)	1.29(3)
O16	1.1012(1)	0.40813(5)	0.7177(2)	1.48(3)
C1	0.7602(2)	0.38184(7)	0.6329(2)	0.95(4)
C2	0.7859(2)	0.42314(6)	0.5616(2)	0.99(4)
C3	0.6493(2)	0.43399(6)	0.4221(2)	0.96(4)
C4	0.5494(2)	0.40313(7)	0.3958(2)	0.99(4)
C5	0.6168(2)	0.36314(6)	0.5015(2)	0.95(4)
C6	0.6678(2)	0.33585(6)	0.3988(2)	1.02(4)
C7	0.8020(2)	0.34677(6)	0.4302(2)	0.87(4)
C8	0.8660(2)	0.37793(6)	0.5654(2)	0.97(4)
C11	0.8039(2)	0.37716(7)	0.8073(2)	1.17(4)
C12	0.7211(2)	0.38563(9)	1.0010(2)	2.44(5)
C21	0.8733(2)	0.46003(7)	0.6677(2)	1.12(4)
C22	0.9751(2)	0.52913(7)	0.6686(3)	2.18(5)
C31	0.6350(2)	0.47232(7)	0.3155(2)	1.24(4)
C32	0.5898(3)	0.54761(7)	0.2681(3)	2.66(6)
C41	0.4062(2)	0.40163(7)	0.2584(2)	1.09(4)
C42	0.2220(2)	0.44582(8)	0.0680(2)	1.92(5)
C51	0.5276(2)	0.33935(7)	0.5674(2)	1.09(4)
C52	0.5326(2)	0.28000(8)	0.7315(3)	2.73(5)
C61	0.5686(2)	0.30791(7)	0.2630(2)	1.28(4)
C62	0.3830(2)	0.25538(8)	0.1879(3)	2.31(5)
C71	0.8872(2)	0.32926(7)	0.3517(2)	1.17(4)
C72	1.0809(2)	0.34578(8)	0.2939(2)	1.76(5)
C81	1.0252(2)	0.37656(7)	0.6684(2)	1.09(4)
C82	1.2222(2)	0.32858(8)	0.7888(3)	1.95(5)
H12A	0.635	0.396	1.012	2.7
H12B	0.741	0.354	1.035	2.7
H12C	0.805	0.404	1.070	2.7
H22A	0.992	0.549	0.595	2.4
H22B	0.914	0.544	0.711	2.4
H22C	1.069	0.521	0.759	2.4
H32A	0.563	0.574	0.313	2.9
H32B	0.684	0.553	0.268	2.9
H32C	0.515	0.543	0.157	2.9
H42A	0.189	0.477	0.052	2.1
H42B	0.239	0.436	-0.024	2.1
H42C	0.147	0.427	0.075	2.1
H52A	0.597	0.256	0.795	3.0
H52B	0.510	0.299	0.803	3.0
H52C	0.442	0.267	0.648	3.0
H62A	0.335	0.236	0.236	2.5
H62B	0.311	0.276	0.109	2.5

Table 21 (cont.). Final Atomic Parameters for $Sb-(COOMe)_8$ at **115 K**

Atom	x	y	z	B(Å^2)
H62C	0.425	0.237	0.133	2.5
H72A	1.144	0.371	0.299	1.9
H72B	1.141	0.321	0.362	1.9
H72C	1.028	0.335	0.182	1.9
H82A	1.245	0.296	0.800	2.1
H82B	1.276	0.343	0.737	2.1
H82C	1.251	0.342	0.896	2.1
H42BA	0.170	0.473	0.072	2.1
H42BB	0.244	0.447	-0.025	2.1
H42BC	0.160	0.420	0.057	2.1
H62BA	0.372	0.227	0.232	2.5
H62BB	0.291	0.272	0.147	2.5
H62BC	0.408	0.250	0.099	2.5

The parameters of the hydrogen atoms were not refined.

Standard deviations are in parentheses.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
$(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos\gamma)*B(1,2) + ac(\cos\beta)*B(1,3) + bc(\cos\alpha)*B(2,3)]$

Table 22. Final Anisotropic Thermal Parameters (U's) for Sb-$(COOMe)_8$ at 115 K

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0211(6)	0.0259(8)	0.0135(5)	0.0062(6)	0.0119(4)	0.0026(6)
O2	0.0182(6)	0.0288(8)	0.0156(6)	0.0053(6)	0.0067(4)	0.0037(6)
O3	0.0228(6)	0.0125(7)	0.0200(6)	-0.0069(5)	0.0108(4)	-0.0033(6)
O4	0.0241(6)	0.0202(7)	0.0158(6)	-0.0031(6)	0.0086(4)	-0.0049(6)
O5	0.0247(6)	0.0107(7)	0.0287(6)	0.0031(6)	0.0155(4)	0.0014(6)
O6	0.0328(7)	0.0237(8)	0.0181(6)	0.0015(6)	0.0152(4)	0.0036(6)
O7	0.0183(6)	0.0164(7)	0.0176(6)	0.0043(6)	0.0030(5)	-0.0003(6)
O8	0.0183(6)	0.0173(7)	0.0223(6)	-0.0022(6)	0.0050(5)	-0.0015(6)
O9	0.0217(6)	0.0161(7)	0.0285(6)	0.0022(6)	0.0166(4)	0.0093(6)
O10	0.0160(6)	0.0218(7)	0.0223(6)	0.0010(6)	0.0111(4)	0.0021(6)
O11	0.0200(6)	0.0160(7)	0.0248(6)	-0.0075(6)	0.0100(5)	-0.0037(6)
O12	0.0268(6)	0.0315(8)	0.0194(6)	-0.0093(6)	0.0124(4)	-0.0094(6)
O13	0.0168(5)	0.0189(7)	0.0184(5)	-0.0019(5)	0.0127(4)	-0.0007(6)
O14	0.0274(6)	0.0164(7)	0.0316(6)	-0.0013(6)	0.0193(4)	-0.0077(6)
O15	0.0141(6)	0.0159(7)	0.0179(6)	0.0037(5)	0.0060(4)	0.0024(6)
O16	0.0160(6)	0.0181(7)	0.0207(6)	-0.0036(6)	0.0070(4)	-0.0038(6)
C1	0.0142(8)	0.0123(9)	0.0129(7)	0.0001(7)	0.0089(5)	-0.0001(7)
C2	0.0140(8)	0.0111(9)	0.0153(8)	-0.0007(7)	0.0090(5)	-0.0010(8)
C3	0.0157(8)	0.0115(9)	0.0125(7)	0.0020(7)	0.0091(5)	-0.0006(7)
C4	0.0168(8)	0.0121(9)	0.0126(7)	0.0007(8)	0.0100(5)	-0.0019(7)
C5	0.0128(8)	0.0107(9)	0.0140(8)	-0.0002(7)	0.0074(6)	0.0014(7)
C6	0.0176(8)	0.0090(9)	0.0134(8)	0.0013(7)	0.0081(6)	0.0015(7)
C7	0.0159(8)	0.0074(9)	0.0107(7)	0.0005(7)	0.0067(5)	0.0013(7)
C8	0.0141(8)	0.0109(9)	0.0142(8)	0.0001(7)	0.0085(5)	0.0006(7)
C11	0.0175(8)	0.014(1)	0.0149(8)	0.0006(8)	0.0084(6)	0.0007(8)
C12	0.040(1)	0.047(1)	0.0127(8)	0.014(1)	0.0175(6)	0.0068(9)
C21	0.0128(8)	0.013(1)	0.0167(8)	0.0019(7)	0.0070(6)	-0.0014(8)
C22	0.038(1)	0.016(1)	0.036(1)	-0.0152(9)	0.0226(7)	-0.0107(9)
C31	0.0135(8)	0.015(1)	0.0166(8)	-0.0015(8)	0.0047(6)	-0.0003(8)
C32	0.041(1)	0.012(1)	0.054(1)	0.0061(9)	0.0263(8)	0.013(1)
C41	0.0158(8)	0.016(1)	0.0146(7)	0.0034(8)	0.0108(5)	0.0012(8)
C42	0.021(1)	0.029(1)	0.0146(9)	0.0074(9)	0.0007(7)	-0.0002(9)
C51	0.0156(8)	0.0115(9)	0.0132(8)	-0.0007(8)	0.0054(6)	-0.0009(8)
C52	0.037(1)	0.030(1)	0.051(1)	0.0050(9)	0.0321(7)	0.0242(9)
C61	0.0144(8)	0.013(1)	0.0220(8)	0.0006(8)	0.0086(6)	-0.0011(8)
C62	0.023(1)	0.022(1)	0.038(1)	-0.0116(9)	0.0089(8)	-0.008(1)
C71	0.0140(8)	0.016(1)	0.0143(8)	0.0005(8)	0.0059(6)	0.0013(8)
C72	0.0179(8)	0.031(1)	0.0263(8)	0.0037(9)	0.0173(6)	0.0026(9)
C81	0.0174(8)	0.017(1)	0.0119(7)	0.0013(8)	0.0111(5)	0.0012(8)
C82	0.0178(9)	0.027(1)	0.025(1)	0.0075(9)	0.0053(7)	0.002(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 23. Interatomic Distances (E) for Sb-$(COOMe)_8$ at 115 K

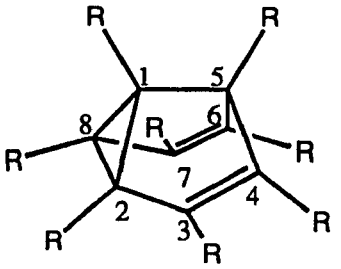
O1	C11	1.337(3)	O15	C82	1.456(2)
O1	C12	1.457(3)	O16	C81	1.199(2)
O2	C11	1.194(2)	C1	C2	1.503(3)
O3	C21	1.329(3)	C1	C5	1.562(2)
O3	C22	1.454(2)	C1	C8	1.504(3)
O4	C21	1.200(2)	C1	C11	1.500(3)
O5	C31	1.318(3)	C2	C3	1.481(2)
O5	C32	1.463(3)	C2	C8	1.602(3)
O6	C31	1.203(3)	C2	C21	1.508(3)
O7	C41	1.332(2)	C3	C4	1.341(3)
O7	C42	1.460(2)	C3	C7	3.079(3)
O8	C41	1.211(2)	C3	C31	1.501(3)
O9	C51	1.334(2)	C4	C5	1.529(3)
O9	C52	1.455(3)	C4	C6	2.385(3)
O10	C51	1.201(3)	C4	C41	1.478(2)
O11	C61	1.335(3)	C5	C6	1.539(3)
O11	C62	1.458(2)	C5	C51	1.513(3)
O12	C61	1.201(3)	C6	C7	1.338(3)
O13	C71	1.338(3)	C6	C61	1.498(2)
O13	C72	1.460(3)	C7	C8	1.484(3)
O14	C71	1.201(3)	C7	C71	1.486(3)
O15	C81	1.335(2)	C8	C81	1.506(2)

Table 24. Angles (°) for Sb-$(COOMe)_8$ at 115 K

C11	O1	C12	114.8(1)	C5	C6	C61	122.7(2)
C21	O3	C22	115.4(2)	C7	C6	C61	125.9(2)
C31	O5	C32	114.5(2)	C6	C7	C8	111.9(2)
C41	O7	C42	116.4(1)	C6	C7	C71	127.0(2)
C51	O9	C52	115.5(2)	C8	C7	C71	121.0(2)
C61	O11	C62	115.5(2)	C1	C8	C2	57.8(1)
C71	O13	C72	115.7(2)	C1	C8	C7	106.1(2)
C81	O15	C82	115.2(1)	C1	C8	C81	122.6(2)
C2	C1	C5	104.5(1)	C2	C8	C7	119.9(1)
C2	C1	C8	64.4(1)	C2	C8	C81	117.0(1)
C2	C1	C11	122.6(2)	C7	C8	C81	118.6(2)
C5	C1	C8	105.2(2)	O1	C11	O2	126.3(2)
C5	C1	C11	123.1(2)	O1	C11	C1	108.9(1)
C8	C1	C11	122.2(1)	O2	C11	C1	124.8(2)
C1	C2	C3	106.8(2)	O3	C21	O4	126.1(2)
C1	C2	C8	57.9(1)	O3	C21	C2	110.0(2)
C1	C2	C21	120.2(2)	O4	C21	C2	123.8(2)
C3	C2	C8	119.8(2)	O5	C31	O6	126.2(2)
C3	C2	C21	118.7(2)	O5	C31	C3	112.3(2)
C8	C2	C21	117.9(1)	O6	C31	C3	121.4(2)
C2	C3	C4	111.7(2)	O7	C41	O8	125.3(1)
C2	C3	C31	122.3(2)	O7	C41	C4	110.6(2)
C4	C3	C31	125.7(1)	O8	C41	C4	124.2(2)
C3	C4	C5	110.0(1)	O9	C51	O10	125.8(2)
C3	C4	C41	125.6(2)	O9	C51	C5	108.9(2)
C5	C4	C6	39.1(1)	O10	C51	C5	125.3(2)
C5	C4	C41	122.4(2)	O11	C61	O12	125.7(2)
C1	C5	C4	103.0(1)	O11	C61	C6	109.8(2)
C1	C5	C6	102.4(2)	O12	C61	C6	124.5(2)
C1	C5	C51	113.5(2)	O13	C71	O14	125.5(2)
C4	C5	C6	102.0(2)	O13	C71	C7	109.7(2)
C4	C5	C51	117.3(2)	O14	C71	C7	124.8(2)
C6	C5	C51	116.7(2)	O15	C81	O16	125.4(2)
C4	C6	C5	38.8(1)	O15	C81	C8	109.4(2)
C5	C6	C7	110.5(2)	O16	C81	C8	125.2(2)

Table 25. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for $Sb-(COOMe)_8$ at **115 K**

Atom	Min.	Int'med.	Max.
O1	0.091	0.132	0.174
O2	0.119	0.135	0.176
O3	0.095	0.136	0.162
O4	0.112	0.149	0.161
O5	0.100	0.142	0.173
O6	0.113	0.156	0.182
O7	0.112	0.129	0.169
O8	0.122	0.139	0.168
O9	0.094	0.132	0.184
O10	0.114	0.142	0.156
O11	0.101	0.155	0.163
O12	0.119	0.146	0.200
O13	0.093	0.135	0.147
O14	0.104	0.146	0.190
O15	0.105	0.136	0.140
O16	0.114	0.140	0.153
C1	0.091	0.111	0.125
C2	0.101	0.105	0.129
C3	0.085	0.111	0.130
C4	0.082	0.116	0.133
C5	0.096	0.109	0.122
C6	0.092	0.111	0.133
C7	0.083	0.102	0.126
C8	0.100	0.105	0.125
C11	0.114	0.118	0.133
C12	0.079	0.169	0.241
C21	0.100	0.121	0.133
C22	0.089	0.162	0.220
C31	0.111	0.124	0.139
C32	0.090	0.188	0.240
C41	0.086	0.119	0.141
C42	0.108	0.151	0.196
C51	0.105	0.116	0.130
C52	0.079	0.174	0.259
C61	0.109	0.119	0.150
C62	0.102	0.184	0.208
C71	0.116	0.121	0.128
C72	0.086	0.162	0.183
C81	0.076	0.128	0.140
C82	0.116	0.167	0.182



R = $COOCH_3$

Octacarbomethoxysemibullvalene
[Sb-(COOMe)$_8$]

Table 8–26. X-ray Crystal Data for Sb-(COOMe)$_8$ at **153 K**

Formula	$C_{24}H_{24}O_{16}$
Formula weight	568.45
Melting point (°C)	162–163.2
Crystal size (mm)	0.10 x 0.29 x 0.35
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	10.450(3)
b (Å)	30.469(3)
c (Å)	9.413(1)
β (°)	116.38(1)
Cell volume (Å^3)	2685.0(18.2)
Z	4
d_{calc} (g cm^{-3})	1.406
μ(Cu $K\alpha$) (cm^{-1})	10.02
Maximum θ (°)	60
Unique reflections	3987
Observed reflections [$I > 3.0\sigma(I)$]	3002
Number of variables	361
R	0.036
R_w	0.045
$(\Delta\rho)_{max}$ (e Å^{-3})	0.20
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.23

Table 27. Final Atomic Parameters for $Sb-(COOMe)_8$ at **153 K**

Atom	x	y	z	B(Å^2)
O1	0.6950(2)	0.38994(5)	0.8374(2)	1.98(3)
O2	0.9164(2)	0.36369(6)	0.9047(2)	2.28(4)
O3	0.9041(2)	0.48930(5)	0.5859(2)	1.94(3)
O4	0.9038(2)	0.46229(5)	0.8085(2)	2.21(4)
O5	0.6027(2)	0.50852(5)	0.3708(2)	2.23(4)
O6	0.6572(2)	0.46868(6)	0.2043(2)	2.55(4)
O7	0.3578(2)	0.44181(5)	0.2175(2)	2.04(4)
O8	0.3479(2)	0.36803(5)	0.1981(2)	2.26(4)
O9	0.6045(2)	0.30564(5)	0.6587(2)	2.10(3)
O10	0.4120(2)	0.34975(5)	0.5494(2)	2.00(3)
O11	0.4980(2)	0.28093(5)	0.3150(2)	2.08(4)
O12	0.5596(2)	0.30985(6)	0.1341(2)	2.74(4)
O13	0.9802(1)	0.36010(5)	0.3540(2)	1.66(3)
O14	0.8794(2)	0.29295(5)	0.3031(2)	2.50(4)
O15	1.0700(1)	0.33492(5)	0.6937(2)	1.75(3)
O16	1.1012(2)	0.40803(5)	0.7202(2)	2.03(4)
C1	0.7613(2)	0.38158(7)	0.6355(2)	1.23(4)
C2	0.7871(2)	0.42284(7)	0.5643(2)	1.37(4)
C3	0.6503(2)	0.43374(7)	0.4249(2)	1.29(4)
C4	0.5510(2)	0.40289(7)	0.3986(2)	1.26(4)
C5	0.6188(2)	0.36298(7)	0.5043(2)	1.27(4)
C6	0.6700(2)	0.33572(7)	0.4017(2)	1.31(4)
C7	0.8037(2)	0.34680(7)	0.4328(2)	1.21(4)
C8	0.8674(2)	0.37777(7)	0.5680(2)	1.27(4)
C11	0.8037(2)	0.37705(7)	0.8089(2)	1.50(5)
C12	0.7204(3)	0.3866(1)	1.0024(3)	3.29(6)
C21	0.8738(2)	0.45971(7)	0.6701(2)	1.53(5)
C22	0.9771(3)	0.52846(8)	0.6715(3)	3.01(6)
C31	0.6368(2)	0.47226(7)	0.3195(3)	1.64(5)
C32	0.5923(3)	0.54732(8)	0.2753(4)	3.83(7)
C41	0.4086(2)	0.40135(7)	0.2615(2)	1.51(5)
C42	0.2261(3)	0.44556(9)	0.0706(3)	2.63(6)
C51	0.5292(2)	0.33906(7)	0.5700(2)	1.42(4)
C52	0.5344(3)	0.27993(9)	0.7344(3)	3.72(6)
C61	0.5709(2)	0.30785(7)	0.2664(3)	1.71(5)
C62	0.3859(3)	0.25540(9)	0.1923(3)	3.18(7)
C71	0.8887(2)	0.32938(7)	0.3540(2)	1.55(5)
C72	1.0818(2)	0.34617(9)	0.2956(3)	2.40(5)
C81	1.0258(2)	0.37665(7)	0.6709(2)	1.45(4)
C82	1.2226(3)	0.32879(9)	0.7901(3)	2.72(6)
H12A	0.634	0.397	1.012	3.6
H12B	0.741	0.355	1.038	3.6
H12C	0.804	0.405	1.070	3.6
H22A	0.995	0.549	0.598	3.3
H22B	0.916	0.544	0.714	3.3
H22C	1.070	0.520	0.762	3.3
H32A	0.566	0.573	0.322	4.1
H32B	0.686	0.553	0.274	4.1
H32C	0.517	0.542	0.164	4.1
H42A	0.189	0.477	0.052	2.8
H42B	0.239	0.436	-0.024	2.8
H42C	0.147	0.427	0.075	2.8
H52A	0.599	0.256	0.798	4.0
H52B	0.512	0.299	0.806	4.0
H52C	0.444	0.267	0.651	4.0
H62A	0.335	0.236	0.236	3.5
H62B	0.311	0.276	0.109	3.5

Table 27 (cont.). Final Atomic Parameters for Sb-$(COOMe)_8$ at **153 K**

Atom	x	y	z	B(Å^2)
H62C	0.425	0.237	0.132	3.5
H72A	1.145	0.371	0.301	2.6
H72B	1.142	0.322	0.363	2.6
H72C	1.029	0.336	0.183	2.6
H82A	1.245	0.297	0.800	2.9
H82B	1.276	0.344	0.738	2.9
H82C	1.251	0.342	0.898	2.9
H42BA	0.170	0.473	0.072	3.6
H42BB	0.244	0.447	-0.025	3.6
H42BC	0.160	0.420	0.057	3.6
H62BA	0.372	0.227	0.232	3.5
H62BB	0.291	0.272	0.147	3.5
H62BC	0.408	0.250	0.099	3.5

The parameters of the hydrogen atoms were not refined.

Standard deviations are in parentheses.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos\gamma)*B(1,2) + ac(\cos\beta)*B(1,3) + bc(\cos\alpha)*B(2,3)]$

Table 28. Final Anisotropic Thermal Parameters (U's) for Sb-$(COOMe)_8$ at **153 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0267(7)	0.0360(9)	0.0179(6)	0.0080(7)	0.0147(4)	0.0042(6)
O2	0.0243(7)	0.042(1)	0.0192(6)	0.0086(7)	0.0082(5)	0.0062(7)
O3	0.0284(7)	0.0182(7)	0.0292(7)	-0.0084(6)	0.0147(5)	-0.0053(6)
O4	0.0344(8)	0.0283(8)	0.0217(6)	-0.0057(7)	0.0127(5)	-0.0076(7)
O5	0.0341(7)	0.0149(8)	0.0412(7)	0.0042(6)	0.0218(5)	0.0025(7)
O6	0.0457(8)	0.0325(9)	0.0262(6)	0.0034(7)	0.0229(5)	0.0065(7)
O7	0.0228(7)	0.0238(8)	0.0229(7)	0.0057(7)	0.0028(5)	0.0000(7)
O8	0.0235(7)	0.0238(8)	0.0309(8)	-0.0034(7)	0.0052(6)	-0.0029(7)
O9	0.0292(6)	0.0213(8)	0.0386(7)	0.0045(6)	0.0235(5)	0.0127(6)
O10	0.0185(6)	0.0308(8)	0.0306(7)	0.0008(6)	0.0143(5)	0.0034(7)
O11	0.0267(7)	0.0197(8)	0.0344(7)	-0.0092(6)	0.0150(5)	-0.0051(7)
O12	0.0364(8)	0.045(1)	0.0255(7)	-0.0156(8)	0.0165(5)	-0.0134(7)
O13	0.0201(6)	0.0248(8)	0.0244(6)	-0.0021(6)	0.0156(4)	-0.0004(6)
O14	0.0370(7)	0.0236(8)	0.0454(7)	-0.0030(7)	0.0283(5)	-0.0121(7)
O15	0.0190(6)	0.0218(8)	0.0251(7)	0.0055(6)	0.0093(5)	0.0033(6)
O16	0.0205(7)	0.0259(8)	0.0281(7)	-0.0057(6)	0.0084(5)	-0.0046(7)
C1	0.0176(8)	0.016(1)	0.0158(8)	0.0005(8)	0.0099(6)	-0.0005(8)
C2	0.0191(9)	0.015(1)	0.0218(8)	-0.0013(8)	0.0123(6)	-0.0004(8)
C3	0.0199(9)	0.015(1)	0.0151(8)	0.0022(8)	0.0092(6)	-0.0007(8)
C4	0.0197(8)	0.015(1)	0.0173(8)	0.0016(8)	0.0115(6)	-0.0011(8)
C5	0.0156(8)	0.016(1)	0.0183(8)	-0.0004(8)	0.0090(6)	0.0009(8)
C6	0.0208(9)	0.013(1)	0.0188(8)	0.0003(8)	0.0110(6)	0.0008(8)
C7	0.0191(9)	0.012(1)	0.0150(8)	0.0007(8)	0.0079(6)	0.0019(8)
C8	0.0160(8)	0.016(1)	0.0192(8)	0.0001(8)	0.0106(6)	0.0005(8)
C11	0.0186(9)	0.019(1)	0.0196(9)	-0.0003(9)	0.0090(6)	-0.0000(9)
C12	0.048(1)	0.065(2)	0.0191(9)	0.018(1)	0.0214(8)	0.010(1)
C21	0.0196(9)	0.019(1)	0.0214(9)	0.0020(8)	0.0108(6)	-0.0000(9)
C22	0.050(1)	0.023(1)	0.052(1)	-0.020(1)	0.0321(8)	-0.017(1)
C31	0.0173(9)	0.019(1)	0.0252(9)	0.0003(9)	0.0085(7)	0.0026(9)
C32	0.057(1)	0.018(1)	0.078(2)	0.009(1)	0.037(1)	0.021(1)
C41	0.0195(9)	0.023(1)	0.0186(8)	0.0032(9)	0.0113(6)	0.0006(9)
C42	0.029(1)	0.039(1)	0.020(1)	0.011(1)	-0.0002(9)	0.001(1)
C51	0.0186(9)	0.016(1)	0.0192(8)	-0.0010(8)	0.0084(6)	0.0002(9)
C52	0.048(1)	0.041(1)	0.073(1)	0.008(1)	0.0447(8)	0.033(1)
C61	0.0192(9)	0.018(1)	0.028(1)	0.0000(9)	0.0113(7)	-0.0026(9)
C62	0.031(1)	0.031(1)	0.055(1)	-0.016(1)	0.015(1)	-0.014(1)
C71	0.0185(9)	0.021(1)	0.0194(9)	0.0006(9)	0.0087(7)	0.0001(9)
C72	0.0227(9)	0.044(1)	0.035(1)	0.004(1)	0.0217(7)	0.002(1)
C81	0.0221(9)	0.021(1)	0.0165(8)	0.0003(9)	0.0128(6)	0.0010(8)
C82	0.021(1)	0.040(1)	0.035(1)	0.012(1)	0.0067(8)	0.007(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 29. Interatomic Distances (Å) for Sb-$(COOMe)_8$ at **153 K**

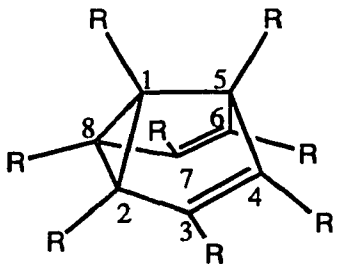
O1	C11	1.337(3)	O15	C82	1.455(3)
O1	C12	1.458(3)	O16	C81	1.194(3)
O2	C11	1.192(2)	C1	C2	1.504(3)
O3	C21	1.329(3)	C1	C5	1.559(2)
O3	C22	1.452(3)	C1	C8	1.507(4)
O4	C21	1.199(3)	C1	C11	1.496(3)
O5	C31	1.317(3)	C2	C3	1.486(2)
O5	C32	1.460(3)	C2	C8	1.602(3)
O6	C31	1.200(3)	C2	C21	1.508(3)
O7	C41	1.333(3)	C3	C4	1.340(3)
O7	C42	1.459(2)	C3	C7	3.080(3)
O8	C41	1.205(3)	C3	C31	1.502(3)
O9	C51	1.330(2)	C4	C5	1.531(3)
O9	C52	1.456(4)	C4	C6	2.388(3)
O10	C51	1.196(3)	C4	C41	1.475(2)
O11	C61	1.331(3)	C5	C6	1.539(3)
O11	C62	1.452(3)	C5	C51	1.518(4)
O12	C61	1.199(3)	C6	C7	1.337(3)
O13	C71	1.338(3)	C6	C61	1.498(3)
O13	C72	1.459(3)	C7	C8	1.483(3)
O14	C71	1.195(3)	C7	C71	1.486(4)
O15	C81	1.337(3)	C8	C81	1.501(3)

Table 30. Angles (°) for Sb-$(COOMe)_8$ at **153 K**

C11	O1	C12	115.1(2)	C5	C6	C61	122.5(2)
C21	O3	C22	115.6(2)	C7	C6	C61	126.2(2)
C31	O5	C32	114.3(2)	C6	C7	C8	112.1(2)
C41	O7	C42	116.4(2)	C6	C7	C71	126.8(2)
C51	O9	C52	115.7(2)	C8	C7	C71	121.0(2)
C61	O11	C62	116.1(2)	C1	C8	C2	57.8(1)
C71	O13	C72	115.9(2)	C1	C8	C7	106.1(2)
C81	O15	C82	115.3(2)	C1	C8	C81	122.4(2)
C2	C1	C5	104.4(1)	C2	C8	C7	119.7(1)
C2	C1	C8	64.3(2)	C2	C8	C81	116.8(2)
C2	C1	C11	122.6(2)	C7	C8	C81	119.0(2)
C5	C1	C8	105.1(2)	O1	C11	O2	126.2(2)
C5	C1	C11	123.1(2)	O1	C11	C1	109.0(2)
C8	C1	C11	122.4(2)	O2	C11	C1	124.8(2)
C1	C2	C3	106.7(2)	O3	C21	O4	125.9(2)
C1	C2	C8	58.0(1)	O3	C21	C2	110.1(2)
C1	C2	C21	120.1(2)	O4	C21	C2	123.9(2)
C3	C2	C8	120.0(2)	O5	C31	O6	126.4(2)
C3	C2	C21	118.5(2)	O5	C31	C3	112.0(2)
C8	C2	C21	118.0(2)	O6	C31	C3	121.6(2)
C2	C3	C4	111.7(2)	O7	C41	O8	125.2(2)
C2	C3	C31	121.9(2)	O7	C41	C4	110.5(2)
C4	C3	C31	126.0(2)	O8	C41	C4	124.3(2)
C3	C4	C5	109.9(2)	O9	C51	O10	126.0(2)
C3	C4	C41	125.6(2)	O9	C51	C5	108.8(2)
C5	C4	C6	39.1(1)	O10	C51	C5	125.1(2)
C5	C4	C41	122.6(2)	O11	C61	O12	125.5(2)
C1	C5	C4	103.3(2)	O11	C61	C6	110.0(2)
C1	C5	C6	102.5(2)	O12	C61	C6	124.5(2)
C1	C5	C51	113.4(2)	O13	C71	O14	125.5(2)
C4	C5	C6	102.1(2)	O13	C71	C7	109.6(2)
C4	C5	C51	117.1(2)	O14	C71	C7	124.8(2)
C6	C5	C51	116.5(2)	O15	C81	O16	125.3(2)
C4	C6	C5	38.8(1)	O15	C81	C8	109.2(2)
C5	C6	C7	110.3(2)	O16	C81	C8	125.5(2)

Table 31. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for $Sb-(COOMe)_8$ at **153 K**

Atom	Min.	Int'med.	Max.
O1	0.109	0.151	0.202
O2	0.131	0.156	0.213
O3	0.116	0.161	0.185
O4	0.129	0.172	0.194
O5	0.118	0.167	0.207
O6	0.129	0.182	0.217
O7	0.126	0.153	0.195
O8	0.137	0.163	0.201
O9	0.108	0.146	0.216
O10	0.121	0.166	0.185
O11	0.115	0.172	0.191
O12	0.137	0.165	0.241
O13	0.107	0.156	0.165
O14	0.120	0.167	0.230
O15	0.121	0.157	0.165
O16	0.129	0.169	0.179
C1	0.108	0.128	0.136
C2	0.116	0.125	0.152
C3	0.110	0.126	0.144
C4	0.104	0.127	0.145
C5	0.115	0.128	0.137
C6	0.112	0.126	0.147
C7	0.105	0.125	0.139
C8	0.111	0.127	0.142
C11	0.134	0.140	0.140
C21	0.126	0.142	0.149
C22	0.109	0.186	0.261
C31	0.131	0.134	0.165
C32	0.106	0.223	0.290
C41	0.115	0.140	0.157
C42	0.121	0.179	0.231
C51	0.126	0.138	0.139
C52	0.098	0.193	0.308
C61	0.130	0.137	0.171
C62	0.119	0.210	0.250
C71	0.134	0.139	0.146
C72	0.103	0.189	0.212
C81	0.104	0.146	0.152
C82	0.122	0.205	0.215



R = $COOCH_3$

Octacarbomethoxysemibullvalene
[Sb-(COOMe)$_8$]

Table 8–32. X-ray Crystal Data for Sb-(COOMe)$_8$ at **181 K**

Formula	$C_{24}H_{24}O_{16}$
Formula weight	568.45
Melting point (°C)	162–163.2
Crystal size (mm)	0.10 x 0.29 x 0.35
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	10.455(2)
b (Å)	30.518(3)
c (Å)	9.416(1)
β (°)	116.26(1)
Cell volume (Å^3)	2694.4(12.2)
Z	4
d_{calc} (g cm^{-3})	1.401
μ(Cu $K\alpha$) (cm^{-1})	9.98
Maximum θ (°)	60
Unique reflections	3999
Observed reflections	2956
[$I > 3.0\sigma(I)$]	
Number of variables	361
R	0.037
R_w	0.045
$(\Delta\rho)_{max}$ (e Å^{-3})	0.21
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.28

Table 33. Final Atomic Parameters for Sb-$(COOMe)_8$ at **181 K**

Atom	x	y	z	B(Å^2)
O1	0.6951(2)	0.39003(5)	0.8383(2)	2.31(4)
O2	0.9160(2)	0.36375(6)	0.9058(2)	2.70(4)
O3	0.9054(2)	0.48897(5)	0.5883(2)	2.24(4)
O4	0.9031(2)	0.46219(6)	0.8097(2)	2.61(4)
O5	0.6041(2)	0.50828(5)	0.3746(2)	2.64(4)
O6	0.6573(2)	0.46889(6)	0.2066(2)	2.98(4)
O7	0.3599(2)	0.44144(5)	0.2194(2)	2.32(4)
O8	0.3496(2)	0.36799(5)	0.2002(2)	2.68(4)
O9	0.6056(2)	0.30566(5)	0.6601(2)	2.42(3)
O10	0.4130(2)	0.34950(5)	0.5506(2)	2.35(4)
O11	0.4999(2)	0.28097(5)	0.3176(2)	2.42(4)
O12	0.5616(2)	0.30974(6)	0.1368(2)	3.29(4)
O13	0.9807(1)	0.36029(5)	0.3553(2)	1.89(3)
O14	0.8807(2)	0.29314(5)	0.3049(2)	2.98(4)
O15	1.0704(2)	0.33493(5)	0.6951(2)	2.10(3)
O16	1.1018(2)	0.40803(5)	0.7221(2)	2.38(4)
C1	0.7620(2)	0.38146(7)	0.6371(2)	1.39(4)
C2	0.7878(2)	0.42276(7)	0.5659(2)	1.43(4)
C3	0.6516(2)	0.43354(7)	0.4273(2)	1.44(4)
C4	0.5526(2)	0.40275(7)	0.4004(2)	1.45(4)
C5	0.6198(2)	0.36286(7)	0.5062(2)	1.41(4)
C6	0.6716(2)	0.33581(7)	0.4038(2)	1.41(4)
C7	0.8051(2)	0.34680(7)	0.4351(2)	1.34(4)
C8	0.8683(2)	0.37781(7)	0.5702(2)	1.41(4)
C11	0.8039(2)	0.37703(7)	0.8103(2)	1.74(5)
C12	0.7191(3)	0.3870(1)	1.0027(3)	3.87(7)
C21	0.8742(2)	0.45959(7)	0.6722(2)	1.79(5)
C22	0.9782(3)	0.52811(8)	0.6742(3)	3.61(6)
C31	0.6374(2)	0.47203(7)	0.3220(3)	1.84(5)
C32	0.5940(3)	0.54714(9)	0.2796(4)	4.64(8)
C41	0.4105(2)	0.40130(7)	0.2633(2)	1.67(5)
C42	0.2292(3)	0.44543(9)	0.0722(3)	3.06(6)
C51	0.5304(2)	0.33908(7)	0.5715(2)	1.69(5)
C52	0.5354(3)	0.2800(1)	0.7358(3)	4.39(7)
C61	0.5731(2)	0.30774(7)	0.2686(3)	1.97(5)
C62	0.3881(3)	0.25549(9)	0.1951(4)	3.73(7)
C71	0.8898(2)	0.32941(7)	0.3554(2)	1.71(5)
C72	1.0826(2)	0.34655(9)	0.2968(3)	2.81(6)
C81	1.0259(2)	0.37658(7)	0.6721(2)	1.64(5)
C82	1.2227(3)	0.32874(9)	0.7913(3)	3.22(6)
H12A	0.632	0.397	1.012	4.3
H12B	0.739	0.356	1.039	4.3
H12C	0.803	0.406	1.071	4.3
H22A	0.997	0.548	0.602	4.0
H22B	0.917	0.543	0.716	4.0
H22C	1.071	0.520	0.765	4.0
H32A	0.568	0.573	0.326	5.1
H32B	0.688	0.552	0.278	5.1
H32C	0.519	0.543	0.169	5.1
H42A	0.193	0.476	0.060	3.4
H42B	0.249	0.438	-0.020	3.4
H42C	0.155	0.425	0.074	3.4
H52A	0.600	0.256	0.799	4.8
H52B	0.513	0.299	0.807	4.8
H52C	0.445	0.267	0.653	4.8
H62A	0.340	0.237	0.244	4.1
H62B	0.316	0.276	0.116	4.1

Table 33 (cont.). Final Atomic Parameters for Sb-$(COOMe)_8$ at **181 K**

Atom	x	y	z	B(Å^2)
H62C	0.430	0.237	0.140	4.1
H72A	1.145	0.372	0.302	3.1
H72B	1.143	0.322	0.364	3.1
H72C	1.030	0.336	0.185	3.1
H82A	1.245	0.297	0.802	3.5
H82B	1.277	0.344	0.740	3.5
H82C	1.251	0.342	0.899	3.5
H42BA	0.164	0.467	0.086	3.4
H42BB	0.253	0.456	-0.014	3.4
H42BC	0.181	0.416	0.043	3.4

The parameters of the hydrogen atoms were not refined.

Standard deviations are in parentheses.

Table 34. Final Anisotropic Thermal Parameters (U's) for Sb-$(COOMe)_8$ at **181 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0315(7)	0.0405(9)	0.0221(6)	0.0099(7)	0.0175(5)	0.0039(7)
O2	0.0271(7)	0.051(1)	0.0227(7)	0.0109(7)	0.0094(5)	0.0080(7)
O3	0.0331(7)	0.0202(8)	0.0356(7)	-0.0103(6)	0.0185(5)	-0.0052(6)
O4	0.0411(8)	0.0336(9)	0.0256(7)	-0.0066(7)	0.0157(5)	-0.0080(7)
O5	0.0399(7)	0.0160(8)	0.0521(8)	0.0053(7)	0.0274(5)	0.0036(7)
O6	0.0554(9)	0.0355(9)	0.0316(7)	0.0040(8)	0.0276(5)	0.0083(7)
O7	0.0257(7)	0.0258(8)	0.0268(7)	0.0068(7)	0.0025(6)	-0.0010(7)
O8	0.0271(8)	0.0288(8)	0.0374(8)	-0.0040(7)	0.0068(6)	-0.0029(7)
O9	0.0320(7)	0.0252(8)	0.0454(7)	0.0055(6)	0.0267(5)	0.0157(7)
O10	0.0211(6)	0.0353(9)	0.0377(7)	0.0013(7)	0.0174(5)	0.0044(7)
O11	0.0296(7)	0.0239(8)	0.0405(8)	-0.0105(7)	0.0174(5)	-0.0054(7)
O12	0.0426(8)	0.056(1)	0.0297(7)	-0.0191(8)	0.0189(6)	-0.0171(8)
O13	0.0221(6)	0.0273(8)	0.0292(6)	-0.0017(6)	0.0176(4)	0.0005(6)
O14	0.0435(7)	0.0271(8)	0.0557(8)	-0.0029(7)	0.0338(5)	-0.0130(7)
O15	0.0208(7)	0.0271(8)	0.0309(7)	0.0063(6)	0.0107(5)	0.0035(7)
O16	0.0213(7)	0.0305(8)	0.0344(8)	-0.0055(7)	0.0084(5)	-0.0059(7)
C1	0.0184(9)	0.019(1)	0.0188(8)	0.0016(8)	0.0110(6)	0.0011(8)
C2	0.0200(9)	0.016(1)	0.0210(8)	-0.0009(8)	0.0114(6)	-0.0020(8)
C3	0.0222(9)	0.016(1)	0.0198(8)	0.0034(8)	0.0125(6)	0.0009(8)
C4	0.0211(9)	0.018(1)	0.0192(8)	0.0026(8)	0.0120(6)	-0.0008(8)
C5	0.0179(8)	0.018(1)	0.0205(8)	-0.0001(8)	0.0108(6)	0.0004(8)
C6	0.0208(9)	0.015(1)	0.0211(8)	0.0002(8)	0.0119(6)	0.0005(8)
C7	0.0210(9)	0.014(1)	0.0182(8)	0.0004(8)	0.0108(6)	0.0011(8)
C8	0.0165(8)	0.018(1)	0.0214(8)	0.0003(8)	0.0109(6)	0.0007(8)
C11	0.0229(9)	0.022(1)	0.0232(9)	0.0012(9)	0.0124(7)	0.0014(9)
C12	0.057(1)	0.079(2)	0.023(1)	0.020(1)	0.0275(8)	0.009(1)
C21	0.0219(9)	0.020(1)	0.0278(9)	0.0008(9)	0.0128(7)	-0.0022(9)
C22	0.060(1)	0.028(1)	0.061(1)	-0.026(1)	0.0375(9)	-0.021(1)
C31	0.021(1)	0.020(1)	0.028(1)	0.0008(9)	0.0100(7)	0.0038(9)
C32	0.071(2)	0.021(1)	0.097(2)	0.013(1)	0.049(1)	0.024(1)
C41	0.0199(9)	0.025(1)	0.0222(9)	0.0038(9)	0.0129(6)	0.0018(9)
C42	0.033(1)	0.043(1)	0.026(1)	0.012(1)	0.001(1)	0.000(1)
C51	0.0210(9)	0.021(1)	0.0242(9)	0.0000(9)	0.0118(6)	0.0013(9)
C52	0.055(1)	0.050(2)	0.085(1)	0.010(1)	0.0519(9)	0.039(1)
C61	0.022(1)	0.021(1)	0.033(1)	-0.0017(9)	0.0136(7)	-0.0039(9)
C62	0.034(1)	0.035(1)	0.068(2)	-0.018(1)	0.018(1)	-0.015(1)
C71	0.0206(9)	0.023(1)	0.0221(9)	0.0015(9)	0.0099(7)	0.0003(9)
C72	0.0258(9)	0.052(2)	0.042(1)	0.004(1)	0.0267(7)	0.003(1)
C81	0.0228(9)	0.026(1)	0.0184(8)	0.0005(9)	0.0132(6)	-0.0005(9)
C82	0.023(1)	0.048(2)	0.044(1)	0.013(1)	0.0087(9)	0.008(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 35. Interatomic Distances (Å) for Sb-$(COOMe)_8$ at **181 K**

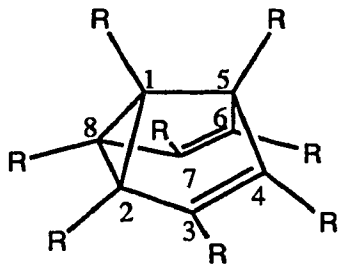
O1	C11	1.336(3)	O15	C82	1.455(3)
O1	C12	1.458(3)	O16	C81	1.200(3)
O2	C11	1.189(2)	C1	C2	1.507(3)
O3	C21	1.327(3)	C1	C5	1.560(2)
O3	C22	1.455(3)	C1	C8	1.504(4)
O4	C21	1.195(3)	C1	C11	1.496(3)
O5	C31	1.320(3)	C2	C3	1.482(2)
O5	C32	1.461(4)	C2	C8	1.600(3)
O6	C31	1.198(3)	C2	C21	1.510(3)
O7	C41	1.326(3)	C3	C4	1.336(3)
O7	C42	1.458(2)	C3	C7	3.080(3)
O8	C41	1.207(3)	C3	C31	1.502(3)
O9	C51	1.332(2)	C4	C5	1.532(3)
O9	C52	1.457(4)	C4	C6	2.385(3)
O10	C51	1.196(3)	C4	C41	1.476(2)
O11	C61	1.333(3)	C5	C6	1.538(3)
O11	C62	1.452(3)	C5	C51	1.512(4)
O12	C61	1.195(3)	C6	C7	1.336(3)
O13	C71	1.339(3)	C6	C61	1.502(3)
O13	C72	1.460(3)	C7	C8	1.485(3)
O14	C71	1.192(3)	C7	C71	1.489(4)
O15	C81	1.338(3)	C8	C81	1.497(3)

Table 36. Angles (°) for Sb-$(COOMe)_8$ at **181 K**

C11	O1	C12	115.4(2)	C5	C6	C61	122.5(2)
C21	O3	C22	115.4(2)	C7	C6	C61	126.0(2)
C31	O5	C32	114.2(2)	C6	C7	C8	112.0(2)
C41	O7	C42	116.8(2)	C6	C7	C71	126.6(2)
C51	O9	C52	115.7(2)	C8	C7	C71	121.4(2)
C61	O11	C62	115.9(2)	C1	C8	C2	58.0(1)
C71	O13	C72	115.8(2)	C1	C8	C7	106.0(2)
C81	O15	C82	115.5(2)	C1	C8	C81	122.8(2)
C2	C1	C5	104.4(1)	C2	C8	C7	119.7(1)
C2	C1	C8	64.2(2)	C2	C8	C81	117.1(2)
C2	C1	C11	122.5(2)	C7	C8	C81	118.6(2)
C5	C1	C8	105.3(2)	O1	C11	O2	126.3(2)
C5	C1	C11	123.1(2)	O1	C11	C1	108.9(2)
C8	C1	C11	122.4(2)	O2	C11	C1	124.8(2)
C1	C2	C3	106.6(2)	O3	C21	O4	126.1(2)
C1	C2	C8	57.8(1)	O3	C21	C2	109.9(2)
C1	C2	C21	120.0(2)	O4	C21	C2	123.9(2)
C3	C2	C8	120.1(2)	O5	C31	O6	126.0(2)
C3	C2	C21	118.6(2)	O5	C31	C3	111.9(2)
C8	C2	C21	117.9(2)	O6	C31	C3	122.1(2)
C2	C3	C4	111.9(2)	O7	C41	O8	125.0(2)
C2	C3	C31	122.1(2)	O7	C41	C4	110.7(2)
C4	C3	C31	125.7(2)	O8	C41	C4	124.3(2)
C3	C4	C5	110.0(2)	O9	C51	O10	125.8(2)
C3	C4	C41	125.6(2)	O9	C51	C5	108.8(2)
C5	C4	C6	39.1(1)	O10	C51	C5	125.4(2)
C5	C4	C41	122.6(2)	O11	C61	O12	125.6(2)
C1	C5	C4	103.1(2)	O11	C61	C6	109.9(2)
C1	C5	C6	102.3(2)	O12	C61	C6	124.6(2)
C1	C5	C51	113.5(2)	O13	C71	O14	125.8(2)
C4	C5	C6	101.9(2)	O13	C71	C7	109.3(2)
C4	C5	C51	117.2(2)	O14	C71	C7	124.9(2)
C6	C5	C51	116.7(2)	O15	C81	O16	125.0(2)
C4	C6	C5	39.0(1)	O15	C81	C8	109.5(2)
C5	C6	C7	110.5(2)	O16	C81	C8	125.5(2)

Table 37. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for $Sb-(COOMe)_8$ at **181 K**

Atom	Min.	Int'med.	Max.
O1	0.121	0.162	0.217
O2	0.140	0.166	0.236
O3	0.120	0.174	0.202
O4	0.143	0.184	0.212
O5	0.122	0.178	0.232
O6	0.138	0.193	0.239
O7	0.133	0.159	0.213
O8	0.150	0.178	0.218
O9	0.115	0.154	0.234
O10	0.127	0.179	0.203
O11	0.125	0.184	0.206
O12	0.146	0.181	0.266
O13	0.114	0.166	0.176
O14	0.135	0.180	0.251
O15	0.130	0.173	0.181
O16	0.135	0.179	0.201
C1	0.116	0.133	0.146
C2	0.122	0.130	0.150
C3	0.115	0.130	0.157
C4	0.112	0.140	0.152
C5	0.121	0.133	0.145
C6	0.121	0.127	0.151
C7	0.117	0.126	0.147
C8	0.116	0.135	0.148
C11	0.138	0.147	0.159
C12	0.109	0.212	0.300
C21	0.133	0.148	0.168
C22	0.114	0.204	0.287
C31	0.137	0.144	0.174
C32	0.121	0.239	0.323
C41	0.118	0.147	0.167
C42	0.138	0.192	0.246
C51	0.136	0.144	0.157
C52	0.109	0.209	0.334
C61	0.141	0.144	0.185
C62	0.126	0.224	0.275
C71	0.139	0.148	0.153
C72	0.102	0.208	0.231
C81	0.112	0.155	0.161
C82	0.131	0.226	0.233



R = $COOCH_3$

Octacarbomethoxysemibullvalene
[Sb-(COOMe)$_8$]

Table 8–38. X-ray Crystal Data for Sb-(COOMe)$_8$ at 236 K

Formula	$C_{24}H_{24}O_{16}$
Formula weight	568.45
Melting point (°C)	162–163.2
Crystal size (mm)	0.10 x 0.29 x 0.35
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	10.475(1)
b (Å)	30.616(2)
c (Å)	9.426(1)
β (°)	116.05(1)
Cell volume (Å^3)	2716.0(7.7)
Z	4
d_{calc} (g cm^{-3})	1.390
μ(Cu $K\alpha$) (cm^{-1})	9.90
Maximum θ (°)	60
Unique reflections	4031
Observed reflections	2839
[$I > 3.0\sigma(I)$]	
Number of variables	361
R	0.040
R_w	0.048
$(\Delta\rho)_{max}$ (e Å^{-3})	0.19
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.25

Table 39. Final Atomic Parameters for Sb-$(COOMe)_8$ at **236 K**

Atom	x	y	z	B(Å^2)
O1	0.6950(2)	0.39015(6)	0.8398(2)	2.94(4)
O2	0.9148(2)	0.36375(7)	0.9083(2)	3.63(5)
O3	0.9071(2)	0.48839(6)	0.5919(2)	3.00(4)
O4	0.9019(2)	0.46209(6)	0.8116(2)	3.54(5)
O5	0.6072(2)	0.50769(6)	0.3811(2)	3.49(5)
O6	0.6583(2)	0.46904(7)	0.2114(2)	3.95(5)
O7	0.3635(2)	0.44091(6)	0.2229(2)	3.12(5)
O8	0.3535(2)	0.36801(6)	0.2039(2)	3.65(5)
O9	0.6073(2)	0.30580(6)	0.6634(2)	3.16(4)
O10	0.4151(2)	0.34925(6)	0.5532(2)	3.10(4)
O11	0.5032(2)	0.28121(6)	0.3213(2)	3.22(4)
O12	0.5664(2)	0.30951(7)	0.1418(2)	4.45(5)
O13	0.9818(2)	0.36045(6)	0.3574(2)	2.51(4)
O14	0.8837(2)	0.29353(6)	0.3096(2)	3.92(5)
O15	1.0710(2)	0.33522(6)	0.6975(2)	2.78(4)
O16	1.1017(2)	0.40790(6)	0.7255(2)	3.24(5)
C1	0.7633(2)	0.38134(8)	0.6402(2)	1.75(5)
C2	0.7892(2)	0.42262(7)	0.5697(3)	1.92(5)
C3	0.6540(2)	0.43327(8)	0.4310(3)	1.84(5)
C4	0.5553(2)	0.40240(8)	0.4038(3)	1.90(5)
C5	0.6218(2)	0.36281(7)	0.5097(3)	1.81(5)
C6	0.6734(2)	0.33569(7)	0.4067(3)	1.89(5)
C7	0.8072(2)	0.34684(7)	0.4385(3)	1.77(5)
C8	0.8696(2)	0.37763(8)	0.5734(3)	1.80(5)
C11	0.8039(2)	0.37707(8)	0.8128(3)	2.36(6)
C12	0.7182(3)	0.3880(1)	1.0041(3)	5.18(9)
C21	0.8742(3)	0.45912(8)	0.6751(3)	2.33(6)
C22	0.9805(3)	0.5272(1)	0.6774(4)	4.86(8)
C31	0.6396(3)	0.47189(8)	0.3269(3)	2.41(6)
C32	0.5958(4)	0.5469(1)	0.2879(5)	6.0(1)
C41	0.4140(2)	0.40081(8)	0.2668(3)	2.24(5)
C42	0.2352(3)	0.4450(1)	0.0760(4)	4.12(8)
C51	0.5323(2)	0.33885(8)	0.5746(3)	2.18(5)
C52	0.5377(3)	0.2801(1)	0.7390(4)	5.77(8)
C61	0.5769(3)	0.30769(8)	0.2735(3)	2.54(6)
C62	0.3927(3)	0.2556(1)	0.1998(4)	4.95(9)
C71	0.8923(2)	0.32971(8)	0.3593(3)	2.19(5)
C72	1.0834(3)	0.3471(1)	0.2987(3)	3.53(7)
C81	1.0267(2)	0.37665(8)	0.6754(3)	2.21(5)
C82	1.2232(3)	0.3289(1)	0.7941(4)	4.28(8)
H12A	0.631	0.398	1.012	5.6
H12B	0.739	0.357	1.042	5.6
H12C	0.801	0.407	1.071	5.6
H22A	1.001	0.547	0.605	5.3
H22B	0.920	0.543	0.719	5.3
H22C	1.072	0.518	0.768	5.3
H32A	0.571	0.573	0.336	6.6
H32B	0.688	0.553	0.284	6.6
H32C	0.520	0.543	0.177	6.6
H42A	0.203	0.476	0.060	4.5
H42B	0.255	0.436	-0.014	4.5
H42C	0.159	0.426	0.080	4.5
H52A	0.602	0.256	0.803	6.3
H52B	0.514	0.299	0.810	6.3
H52C	0.448	0.267	0.656	6.3
H62A	0.344	0.237	0.248	5.4
H62B	0.321	0.276	0.120	5.4

Table 39 (cont.). Final Atomic Parameters for Sb-$(COOMe)_8$ at **236 K**

Atom	x	y	z	B($Å^2$)
H62C	0.435	0.237	0.146	5.4
H72A	1.145	0.373	0.302	3.9
H72B	1.144	0.323	0.366	3.9
H72C	1.031	0.337	0.187	3.9
H82A	1.246	0.297	0.804	4.7
H82B	1.277	0.344	0.743	4.7
H82C	1.251	0.342	0.902	4.7
H42BA	0.169	0.466	0.090	4.5
H42BB	0.260	0.456	-0.009	4.5
H42BC	0.188	0.416	0.044	4.5

The parameters of the hydrogen atoms were not refined.

Standard deviations are in parentheses.

Table 40. Final Anisotropic Thermal Parameters (U's) for Sb-$(COOMe)_8$ at **236 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0386(8)	0.053(1)	0.0276(7)	0.0109(8)	0.0213(5)	0.0056(8)
O2	0.0337(9)	0.072(1)	0.0287(8)	0.0163(9)	0.0105(6)	0.0103(9)
O3	0.0442(9)	0.0280(9)	0.0459(9)	-0.0144(7)	0.0235(6)	-0.0080(8)
O4	0.055(1)	0.046(1)	0.0344(8)	-0.0124(9)	0.0207(7)	-0.0143(8)
O5	0.0533(9)	0.0212(9)	0.069(1)	0.0071(8)	0.0371(7)	0.0053(8)
O6	0.075(1)	0.047(1)	0.0410(8)	0.0058(9)	0.0372(6)	0.0108(8)
O7	0.0362(9)	0.0349(9)	0.0354(9)	0.0097(8)	0.0045(7)	-0.0008(8)
O8	0.036(1)	0.038(1)	0.051(1)	-0.0046(9)	0.0064(8)	-0.0038(9)
O9	0.0419(8)	0.0327(9)	0.0595(9)	0.0075(7)	0.0350(6)	0.0196(8)
O10	0.0276(7)	0.044(1)	0.0538(9)	0.0024(8)	0.0251(6)	0.0073(8)
O11	0.0396(9)	0.0300(9)	0.056(1)	-0.0149(8)	0.0243(7)	-0.0079(8)
O12	0.059(1)	0.075(1)	0.0403(9)	-0.030(1)	0.0268(7)	-0.024(1)
O13	0.0290(7)	0.0361(9)	0.0390(7)	-0.0033(7)	0.0229(5)	-0.0006(7)
O14	0.0592(9)	0.034(1)	0.0757(9)	-0.0058(8)	0.0479(6)	-0.0190(8)
O15	0.0274(8)	0.0347(9)	0.0427(8)	0.0081(7)	0.0147(6)	0.0056(8)
O16	0.0274(8)	0.040(1)	0.048(1)	-0.0070(8)	0.0094(7)	-0.0085(9)
C1	0.024(1)	0.024(1)	0.0218(9)	0.0001(9)	0.0131(7)	-0.0008(9)
C2	0.026(1)	0.021(1)	0.029(1)	-0.0010(9)	0.0151(7)	-0.002(1)
C3	0.026(1)	0.023(1)	0.025(1)	0.0030(9)	0.0145(7)	0.0011(9)
C4	0.025(1)	0.024(1)	0.026(1)	0.003(1)	0.0136(7)	-0.001(1)
C5	0.023(1)	0.021(1)	0.027(1)	-0.0023(9)	0.0130(7)	0.0000(9)
C6	0.027(1)	0.020(1)	0.029(1)	-0.0014(9)	0.0151(7)	-0.001(1)
C7	0.025(1)	0.018(1)	0.027(1)	-0.0005(9)	0.0143(7)	-0.0003(9)
C8	0.020(1)	0.025(1)	0.026(1)	0.0000(9)	0.0114(7)	-0.0007(9)
C11	0.032(1)	0.031(1)	0.031(1)	0.004(1)	0.0174(8)	0.002(1)
C12	0.074(2)	0.105(3)	0.031(1)	0.026(2)	0.036(1)	0.013(2)
C21	0.027(1)	0.029(1)	0.035(1)	-0.000(1)	0.0150(8)	-0.005(1)
C22	0.079(2)	0.038(2)	0.084(2)	-0.034(1)	0.051(1)	-0.025(1)
C31	0.029(1)	0.026(1)	0.037(1)	0.004(1)	0.0146(8)	0.006(1)
C32	0.090(2)	0.029(2)	0.121(2)	0.017(2)	0.059(2)	0.033(2)
C41	0.028(1)	0.032(1)	0.027(1)	0.003(1)	0.0141(8)	0.002(1)
C42	0.044(2)	0.060(2)	0.033(1)	0.017(1)	-0.002(1)	0.001(1)
C51	0.028(1)	0.025(1)	0.033(1)	-0.001(1)	0.0163(8)	0.002(1)
C52	0.072(2)	0.062(2)	0.115(2)	0.012(1)	0.069(1)	0.050(1)
C61	0.029(1)	0.027(1)	0.043(1)	-0.004(1)	0.0181(8)	-0.006(1)
C62	0.047(2)	0.044(2)	0.092(2)	-0.024(1)	0.024(1)	-0.022(2)
C71	0.027(1)	0.029(1)	0.030(1)	0.002(1)	0.0140(8)	-0.000(1)
C72	0.030(1)	0.065(2)	0.053(1)	0.004(1)	0.0314(8)	0.005(1)
C81	0.028(1)	0.035(1)	0.024(1)	0.001(1)	0.0157(7)	0.000(1)
C82	0.032(1)	0.063(2)	0.059(2)	0.019(1)	0.012(1)	0.010(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 41. Interatomic Distances (Å) Sb-$(COOMe)_8$ at **236 K**

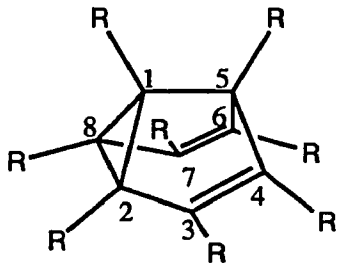
O1	C11	1.335(4)	O15	C82	1.461(3)
O1	C12	1.461(4)	O16	C81	1.195(3)
O2	C11	1.187(3)	C1	C2	1.507(3)
O3	C21	1.332(3)	C1	C5	1.559(3)
O3	C22	1.451(3)	C1	C8	1.505(4)
O4	C21	1.192(3)	C1	C11	1.495(3)
O5	C31	1.315(3)	C2	C3	1.482(3)
O5	C32	1.462(4)	C2	C8	1.607(3)
O6	C31	1.192(4)	C2	C21	1.501(3)
O7	C41	1.329(3)	C3	C4	1.340(3)
O7	C42	1.451(3)	C3	C7	3.080(3)
O8	C41	1.196(3)	C3	C31	1.501(4)
O9	C51	1.328(3)	C4	C5	1.530(3)
O9	C52	1.455(5)	C4	C6	2.382(3)
O10	C51	1.197(3)	C4	C41	1.477(3)
O11	C61	1.328(4)	C5	C6	1.544(4)
O11	C62	1.449(3)	C5	C51	1.516(4)
O12	C61	1.199(4)	C6	C7	1.342(3)
O13	C71	1.334(3)	C6	C61	1.490(3)
O13	C72	1.457(4)	C7	C8	1.484(3)
O14	C71	1.191(3)	C7	C71	1.486(4)
O15	C81	1.335(3)	C8	C81	1.498(3)

Table 42. Angles (°) for Sb-$(COOMe)_8$ at **236 K**

C11	O1	C12	115.5(2)	C5	C6	C61	122.9(2)
C21	O3	C22	115.7(2)	C7	C6	C61	126.2(3)
C31	O5	C32	114.7(3)	C6	C7	C8	112.1(2)
C41	O7	C42	116.9(2)	C6	C7	C71	126.5(2)
C51	O9	C52	115.9(2)	C8	C7	C71	121.2(2)
C61	O11	C62	116.3(2)	C1	C8	C2	57.8(2)
C71	O13	C72	116.2(2)	C1	C8	C7	106.1(2)
C81	O15	C82	115.6(2)	C1	C8	C81	122.6(2)
C2	C1	C5	104.5(2)	C2	C8	C7	119.8(2)
C2	C1	C8	64.5(2)	C2	C8	C81	116.7(2)
C2	C1	C11	122.2(2)	C7	C8	C81	118.9(2)
C5	C1	C8	105.3(2)	O1	C11	O2	126.4(3)
C5	C1	C11	123.0(2)	O1	C11	C1	108.8(2)
C8	C1	C11	122.7(2)	O2	C11	C1	124.8(3)
C1	C2	C3	106.7(2)	O3	C21	O4	125.6(2)
C1	C2	C8	57.7(2)	O3	C21	C2	110.0(2)
C1	C2	C21	120.1(2)	O4	C21	C2	124.3(3)
C3	C2	C8	119.8(2)	O5	C31	O6	126.2(3)
C3	C2	C21	118.7(2)	O5	C31	C3	111.8(2)
C8	C2	C21	118.1(2)	O6	C31	C3	122.0(2)
C2	C3	C4	111.8(2)	O7	C41	O8	124.7(2)
C2	C3	C31	122.2(2)	O7	C41	C4	110.5(2)
C4	C3	C31	125.6(2)	O8	C41	C4	124.8(2)
C3	C4	C5	110.0(2)	O9	C51	O10	126.0(3)
C3	C4	C41	125.7(2)	O9	C51	C5	108.9(2)
C5	C4	C6	39.4(1)	O10	C51	C5	125.1(2)
C5	C4	C41	122.6(2)	O11	C61	O12	125.3(2)
C1	C5	C4	103.3(2)	O11	C61	C6	110.3(2)
C1	C5	C6	102.6(2)	O12	C61	C6	124.5(3)
C1	C5	C51	113.6(2)	O13	C71	O14	125.6(3)
C4	C5	C6	101.6(2)	O13	C71	C7	109.8(2)
C4	C5	C51	117.5(2)	O14	C71	C7	124.6(3)
C6	C5	C51	116.3(2)	O15	C81	O16	125.1(2)
C4	C6	C5	39.0(1)	O15	C81	C8	109.1(2)
C5	C6	C7	110.0(2)	O16	C81	C8	125.7(2)

Table 43. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-(COOMe)8 at **236 K**

Atom	Min.	Int'med.	Max.
O1	0.138	0.184	0.243
O2	0.154	0.190	0.279
O3	0.140	0.200	0.233
O4	0.157	0.214	0.253
O5	0.140	0.202	0.269
O6	0.156	0.221	0.277
O7	0.156	0.185	0.245
O8	0.172	0.202	0.262
O9	0.136	0.174	0.267
O10	0.140	0.201	0.240
O11	0.137	0.211	0.243
O12	0.168	0.204	0.315
O13	0.133	0.190	0.204
O14	0.147	0.200	0.296
O15	0.148	0.194	0.214
O16	0.153	0.205	0.240
C1	0.131	0.156	0.159
C2	0.143	0.148	0.175
C3	0.137	0.149	0.170
C4	0.137	0.161	0.166
C5	0.134	0.152	0.166
C6	0.139	0.150	0.173
C7	0.134	0.145	0.168
C8	0.135	0.156	0.161
C11	0.154	0.172	0.190
C12	0.131	0.244	0.346
C21	0.153	0.166	0.194
C22	0.137	0.238	0.331
C31	0.152	0.170	0.199
C32	0.136	0.275	0.364
C41	0.155	0.166	0.184
C42	0.149	0.225	0.290
C51	0.148	0.165	0.184
C52	0.125	0.239	0.382
C61	0.153	0.166	0.213
C62	0.142	0.256	0.320
C71	0.154	0.172	0.172
C72	0.117	0.230	0.260
C81	0.137	0.172	0.189
C82	0.151	0.261	0.268



R = $COOCH_3$

Octacarbomethoxysemibullvalene
[Sb-(COOMe)$_8$]

Table 8–44. X-ray Crystal Data for Sb-(COOMe)$_8$ at **294 K**

Formula	$C_{24}H_{24}O_{16}$
Formula weight	568.45
Melting point (°C)	162–163.2
Crystal size (mm)	0.10 x 0.29 x 0.35
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	10.498(1)
b (Å)	30.719(1)
c (Å)	9.440(1)
β (°)	115.885(1)
Cell volume (Å^3)	2738.8(6.5)
Z	4
d_{calc} (g cm^{-3})	1.379
μ(Cu $K\alpha$) (cm^{-1})	9.82
Maximum θ (°)	60
Unique reflections	4069
Observed reflections	2706
[$I > 3.0\sigma(I)$]	
Number of variables	361
R	0.042
R_w	0.050
$(\Delta\rho)_{max}$ (e Å^{-3})	0.20
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.19

Table 45. Final Atomic Parameters for Sb-$(COOMe)_8$ at **294 K**

Atom	x	y	z	B(Å^2)
O1	0.6952(2)	0.39038(7)	0.8409(2)	3.82(5)
O2	0.9136(2)	0.36360(8)	0.9102(2)	4.66(6)
O3	0.9087(2)	0.48769(6)	0.5955(2)	3.89(5)
O4	0.9007(2)	0.46183(7)	0.8131(2)	4.73(6)
O5	0.6097(2)	0.50711(6)	0.3863(3)	4.49(5)
O6	0.6591(2)	0.46911(7)	0.2153(2)	5.05(6)
O7	0.3671(2)	0.44034(7)	0.2257(2)	4.09(5)
O8	0.3570(2)	0.36787(7)	0.2073(3)	4.81(6)
O9	0.6084(2)	0.30586(6)	0.6653(2)	4.06(5)
O10	0.4169(2)	0.34908(7)	0.5546(2)	3.99(5)
O11	0.5068(2)	0.28153(6)	0.3246(2)	4.15(5)
O12	0.5702(2)	0.30938(8)	0.1460(2)	5.89(6)
O13	0.9822(2)	0.36079(6)	0.3592(2)	3.26(4)
O14	0.8867(2)	0.29390(7)	0.3137(2)	5.10(5)
O15	1.0718(2)	0.33546(6)	0.6996(2)	3.67(5)
O16	1.1012(2)	0.40780(7)	0.7286(3)	4.24(5)
C1	0.7640(2)	0.38127(8)	0.6421(3)	2.20(6)
C2	0.7899(3)	0.42246(8)	0.5726(3)	2.38(6)
C3	0.6559(3)	0.43292(8)	0.4341(3)	2.30(6)
C4	0.5576(3)	0.40189(9)	0.4062(3)	2.45(6)
C5	0.6238(2)	0.36261(8)	0.5121(3)	2.27(6)
C6	0.6759(3)	0.33574(8)	0.4098(3)	2.42(6)
C7	0.8094(3)	0.34697(8)	0.4418(3)	2.25(5)
C8	0.8709(2)	0.37754(8)	0.5764(3)	2.31(6)
C11	0.8039(3)	0.37701(9)	0.8146(3)	3.04(6)
C12	0.7164(4)	0.3886(2)	1.0047(3)	6.6(1)
C21	0.8745(3)	0.45890(9)	0.6776(3)	3.09(7)
C22	0.9827(4)	0.5262(1)	0.6805(4)	6.4(1)
C31	0.6413(3)	0.47159(9)	0.3315(3)	3.07(7)
C32	0.5973(5)	0.5464(1)	0.2948(5)	8.0(1)
C41	0.4173(3)	0.40050(9)	0.2700(3)	2.93(6)
C42	0.2399(4)	0.4446(1)	0.0792(4)	5.4(1)
C51	0.5336(3)	0.33869(9)	0.5766(3)	2.85(6)
C52	0.5384(4)	0.2799(1)	0.7397(4)	7.3(1)
C61	0.5802(3)	0.30789(9)	0.2771(3)	3.24(7)
C62	0.3969(4)	0.2559(1)	0.2035(5)	6.4(1)
C71	0.8943(3)	0.33001(9)	0.3623(3)	2.76(6)
C72	1.0839(3)	0.3476(1)	0.2999(4)	4.68(8)
C81	1.0273(3)	0.37667(9)	0.6782(3)	2.81(6)
C82	1.2231(3)	0.3291(1)	0.7952(5)	5.7(1)
H12A	0.629	0.399	1.012	7.2
H12B	0.736	0.358	1.043	7.2
H12C	0.799	0.407	1.071	7.2
H22A	1.004	0.546	0.608	7.0
H22B	0.922	0.542	0.721	7.0
H22C	1.074	0.517	0.771	7.0
H32A	0.574	0.572	0.346	8.7
H32B	0.690	0.552	0.291	8.7
H32C	0.521	0.542	0.186	8.7
H42A	0.227	0.476	0.043	5.9
H42B	0.246	0.426	-0.004	5.9
H42C	0.154	0.435	0.094	5.9
H52A	0.603	0.256	0.803	8.0
H52B	0.513	0.299	0.810	8.0
H52C	0.450	0.267	0.656	8.0
H62A	0.349	0.237	0.253	7.0
H62B	0.326	0.276	0.125	7.0

Table 45 (cont.). Final Atomic Parameters for $Sb-(COOMe)_8$ at **294 K**

Atom	x	y	z	B($Å^2$)
H62C	0.440	0.237	0.150	7.0
H72A	1.144	0.373	0.302	5.1
H72B	1.145	0.324	0.367	5.1
H72C	1.031	0.337	0.189	5.1
H82A	1.245	0.297	0.804	6.2
H82B	1.277	0.344	0.745	6.2
H82C	1.251	0.341	0.903	6.2
H42BA	0.184	0.471	0.083	5.9
H42BB	0.265	0.448	-0.011	5.9
H42BC	0.178	0.418	0.062	5.9

The parameters of the hydrogen atoms were not refined.

Standard deviations are in parentheses.

Table 46. Final Anisotropic Thermal Parameters (U's) for Sb-$(COOMe)_8$ at **294 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0478(9)	0.070(1)	0.0364(8)	0.0142(9)	0.0266(6)	0.0060(9)
O2	0.043(1)	0.094(2)	0.0378(9)	0.021(1)	0.0153(7)	0.013(1)
O3	0.056(1)	0.036(1)	0.061(1)	-0.0172(9)	0.0307(7)	-0.0096(9)
O4	0.077(1)	0.060(1)	0.0462(9)	-0.018(1)	0.0293(8)	-0.019(1)
O5	0.071(1)	0.028(1)	0.084(1)	0.0113(9)	0.0466(8)	0.0063(9)
O6	0.097(1)	0.058(1)	0.0542(9)	0.007(1)	0.0487(7)	0.013(1)
O7	0.047(1)	0.046(1)	0.046(1)	0.013(1)	0.0050(9)	0.000(1)
O8	0.045(1)	0.051(1)	0.066(1)	-0.007(1)	0.005(1)	-0.005(1)
O9	0.0531(9)	0.042(1)	0.077(1)	0.0091(8)	0.0445(7)	0.0255(9)
O10	0.0339(8)	0.059(1)	0.068(1)	0.0041(9)	0.0308(7)	0.011(1)
O11	0.049(1)	0.040(1)	0.072(1)	-0.0184(9)	0.0292(8)	-0.011(1)
O12	0.079(1)	0.099(2)	0.054(1)	-0.041(1)	0.0357(8)	-0.033(1)
O13	0.0376(8)	0.047(1)	0.0503(8)	-0.0039(8)	0.0295(6)	-0.0012(9)
O14	0.077(1)	0.043(1)	0.100(1)	-0.006(1)	0.0632(7)	-0.024(1)
O15	0.0351(9)	0.047(1)	0.055(1)	0.0106(9)	0.0178(7)	0.0058(9)
O16	0.035(1)	0.051(1)	0.064(1)	-0.0081(9)	0.0109(8)	-0.010(1)
C1	0.029(1)	0.030(1)	0.028(1)	0.002(1)	0.0149(8)	0.000(1)
C2	0.033(1)	0.027(1)	0.033(1)	-0.003(1)	0.0169(8)	-0.002(1)
C3	0.033(1)	0.028(1)	0.031(1)	0.004(1)	0.0176(8)	0.002(1)
C4	0.031(1)	0.032(1)	0.033(1)	0.003(1)	0.0168(8)	0.001(1)
C5	0.028(1)	0.026(1)	0.035(1)	0.000(1)	0.0161(8)	0.003(1)
C6	0.032(1)	0.027(1)	0.038(1)	-0.001(1)	0.0199(8)	-0.002(1)
C7	0.031(1)	0.023(1)	0.035(1)	-0.000(1)	0.0171(8)	-0.001(1)
C8	0.028(1)	0.032(1)	0.031(1)	0.000(1)	0.0162(8)	-0.002(1)
C11	0.038(1)	0.043(2)	0.038(1)	0.006(1)	0.0195(9)	0.004(1)
C12	0.095(2)	0.133(3)	0.044(1)	0.029(2)	0.048(1)	0.012(2)
C21	0.037(1)	0.036(1)	0.047(1)	-0.004(1)	0.021(1)	-0.009(1)
C22	0.101(2)	0.050(2)	0.112(2)	-0.042(2)	0.065(2)	-0.035(2)
C31	0.038(1)	0.034(1)	0.046(1)	0.003(1)	0.019(1)	0.005(1)
C32	0.127(3)	0.037(2)	0.158(3)	0.024(2)	0.078(2)	0.039(2)
C41	0.033(1)	0.040(1)	0.040(1)	0.003(1)	0.0182(9)	0.002(1)
C42	0.057(2)	0.078(2)	0.044(2)	0.022(2)	-0.003(2)	0.004(2)
C51	0.037(1)	0.033(1)	0.045(1)	-0.001(1)	0.0241(9)	0.004(1)
C52	0.089(2)	0.086(2)	0.139(2)	0.014(2)	0.083(1)	0.066(2)
C61	0.038(1)	0.034(1)	0.053(1)	-0.007(1)	0.022(1)	-0.011(1)
C62	0.061(2)	0.055(2)	0.114(3)	-0.030(2)	0.028(2)	-0.027(2)
C71	0.035(1)	0.036(1)	0.037(1)	0.004(1)	0.0187(9)	-0.002(1)
C72	0.043(1)	0.084(2)	0.071(1)	0.004(1)	0.0437(9)	0.002(2)
C81	0.033(1)	0.046(2)	0.032(1)	0.002(1)	0.0185(8)	-0.001(1)
C82	0.040(2)	0.083(2)	0.078(2)	0.023(2)	0.011(2)	0.008(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 47. Interatomic Distances (Å) for Sb-$(COOMe)_8$ at **294 K**

O1	C11	1.334(4)	O15	C82	1.458(3)
O1	C12	1.463(4)	O16	C81	1.192(3)
O2	C11	1.185(3)	C1	C2	1.504(4)
O3	C21	1.324(4)	C1	C5	1.557(3)
O3	C22	1.451(4)	C1	C8	1.505(4)
O4	C21	1.189(4)	C1	C11	1.500(4)
O5	C31	1.310(4)	C2	C3	1.478(3)
O5	C32	1.457(5)	C2	C8	1.614(4)
O6	C31	1.193(4)	C2	C21	1.502(3)
O7	C41	1.326(3)	C3	C4	1.344(4)
O7	C42	1.449(3)	C3	C7	3.078(4)
O8	C41	1.195(3)	C3	C31	1.497(4)
O9	C51	1.327(3)	C4	C5	1.527(3)
O9	C52	1.457(5)	C4	C6	2.374(4)
O10	C51	1.193(3)	C4	C41	1.473(3)
O11	C61	1.324(4)	C5	C6	1.541(4)
O11	C62	1.452(4)	C5	C51	1.519(4)
O12	C61	1.197(4)	C6	C7	1.344(4)
O13	C71	1.331(3)	C6	C61	1.487(3)
O13	C72	1.462(4)	C7	C8	1.482(3)
O14	C71	1.190(3)	C7	C71	1.487(4)
O15	C81	1.334(3)	C8	C81	1.497(3)

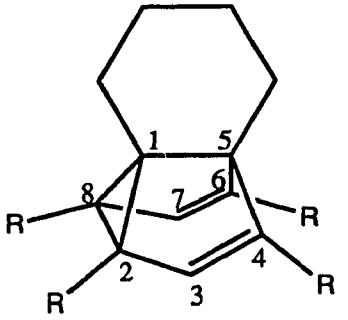
Table 48. Angles (°) for Sb-$(COOMe)_8$ at **294 K**

C11	O1	C12	115.9(2)	C5	C6	C61	122.8(2)
C21	O3	C22	115.9(3)	C7	C6	C61	126.2(3)
C31	O5	C32	115.5(3)	C6	C7	C8	112.1(3)
C41	O7	C42	117.3(2)	C6	C7	C71	126.4(2)
C51	O9	C52	115.9(2)	C8	C7	C71	121.4(2)
C61	O11	C62	116.4(3)	C1	C8	C2	57.5(2)
C71	O13	C72	116.1(2)	C1	C8	C7	106.1(2)
C81	O15	C82	115.8(2)	C1	C8	C81	122.8(2)
C2	C1	C5	104.7(2)	C2	C8	C7	119.6(2)
C2	C1	C8	64.9(2)	C2	C8	C81	116.7(2)
C2	C1	C11	122.0(2)	C7	C8	C81	119.0(2)
C5	C1	C8	105.4(2)	O1	C11	O2	126.2(3)
C5	C1	C11	122.9(2)	O1	C11	C1	108.6(2)
C8	C1	C11	122.4(2)	O2	C11	C1	125.1(3)
C1	C2	C3	106.6(2)	O3	C21	O4	125.8(3)
C1	C2	C8	57.6(2)	O3	C21	C2	110.2(2)
C1	C2	C21	120.4(2)	O4	C21	C2	124.0(3)
C3	C2	C8	119.6(2)	O5	C31	O6	125.7(3)
C3	C2	C21	118.8(2)	O5	C31	C3	112.2(3)
C8	C2	C21	117.9(2)	O6	C31	C3	122.1(3)
C2	C3	C4	111.8(2)	O7	C41	O8	124.5(2)
C2	C3	C31	122.3(2)	O7	C41	C4	110.9(2)
C4	C3	C31	125.6(2)	O8	C41	C4	124.6(2)
C3	C4	C5	109.9(2)	O9	C51	O10	126.4(3)
C3	C4	C41	125.5(2)	O9	C51	C5	108.7(2)
C5	C4	C6	39.5(1)	O10	C51	C5	124.9(2)
C5	C4	C41	123.0(2)	O11	C61	O12	124.9(2)
C1	C5	C4	103.2(2)	O11	C61	C6	110.2(3)
C1	C5	C6	102.6(2)	O12	C61	C6	124.9(3)
C1	C5	C51	113.7(2)	O13	C71	O14	125.8(3)
C4	C5	C6	101.4(2)	O13	C71	C7	109.7(2)
C4	C5	C51	117.4(2)	O14	C71	C7	124.6(3)
C6	C5	C51	116.4(2)	O15	C81	O16	125.2(2)
C4	C6	C5	39.1(1)	O15	C81	C8	109.1(2)
C5	C6	C7	110.1(2)	O16	C81	C8	125.6(2)

Table 49. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for $Sb-(COOMe)_8$ at **294 K**

Atom	Min.	Int'med.	Max.
O1	0.159	0.207	0.277
O2	0.179	0.208	0.319
O3	0.163	0.228	0.264
O4	0.180	0.242	0.298
O5	0.159	0.236	0.299
O6	0.179	0.246	0.315
O7	0.177	0.215	0.279
O8	0.189	0.233	0.305
O9	0.152	0.198	0.303
O10	0.157	0.228	0.274
O11	0.159	0.238	0.275
O12	0.190	0.233	0.366
O13	0.153	0.216	0.232
O14	0.165	0.228	0.339
O15	0.170	0.228	0.243
O16	0.174	0.231	0.278
C1	0.153	0.169	0.178
C2	0.159	0.171	0.189
C3	0.154	0.165	0.191
C4	0.159	0.179	0.189
C5	0.154	0.163	0.190
C6	0.160	0.164	0.198
C7	0.151	0.165	0.188
C8	0.152	0.176	0.184
C11	0.178	0.190	0.219
C12	0.152	0.283	0.386
C21	0.177	0.186	0.227
C22	0.162	0.273	0.377
C31	0.178	0.194	0.218
C32	0.160	0.328	0.415
C41	0.174	0.197	0.206
C42	0.169	0.263	0.330
C51	0.161	0.187	0.217
C52	0.141	0.273	0.430
C61	0.168	0.192	0.241
C62	0.163	0.292	0.361
C71	0.165	0.195	0.198
C72	0.138	0.273	0.290
C81	0.157	0.189	0.216
C82	0.171	0.298	0.314

8.4 SB-6



R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Table 8–50. X-ray Crystal Data for Sb-6 at **115 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	117-118
Crystal size (mm)	0.21 x 0.25 x 0.33
Crystal system	monoclinic
Space group	*P2/n*
a (Å)	41.319(3)
b (Å)	7.317(1)
c (Å)	12.104(1)
β (°)	98.00(1)
Cell volume (Å^3)	3623.74(2.87)
Z	8
d_{calc} (g cm^{-3})	1.431
μ(Cu $K\alpha$) (cm^{-1})	8.92
Maximum θ (°)	60
Unique reflections	5375
Observed reflections [$I > 3.0\sigma(I)$]	3543
Number of variables	505
R	0.046
R_w	0.054
$(\Delta\rho)_{max}$ (e Å^{-3})	0.29
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.33

Table 51. Final Atomic Parameters for Sb-6 at 115 K

Atom	x	y	z	B(Å^2)
O1	0.55485(5)	0.1442(3)	0.2594(2)	1.10(5)
O2	0.55547(5)	0.4165(3)	0.3458(2)	1.54(5)
O3	0.69172(5)	0.4023(3)	0.3891(2)	1.54(5)
O4	0.70560(5)	0.1108(4)	0.3606(2)	1.83(5)
O5	0.68200(5)	0.0785(4)	0.7606(2)	1.79(5)
O6	0.70733(5)	0.0293(4)	0.6114(2)	2.14(6)
O7	0.56005(5)	0.1170(4)	0.6703(2)	1.49(5)
O8	0.53639(5)	0.0930(4)	0.4913(2)	1.76(5)
C1	0.60499(7)	0.0028(5)	0.4384(3)	0.89(6)
C2	0.59660(8)	0.1962(5)	0.4080(3)	0.95(6)
C3	0.62702(8)	0.2899(5)	0.3894(3)	1.09(7)
C4	0.65269(8)	0.1768(5)	0.4083(3)	1.04(7)
C5	0.64303(7)	0.0008(5)	0.4634(3)	0.97(6)
C6	0.64939(8)	0.0545(5)	0.5868(3)	1.11(7)
C7	0.62287(8)	0.1299(5)	0.6206(3)	1.19(7)
C8	0.59457(8)	0.1161(5)	0.5332(3)	1.05(7)
C9	0.58918(8)	-0.1675(5)	0.3880(3)	1.15(7)
C10	0.60487(8)	-0.2180(5)	0.2843(3)	1.38(7)
C11	0.64296(8)	-0.2141(5)	0.3044(3)	1.30(7)
C12	0.65708(8)	-0.1776(5)	0.4262(3)	1.17(7)
C15	0.56623(8)	0.2641(5)	0.3381(3)	1.06(7)
C16	0.68615(8)	0.2204(5)	0.3853(3)	1.21(7)
C17	0.68252(8)	0.0523(5)	0.6516(3)	1.20(7)
C18	0.56036(8)	0.1077(5)	0.5595(3)	1.11(7)
C19	0.52866(8)	0.2101(5)	0.1773(3)	1.52(7)
C20	0.72307(8)	0.4575(6)	0.3592(3)	2.16(8)
C21	0.71377(8)	0.0746(6)	0.8293(3)	1.88(8)
C22	0.52777(8)	0.1064(6)	0.7054(3)	1.72(7)
O1'	0.44777(5)	0.3640(3)	-0.0509(2)	1.26(5)
O2'	0.44734(5)	0.0969(3)	0.0405(2)	1.67(5)
O3'	0.30996(5)	0.0972(3)	-0.0605(2)	1.59(5)
O4'	0.29606(5)	0.3873(3)	-0.1061(2)	1.68(5)
O5'	0.31753(5)	0.4213(4)	0.3184(2)	1.87(5)
O6'	0.29184(5)	0.4667(4)	0.1443(2)	2.09(5)
O7'	0.43820(5)	0.3736(4)	0.3518(2)	1.46(5)
O8'	0.46281(5)	0.4442(3)	0.2029(2)	1.46(5)
C1'	0.39504(7)	0.5037(5)	0.0746(3)	0.87(6)
C2'	0.40434(8)	0.3120(5)	0.0519(3)	0.95(6)
C3'	0.37469(8)	0.2159(5)	0.0020(3)	0.96(6)
C4'	0.34850(8)	0.3243(5)	-0.0041(3)	1.02(7)
C5'	0.35692(7)	0.5012(5)	0.0603(3)	0.94(6)
C6'	0.34992(8)	0.4460(5)	0.1768(3)	1.18(7)
C7'	0.37626(8)	0.3738(5)	0.2373(3)	1.15(7)
C8'	0.40517(7)	0.3930(5)	0.1796(3)	1.06(7)
C9'	0.41055(8)	0.6761(5)	0.0397(3)	1.10(7)
C10'	0.39529(8)	0.7223(5)	-0.0798(3)	1.38(7)
C11'	0.35713(8)	0.7193(5)	-0.0982(3)	1.20(7)
C12'	0.34242(8)	0.6788(5)	0.0095(3)	1.11(7)
C15'	0.43577(8)	0.2457(5)	0.0168(3)	1.12(7)
C16'	0.31526(8)	0.2783(5)	-0.0609(3)	1.19(7)
C17'	0.31656(8)	0.4456(5)	0.2083(3)	1.19(7)
C18'	0.43844(8)	0.4069(5)	0.2436(3)	1.07(6)
C19'	0.47578(8)	0.2999(5)	-0.1013(3)	1.87(7)
C20'	0.27870(8)	0.0406(6)	-0.1214(3)	2.02(8)
C21'	0.28571(8)	0.4250(6)	0.3574(3)	1.96(8)
C22'	0.46931(8)	0.3896(6)	0.4243(3)	1.71(8)

Table 51 (cont.). Final Atomic Parameters for Sb-6 at **115 K**

Atom	x	y	z	B(Å^2)
H3	0.628	0.420	0.366	1.2
H7	0.622	0.188	0.695	1.3
H9A	0.565	-0.146	0.366	1.2
H9B	0.592	-0.269	0.443	1.2
H10A	0.597	-0.129	0.223	1.5
H10B	0.598	-0.344	0.260	1.5
H11A	0.651	-0.116	0.257	1.4
H11B	0.651	-0.335	0.282	1.4
H12A	0.651	-0.280	0.474	1.2
H12B	0.681	-0.168	0.433	1.2
H19A	0.522	0.111	0.122	1.6
H19B	0.510	0.247	0.215	1.6
H19C	0.536	0.318	0.138	1.6
H20A	0.725	0.594	0.364	2.3
H20B	0.741	0.400	0.412	2.3
H20C	0.725	0.417	0.281	2.3
H21A	0.711	0.095	0.909	2.0
H21B	0.724	-0.047	0.822	2.0
H21C	0.728	0.173	0.805	2.0
H22A	0.530	0.114	0.789	1.9
H22B	0.514	0.210	0.672	1.9
H22C	0.517	-0.012	0.680	1.9
H3'	0.374	0.086	-0.024	1.0
H7'	0.376	0.314	0.312	1.2
H9A'	0.435	0.657	0.043	1.2
H9B'	0.406	0.778	0.091	1.2
H10A'	0.403	0.631	-0.132	1.5
H10B'	0.403	0.847	-0.098	1.5
H11A'	0.350	0.623	-0.154	1.3
H11B'	0.349	0.841	-0.127	1.3
H12A'	0.348	0.781	0.064	1.2
H12B'	0.318	0.666	-0.008	1.2
H19A'	0.483	0.398	-0.150	2.0
H19B'	0.494	0.270	-0.041	2.0
H19C'	0.470	0.188	-0.147	2.0
H20A'	0.277	-0.095	-0.117	2.2
H20B'	0.261	0.099	-0.088	2.2
H20C'	0.277	0.079	-0.201	2.2
H21A'	0.289	0.406	0.440	2.1
H21B'	0.275	0.546	0.339	2.1
H21C'	0.272	0.325	0.320	2.1
H22A'	0.466	0.362	0.503	1.9
H22B'	0.485	0.301	0.400	1.9
H22C'	0.478	0.517	0.420	1.9
H22BA	0.528	0.018	0.769	1.9
H22BB	0.521	0.230	0.730	1.9
H22BC	0.512	0.066	0.641	1.9
H19BA'	0.480	0.168	-0.083	1.6
H19BB'	0.471	0.316	-0.184	1.6
H19BC'	0.496	0.372	-0.071	1.6
H22BA'	0.466	0.445	0.497	1.9
H22BB'	0.479	0.266	0.438	1.9
H22BC'	0.484	0.469	0.388	1.9

The parameters of the hydrogen atoms were not refined.

Table 52. Final Anisotropic Thermal Parameters (U's) for Sb-6 at **115 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.014(1)	0.013(1)	0.014(1)	0.001(1)	0.0008(9)	0.001(1)
O2	0.015(1)	0.017(1)	0.026(1)	0.004(1)	0.003(1)	-0.001(1)
O3	0.013(1)	0.019(1)	0.029(1)	-0.006(1)	0.0107(9)	0.000(1)
O4	0.016(1)	0.024(1)	0.032(1)	0.006(1)	0.0131(9)	0.001(1)
O5	0.013(1)	0.042(2)	0.013(1)	0.003(1)	0.0003(9)	-0.004(1)
O6	0.012(1)	0.051(2)	0.019(1)	0.003(1)	0.004(1)	-0.007(1)
O7	0.015(1)	0.028(1)	0.016(1)	-0.002(1)	0.0090(9)	-0.002(1)
O8	0.015(1)	0.035(2)	0.017(1)	-0.004(1)	0.0024(9)	0.002(1)
C1	0.008(1)	0.014(2)	0.012(1)	0.001(1)	0.001(1)	0.000(1)
C2	0.012(2)	0.016(2)	0.010(1)	-0.000(1)	0.005(1)	0.001(1)
C3	0.015(2)	0.014(2)	0.014(2)	0.001(2)	0.005(1)	0.001(1)
C4	0.015(2)	0.016(2)	0.010(1)	-0.000(2)	0.005(1)	-0.001(1)
C5	0.009(1)	0.016(2)	0.012(1)	0.000(1)	0.003(1)	0.001(1)
C6	0.016(2)	0.015(2)	0.012(2)	-0.003(2)	0.005(1)	0.002(1)
C7	0.016(2)	0.016(2)	0.013(2)	-0.003(2)	0.004(1)	0.000(1)
C8	0.017(2)	0.013(2)	0.011(1)	-0.000(2)	0.005(1)	0.001(1)
C9	0.014(2)	0.014(2)	0.016(2)	-0.002(2)	0.003(1)	0.002(1)
C10	0.020(2)	0.016(2)	0.017(2)	0.001(2)	0.003(1)	-0.004(2)
C11	0.020(2)	0.016(2)	0.015(2)	0.000(2)	0.006(1)	-0.000(2)
C12	0.016(2)	0.011(2)	0.018(2)	0.006(1)	0.005(1)	-0.000(1)
C15	0.011(2)	0.014(2)	0.017(2)	-0.001(1)	0.008(1)	0.003(1)
C16	0.015(2)	0.018(2)	0.014(2)	-0.000(2)	0.004(1)	0.001(2)
C17	0.016(2)	0.015(2)	0.015(2)	0.000(2)	0.004(1)	-0.003(1)
C18	0.017(2)	0.011(2)	0.015(2)	0.000(2)	0.005(1)	0.002(2)
C19	0.017(2)	0.020(2)	0.019(2)	0.003(2)	-0.004(1)	0.004(2)
C20	0.018(2)	0.030(2)	0.038(2)	-0.008(2)	0.017(1)	0.005(2)
C21	0.011(2)	0.042(2)	0.017(2)	0.007(2)	-0.003(1)	-0.002(2)
C22	0.015(2)	0.031(2)	0.022(2)	-0.002(2)	0.015(1)	0.000(2)
O1'	0.015(1)	0.015(1)	0.020(1)	0.002(1)	0.0105(9)	0.001(1)
O2'	0.018(1)	0.018(1)	0.029(1)	0.006(1)	0.008(1)	0.004(1)
O3'	0.013(1)	0.019(1)	0.027(1)	-0.004(1)	-0.003(1)	-0.004(1)
O4'	0.017(1)	0.021(1)	0.024(1)	0.003(1)	-0.003(1)	-0.001(1)
O5'	0.013(1)	0.044(2)	0.016(1)	0.007(1)	0.0076(9)	0.006(1)
O6'	0.013(1)	0.047(2)	0.020(1)	0.003(1)	0.003(1)	0.005(1)
O7'	0.012(1)	0.030(1)	0.013(1)	-0.003(1)	0.0002(9)	0.002(1)
O8'	0.012(1)	0.024(1)	0.020(1)	-0.001(1)	0.0046(9)	-0.001(1)
C1'	0.009(1)	0.012(2)	0.013(1)	0.001(1)	0.003(1)	-0.001(1)
C2'	0.012(2)	0.013(2)	0.011(1)	-0.003(1)	0.003(1)	-0.003(1)
C3'	0.014(2)	0.015(2)	0.008(1)	-0.002(1)	0.003(1)	0.001(1)
C4'	0.014(2)	0.014(2)	0.012(1)	-0.000(1)	0.004(1)	-0.000(1)
C5'	0.008(1)	0.015(2)	0.013(1)	0.002(1)	0.002(1)	0.001(1)
C6'	0.016(2)	0.016(2)	0.013(2)	-0.001(2)	0.004(1)	-0.000(1)
C7'	0.013(2)	0.019(2)	0.012(1)	-0.002(2)	0.004(1)	0.000(2)
C8'	0.008(1)	0.018(2)	0.014(2)	-0.001(1)	0.003(1)	-0.000(2)
C9'	0.013(2)	0.014(2)	0.016(2)	-0.001(1)	0.005(1)	-0.001(1)
C10'	0.020(2)	0.015(2)	0.018(2)	0.001(2)	0.007(1)	0.004(2)
C11'	0.015(2)	0.016(2)	0.015(2)	0.002(2)	0.005(1)	0.002(2)
C12'	0.014(2)	0.015(2)	0.014(2)	0.002(2)	0.006(1)	0.002(1)
C15'	0.013(2)	0.014(2)	0.016(2)	-0.004(1)	0.001(1)	-0.001(1)
C16'	0.016(2)	0.018(2)	0.012(2)	-0.005(2)	0.006(1)	-0.003(1)
C17'	0.019(2)	0.017(2)	0.011(1)	0.000(2)	0.004(1)	0.002(1)
C18'	0.015(2)	0.013(2)	0.012(1)	0.001(2)	0.000(1)	-0.001(1)
C19'	0.022(2)	0.023(2)	0.030(2)	0.005(2)	0.019(1)	0.002(2)
C20'	0.015(2)	0.030(2)	0.030(2)	-0.008(2)	-0.006(2)	-0.004(2)
C21'	0.017(2)	0.044(3)	0.016(2)	0.007(2)	0.013(1)	0.003(2)
C22'	0.012(2)	0.034(2)	0.017(2)	-0.002(2)	-0.005(1)	-0.000(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 53. Interatomic Distances (Å) for Sb-6 at **115 K**

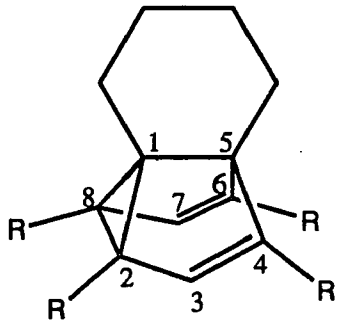
		Unprimed	Primed
O1	C15	1.332(4)	1.334(4)
O1	C19	1.446(4)	1.458(4)
O2	C15	1.209(4)	1.208(4)
O3	C16	1.350(4)	1.343(4)
O3	C20	1.450(4)	1.456(4)
O4	C16	1.202(4)	1.202(4)
O5	C17	1.337(4)	1.340(4)
O5	C21	1.453(4)	1.457(4)
O6	C17	1.206(4)	1.203(4)
O7	C18	1.345(4)	1.334(4)
O7	C22	1.458(4)	1.457(4)
O8	C18	1.202(4)	1.212(4)
C1	C2	1.491(5)	1.490(5)
C1	C5	1.559(4)	1.561(4)
C1	C8	1.525(5)	1.517(4)
C1	C9	1.497(5)	1.501(5)
C2	C3	1.476(5)	1.468(4)
C2	C8	1.638(4)	1.652(4)
C2	C15	1.497(4)	1.502(5)
C3	C4	1.340(5)	1.335(5)
C3	C7	3.060(5)	3.066(4)
C4	C5	1.528(5)	1.526(5)
C4	C6	2.360(5)	2.356(5)
C4	C16	1.482(5)	1.487(4)
C5	C6	1.532(4)	1.532(5)
C5	C12	1.522(5)	1.524(5)
C6	C7	1.341(5)	1.333(4)
C6	C17	1.480(4)	1.481(5)
C7	C8	1.467(4)	1.472(5)
C8	C18	1.493(5)	1.484(4)
C9	C10	1.536(5)	1.533(4)
C10	C11	1.559(5)	1.562(5)
C11	C12	1.532(4)	1.542(5)

Table 54. Angles (°) for Sb-6 at **115 K**

			Unprimed	Primed
C15	O1	C19	115.3(3)	115.6(3)
C16	O3	C20	114.9(3)	114.4(3)
C17	O5	C21	115.1(3)	114.6(2)
C18	O7	C22	115.1(2)	116.8(3)
C2	C1	C5	104.5(3)	104.5(3)
C2	C1	C8	65.8(2)	66.7(2)
C2	C1	C9	128.0(3)	127.4(3)
C5	C1	C8	104.0(2)	104.1(3)
C5	C1	C9	116.3(3)	116.2(3)
C8	C1	C9	127.3(3)	127.3(3)
C1	C2	C3	107.7(3)	107.8(3)
C1	C2	C8	58.1(2)	57.5(2)
C1	C2	C15	127.0(3)	127.7(3)
C3	C2	C8	117.5(2)	117.7(3)
C3	C2	C15	115.1(3)	115.7(3)
C8	C2	C15	119.6(3)	118.3(2)
C2	C3	C4	111.0(3)	111.2(3)
C3	C4	C5	110.3(3)	110.5(3)
C3	C4	C16	124.9(3)	125.5(3)
C5	C4	C6	39.6(2)	39.7(2)
C5	C4	C16	124.8(3)	124.0(3)
C1	C5	C4	103.0(3)	102.8(3)
C1	C5	C6	102.6(3)	102.6(2)
C1	C5	C12	111.5(3)	111.6(3)
C4	C5	C6	100.9(3)	100.8(3)
C4	C5	C12	117.4(3)	117.9(2)
C6	C5	C12	119.2(3)	118.8(3)
C4	C6	C5	39.5(2)	39.5(2)
C5	C6	C7	111.5(3)	111.5(3)
C5	C6	C17	122.3(3)	122.6(3)
C7	C6	C17	125.3(3)	125.1(3)
C6	C7	C8	110.8(3)	110.9(3)
C1	C8	C2	56.1(2)	55.9(2)
C1	C8	C7	107.4(3)	107.5(3)
C1	C8	C18	120.8(3)	121.9(3)
C2	C8	C7	120.3(3)	119.8(3)
C2	C8	C18	112.5(2)	114.2(3)
C7	C8	C18	122.2(3)	120.9(3)
C1	C9	C10	108.9(3)	108.3(3)
C9	C10	C11	113.6(3)	113.9(3)
C10	C11	C12	113.2(3)	113.0(2)
C5	C12	C11	108.9(3)	109.0(3)
O1	C15	O2	124.4(3)	124.2(3)
O1	C15	C2	111.7(3)	111.9(3)
O2	C15	C2	123.4(3)	123.6(3)
O3	C16	O4	123.3(3)	124.0(3)
O3	C16	C4	111.4(3)	111.3(3)
O4	C16	C4	125.2(3)	124.7(3)
O5	C17	O6	123.3(3)	124.3(3)
O5	C17	C6	112.4(3)	110.9(3)
O6	C17	C6	124.3(3)	124.8(3)
O7	C18	O8	124.6(3)	124.1(3)
O7	C18	C8	110.5(2)	111.5(3)
O8	C18	C8	124.9(3)	124.4(3)

Table 55. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-6 at **115 K**

	Unprimed			Primed		
Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O1	0.110	0.118	0.125	0.088	0.121	0.159
O2	0.110	0.140	0.164	0.110	0.139	0.179
O3	0.080	0.145	0.177	0.094	0.145	0.175
O4	0.089	0.160	0.190	0.115	0.145	0.171
O5	0.107	0.116	0.208	0.087	0.130	0.215
O6	0.103	0.135	0.229	0.111	0.137	0.220
O7	0.087	0.142	0.170	0.106	0.118	0.174
O8	0.118	0.130	0.191	0.103	0.141	0.158
C1	0.089	0.109	0.118	0.084	0.112	0.117
C2	0.080	0.117	0.126	0.096	0.101	0.129
C3	0.101	0.117	0.132	0.084	0.114	0.129
C4	0.085	0.123	0.130	0.101	0.118	0.122
C5	0.093	0.109	0.128	0.085	0.113	0.125
C6	0.091	0.124	0.136	0.108	0.126	0.131
C7	0.108	0.122	0.137	0.100	0.119	0.139
C8	0.091	0.116	0.135	0.088	0.120	0.135
C9	0.103	0.124	0.132	0.102	0.115	0.135
C10	0.110	0.139	0.145	0.108	0.128	0.156
C11	0.111	0.128	0.145	0.107	0.119	0.142
C12	0.083	0.129	0.144	0.098	0.114	0.140
C15	0.074	0.120	0.142	0.098	0.126	0.130
C16	0.112	0.126	0.133	0.096	0.115	0.151
C17	0.107	0.126	0.135	0.097	0.130	0.138
C18	0.102	0.117	0.134	0.105	0.114	0.128
C19	0.097	0.149	0.161	0.086	0.151	0.202
C20	0.071	0.185	0.207	0.090	0.181	0.189
C21	0.089	0.139	0.211	0.065	0.153	0.216
C22	0.059	0.173	0.179	0.086	0.152	0.186



R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Table 8–56. X-ray Crystal Data for Sb-6 at **153 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	117–118
Crystal size (mm)	0.21 x 0.25 x 0.33
Crystal system	monoclinic
Space group	*P2/n*
a (Å)	41.364(2)
b (Å)	7.341(1)
c (Å)	12.140(1)
β (°)	98.07(1)
Cell volume (Å^3)	3649.91(2.74)
Z	8
d_{calc} (g cm^{-3})	1.421
μ(Cu $K\alpha$) (cm^{-1})	8.86
Maximum θ(°)	60
Unique reflections	5419
Observed reflections [$I > 3.0\sigma(I)$]	3465
Number of variables	505
R	0.047
R_w	0.055
$(\Delta\rho)_{max}$ (e Å^{-3})	0.25
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.28

Table 57. Final Atomic Parameters for Sb-6 at 153 K

Atom	x	y	z	B(Å^2)
O1	0.55512(5)	0.1475(3)	0.2603(2)	1.43(5)
O2	0.55582(6)	0.4180(3)	0.3475(2)	2.18(5)
O3	0.69174(5)	0.4030(4)	0.3894(2)	2.07(5)
O4	0.70569(6)	0.1132(4)	0.3621(2)	2.60(6)
O5	0.68215(6)	0.0803(4)	0.7601(2)	2.48(6)
O6	0.70732(6)	0.0297(4)	0.6123(2)	3.04(6)
O7	0.56033(5)	0.1191(4)	0.6695(2)	2.06(5)
O8	0.53666(6)	0.0935(4)	0.4914(2)	2.46(6)
C1	0.60532(8)	0.0052(5)	0.4385(3)	1.23(7)
C2	0.59699(8)	0.1987(5)	0.4083(3)	1.32(7)
C3	0.62729(8)	0.2901(5)	0.3894(3)	1.44(7)
C4	0.65290(8)	0.1790(5)	0.4088(3)	1.43(7)
C5	0.64334(8)	0.0023(5)	0.4637(3)	1.25(7)
C6	0.64953(8)	0.0559(5)	0.5872(3)	1.52(7)
C7	0.62295(8)	0.1305(5)	0.6203(3)	1.53(7)
C8	0.59476(8)	0.1179(5)	0.5333(3)	1.36(7)
C9	0.58929(8)	-0.1642(5)	0.3879(3)	1.61(7)
C10	0.60519(9)	-0.2148(5)	0.2847(3)	1.91(8)
C11	0.64307(9)	-0.2118(5)	0.3052(3)	1.71(7)
C12	0.65731(8)	-0.1747(5)	0.4268(3)	1.51(7)
C15	0.56662(8)	0.2669(5)	0.3392(3)	1.50(7)
C16	0.68625(8)	0.2223(5)	0.3861(3)	1.61(7)
C17	0.68269(8)	0.0523(5)	0.6521(3)	1.58(7)
C18	0.56070(8)	0.1089(5)	0.5595(3)	1.61(7)
C19	0.52875(9)	0.2128(5)	0.1789(3)	1.99(8)
C20	0.72317(9)	0.4584(6)	0.3603(3)	2.94(9)
C21	0.71355(9)	0.0738(6)	0.8294(3)	2.62(9)
C22	0.52806(9)	0.1078(6)	0.7048(3)	2.40(8)
O1'	0.44779(5)	0.3608(3)	-0.0507(2)	1.79(5)
O2'	0.44716(6)	0.0957(4)	0.0410(2)	2.38(6)
O3'	0.31000(6)	0.0964(4)	-0.0606(2)	2.24(5)
O4'	0.29627(6)	0.3850(4)	-0.1063(2)	2.39(6)
O5'	0.31770(6)	0.4212(4)	0.3167(2)	2.65(6)
O6'	0.29187(6)	0.4642(4)	0.1435(2)	2.87(6)
O7'	0.43826(6)	0.3730(4)	0.3513(2)	2.18(6)
O8'	0.46264(5)	0.4445(4)	0.2027(2)	1.97(5)
C1'	0.39500(7)	0.5012(5)	0.0744(3)	1.13(7)
C2'	0.40424(8)	0.3111(5)	0.0510(3)	1.44(7)
C3'	0.37476(8)	0.2139(5)	0.0026(3)	1.40(7)
C4'	0.34860(8)	0.3217(5)	-0.0033(3)	1.51(7)
C5'	0.35703(7)	0.4997(5)	0.0602(3)	1.17(7)
C6'	0.34994(8)	0.4427(5)	0.1756(3)	1.56(7)
C7'	0.37633(8)	0.3731(5)	0.2362(3)	1.46(7)
C8'	0.40507(8)	0.3926(5)	0.1796(3)	1.54(7)
C9'	0.41038(8)	0.6739(5)	0.0392(3)	1.50(7)
C10'	0.39518(9)	0.7192(5)	-0.0797(3)	1.74(7)
C11'	0.35723(9)	0.7164(5)	-0.0979(3)	1.72(7)
C12'	0.34256(8)	0.6765(5)	0.0092(3)	1.55(7)
C15'	0.43551(8)	0.2438(5)	0.0168(3)	1.57(7)
C16'	0.31542(8)	0.2761(5)	-0.0606(3)	1.56(7)
C17'	0.31672(8)	0.4437(5)	0.2073(3)	1.59(7)
C18'	0.43847(8)	0.4073(5)	0.2434(3)	1.44(7)
C19'	0.47597(9)	0.2989(6)	-0.0995(3)	2.52(8)
C20'	0.27879(9)	0.0391(6)	-0.1219(3)	2.79(9)
C21'	0.28591(9)	0.4250(6)	0.3559(3)	2.57(9)
C22'	0.46915(9)	0.3883(6)	0.4237(3)	2.27(8)

Table 57 (cont.). Final Atomic Parameters for Sb-6 at 153 K

Atom	x	y	z	B(Å^2)
H3	0.628	0.420	0.366	1.2
H7	0.622	0.188	0.695	1.3
H9A	0.565	-0.146	0.366	1.3
H9B	0.593	-0.269	0.443	1.3
H10A	0.597	-0.130	0.224	1.5
H10B	0.598	-0.344	0.260	1.5
H11A	0.651	-0.116	0.257	1.4
H11B	0.651	-0.335	0.282	1.4
H12A	0.651	-0.280	0.474	1.3
H12B	0.681	-0.168	0.433	1.3
H19A	0.522	0.111	0.122	1.7
H19B	0.510	0.247	0.215	1.7
H19C	0.536	0.318	0.138	1.7
H20A	0.725	0.593	0.364	2.4
H20B	0.741	0.400	0.411	2.4
H20C	0.725	0.418	0.281	2.4
H21A	0.711	0.095	0.909	2.1
H21B	0.724	-0.047	0.822	2.1
H21C	0.728	0.173	0.805	2.1
H22A	0.530	0.114	0.788	1.9
H22B	0.514	0.209	0.672	1.9
H22C	0.517	-0.012	0.680	1.9
H3'	0.374	0.087	-0.024	1.1
H7'	0.376	0.315	0.312	1.3
H9A'	0.435	0.658	0.043	1.2
H9B'	0.406	0.778	0.091	1.2
H10A'	0.403	0.631	-0.131	1.5
H10B'	0.403	0.847	-0.098	1.5
H11A'	0.350	0.623	-0.154	1.3
H11B'	0.349	0.841	-0.127	1.3
H12A'	0.348	0.781	0.064	1.2
H12B'	0.318	0.666	-0.008	1.2
H19A'	0.483	0.397	-0.150	2.1
H19B'	0.494	0.270	-0.041	2.1
H19C'	0.469	0.189	-0.147	2.1
H20A'	0.277	-0.095	-0.117	2.2
H20B'	0.261	0.099	-0.088	2.2
H20C'	0.277	0.079	-0.201	2.2
H21A'	0.289	0.406	0.440	2.2
H21B'	0.275	0.546	0.339	2.2
H21C'	0.272	0.326	0.320	2.2
H22A'	0.466	0.362	0.503	1.9
H22B'	0.485	0.302	0.400	1.9
H22C'	0.478	0.516	0.420	1.9
H22BA	0.528	0.018	0.769	1.9
H22BB	0.521	0.230	0.730	1.9
H22BC	0.512	0.066	0.641	1.9
H19BA'	0.480	0.168	-0.083	2.1
H19BB'	0.471	0.316	-0.184	2.1
H19BC'	0.496	0.372	-0.071	2.1
H22BA'	0.466	0.445	0.497	1.9
H22BB'	0.479	0.266	0.438	1.9
H22BC'	0.484	0.469	0.388	1.9

The parameters of the hydrogen atoms were not refined.

Table 58. Final Anisotropic Thermal Parameters (U's) for Sb-6 at **153 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.018(1)	0.017(1)	0.020(1)	0.002(1)	0.0018(9)	0.000(1)
O2	0.024(1)	0.020(1)	0.038(1)	0.007(1)	0.003(1)	-0.003(1)
O3	0.017(1)	0.024(1)	0.040(1)	-0.008(1)	0.014(1)	-0.000(1)
O4	0.022(1)	0.033(2)	0.048(1)	0.008(1)	0.019(1)	0.001(1)
O5	0.022(1)	0.055(2)	0.017(1)	0.007(1)	0.001(1)	-0.005(1)
O6	0.016(1)	0.073(2)	0.026(1)	0.001(1)	0.005(1)	-0.010(2)
O7	0.019(1)	0.040(2)	0.021(1)	-0.002(1)	0.009(1)	-0.003(1)
O8	0.019(1)	0.050(2)	0.025(1)	-0.004(1)	0.005(1)	0.004(1)
C1	0.013(2)	0.018(2)	0.016(2)	0.000(2)	0.002(1)	0.003(2)
C2	0.014(2)	0.020(2)	0.017(2)	0.000(2)	0.004(1)	0.000(2)
C3	0.017(2)	0.017(2)	0.021(2)	0.000(2)	0.005(1)	-0.001(2)
C4	0.018(2)	0.020(2)	0.017(2)	-0.000(2)	0.005(1)	-0.001(2)
C5	0.013(2)	0.019(2)	0.015(2)	-0.001(2)	0.003(1)	0.003(2)
C6	0.022(2)	0.021(2)	0.016(2)	-0.001(2)	0.004(1)	0.000(2)
C7	0.020(2)	0.022(2)	0.017(2)	-0.004(2)	0.006(1)	-0.001(2)
C8	0.017(2)	0.021(2)	0.015(2)	-0.000(2)	0.007(1)	0.002(2)
C9	0.020(2)	0.017(2)	0.024(2)	-0.001(2)	0.001(1)	0.001(2)
C10	0.030(2)	0.022(2)	0.020(2)	0.003(2)	-0.001(2)	-0.003(2)
C11	0.027(2)	0.018(2)	0.021(2)	0.004(2)	0.007(1)	-0.000(2)
C12	0.022(2)	0.017(2)	0.020(2)	0.004(2)	0.006(1)	0.001(2)
C15	0.015(2)	0.020(2)	0.024(2)	-0.003(2)	0.009(1)	0.004(2)
C16	0.020(2)	0.024(2)	0.019(2)	-0.002(2)	0.006(1)	0.002(2)
C17	0.019(2)	0.020(2)	0.021(2)	-0.000(2)	0.004(1)	0.000(2)
C18	0.019(2)	0.022(2)	0.021(2)	-0.003(2)	0.005(1)	-0.002(2)
C19	0.019(2)	0.025(2)	0.030(2)	0.003(2)	-0.003(2)	0.006(2)
C20	0.021(2)	0.043(3)	0.052(2)	-0.013(2)	0.020(2)	0.005(2)
C21	0.022(2)	0.054(3)	0.022(2)	0.008(2)	-0.006(2)	-0.005(2)
C22	0.021(2)	0.041(2)	0.034(2)	-0.004(2)	0.020(1)	0.002(2)
O1'	0.024(1)	0.021(1)	0.026(1)	0.005(1)	0.014(1)	0.002(1)
O2'	0.025(1)	0.024(1)	0.045(1)	0.009(1)	0.014(1)	0.009(1)
O3'	0.018(1)	0.025(1)	0.039(1)	-0.007(1)	-0.005(1)	-0.002(1)
O4'	0.024(1)	0.029(2)	0.034(1)	0.006(1)	-0.007(1)	0.000(1)
O5'	0.016(1)	0.063(2)	0.023(1)	0.009(1)	0.008(1)	0.007(1)
O6'	0.019(1)	0.065(2)	0.025(1)	0.002(1)	0.005(1)	0.011(1)
O7'	0.018(1)	0.045(2)	0.019(1)	-0.005(1)	-0.000(1)	0.002(1)
O8'	0.014(1)	0.034(2)	0.028(1)	-0.003(1)	0.005(1)	-0.001(1)
C1'	0.011(1)	0.016(2)	0.017(2)	-0.002(2)	0.005(1)	-0.002(2)
C2'	0.015(2)	0.018(2)	0.022(2)	-0.002(2)	0.004(1)	-0.002(2)
C3'	0.020(2)	0.017(2)	0.016(2)	-0.001(2)	0.004(1)	0.000(2)
C4'	0.016(2)	0.021(2)	0.021(2)	-0.000(2)	0.004(1)	-0.001(2)
C5'	0.013(2)	0.017(2)	0.016(2)	0.001(2)	0.005(1)	-0.001(1)
C6'	0.019(2)	0.021(2)	0.020(2)	0.000(2)	0.006(1)	0.001(2)
C7'	0.017(2)	0.021(2)	0.018(2)	-0.003(2)	0.004(1)	-0.002(2)
C8'	0.012(2)	0.026(2)	0.021(2)	-0.002(2)	0.003(1)	-0.000(2)
C9'	0.020(2)	0.015(2)	0.024(2)	-0.003(2)	0.009(1)	-0.001(2)
C10'	0.027(2)	0.019(2)	0.022(2)	0.001(2)	0.010(1)	0.004(2)
C11'	0.026(2)	0.018(2)	0.023(2)	0.002(2)	0.010(1)	0.004(2)
C12'	0.020(2)	0.020(2)	0.019(2)	0.004(2)	0.006(1)	0.002(2)
C15'	0.018(2)	0.021(2)	0.020(2)	-0.004(2)	0.001(1)	-0.002(2)
C16'	0.017(2)	0.024(2)	0.019(2)	-0.002(2)	0.006(1)	-0.004(2)
C17'	0.020(2)	0.022(2)	0.019(2)	0.002(2)	0.006(1)	0.006(2)
C18'	0.018(2)	0.018(2)	0.018(2)	0.002(2)	0.003(1)	-0.001(2)
C19'	0.028(2)	0.033(2)	0.040(2)	0.006(2)	0.023(2)	0.002(2)
C20'	0.020(2)	0.037(3)	0.046(2)	-0.010(2)	-0.008(2)	-0.009(2)
C21'	0.023(2)	0.055(3)	0.024(2)	0.008(2)	0.014(1)	0.007(2)
C22'	0.020(2)	0.036(2)	0.028(2)	-0.004(2)	-0.004(2)	-0.006(2)

The form of the anisotropic displacement parameter is:
$\exp(-2p^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)])$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 59. Interatomic Distances (Å) for Sb-6 at **153 K**

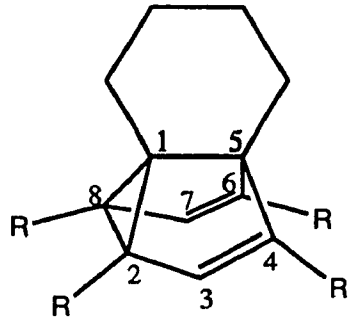
		Unprimed	Primed
O1	C15	1.336(4)	1.335(4)
O1	C19	1.447(4)	1.453(5)
O2	C15	1.205(4)	1.209(4)
O3	C16	1.346(5)	1.338(5)
O3	C20	1.453(5)	1.459(4)
O4	C16	1.199(5)	1.205(4)
O5	C17	1.330(4)	1.333(4)
O5	C21	1.446(4)	1.460(5)
O6	C17	1.198(4)	1.207(4)
O7	C18	1.340(4)	1.335(4)
O7	C22	1.460(4)	1.449(4)
O8	C18	1.206(4)	1.207(4)
C1	C2	1.496(5)	1.485(5)
C1	C5	1.560(4)	1.556(4)
C1	C8	1.529(5)	1.513(5)
C1	C9	1.499(5)	1.507(5)
C2	C3	1.468(5)	1.463(5)
C2	C8	1.644(5)	1.667(5)
C2	C15	1.495(4)	1.497(5)
C3	C4	1.331(5)	1.334(5)
C3	C4	3.067(5)	3.059(5)
C4	C5	1.536(5)	1.532(5)
C4	C6	2.369(5)	2.340(5)
C4	C16	1.479(5)	1.487(5)
C5	C6	1.536(4)	1.530(5)
C5	C12	1.515(5)	1.523(5)
C6	C7	1.340(5)	1.330(5)
C6	C17	1.483(4)	1.478(5)
C7	C8	1.463(4)	1.461(5)
C8	C18	1.489(5)	1.490(4)
C9	C10	1.541(5)	1.527(5)
C10	C11	1.552(5)	1.555(5)
C11	C12	1.535(5)	1.538(5)

Table 60. Angles (°) for Sb-6 at **153 K**

			Unprimed	Primed
C15	O1	C19	115.5(3)	116.4(3)
C16	O3	C20	114.9(3)	114.9(3)
C17	O5	C21	115.5(3)	114.8(2)
C18	O7	C22	115.3(2)	117.0(3)
C2	C1	C5	104.6(3)	104.8(3)
C2	C1	C8	65.8(2)	67.5(2)
C2	C1	C9	127.9(3)	127.3(3)
C5	C1	C8	104.3(2)	104.1(3)
C5	C1	C9	116.4(3)	115.7(3)
C8	C1	C9	126.9(3)	127.3(3)
C1	C2	C3	107.5(3)	108.2(3)
C1	C2	C8	58.1(2)	57.0(2)
C1	C2	C15	127.0(3)	128.2(3)
C3	C2	C8	117.9(3)	117.2(3)
C3	C2	C15	115.4(3)	115.6(3)
C8	C2	C15	119.1(3)	118.3(3)
C2	C3	C4	111.6(3)	110.9(3)
C3	C4	C5	110.3(3)	110.7(3)
C3	C4	C16	125.2(3)	125.5(3)
C5	C4	C6	39.6(2)	40.1(2)
C5	C4	C16	124.5(3)	123.8(3)
C1	C5	C4	102.5(3)	102.5(3)
C1	C5	C6	102.3(3)	102.7(2)
C1	C5	C12	111.7(3)	111.8(3)
C4	C5	C6	100.9(3)	99.7(3)
C4	C5	C12	117.7(3)	118.3(3)
C6	C5	C12	119.4(3)	119.3(3)
C4	C6	C5	39.5(2)	40.2(2)
C5	C6	C7	111.5(3)	111.3(3)
C5	C6	C17	121.9(3)	122.8(3)
C7	C6	C17	125.8(3)	125.4(3)
C6	C7	C8	111.2(3)	111.2(3)
C1	C8	C2	56.1(2)	55.4(2)
C1	C8	C7	107.1(3)	107.6(3)
C1	C8	C18	121.0(3)	121.7(3)
C2	C8	C7	120.1(3)	119.6(3)
C2	C8	C18	113.0(3)	114.1(3)
C7	C8	C18	122.0(3)	121.2(3)
C1	C9	C10	108.6(3)	108.5(3)
C9	C10	C11	113.7(3)	113.9(3)
C10	C11	C12	113.5(3)	113.1(3)
C5	C12	C11	109.0(3)	109.0(3)
O1	C15	O2	124.4(3)	123.7(3)
O1	C15	C2	111.7(3)	112.1(3)
O2	C15	C2	123.6(3)	124.0(3)
O3	C16	O4	123.3(3)	123.7(3)
O3	C16	C4	111.3(3)	111.4(3)
O4	C16	C4	125.2(3)	124.8(3)
O5	C17	O6	123.5(3)	124.0(3)
O5	C17	C6	112.3(3)	111.1(3)
O6	C17	C6	124.3(3)	124.9(3)
O7	C18	O8	124.4(3)	124.4(3)
O7	C18	C8	110.7(3)	111.3(3)
O8	C18	C8	124.8(3)	124.3(3)

Table 61. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-6 at **153 K**

	Unprimed			Primed		
Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O1	0.122	0.138	0.143	0.110	0.142	0.189
O2	0.122	0.168	0.199	0.124	0.153	0.227
O3	0.089	0.166	0.207	0.109	0.171	0.210
O4	0.105	0.186	0.230	0.128	0.174	0.210
O5	0.128	0.142	0.240	0.108	0.154	0.256
O6	0.123	0.157	0.275	0.135	0.152	0.260
O7	0.113	0.158	0.202	0.125	0.146	0.214
O8	0.130	0.158	0.227	0.113	0.166	0.186
C1	0.114	0.117	0.141	0.093	0.120	0.142
C2	0.111	0.134	0.140	0.117	0.131	0.154
C3	0.124	0.133	0.147	0.125	0.130	0.144
C4	0.122	0.139	0.142	0.124	0.141	0.148
C5	0.108	0.120	0.146	0.101	0.129	0.132
C6	0.123	0.141	0.151	0.126	0.142	0.153
C7	0.116	0.136	0.161	0.124	0.131	0.152
C8	0.101	0.140	0.147	0.107	0.144	0.162
C9	0.129	0.137	0.161	0.115	0.127	0.166
C10	0.132	0.148	0.183	0.119	0.143	0.177
C11	0.125	0.142	0.170	0.123	0.138	0.177
C12	0.121	0.132	0.159	0.122	0.133	0.162
C15	0.091	0.148	0.165	0.121	0.144	0.156
C16	0.121	0.149	0.156	0.118	0.134	0.165
C17	0.137	0.140	0.147	0.117	0.138	0.166
C18	0.129	0.138	0.159	0.127	0.137	0.141
C19	0.118	0.161	0.190	0.105	0.180	0.229
C20	0.080	0.222	0.237	0.104	0.203	0.233
C21	0.117	0.168	0.240	0.102	0.170	0.242
C22	0.082	0.204	0.207	0.123	0.178	0.199



R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Table 8–62. X-ray Crystal Data for Sb-6 at **181 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	117–118
Crystal size (mm)	0.32 x 0.50 x 0.64
Crystal system	monoclinic
Space group	*P2/n*
a (Å)	41.388(2)
b (Å)	7.358(3)
c (Å)	12.163(2)
β (°)	98.11(1)
Cell volume ($Å^3$)	3666.90(4.90)
Z	8
d_{calc} (g cm^{-3})	1.414
μ(Cu $K\alpha$) (cm^{-1})	8.82
Maximum θ(°)	60
Unique reflections	5438
Observed reflections [$I > 3.0\sigma(I)$]	4260
Number of variables	505
R	0.046
R_w	0.060
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.23
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.29

Table 63. Final Atomic Parameters for SB-6 at **181 K**

Atom	x	y	z	B(Å^2)
O1	0.55533(4)	0.1495(2)	0.2609(1)	2.03(3)
O2	0.55595(4)	0.4186(3)	0.3481(2)	2.82(4)
O3	0.69198(4)	0.4030(3)	0.3898(2)	2.64(4)
O4	0.70572(4)	0.1146(3)	0.3626(2)	3.30(4)
O5	0.68203(4)	0.0799(3)	0.7598(1)	3.10(4)
O6	0.70735(4)	0.0305(3)	0.6126(2)	3.82(5)
O7	0.56038(4)	0.1206(3)	0.6685(1)	2.65(4)
O8	0.53698(4)	0.0932(3)	0.4916(1)	3.03(4)
C1	0.60536(5)	0.0080(3)	0.4387(2)	1.61(5)
C2	0.59714(5)	0.2000(3)	0.4088(2)	1.72(5)
C3	0.62741(5)	0.2923(4)	0.3904(2)	1.83(5)
C4	0.65300(5)	0.1803(4)	0.4097(2)	1.79(5)
C5	0.64358(5)	0.0034(4)	0.4644(2)	1.62(5)
C6	0.64978(6)	0.0570(4)	0.5873(2)	1.93(5)
C7	0.62315(6)	0.1306(4)	0.6202(2)	1.98(5)
C8	0.59483(6)	0.1186(4)	0.5329(2)	1.88(5)
C9	0.58953(6)	-0.1619(4)	0.3878(2)	2.02(5)
C10	0.60519(6)	-0.2129(4)	0.2854(2)	2.38(5)
C11	0.64312(6)	-0.2098(4)	0.3059(2)	2.22(5)
C12	0.65737(6)	-0.1727(4)	0.4267(2)	2.04(5)
C15	0.56671(5)	0.2682(4)	0.3398(2)	1.96(5)
C16	0.68653(6)	0.2234(4)	0.3868(2)	2.07(5)
C17	0.68269(6)	0.0548(4)	0.6522(2)	2.11(5)
C18	0.56089(6)	0.1095(4)	0.5594(2)	1.96(5)
C19	0.52879(6)	0.2140(4)	0.1799(2)	2.64(6)
C20	0.72340(6)	0.4592(4)	0.3609(3)	3.48(6)
C21	0.71364(7)	0.0761(5)	0.8294(2)	3.40(7)
C22	0.52834(6)	0.1075(4)	0.7041(2)	3.03(6)
O1'	0.44784(4)	0.3594(2)	-0.0506(1)	2.20(3)
O2'	0.44704(4)	0.0954(3)	0.0409(2)	3.12(4)
O3'	0.30995(4)	0.0965(3)	-0.0608(2)	2.83(4)
O4'	0.29651(4)	0.3837(3)	-0.1061(2)	3.03(4)
O5'	0.31769(4)	0.4201(3)	0.3154(1)	3.23(4)
O6'	0.29189(4)	0.4627(3)	0.1431(2)	3.55(5)
O7'	0.43804(4)	0.3729(3)	0.3508(1)	2.65(4)
O8'	0.46245(4)	0.4440(3)	0.2029(1)	2.62(4)
C1'	0.39511(5)	0.5000(3)	0.0743(2)	1.58(5)
C2'	0.40416(5)	0.3096(4)	0.0506(2)	1.92(5)
C3'	0.37471(6)	0.2131(4)	0.0025(2)	1.77(5)
C4'	0.34846(5)	0.3214(4)	-0.0029(2)	1.83(5)
C5'	0.35690(5)	0.4984(3)	0.0598(2)	1.51(4)
C6'	0.34973(6)	0.4414(4)	0.1746(2)	2.21(5)
C7'	0.37641(6)	0.3717(4)	0.2356(2)	1.88(5)
C8'	0.40506(6)	0.3934(4)	0.1799(2)	1.99(5)
C9'	0.41045(6)	0.6716(4)	0.0390(2)	2.06(5)
C10'	0.39501(6)	0.7182(4)	-0.0797(2)	2.21(5)
C11'	0.35709(6)	0.7146(4)	-0.0976(2)	2.21(5)
C12'	0.34257(6)	0.6737(4)	0.0089(2)	1.92(5)
C15'	0.43564(6)	0.2436(4)	0.0167(2)	2.00(5)
C16'	0.31539(6)	0.2751(4)	-0.0602(2)	2.18(5)
C17'	0.31668(6)	0.4420(4)	0.2066(2)	2.19(5)
C18'	0.43826(6)	0.4057(4)	0.2436(2)	1.95(5)
C19'	0.47599(6)	0.2971(4)	-0.0992(2)	3.08(6)
C20'	0.27888(7)	0.0400(4)	-0.1215(3)	3.54(7)
C21'	0.28643(6)	0.4258(5)	0.3563(2)	3.37(7)
C22'	0.46914(6)	0.3875(4)	0.4230(2)	2.79(6)

Table 63 (cont.). Final Atomic Parameters for SB-6 at **181 K**

Atom	x	y	z	B(Å^2)
H3	0.629	0.422	0.367	2.0
H7	0.623	0.187	0.695	2.2
H9A	0.566	-0.140	0.365	2.2
H9B	0.593	-0.263	0.443	2.2
H10A	0.598	-0.125	0.225	2.6
H10B	0.598	-0.338	0.262	2.6
H11A	0.651	-0.113	0.258	2.4
H11B	0.651	-0.330	0.284	2.4
H12A	0.652	-0.275	0.475	2.2
H12B	0.682	-0.163	0.433	2.2
H19A	0.522	0.116	0.125	2.9
H19B	0.510	0.248	0.218	2.9
H19C	0.536	0.323	0.141	2.9
H20A	0.725	0.595	0.365	3.8
H20B	0.741	0.403	0.414	3.8
H20C	0.725	0.419	0.284	3.8
H21A	0.711	0.096	0.909	3.7
H21B	0.724	-0.045	0.822	3.7
H21C	0.728	0.174	0.805	3.7
H22A	0.531	0.118	0.787	3.3
H22B	0.514	0.208	0.670	3.3
H22C	0.518	-0.012	0.680	3.3
H3'	0.374	0.084	-0.023	1.9
H7'	0.377	0.313	0.310	2.1
H9A'	0.434	0.653	0.041	2.3
H9B'	0.407	0.773	0.090	2.3
H10A'	0.403	0.628	-0.131	2.4
H10B'	0.402	0.843	-0.098	2.4
H11A'	0.350	0.619	-0.154	2.4
H11B'	0.349	0.836	-0.126	2.4
H12A'	0.348	0.776	0.063	2.1
H12B'	0.318	0.661	-0.009	2.1
H19A'	0.483	0.395	-0.148	3.4
H19B'	0.494	0.268	-0.039	3.4
H19C'	0.470	0.186	-0.144	3.4
H20A'	0.277	-0.095	-0.118	3.9
H20B'	0.261	0.098	-0.088	3.9
H20C'	0.278	0.078	-0.201	3.9
H21A'	0.290	0.408	0.439	3.7
H21B'	0.276	0.546	0.338	3.7
H21C'	0.272	0.327	0.320	3.7
H22A'	0.466	0.360	0.501	3.1
H22B'	0.485	0.299	0.398	3.1
H22C'	0.478	0.514	0.419	3.1
H22BA	0.529	0.019	0.767	3.3
H22BB	0.522	0.230	0.730	3.3
H22BC	0.512	0.065	0.641	3.3
H19BA'	0.480	0.164	-0.082	3.4
H19BB'	0.472	0.315	-0.181	3.4
H19BC'	0.496	0.366	-0.065	3.4
H22BA'	0.466	0.444	0.495	3.1
H22BB'	0.479	0.263	0.437	3.1
H22BC'	0.484	0.465	0.387	3.1

The parameters of the hydrogen atoms were not refined.

Table 64. Final Anisotropic Thermal Parameters (U's) for SB-6 at **181 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0207(8)	0.0288(9)	0.0270(8)	0.0025(8)	0.0009(7)	-0.0001(8)
O2	0.0289(9)	0.031(1)	0.047(1)	0.0089(8)	0.0043(8)	-0.0030(9)
O3	0.0206(8)	0.035(1)	0.048(1)	-0.0074(8)	0.0144(7)	0.0023(9)
O4	0.0265(9)	0.044(1)	0.060(1)	0.0080(9)	0.0224(8)	0.003(1)
O5	0.0240(8)	0.070(1)	0.0225(8)	0.009(1)	0.0005(7)	-0.0036(9)
O6	0.0221(9)	0.091(2)	0.0320(9)	0.003(1)	0.0049(8)	-0.013(1)
O7	0.0234(8)	0.052(1)	0.0279(8)	-0.0034(9)	0.0129(7)	-0.0021(9)
O8	0.0210(8)	0.065(1)	0.0298(9)	-0.0054(9)	0.0051(7)	0.002(1)
C1	0.017(1)	0.023(1)	0.021(1)	0.002(1)	0.0029(9)	-0.000(1)
C2	0.019(1)	0.025(1)	0.022(1)	0.002(1)	0.0059(9)	0.002(1)
C3	0.019(1)	0.025(1)	0.026(1)	-0.002(1)	0.0068(9)	-0.002(1)
C4	0.019(1)	0.026(1)	0.024(1)	-0.001(1)	0.0065(9)	-0.001(1)
C5	0.016(1)	0.025(1)	0.022(1)	0.001(1)	0.0039(9)	0.001(1)
C6	0.021(1)	0.030(1)	0.023(1)	-0.002(1)	0.0042(9)	0.001(1)
C7	0.023(1)	0.030(1)	0.023(1)	-0.004(1)	0.0066(9)	-0.001(1)
C8	0.022(1)	0.026(1)	0.025(1)	-0.001(1)	0.0087(9)	0.001(1)
C9	0.026(1)	0.023(1)	0.028(1)	-0.004(1)	0.001(1)	0.003(1)
C10	0.032(1)	0.031(1)	0.026(1)	0.003(1)	0.001(1)	-0.001(1)
C11	0.032(1)	0.026(1)	0.027(1)	0.003(1)	0.007(1)	-0.000(1)
C12	0.024(1)	0.026(1)	0.028(1)	0.003(1)	0.004(1)	0.001(1)
C15	0.017(1)	0.030(1)	0.030(1)	-0.002(1)	0.0105(9)	0.001(1)
C16	0.020(1)	0.035(1)	0.025(1)	-0.001(1)	0.0062(9)	0.002(1)
C17	0.023(1)	0.033(1)	0.024(1)	-0.000(1)	0.004(1)	-0.001(1)
C18	0.021(1)	0.029(1)	0.026(1)	-0.001(1)	0.0084(9)	0.001(1)
C19	0.024(1)	0.038(2)	0.036(1)	0.004(1)	-0.006(1)	0.004(1)
C20	0.024(1)	0.051(2)	0.061(2)	-0.011(1)	0.019(1)	0.007(2)
C21	0.027(1)	0.073(2)	0.027(1)	0.010(2)	-0.005(1)	-0.004(1)
C22	0.027(1)	0.053(2)	0.040(1)	-0.007(1)	0.022(1)	-0.003(1)
O1'	0.0263(8)	0.029(1)	0.0317(8)	0.0041(8)	0.0157(7)	0.0032(8)
O2'	0.0304(9)	0.033(1)	0.058(1)	0.0108(9)	0.0175(8)	0.0075(9)
O3'	0.0217(8)	0.034(1)	0.048(1)	-0.0072(8)	-0.0068(8)	-0.0007(9)
O4'	0.0274(9)	0.041(1)	0.043(1)	0.0070(9)	-0.0086(8)	0.000(1)
O5'	0.0203(8)	0.076(1)	0.0283(9)	0.008(1)	0.0088(7)	0.008(1)
O6'	0.0206(8)	0.083(2)	0.0322(9)	0.005(1)	0.0056(7)	0.011(1)
O7'	0.0202(8)	0.054(1)	0.0254(8)	-0.0036(9)	-0.0012(7)	0.0026(9)
O8'	0.0175(8)	0.049(1)	0.0330(9)	-0.0017(9)	0.0049(7)	0.0010(9)
C1'	0.017(1)	0.023(1)	0.020(1)	-0.001(1)	0.0056(9)	-0.001(1)
C2'	0.016(1)	0.025(1)	0.032(1)	0.001(1)	0.006(1)	-0.001(1)
C3'	0.020(1)	0.027(1)	0.021(1)	-0.003(1)	0.0045(9)	0.001(1)
C4'	0.017(1)	0.027(1)	0.026(1)	-0.001(1)	0.003(1)	-0.001(1)
C5'	0.015(1)	0.022(1)	0.020(1)	0.001(1)	0.0044(9)	-0.002(1)
C6'	0.022(1)	0.036(2)	0.027(1)	-0.000(1)	0.007(1)	0.002(1)
C7'	0.020(1)	0.032(1)	0.020(1)	-0.001(1)	0.0045(9)	0.001(1)
C8'	0.018(1)	0.032(1)	0.026(1)	-0.001(1)	0.0034(9)	0.003(1)
C9'	0.023(1)	0.026(1)	0.031(1)	-0.002(1)	0.008(1)	-0.002(1)
C10'	0.030(1)	0.027(1)	0.029(1)	0.003(1)	0.013(1)	0.003(1)
C11'	0.028(1)	0.030(1)	0.027(1)	0.003(1)	0.007(1)	0.003(1)
C12'	0.023(1)	0.023(1)	0.027(1)	0.003(1)	0.007(1)	0.001(1)
C15'	0.017(1)	0.029(1)	0.030(1)	-0.002(1)	0.002(1)	-0.004(1)
C16'	0.020(1)	0.037(2)	0.026(1)	-0.002(1)	0.005(1)	-0.004(1)
C17'	0.021(1)	0.037(2)	0.026(1)	0.002(1)	0.007(1)	0.005(1)
C18'	0.021(1)	0.028(1)	0.025(1)	0.001(1)	0.0023(9)	-0.001(1)
C19'	0.033(1)	0.040(2)	0.050(1)	0.007(1)	0.026(1)	0.001(1)
C20'	0.025(1)	0.049(2)	0.055(2)	-0.011(1)	-0.011(1)	-0.006(2)
C21'	0.024(1)	0.076(2)	0.031(1)	0.009(1)	0.014(1)	0.008(1)
C22'	0.021(1)	0.054(2)	0.028(1)	-0.001(1)	-0.006(1)	-0.003(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 65. Interatomic Distances (Å) for Sb-6 at **181 K**

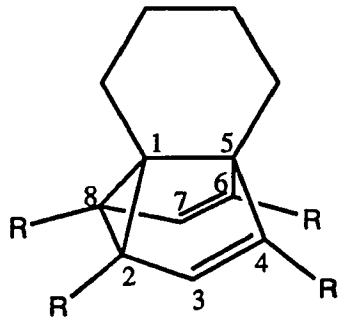
		Unprimed	Primed
O1	C15	1.334(3)	1.329(3)
O1	C19	1.448(3)	1.453(3)
O2	C15	1.203(3)	1.208(3)
O3	C16	1.340(3)	1.334(3)
O3	C20	1.454(3)	1.450(3)
O4	C16	1.194(3)	1.199(3)
O5	C17	1.325(3)	1.328(3)
O5	C21	1.455(3)	1.451(3)
O6	C17	1.202(3)	1.204(3)
O7	C18	1.332(3)	1.327(3)
O7	C22	1.456(3)	1.457(3)
O8	C18	1.202(3)	1.211(3)
C1	C2	1.486(4)	1.489(4)
C1	C5	1.569(3)	1.566(3)
C1	C8	1.518(3)	1.512(3)
C1	C9	1.504(3)	1.503(4)
C2	C3	1.470(3)	1.460(3)
C2	C8	1.639(3)	1.685(3)
C2	C15	1.498(3)	1.502(3)
C3	C4	1.336(3)	1.341(3)
C3	C7	3.066(3)	3.058(3)
C4	C5	1.537(4)	1.525(3)
C4	C6	2.364(3)	2.325(3)
C4	C16	1.487(3)	1.485(3)
C5	C6	1.531(3)	1.526(3)
C5	C12	1.512(4)	1.515(3)
C6	C7	1.339(4)	1.343(3)
C6	C17	1.475(3)	1.475(4)
C7	C8	1.469(3)	1.455(3)
C8	C18	1.487(3)	1.482(3)
C9	C10	1.529(4)	1.533(3)
C10	C11	1.555(4)	1.554(3)
C11	C12	1.529(3)	1.532(4)

Table 66. Angles (°) for Sb-6 at **181 K**

			Unprimed	Primed
C15	O1	C19	115.6(2)	116.4(2)
C16	O3	C20	115.3(2)	115.0(2)
C17	O5	C21	115.5(2)	115.7(2)
C18	O7	C22	115.8(2)	116.8(2)
C2	C1	C5	105.0(2)	104.4(2)
C2	C1	C8	66.1(2)	68.3(2)
C2	C1	C9	128.2(2)	127.4(2)
C5	C1	C8	104.4(2)	104.0(2)
C5	C1	C9	115.6(2)	115.8(2)
C8	C1	C9	127.0(2)	127.1(2)
C1	C2	C3	107.8(2)	108.5(2)
C1	C2	C8	57.9(2)	56.5(1)
C1	C2	C15	126.9(2)	127.5(2)
C3	C2	C8	118.1(2)	117.4(2)
C3	C2	C15	115.3(2)	116.1(2)
C8	C2	C15	119.0(2)	118.0(2)
C2	C3	C4	111.1(2)	110.8(2)
C3	C4	C5	110.8(2)	110.9(2)
C3	C4	C16	125.0(2)	125.0(2)
C5	C4	C6	39.5(1)	40.3(1)
C5	C4	C16	124.2(2)	124.2(2)
C1	C5	C4	101.8(2)	102.7(2)
C1	C5	C6	102.4(2)	102.9(2)
C1	C5	C12	111.8(2)	111.7(2)
C4	C5	C6	100.8(2)	99.3(2)
C4	C5	C12	117.7(2)	118.3(2)
C6	C5	C12	119.9(2)	119.6(2)
C4	C6	C5	39.7(1)	40.3(1)
C5	C6	C7	111.4(2)	111.1(2)
C5	C6	C17	122.3(2)	123.2(2)
C7	C6	C17	125.5(2)	125.2(2)
C6	C7	C8	111.5(2)	111.2(2)
C1	C8	C2	56.0(1)	55.2(1)
C1	C8	C7	107.0(2)	108.1(2)
C1	C8	C18	121.4(2)	122.3(2)
C2	C8	C7	120.0(2)	118.8(2)
C2	C8	C18	113.3(2)	114.0(2)
C7	C8	C18	121.8(2)	121.3(2)
C1	C9	C10	109.2(2)	108.7(2)
C9	C10	C11	113.6(2)	114.0(2)
C10	C11	C12	113.6(2)	113.2(2)
C5	C12	C11	109.5(2)	109.6(2)
O1	C15	O2	124.5(2)	124.0(2)
O1	C15	C2	111.5(2)	112.4(2)
O2	C15	C2	123.6(2)	123.3(2)
O3	C16	O4	123.5(2)	123.7(2)
O3	C16	C4	111.3(2)	111.9(2)
O4	C16	C4	125.1(2)	124.3(2)
O5	C17	O6	123.6(2)	124.0(2)
O5	C17	C6	112.4(2)	111.3(2)
O6	C17	C6	124.0(2)	124.7(2)
O7	C18	O8	124.2(2)	124.3(2)
O7	C18	C8	111.2(2)	111.6(2)
O8	C18	C8	124.5(2)	124.0(2)

Table 67. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-6 at **181 K**

	Unprimed			Primed		
Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O1	0.140	0.166	0.173	0.122	0.165	0.203
O2	0.143	0.195	0.221	0.140	0.187	0.254
O3	0.114	0.195	0.222	0.127	0.191	0.234
O4	0.125	0.209	0.257	0.140	0.204	0.232
O5	0.144	0.157	0.269	0.128	0.168	0.279
O6	0.146	0.172	0.307	0.141	0.173	0.292
O7	0.121	0.183	0.230	0.135	0.167	0.234
O8	0.140	0.173	0.256	0.130	0.182	0.222
C1	0.129	0.144	0.154	0.122	0.144	0.155
C2	0.127	0.148	0.164	0.123	0.159	0.179
C3	0.129	0.155	0.170	0.130	0.148	0.168
C4	0.130	0.155	0.164	0.131	0.159	0.165
C5	0.123	0.146	0.159	0.119	0.141	0.153
C6	0.142	0.152	0.174	0.139	0.168	0.191
C7	0.137	0.155	0.180	0.133	0.146	0.180
C8	0.129	0.163	0.168	0.132	0.157	0.183
C9	0.141	0.157	0.180	0.140	0.159	0.182
C10	0.158	0.169	0.191	0.140	0.161	0.196
C11	0.155	0.165	0.183	0.155	0.161	0.184
C12	0.146	0.165	0.171	0.137	0.156	0.173
C15	0.111	0.172	0.181	0.128	0.162	0.183
C16	0.132	0.161	0.188	0.140	0.157	0.197
C17	0.149	0.156	0.183	0.137	0.158	0.198
C18	0.129	0.168	0.172	0.144	0.157	0.170
C19	0.135	0.195	0.210	0.123	0.200	0.249
C20	0.112	0.233	0.256	0.126	0.231	0.255
C21	0.139	0.185	0.275	0.121	0.185	0.282
C22	0.110	0.213	0.241	0.125	0.189	0.233



R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Table 8–68 X-ray Crystal Data for Sb-6 at **181 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	117–118
Crystal size (mm)	0.21 x 0.25 x 0.33
Crystal system	monoclinic
Space group	*P2/n*
a (Å)	41.319(2)
b (Å)	7.361(1)
c (Å)	12.163(1)
β (°)	98.10(1)
Cell volume ($Å^3$)	3668.68(2.61)
Z	8
d_{calc} (g cm^{-3})	1.414
μ(Cu $K\alpha$) (cm^{-1})	8.81
Maximum θ (°)	60
Unique reflections	5445
Observed reflections [$I > 3.0\sigma(I)$]	3378
Number of variables	505
R	0.047
R_w	0.053
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.24
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.23

Table 69. Final Atomic Parameters for Sb-6 at **181 K**

Atom	x	y	z	B(Å^2)
O1	0.55538(5)	0.1498(3)	0.2608(2)	1.75(5)
O2	0.55591(6)	0.4184(3)	0.3483(2)	2.59(6)
O3	0.69190(5)	0.4031(4)	0.3896(2)	2.48(5)
O4	0.70573(6)	0.1144(4)	0.3624(2)	3.08(6)
O5	0.68213(6)	0.0811(4)	0.7600(2)	2.99(6)
O6	0.70731(6)	0.0306(5)	0.6125(2)	3.58(7)
O7	0.56044(5)	0.1204(4)	0.6691(2)	2.48(5)
O8	0.53696(6)	0.0929(4)	0.4919(2)	2.80(6)
C1	0.60540(8)	0.0062(5)	0.4388(3)	1.43(7)
C2	0.59707(8)	0.1992(5)	0.4085(3)	1.42(7)
C3	0.62755(8)	0.2923(5)	0.3899(3)	1.61(7)
C4	0.65314(8)	0.1805(5)	0.4103(3)	1.64(7)
C5	0.64347(7)	0.0042(5)	0.4640(3)	1.40(6)
C6	0.64977(8)	0.0573(5)	0.5869(3)	1.63(7)
C7	0.62314(8)	0.1313(5)	0.6200(3)	1.84(7)
C8	0.59490(8)	0.1183(5)	0.5329(3)	1.66(7)
C9	0.58922(8)	-0.1621(5)	0.3878(3)	1.85(7)
C10	0.60531(9)	-0.2123(5)	0.2857(3)	2.13(8)
C11	0.64320(8)	-0.2098(5)	0.3060(3)	1.93(7)
C12	0.65742(8)	-0.1732(5)	0.4268(3)	1.86(7)
C15	0.56677(8)	0.2685(5)	0.3400(3)	1.79(7)
C16	0.68649(8)	0.2231(5)	0.3864(3)	1.77(7)
C17	0.68257(8)	0.0544(5)	0.6523(3)	1.89(7)
C18	0.56081(8)	0.1093(5)	0.5593(3)	1.89(7)
C19	0.52894(9)	0.2140(5)	0.1802(3)	2.44(8)
C20	0.72338(9)	0.4584(6)	0.3612(3)	3.15(9)
C21	0.71364(9)	0.0745(6)	0.8292(3)	3.15(9)
C22	0.52827(9)	0.1078(6)	0.7047(3)	2.79(8)
O1'	0.44782(5)	0.3596(3)	-0.0506(2)	2.00(5)
O2'	0.44705(6)	0.0958(4)	0.0409(2)	2.83(6)
O3'	0.31001(6)	0.0965(4)	-0.0603(2)	2.53(6)
O4'	0.29654(6)	0.3838(4)	-0.1061(2)	2.89(6)
O5'	0.31780(6)	0.4203(4)	0.3155(2)	3.05(6)
O6'	0.29195(6)	0.4628(4)	0.1429(2)	3.36(6)
O7'	0.43810(5)	0.3729(4)	0.3507(2)	2.46(6)
O8'	0.46239(5)	0.4441(4)	0.2027(2)	2.36(5)
C1'	0.39514(8)	0.5004(5)	0.0739(3)	1.42(7)
C2'	0.40415(8)	0.3102(5)	0.0507(3)	1.73(7)
C3'	0.37489(8)	0.2133(5)	0.0027(3)	1.52(7)
C4'	0.34839(8)	0.3206(5)	-0.0032(3)	1.68(7)
C5'	0.35693(7)	0.4984(5)	0.0594(3)	1.38(7)
C6'	0.34991(8)	0.4412(5)	0.1744(3)	1.89(7)
C7'	0.37626(8)	0.3719(5)	0.2356(3)	1.66(7)
C8'	0.40509(8)	0.3935(5)	0.1799(3)	1.75(7)
C9'	0.41052(8)	0.6718(5)	0.0391(3)	1.79(7)
C10'	0.39516(9)	0.7173(5)	-0.0798(3)	2.05(7)
C11'	0.35724(9)	0.7148(5)	-0.0976(3)	2.07(8)
C12'	0.34243(8)	0.6744(5)	0.0087(3)	1.71(7)
C15'	0.43545(8)	0.2429(5)	0.0163(3)	1.76(7)
C16'	0.31537(8)	0.2754(5)	-0.0601(3)	1.86(7)
C17'	0.31660(8)	0.4424(5)	0.2065(3)	2.05(8)
C18'	0.43816(8)	0.4062(5)	0.2431(3)	1.71(7)
C19'	0.47604(9)	0.2974(6)	-0.0985(3)	2.91(9)
C20'	0.27901(9)	0.0389(6)	-0.1216(4)	3.3(1)
C21'	0.28638(9)	0.4258(6)	0.3555(3)	3.02(9)
C22'	0.46910(9)	0.3879(6)	0.4235(3)	2.64(9)

Table 69 (cont.). Final Atomic Parameters for Sb-6 at **181 K**

Atom	x	y	z	B(Å^2)
H3	0.629	0.422	0.367	2.0
H7	0.623	0.187	0.695	2.2
H9A	0.566	-0.140	0.365	2.2
H9B	0.593	-0.263	0.443	2.2
H10A	0.598	-0.125	0.225	2.6
H10B	0.598	-0.338	0.262	2.6
H11A	0.651	-0.113	0.258	2.4
H11B	0.651	-0.330	0.284	2.4
H12A	0.652	-0.275	0.475	2.2
H12B	0.682	-0.163	0.433	2.2
H19A	0.522	0.116	0.125	2.9
H19B	0.510	0.248	0.218	2.9
H19C	0.536	0.323	0.141	2.9
H20A	0.725	0.595	0.365	3.8
H20B	0.741	0.403	0.414	3.8
H20C	0.725	0.419	0.284	3.8
H21A	0.711	0.096	0.909	3.7
H21B	0.724	-0.045	0.822	3.7
H21C	0.728	0.174	0.805	3.7
H22A	0.531	0.118	0.787	3.3
H22B	0.514	0.208	0.670	3.3
H22C	0.518	-0.012	0.680	3.3
H3'	0.374	0.084	-0.023	1.9
H7'	0.377	0.313	0.310	2.1
H9A'	0.434	0.653	0.041	2.3
H9B'	0.407	0.773	0.090	2.3
H10A'	0.403	0.628	-0.131	2.4
H10B'	0.402	0.843	-0.098	2.4
H11A'	0.350	0.619	-0.154	2.4
H11B'	0.349	0.836	-0.126	2.4
H12A'	0.348	0.776	0.063	2.1
H12B'	0.318	0.661	-0.009	2.1
H19A'	0.483	0.395	-0.148	3.4
H19B'	0.494	0.268	-0.039	3.4
H19C'	0.470	0.186	-0.144	3.4
H20A'	0.277	-0.095	-0.118	3.9
H20B'	0.261	0.098	-0.088	3.9
H20C'	0.278	0.078	-0.201	3.9
H21A'	0.290	0.408	0.439	3.7
H21B'	0.276	0.546	0.338	3.7
H21C'	0.272	0.327	0.320	3.7
H22A'	0.466	0.360	0.501	3.1
H22B'	0.485	0.299	0.398	3.1
H22C'	0.478	0.514	0.419	3.1
H22BA	0.529	0.019	0.767	3.3
H22BB	0.522	0.230	0.730	3.3
H22BC	0.512	0.065	0.641	3.3
H19BA'	0.480	0.164	-0.082	3.4
H19BB'	0.472	0.315	-0.181	3.4
H19BC'	0.496	0.366	-0.065	3.4
H22BA'	0.466	0.444	0.495	3.1
H22BB'	0.479	0.263	0.437	3.1
H22BC'	0.484	0.465	0.387	3.1

The parameters of the hydrogen atoms were not refined.

Table 70. Final Anisotropic Thermal Parameters (U's) for Sb-6 at **181 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.019(1)	0.022(1)	0.025(1)	0.004(1)	0.001(1)	0.003(1)
O2	0.028(1)	0.025(1)	0.045(1)	0.008(1)	0.006(1)	-0.005(1)
O3	0.022(1)	0.029(1)	0.046(1)	-0.008(1)	0.016(1)	0.000(1)
O4	0.025(1)	0.039(2)	0.058(2)	0.008(1)	0.023(1)	0.003(1)
O5	0.023(1)	0.070(2)	0.020(1)	0.011(1)	0.001(1)	-0.005(1)
O6	0.021(1)	0.085(2)	0.031(1)	0.003(2)	0.006(1)	-0.013(2)
O7	0.025(1)	0.046(2)	0.026(1)	-0.005(1)	0.015(1)	-0.003(1)
O8	0.022(1)	0.058(2)	0.027(1)	-0.007(1)	0.006(1)	0.002(1)
C1	0.017(2)	0.019(2)	0.019(2)	-0.001(2)	0.007(1)	0.002(2)
C2	0.017(2)	0.019(2)	0.019(2)	0.001(2)	0.005(1)	0.003(2)
C3	0.020(2)	0.019(2)	0.024(2)	-0.003(2)	0.008(1)	-0.001(2)
C4	0.023(2)	0.022(2)	0.018(2)	0.001(2)	0.007(1)	-0.000(2)
C5	0.015(2)	0.018(2)	0.019(2)	0.001(2)	0.003(1)	-0.000(2)
C6	0.024(2)	0.021(2)	0.018(2)	-0.000(2)	0.006(1)	0.002(2)
C7	0.021(2)	0.028(2)	0.021(2)	-0.007(2)	0.005(1)	-0.001(2)
C8	0.022(2)	0.024(2)	0.019(2)	-0.001(2)	0.009(1)	0.001(2)
C9	0.026(2)	0.017(2)	0.027(2)	-0.005(2)	0.003(1)	0.000(2)
C10	0.031(2)	0.026(2)	0.024(2)	0.004(2)	0.003(2)	-0.003(2)
C11	0.029(2)	0.020(2)	0.025(2)	0.003(2)	0.007(1)	-0.000(2)
C12	0.023(2)	0.021(2)	0.027(2)	0.006(2)	0.005(1)	0.001(2)
C15	0.018(2)	0.024(2)	0.029(2)	-0.003(2)	0.013(1)	0.001(2)
C16	0.021(2)	0.025(2)	0.022(2)	0.002(2)	0.007(1)	0.003(2)
C17	0.019(2)	0.029(2)	0.025(2)	-0.002(2)	0.006(1)	-0.002(2)
C18	0.022(2)	0.026(2)	0.025(2)	0.001(2)	0.008(1)	0.001(2)
C19	0.023(2)	0.032(2)	0.035(2)	0.004(2)	-0.004(2)	0.004(2)
C20	0.024(2)	0.044(3)	0.057(2)	-0.013(2)	0.020(2)	0.005(2)
C21	0.024(2)	0.071(3)	0.021(2)	0.010(2)	-0.007(2)	-0.005(2)
C22	0.026(2)	0.047(3)	0.037(2)	-0.006(2)	0.022(1)	0.001(2)
O1'	0.026(1)	0.024(1)	0.030(1)	0.004(1)	0.0159(9)	0.001(1)
O2'	0.030(1)	0.027(1)	0.054(1)	0.010(1)	0.017(1)	0.009(1)
O3'	0.021(1)	0.027(1)	0.044(1)	-0.007(1)	-0.007(1)	-0.001(1)
O4'	0.031(1)	0.036(2)	0.040(1)	0.005(1)	-0.008(1)	-0.001(1)
O5'	0.021(1)	0.069(2)	0.028(1)	0.008(1)	0.010(1)	0.009(1)
O6'	0.022(1)	0.077(2)	0.030(1)	0.006(1)	0.007(1)	0.012(2)
O7'	0.019(1)	0.050(2)	0.023(1)	-0.005(1)	-0.001(1)	0.004(1)
O8'	0.018(1)	0.042(2)	0.031(1)	-0.004(1)	0.007(1)	-0.001(1)
C1'	0.016(2)	0.019(2)	0.019(2)	-0.001(2)	0.006(1)	-0.000(2)
C2'	0.018(2)	0.019(2)	0.029(2)	-0.003(2)	0.005(1)	-0.002(2)
C3'	0.020(2)	0.019(2)	0.020(2)	0.000(2)	0.005(1)	-0.003(2)
C4'	0.018(2)	0.022(2)	0.023(2)	-0.002(2)	0.001(1)	-0.000(2)
C5'	0.014(2)	0.020(2)	0.019(2)	0.004(2)	0.004(1)	-0.001(2)
C6'	0.024(2)	0.029(2)	0.021(2)	0.001(2)	0.008(1)	0.005(2)
C7'	0.019(2)	0.026(2)	0.018(2)	-0.004(2)	0.002(1)	0.001(2)
C8'	0.015(2)	0.030(2)	0.022(2)	-0.003(2)	0.004(1)	0.002(2)
C9'	0.025(2)	0.017(2)	0.028(2)	-0.004(2)	0.010(1)	-0.002(2)
C10'	0.034(2)	0.017(2)	0.029(2)	0.001(2)	0.014(1)	0.002(2)
C11'	0.033(2)	0.023(2)	0.024(2)	0.004(2)	0.010(1)	0.003(2)
C12'	0.023(2)	0.022(2)	0.022(2)	0.002(2)	0.007(1)	-0.000(2)
C15'	0.019(2)	0.019(2)	0.028(2)	-0.002(2)	0.003(1)	0.001(2)
C16'	0.022(2)	0.025(2)	0.024(2)	0.001(2)	0.005(1)	-0.005(2)
C17'	0.022(2)	0.033(2)	0.023(2)	0.004(2)	0.005(1)	0.008(2)
C18'	0.020(2)	0.022(2)	0.023(2)	0.000(2)	0.004(1)	-0.001(2)
C19'	0.033(2)	0.036(2)	0.048(2)	0.007(2)	0.027(2)	0.004(2)
C20'	0.023(2)	0.043(3)	0.056(3)	-0.011(2)	-0.012(2)	-0.009(2)
C21'	0.027(2)	0.064(3)	0.028(2)	0.010(2)	0.016(1)	0.008(2)
C22'	0.024(2)	0.045(3)	0.029(2)	0.001(2)	-0.005(2)	-0.002(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 71. Interatomic Distances (Å) for Sb-6 at **181 K**

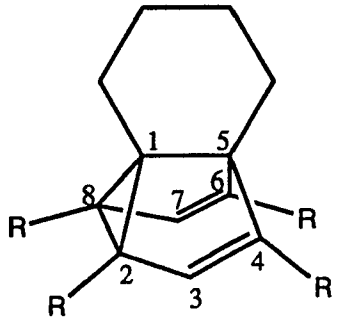
		Unprimed	Primed
O1	C15	1.337(4)	1.334(4)
O1	C19	1.442(4)	1.452(5)
O2	C15	1.201(4)	1.204(4)
O3	C16	1.343(5)	1.336(4)
O3	C20	1.452(5)	1.453(4)
O4	C16	1.193(4)	1.197(4)
O5	C17	1.327(4)	1.329(4)
O5	C21	1.450(4)	1.452(4)
O6	C17	1.206(4)	1.200(4)
O7	C18	1.339(4)	1.331(4)
O7	C22	1.460(4)	1.457(4)
O8	C18	1.197(4)	1.210(4)
C1	C2	1.495(5)	1.486(5)
C1	C5	1.563(4)	1.567(4)
C1	C8	1.524(5)	1.517(5)
C1	C9	1.500(5)	1.500(5)
C2	C3	1.481(5)	1.455(5)
C2	C8	1.640(5)	1.683(5)
C2	C15	1.494(4)	1.500(5)
C3	C4	1.336(5)	1.345(5)
C3	C7	3.069(5)	3.057(5)
C4	C5	1.532(5)	1.530(5)
C4	C6	2.354(5)	2.328(5)
C4	C16	1.484(5)	1.480(4)
C5	C6	1.531(4)	1.527(5)
C5	C12	1.522(5)	1.521(5)
C6	C7	1.341(5)	1.332(4)
C6	C17	1.474(4)	1.485(5)
C7	C8	1.466(4)	1.461(5)
C8	C18	1.492(5)	1.476(4)
C9	C10	1.534(5)	1.533(5)
C10	C11	1.553(5)	1.554(5)
C11	C12	1.528(5)	1.536(5)

Table 72. Angles (°) for Sb-6 at **181 K**

			Unprimed	Primed
C15	O1	C19	115.6(3)	116.2(3)
C16	O3	C20	114.8(3)	115.0(3)
C17	O5	C21	115.6(3)	114.9(2)
C18	O7	C22	115.5(2)	117.4(3)
C2	C1	C5	104.4(3)	104.2(3)
C2	C1	C8	65.8(2)	68.1(2)
C2	C1	C9	127.5(3)	127.6(3)
C5	C1	C8	104.1(2)	103.9(3)
C5	C1	C9	116.9(3)	116.0(3)
C8	C1	C9	126.9(3)	126.9(3)
C1	C2	C3	107.8(3)	108.7(3)
C1	C2	C8	57.9(2)	56.8(2)
C1	C2	C15	127.4(3)	127.9(3)
C3	C2	C8	117.9(2)	117.5(3)
C3	C2	C15	115.0(3)	115.4(3)
C8	C2	C15	119.2(3)	118.3(3)
C2	C3	C4	110.9(3)	111.1(3)
C3	C4	C5	110.7(3)	110.2(3)
C3	C4	C16	124.6(3)	125.8(3)
C5	C4	C6	39.8(2)	40.4(2)
C5	C4	C16	124.7(3)	123.9(3)
C1	C5	C4	103.0(3)	102.9(3)
C1	C5	C6	102.6(3)	102.6(2)
C1	C5	C12	111.3(3)	111.8(3)
C4	C5	C6	100.5(3)	99.2(3)
C4	C5	C12	117.8(3)	118.5(2)
C6	C5	C12	119.4(3)	119.4(3)
C4	C6	C5	39.8(2)	40.5(2)
C5	C6	C7	111.3(3)	111.8(3)
C5	C6	C17	122.7(3)	122.9(3)
C7	C6	C17	125.2(3)	124.9(3)
C6	C7	C8	111.2(3)	110.9(3)
C1	C8	C2	56.3(2)	55.0(2)
C1	C8	C7	107.2(3)	108.0(3)
C1	C8	C18	121.1(3)	122.1(3)
C2	C8	C7	120.1(3)	118.7(3)
C2	C8	C18	113.0(2)	114.0(3)
C7	C8	C18	122.0(3)	121.6(3)
C1	C9	C10	108.3(3)	108.3(3)
C9	C10	C11	114.4(3)	113.9(3)
C10	C11	C12	113.5(3)	113.6(3)
C5	C12	C11	109.1(3)	108.9(3)
O1	C15	O2	124.3(3)	123.8(3)
O1	C15	C2	111.2(3)	112.2(3)
O2	C15	C2	124.1(3)	123.9(3)
O3	C16	O4	123.7(3)	124.0(3)
O3	C16	C4	111.0(3)	111.4(3)
O4	C16	C4	125.3(3)	124.5(3)
O5	C17	O6	123.3(3)	124.6(3)
O5	C17	C6	113.0(3)	110.8(3)
O6	C17	C6	123.7(3)	124.6(3)
O7	C18	O8	124.4(3)	123.9(3)
O7	C18	C8	110.8(3)	111.7(3)
O8	C18	C8	124.8(3)	124.3(3)

Table 73. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-6 at **181 K**

	Unprimed			Primed		
Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O1	0.126	0.153	0.165	0.114	0.155	0.198
O2	0.129	0.186	0.217	0.134	0.170	0.247
O3	0.110	0.180	0.223	0.119	0.175	0.226
O4	0.116	0.198	0.254	0.148	0.188	0.229
O5	0.139	0.146	0.270	0.125	0.168	0.268
O6	0.141	0.169	0.296	0.142	0.165	0.283
O7	0.112	0.182	0.221	0.132	0.156	0.227
O8	0.137	0.168	0.243	0.126	0.176	0.207
C1	0.110	0.140	0.150	0.116	0.138	0.146
C2	0.121	0.130	0.149	0.121	0.145	0.173
C3	0.121	0.139	0.165	0.124	0.140	0.151
C4	0.123	0.150	0.157	0.130	0.151	0.155
C5	0.123	0.136	0.139	0.103	0.140	0.150
C6	0.124	0.147	0.158	0.124	0.156	0.179
C7	0.129	0.144	0.181	0.130	0.135	0.167
C8	0.117	0.154	0.161	0.115	0.148	0.176
C9	0.123	0.163	0.169	0.123	0.140	0.182
C10	0.146	0.160	0.184	0.129	0.144	0.201
C11	0.137	0.153	0.177	0.140	0.147	0.193
C12	0.128	0.161	0.169	0.130	0.148	0.162
C15	0.100	0.158	0.182	0.132	0.144	0.170
C16	0.132	0.145	0.169	0.134	0.153	0.171
C17	0.133	0.156	0.173	0.136	0.145	0.197
C18	0.136	0.160	0.167	0.140	0.146	0.155
C19	0.136	0.183	0.202	0.117	0.187	0.249
C20	0.095	0.224	0.246	0.110	0.219	0.259
C21	0.117	0.178	0.273	0.114	0.183	0.261
C22	0.099	0.213	0.225	0.136	0.191	0.213



R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Table 8–74. X-ray Crystal Data for Sb-6 at **208 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	117–118
Crystal size (mm)	0.32 x 0.50 x 0.64
Crystal system	monoclinic
Space group	*P2/n*
a (Å)	41.423(2)
b (Å)	7.379(4)
c (Å)	12.188(2)
β (°)	98.14(1)
Cell volume ($Å^3$)	3687.99(5.57)
Z	8
d_{calc} (g cm^{-3})	1.406
μ(Cu $K\alpha$) (cm^{-1})	8.77
Maximum θ (°)	60
Unique reflections	5471
Observed reflections [$I > 3.0\sigma(I)$]	4266
Number of variables	505
R	0.045
R_w	0.060
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.23
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.28

Table 75. Final Atomic Parameters for Sb-6 at **208 K**

Atom	x	y	z	B(Å^2)
O1	0.55558(4)	0.1514(2)	0.2616(1)	2.18(3)
O2	0.55619(4)	0.4195(3)	0.3489(2)	3.14(4)
O3	0.69212(4)	0.4031(3)	0.3900(2)	2.94(4)
O4	0.70579(4)	0.1155(3)	0.3629(2)	3.76(4)
O5	0.68207(4)	0.0809(3)	0.7593(1)	3.51(5)
O6	0.70733(4)	0.0307(4)	0.6129(2)	4.32(5)
O7	0.56063(4)	0.1219(3)	0.6684(1)	2.94(4)
O8	0.53728(4)	0.0933(3)	0.4916(2)	3.44(4)
C1	0.60551(5)	0.0093(3)	0.4388(2)	1.75(5)
C2	0.59735(6)	0.2014(3)	0.4089(2)	1.86(5)
C3	0.62764(6)	0.2932(4)	0.3906(2)	1.97(5)
C4	0.65315(6)	0.1810(4)	0.4105(2)	1.91(5)
C5	0.64368(5)	0.0053(4)	0.4642(2)	1.81(5)
C6	0.64988(6)	0.0580(4)	0.5869(2)	2.01(5)
C7	0.62339(6)	0.1323(4)	0.6202(2)	2.17(5)
C8	0.59498(6)	0.1191(4)	0.5327(2)	2.06(5)
C9	0.58970(6)	-0.1598(4)	0.3879(2)	2.19(5)
C10	0.60550(6)	-0.2105(4)	0.2856(2)	2.57(6)
C11	0.64323(6)	-0.2076(4)	0.3064(2)	2.48(5)
C12	0.65752(6)	-0.1707(4)	0.4272(2)	2.24(5)
C15	0.56689(6)	0.2692(4)	0.3404(2)	2.09(5)
C16	0.68667(6)	0.2250(4)	0.3875(2)	2.26(5)
C17	0.68276(6)	0.0550(4)	0.6519(2)	2.40(5)
C18	0.56113(6)	0.1105(4)	0.5594(2)	2.20(5)
C19	0.52883(6)	0.2152(4)	0.1810(2)	2.90(6)
C20	0.72350(7)	0.4594(5)	0.3617(3)	3.97(7)
C21	0.71349(7)	0.0764(5)	0.8292(2)	3.80(7)
C22	0.52865(6)	0.1087(5)	0.7043(2)	3.42(6)
O1'	0.44781(4)	0.3576(2)	-0.0505(1)	2.47(4)
O2'	0.44687(4)	0.0948(3)	0.0402(2)	3.51(4)
O3'	0.31002(4)	0.0969(3)	-0.0604(2)	3.12(4)
O4'	0.29673(4)	0.3824(3)	-0.1062(2)	3.37(4)
O5'	0.31777(4)	0.4194(3)	0.3140(2)	3.65(5)
O6'	0.29189(4)	0.4610(3)	0.1425(2)	4.02(5)
O7'	0.43803(4)	0.3727(3)	0.3505(1)	2.92(4)
O8'	0.46228(4)	0.4434(3)	0.2031(2)	2.94(4)
C1'	0.39512(5)	0.4986(3)	0.0741(2)	1.69(5)
C2'	0.40417(6)	0.3088(4)	0.0502(2)	2.07(5)
C3'	0.37472(6)	0.2122(4)	0.0024(2)	1.89(5)
C4'	0.34835(6)	0.3204(4)	-0.0022(2)	2.03(5)
C5'	0.35696(5)	0.4969(3)	0.0597(2)	1.67(5)
C6'	0.34977(6)	0.4397(4)	0.1734(2)	2.46(5)
C7'	0.37644(6)	0.3706(4)	0.2353(2)	2.06(5)
C8'	0.40508(6)	0.3933(4)	0.1801(2)	2.20(5)
C9'	0.41041(6)	0.6698(4)	0.0388(2)	2.19(5)
C10'	0.39501(6)	0.7155(4)	-0.0798(2)	2.48(5)
C11'	0.35713(6)	0.7127(4)	-0.0975(2)	2.46(5)
C12'	0.34256(6)	0.6720(4)	0.0088(2)	2.12(5)
C15'	0.43552(6)	0.2422(4)	0.0162(2)	2.22(5)
C16'	0.31541(6)	0.2741(4)	-0.0597(2)	2.22(5)
C17'	0.31675(6)	0.4406(4)	0.2059(2)	2.45(5)
C18'	0.43821(6)	0.4054(4)	0.2434(2)	2.18(5)
C19'	0.47612(7)	0.2956(4)	-0.0985(2)	3.41(6)
C20'	0.27898(7)	0.0387(5)	-0.1211(3)	3.99(7)
C21'	0.28662(6)	0.4261(5)	0.3551(2)	3.73(7)
C22'	0.46906(6)	0.3865(4)	0.4224(2)	3.16(6)

Table 75 (cont.). Final Atomic Parameters for Sb-6 at **208 K**

Atom	x	y	z	B(Å^2)
H3	0.629	0.422	0.366	2.2
H7	0.623	0.189	0.695	2.4
H9A	0.566	-0.138	0.365	2.4
H9B	0.593	-0.261	0.443	2.4
H10A	0.598	-0.122	0.225	2.8
H10B	0.598	-0.335	0.262	2.8
H11A	0.651	-0.111	0.259	2.7
H11B	0.651	-0.328	0.285	2.7
H12A	0.652	-0.272	0.475	2.5
H12B	0.682	-0.161	0.434	2.5
H19A	0.522	0.117	0.126	3.2
H19B	0.510	0.248	0.220	3.2
H19C	0.536	0.324	0.142	3.2
H20A	0.725	0.594	0.366	4.4
H20B	0.741	0.404	0.415	4.4
H20C	0.726	0.419	0.285	4.4
H21A	0.710	0.097	0.908	4.2
H21B	0.724	-0.045	0.822	4.2
H21C	0.728	0.173	0.805	4.2
H22A	0.531	0.119	0.787	3.8
H22B	0.514	0.209	0.670	3.8
H22C	0.519	-0.011	0.681	3.8
H3'	0.374	0.083	-0.023	2.1
H7'	0.377	0.312	0.309	2.3
H9A'	0.434	0.652	0.041	2.4
H9B'	0.406	0.771	0.090	2.4
H10A'	0.403	0.625	-0.131	2.7
H10B'	0.402	0.839	-0.098	2.7
H11A'	0.350	0.618	-0.154	2.7
H11B'	0.349	0.834	-0.126	2.7
H12A'	0.348	0.774	0.063	2.3
H12B'	0.318	0.659	-0.009	2.3
H19A'	0.483	0.393	-0.147	3.8
H19B'	0.494	0.267	-0.038	3.8
H19C'	0.470	0.184	-0.144	3.8
H20A'	0.277	-0.096	-0.117	4.4
H20B'	0.261	0.096	-0.088	4.4
H20C'	0.278	0.076	-0.200	4.4
H21A'	0.290	0.409	0.437	4.1
H21B'	0.276	0.546	0.337	4.1
H21C'	0.272	0.328	0.320	4.1
H22A'	0.466	0.359	0.500	3.5
H22B'	0.485	0.298	0.398	3.5
H22C'	0.478	0.512	0.418	3.5
H19BA'	0.480	0.164	-0.082	3.8
H19BB'	0.472	0.315	-0.181	3.8
H19BC'	0.496	0.366	-0.065	3.8

The parameters of the hydrogen atoms were not refined.

Table 76. Final Anisotropic Thermal Parameters (U's) for Sb-6 at **208 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0238(8)	0.0285(9)	0.0300(8)	0.0043(8)	0.0013(7)	0.0011(8)
O2	0.034(1)	0.031(1)	0.054(1)	0.0101(9)	0.0040(9)	-0.0048(9)
O3	0.0239(8)	0.037(1)	0.054(1)	-0.0081(8)	0.0164(8)	0.0023(9)
O4	0.0317(9)	0.046(1)	0.070(1)	0.0081(9)	0.0269(8)	0.004(1)
O5	0.0277(9)	0.080(2)	0.0242(9)	0.011(1)	0.0000(7)	-0.006(1)
O6	0.0263(9)	0.103(2)	0.035(1)	0.004(1)	0.0056(8)	-0.015(1)
O7	0.0278(9)	0.055(1)	0.0316(9)	-0.0039(9)	0.0133(7)	-0.0023(9)
O8	0.0237(9)	0.072(1)	0.035(1)	-0.009(1)	0.0048(8)	0.003(1)
C1	0.020(1)	0.024(1)	0.023(1)	-0.000(1)	0.0044(9)	0.002(1)
C2	0.020(1)	0.025(1)	0.027(1)	0.001(1)	0.0070(9)	0.002(1)
C3	0.022(1)	0.023(1)	0.030(1)	-0.002(1)	0.008(1)	-0.000(1)
C4	0.022(1)	0.026(1)	0.025(1)	0.000(1)	0.0072(9)	-0.001(1)
C5	0.018(1)	0.025(1)	0.026(1)	0.001(1)	0.0037(9)	0.001(1)
C6	0.024(1)	0.027(1)	0.025(1)	-0.001(1)	0.004(1)	0.000(1)
C7	0.024(1)	0.033(1)	0.026(1)	-0.003(1)	0.006(1)	-0.002(1)
C8	0.025(1)	0.029(1)	0.026(1)	-0.001(1)	0.008(1)	-0.000(1)
C9	0.028(1)	0.024(1)	0.030(1)	-0.004(1)	0.002(1)	0.002(1)
C10	0.037(1)	0.029(1)	0.030(1)	0.004(1)	0.001(1)	-0.003(1)
C11	0.038(1)	0.028(1)	0.029(1)	0.003(1)	0.006(1)	-0.003(1)
C12	0.027(1)	0.027(1)	0.032(1)	0.005(1)	0.005(1)	0.001(1)
C15	0.020(1)	0.027(1)	0.034(1)	-0.003(1)	0.011(1)	0.003(1)
C16	0.023(1)	0.035(1)	0.029(1)	-0.000(1)	0.007(1)	0.003(1)
C17	0.026(1)	0.036(2)	0.029(1)	0.001(1)	0.004(1)	-0.003(1)
C18	0.024(1)	0.030(1)	0.031(1)	-0.003(1)	0.010(1)	0.001(1)
C19	0.028(1)	0.040(2)	0.039(1)	0.005(1)	-0.006(1)	0.007(1)
C20	0.028(1)	0.054(2)	0.074(2)	-0.014(1)	0.022(1)	0.006(2)
C21	0.032(1)	0.078(2)	0.030(1)	0.013(2)	-0.007(1)	-0.005(2)
C22	0.033(1)	0.059(2)	0.045(1)	-0.009(1)	0.025(1)	-0.004(1)
O1'	0.0318(9)	0.030(1)	0.0354(9)	0.0052(8)	0.0174(7)	0.0026(8)
O2'	0.0333(9)	0.035(1)	0.069(1)	0.0128(9)	0.0201(9)	0.011(1)
O3'	0.0250(9)	0.035(1)	0.055(1)	-0.0084(9)	-0.0069(9)	-0.001(1)
O4'	0.033(1)	0.044(1)	0.047(1)	0.007(1)	-0.0111(9)	-0.000(1)
O5'	0.0228(9)	0.085(2)	0.0328(9)	0.009(1)	0.0100(7)	0.009(1)
O6'	0.0233(9)	0.092(2)	0.038(1)	0.006(1)	0.0063(8)	0.014(1)
O7'	0.0227(8)	0.059(1)	0.0275(9)	-0.0044(9)	-0.0015(7)	0.0033(9)
O8'	0.0203(8)	0.055(1)	0.0364(9)	-0.0016(9)	0.0037(7)	0.0005(9)
C1'	0.017(1)	0.025(1)	0.022(1)	-0.001(1)	0.0048(9)	-0.002(1)
C2'	0.017(1)	0.024(1)	0.038(1)	0.001(1)	0.006(1)	-0.002(1)
C3'	0.023(1)	0.023(1)	0.025(1)	-0.003(1)	0.004(1)	-0.000(1)
C4'	0.019(1)	0.027(1)	0.030(1)	-0.001(1)	0.003(1)	0.000(1)
C5'	0.017(1)	0.024(1)	0.022(1)	0.002(1)	0.0053(9)	-0.003(1)
C6'	0.024(1)	0.038(2)	0.033(1)	0.001(1)	0.007(1)	0.005(1)
C7'	0.022(1)	0.033(1)	0.023(1)	-0.000(1)	0.004(1)	0.002(1)
C8'	0.020(1)	0.036(2)	0.028(1)	-0.002(1)	0.003(1)	0.004(1)
C9'	0.025(1)	0.025(1)	0.034(1)	-0.002(1)	0.009(1)	-0.002(1)
C10'	0.036(1)	0.028(1)	0.033(1)	0.003(1)	0.014(1)	0.005(1)
C11'	0.034(1)	0.029(1)	0.032(1)	0.003(1)	0.009(1)	0.004(1)
C12'	0.027(1)	0.025(1)	0.029(1)	0.004(1)	0.007(1)	0.000(1)
C15'	0.020(1)	0.028(1)	0.036(1)	-0.001(1)	0.003(1)	-0.003(1)
C16'	0.022(1)	0.034(1)	0.028(1)	0.001(1)	0.004(1)	-0.003(1)
C17'	0.025(1)	0.040(2)	0.030(1)	0.003(1)	0.009(1)	0.008(1)
C18'	0.022(1)	0.030(1)	0.030(1)	0.002(1)	0.003(1)	0.001(1)
C19'	0.038(1)	0.043(2)	0.055(2)	0.009(1)	0.029(1)	0.002(1)
C20'	0.030(1)	0.054(2)	0.061(2)	-0.014(1)	-0.015(1)	-0.007(2)
C21'	0.029(1)	0.080(2)	0.036(1)	0.010(2)	0.017(1)	0.010(2)
C22'	0.028(1)	0.057(2)	0.032(1)	-0.003(1)	-0.006(1)	-0.005(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 77. Interatomic Distances (Å) for Sb-6 at **208 K**

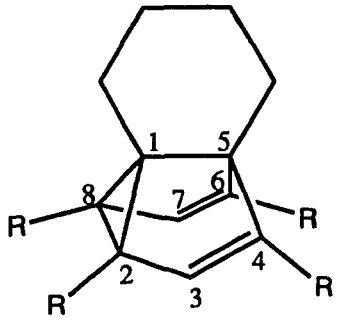
		Unprimed	Primed
O1	C15	1.331(3)	1.327(3)
O1	C19	1.451(3)	1.456(3)
O2	C15	1.204(3)	1.204(3)
O3	C16	1.333(3)	1.326(3)
O3	C20	1.452(3)	1.454(3)
O4	C16	1.199(3)	1.198(3)
O5	C17	1.326(3)	1.322(3)
O5	C21	1.452(3)	1.450(3)
O6	C17	1.197(3)	1.206(3)
O7	C18	1.334(3)	1.328(3)
O7	C22	1.456(3)	1.453(3)
O8	C18	1.202(3)	1.205(3)
C1	C2	1.491(4)	1.489(4)
C1	C5	1.568(3)	1.566(3)
C1	C8	1.516(4)	1.514(3)
C1	C9	1.502(3)	1.503(4)
C2	C3	1.470(3)	1.460(3)
C2	C8	1.641(3)	1.697(4)
C2	C15	1.497(3)	1.501(4)
C3	C4	1.337(3)	1.348(3)
C3	C7	3.068(4)	3.061(3)
C4	C5	1.529(4)	1.522(4)
C4	C6	2.355(3)	2.307(4)
C4	C16	1.490(3)	1.483(3)
C5	C6	1.531(3)	1.518(4)
C5	C12	1.514(4)	1.518(3)
C6	C7	1.340(4)	1.347(3)
C6	C17	1.476(3)	1.477(4)
C7	C8	1.476(3)	1.454(4)
C8	C18	1.486(4)	1.479(3)
C9	C10	1.534(4)	1.533(3)
C10	C11	1.548(4)	1.553(4)
C11	C12	1.532(3)	1.535(4)

Table 78. Angles (°) for Sb-6 at **208 K**

			Unprimed	Primed
C15	O1	C19	115.7(2)	116.4(2)
C16	O3	C20	115.5(2)	115.5(2)
C17	O5	C21	115.7(2)	115.8(2)
C18	O7	C22	116.0(2)	116.9(2)
C2	C1	C5	104.7(2)	104.4(2)
C2	C1	C8	66.2(2)	68.8(2)
C2	C1	C9	128.2(2)	127.4(2)
C5	C1	C8	104.5(2)	103.9(2)
C5	C1	C9	115.8(2)	115.7(2)
C8	C1	C9	126.9(2)	126.9(2)
C1	C2	C3	107.8(2)	108.5(2)
C1	C2	C8	57.6(2)	56.3(2)
C1	C2	C15	126.7(2)	127.8(2)
C3	C2	C8	118.2(2)	117.3(2)
C3	C2	C15	115.6(2)	115.9(2)
C8	C2	C15	118.7(2)	118.2(2)
C2	C3	C4	110.9(2)	110.7(2)
C3	C4	C5	111.0(2)	110.8(2)
C3	C4	C16	124.4(2)	124.7(2)
C5	C4	C6	39.7(1)	40.6(1)
C5	C4	C16	124.6(2)	124.5(2)
C1	C5	C4	102.3(2)	102.9(2)
C1	C5	C6	102.3(2)	103.1(2)
C1	C5	C12	111.8(2)	111.8(2)
C4	C5	C6	100.6(2)	98.8(2)
C4	C5	C12	118.0(2)	118.3(2)
C6	C5	C12	119.4(2)	119.6(2)
C4	C6	C5	39.6(1)	40.7(1)
C5	C6	C7	111.7(2)	111.4(2)
C5	C6	C17	122.4(2)	123.5(2)
C7	C6	C17	125.2(2)	124.7(2)
C6	C7	C8	110.9(2)	110.8(2)
C1	C8	C2	56.2(2)	54.9(1)
C1	C8	C7	107.2(2)	108.2(2)
C1	C8	C18	121.6(2)	122.4(2)
C2	C8	C7	119.7(2)	118.5(2)
C2	C8	C18	113.5(2)	113.9(2)
C7	C8	C18	121.7(2)	121.5(2)
C1	C9	C10	109.1(2)	108.6(2)
C9	C10	C11	113.6(2)	113.9(2)
C10	C11	C12	113.8(2)	113.3(2)
C5	C12	C11	109.1(2)	109.5(2)
O1	C15	O2	124.6(2)	123.9(2)
O1	C15	C2	111.5(2)	112.4(2)
O2	C15	C2	123.5(2)	123.5(2)
O3	C16	O4	123.7(2)	123.9(2)
O3	C16	C4	111.7(2)	111.9(2)
O4	C16	C4	124.5(3)	124.0(2)
O5	C17	O6	123.5(2)	123.9(2)
O5	C17	C6	112.4(2)	111.5(2)
O6	C17	C6	124.1(2)	124.6(2)
O7	C18	O8	124.4(2)	124.3(2)
O7	C18	C8	111.4(2)	111.6(2)
O8	C18	C8	124.2(2)	124.1(2)

Table 79. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-6 at **208 K**

	Unprimed			Primed		
Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O1	0.144	0.175	0.178	0.135	0.171	0.215
O2	0.147	0.202	0.238	0.144	0.192	0.276
O3	0.123	0.202	0.236	0.135	0.197	0.249
O4	0.137	0.216	0.278	0.149	0.210	0.249
O5	0.150	0.166	0.289	0.137	0.180	0.296
O6	0.158	0.181	0.326	0.150	0.185	0.310
O7	0.137	0.192	0.237	0.141	0.175	0.246
O8	0.148	0.187	0.272	0.142	0.191	0.234
C1	0.138	0.149	0.158	0.127	0.147	0.163
C2	0.133	0.154	0.171	0.128	0.157	0.194
C3	0.139	0.155	0.178	0.143	0.159	0.161
C4	0.138	0.161	0.166	0.138	0.165	0.175
C5	0.134	0.156	0.162	0.121	0.147	0.164
C6	0.153	0.159	0.166	0.149	0.173	0.203
C7	0.149	0.160	0.186	0.147	0.152	0.184
C8	0.144	0.166	0.173	0.140	0.161	0.195
C9	0.147	0.166	0.185	0.147	0.158	0.191
C10	0.163	0.171	0.205	0.152	0.164	0.210
C11	0.155	0.177	0.198	0.162	0.168	0.198
C12	0.147	0.175	0.182	0.144	0.166	0.179
C15	0.123	0.167	0.191	0.139	0.166	0.194
C16	0.143	0.170	0.191	0.148	0.163	0.189
C17	0.160	0.167	0.194	0.144	0.165	0.212
C18	0.137	0.177	0.184	0.148	0.175	0.175
C19	0.143	0.202	0.221	0.132	0.208	0.262
C20	0.120	0.244	0.277	0.125	0.245	0.276
C21	0.143	0.200	0.289	0.133	0.200	0.290
C22	0.118	0.224	0.256	0.140	0.206	0.241



R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Table 8–80. X-ray Crystal Data for Sb-6 at **208 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	117–118
Crystal size (mm)	0.21 x 0.25 x 0.33
Crystal system	monoclinic
Space group	*P2/n*
a (Å)	41.421(2)
b (Å)	7.382(1)
c (Å)	12.186(1)
β (°)	98.14(1)
Cell volume (Å^3)	3688.69(2.32)
Z	8
d_{calc} (g cm^{-3})	1.406
μ(Cu $K\alpha$) (cm^{-1})	8.77
Maximum θ (°)	60
Unique reflections	5477
Observed reflections [$I > 3.0\sigma(I)$]	3267
Number of variables	505
R	0.049
R_w	0.056
$(\Delta\rho)_{max}$ (e Å^{-3})	0.24
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.22

Table 81. Final Atomic Parameters for Sb-6 at **208 K**

Atom	x	y	z	B(Å^2)
O1	0.55553(6)	0.1514(4)	0.2615(2)	1.93(5)
O2	0.55611(6)	0.4198(4)	0.3490(2)	3.01(6)
O3	0.69207(6)	0.4033(4)	0.3903(2)	2.82(6)
O4	0.70584(6)	0.1156(4)	0.3633(2)	3.61(7)
O5	0.68208(6)	0.0817(5)	0.7594(2)	3.34(7)
O6	0.70741(6)	0.0311(5)	0.6130(2)	4.22(8)
O7	0.56064(6)	0.1215(4)	0.6688(2)	2.81(6)
O8	0.53723(6)	0.0937(4)	0.4914(2)	3.17(7)
C1	0.60547(8)	0.0092(5)	0.4388(3)	1.60(7)
C2	0.59738(9)	0.2010(5)	0.4091(3)	1.71(8)
C3	0.62774(9)	0.2931(5)	0.3909(3)	1.88(8)
C4	0.65322(9)	0.1812(5)	0.4105(3)	1.78(8)
C5	0.64370(8)	0.0049(6)	0.4648(3)	1.67(7)
C6	0.64992(9)	0.0577(5)	0.5870(3)	1.87(8)
C7	0.62318(9)	0.1325(6)	0.6201(3)	1.98(8)
C8	0.59511(9)	0.1201(5)	0.5335(3)	1.89(8)
C9	0.58953(9)	-0.1595(5)	0.3879(3)	1.92(8)
C10	0.6055(1)	-0.2102(6)	0.2853(3)	2.43(9)
C11	0.6432(1)	-0.2081(6)	0.3065(3)	2.34(9)
C12	0.65771(9)	-0.1714(5)	0.4271(3)	2.00(8)
C15	0.56701(9)	0.2693(5)	0.3405(3)	1.98(8)
C16	0.68656(9)	0.2237(6)	0.3870(3)	2.27(8)
C17	0.68262(9)	0.0542(6)	0.6519(3)	2.19(8)
C18	0.56083(9)	0.1105(6)	0.5590(3)	2.08(8)
C19	0.5290(1)	0.2157(6)	0.1810(3)	2.73(9)
C20	0.7234(1)	0.4586(7)	0.3622(4)	3.7(1)
C21	0.7136(1)	0.0751(7)	0.8297(3)	3.6(1)
C22	0.52862(9)	0.1089(7)	0.7045(3)	3.2(1)
O1'	0.44786(6)	0.3579(4)	-0.0505(2)	2.31(6)
O2'	0.44678(7)	0.0945(4)	0.0405(3)	3.44(7)
O3'	0.31000(6)	0.0959(4)	-0.0605(2)	2.89(6)
O4'	0.29670(7)	0.3826(4)	-0.1063(2)	3.25(7)
O5'	0.31784(6)	0.4193(5)	0.3140(2)	3.37(7)
O6'	0.29201(6)	0.4615(5)	0.1423(2)	3.77(7)
O7'	0.43808(6)	0.3720(4)	0.3504(2)	2.68(6)
O8'	0.46219(6)	0.4435(4)	0.2031(2)	2.76(6)
C1'	0.39517(8)	0.4973(5)	0.0739(3)	1.53(7)
C2'	0.40414(9)	0.3082(5)	0.0503(3)	1.94(8)
C3'	0.37468(9)	0.2126(5)	0.0025(3)	1.76(8)
C4'	0.34840(9)	0.3213(6)	-0.0022(3)	1.98(8)
C5'	0.35696(8)	0.4971(5)	0.0594(3)	1.43(7)
C6'	0.34978(9)	0.4384(6)	0.1735(3)	2.31(9)
C7'	0.37638(8)	0.3708(6)	0.2349(3)	1.86(8)
C8'	0.40499(8)	0.3934(6)	0.1801(3)	2.05(8)
C9'	0.41040(9)	0.6696(5)	0.0385(3)	1.97(8)
C10'	0.3951(1)	0.7151(6)	-0.0797(3)	2.32(8)
C11'	0.3572(1)	0.7118(6)	-0.0977(3)	2.35(9)
C12'	0.34264(9)	0.6719(6)	0.0088(3)	2.04(8)
C15'	0.43533(9)	0.2426(5)	0.0163(3)	2.00(8)
C16'	0.31544(9)	0.2746(6)	-0.0593(3)	1.95(8)
C17'	0.31665(9)	0.4408(6)	0.2055(3)	2.21(9)
C18'	0.43818(9)	0.4069(6)	0.2430(3)	1.99(8)
C19'	0.4761(1)	0.2962(6)	-0.0978(4)	3.2(1)
C20'	0.2790(1)	0.0379(7)	-0.1215(4)	4.0(1)
C21'	0.2865(1)	0.4268(7)	0.3545(3)	3.6(1)
C22'	0.4692(1)	0.3873(7)	0.4235(3)	3.2(1)

Table 81 (cont.). Final Atomic Parameters for Sb-6 at **208 K**

Atom	x	y	z	B(Å^2)
H3	0.629	0.422	0.366	2.2
H7	0.623	0.189	0.695	2.4
H9A	0.566	-0.138	0.365	2.4
H9B	0.593	-0.261	0.443	2.4
H10A	0.598	-0.122	0.225	2.8
H10B	0.598	-0.335	0.262	2.8
H11A	0.651	-0.111	0.259	2.7
H11B	0.651	-0.328	0.285	2.7
H12A	0.652	-0.272	0.475	2.5
H12B	0.682	-0.161	0.434	2.5
H19A	0.522	0.117	0.126	3.2
H19B	0.510	0.248	0.220	3.2
H19C	0.536	0.324	0.142	3.2
H20A	0.725	0.594	0.366	4.4
H20B	0.741	0.404	0.415	4.4
H20C	0.726	0.419	0.285	4.4
H21A	0.710	0.097	0.908	4.2
H21B	0.724	-0.045	0.822	4.2
H21C	0.728	0.173	0.805	4.2
H22A	0.531	0.119	0.787	3.8
H22B	0.514	0.209	0.670	3.8
H22C	0.519	-0.011	0.681	3.8
H3'	0.374	0.083	-0.023	2.1
H7'	0.377	0.312	0.309	2.3
H9A'	0.434	0.652	0.041	2.4
H9B'	0.406	0.771	0.090	2.4
H10A'	0.403	0.625	-0.131	2.7
H10B'	0.402	0.839	-0.098	2.7
H11A'	0.350	0.618	-0.154	2.7
H11B'	0.349	0.834	-0.126	2.7
H12A'	0.348	0.774	0.063	2.3
H12B'	0.318	0.659	-0.009	2.3
H19A'	0.483	0.393	-0.147	3.8
H19B'	0.494	0.267	-0.038	3.8
H19C'	0.470	0.184	-0.144	3.8
H20A'	0.277	-0.096	-0.117	4.4
H20B'	0.261	0.096	-0.088	4.4
H20C'	0.278	0.076	-0.200	4.4
H21A'	0.290	0.409	0.437	4.1
H21B'	0.276	0.546	0.337	4.1
H21C'	0.272	0.328	0.320	4.1
H22A'	0.466	0.359	0.500	3.5
H22B'	0.485	0.298	0.398	3.5
H22C'	0.478	0.512	0.418	3.5
H19BA'	0.480	0.164	-0.082	3.8
H19BB'	0.472	0.315	-0.181	3.8
H19BC'	0.496	0.366	-0.065	3.8

The parameters of the hydrogen atoms were not refined.

Table 82. Final Anisotropic Thermal Parameters (U's) for Sb-6 at **208 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.022(1)	0.022(1)	0.029(1)	0.004(1)	0.003(1)	0.004(1)
O2	0.032(1)	0.029(2)	0.053(2)	0.012(1)	0.003(1)	-0.004(2)
O3	0.024(1)	0.031(2)	0.056(2)	-0.009(1)	0.019(1)	0.003(1)
O4	0.029(1)	0.044(2)	0.071(2)	0.009(1)	0.028(1)	0.006(2)
O5	0.027(1)	0.073(2)	0.026(1)	0.010(2)	0.000(1)	-0.006(2)
O6	0.023(1)	0.102(3)	0.036(2)	0.004(2)	0.005(1)	-0.014(2)
O7	0.028(1)	0.053(2)	0.029(1)	-0.006(1)	0.017(1)	-0.004(1)
O8	0.023(1)	0.067(2)	0.030(1)	-0.007(2)	0.004(1)	0.003(2)
C1	0.018(2)	0.022(2)	0.023(2)	0.001(2)	0.008(1)	0.002(2)
C2	0.022(2)	0.019(2)	0.024(2)	0.001(2)	0.005(2)	0.003(2)
C3	0.023(2)	0.021(2)	0.029(2)	0.000(2)	0.007(2)	-0.001(2)
C4	0.023(2)	0.022(2)	0.023(2)	0.001(2)	0.005(2)	0.000(2)
C5	0.019(2)	0.021(2)	0.023(2)	-0.000(2)	0.005(1)	0.002(2)
C6	0.023(2)	0.024(2)	0.024(2)	-0.001(2)	0.005(2)	0.001(2)
C7	0.026(2)	0.026(2)	0.023(2)	-0.005(2)	0.006(2)	-0.002(2)
C8	0.027(2)	0.023(2)	0.024(2)	-0.002(2)	0.010(1)	-0.000(2)
C9	0.025(2)	0.020(2)	0.028(2)	-0.002(2)	0.002(2)	0.002(2)
C10	0.039(2)	0.028(2)	0.025(2)	0.001(2)	0.001(2)	-0.005(2)
C11	0.036(2)	0.026(2)	0.027(2)	0.002(2)	0.008(2)	-0.003(2)
C12	0.026(2)	0.022(2)	0.028(2)	0.004(2)	0.005(2)	-0.002(2)
C15	0.020(2)	0.025(2)	0.032(2)	-0.003(2)	0.010(2)	0.004(2)
C16	0.027(2)	0.035(2)	0.026(2)	0.001(2)	0.010(2)	0.003(2)
C17	0.027(2)	0.031(2)	0.026(2)	0.002(2)	0.005(2)	-0.002(2)
C18	0.029(2)	0.025(2)	0.027(2)	-0.003(2)	0.009(2)	-0.001(2)
C19	0.027(2)	0.035(2)	0.039(2)	0.002(2)	-0.005(2)	0.005(2)
C20	0.030(2)	0.050(3)	0.067(3)	-0.014(2)	0.026(2)	0.006(3)
C21	0.032(2)	0.073(4)	0.028(2)	0.010(3)	-0.006(2)	-0.005(2)
C22	0.030(2)	0.056(3)	0.042(2)	-0.006(2)	0.025(2)	-0.001(2)
O1'	0.030(1)	0.026(2)	0.035(1)	0.005(1)	0.016(1)	0.001(1)
O2'	0.034(1)	0.033(2)	0.067(2)	0.013(1)	0.021(1)	0.012(2)
O3'	0.026(1)	0.029(2)	0.051(2)	-0.010(1)	-0.009(1)	-0.003(1)
O4'	0.035(2)	0.038(2)	0.045(2)	0.006(2)	-0.011(1)	0.001(2)
O5'	0.021(1)	0.079(2)	0.030(1)	0.008(2)	0.011(1)	0.010(2)
O6'	0.023(1)	0.085(3)	0.036(2)	0.006(2)	0.006(1)	0.016(2)
O7'	0.022(1)	0.053(2)	0.026(1)	-0.005(1)	-0.002(1)	0.003(1)
O8'	0.016(1)	0.052(2)	0.037(1)	-0.002(1)	0.005(1)	-0.002(1)
C1'	0.016(2)	0.024(2)	0.020(2)	-0.001(2)	0.008(1)	0.000(2)
C2'	0.017(2)	0.022(2)	0.035(2)	0.001(2)	0.007(2)	-0.001(2)
C3'	0.023(2)	0.021(2)	0.024(2)	-0.001(2)	0.004(2)	0.001(2)
C4'	0.019(2)	0.026(2)	0.031(2)	-0.000(2)	0.004(2)	-0.003(2)
C5'	0.017(2)	0.020(2)	0.017(2)	0.002(2)	0.004(1)	-0.001(2)
C6'	0.027(2)	0.035(3)	0.026(2)	0.000(2)	0.007(2)	0.005(2)
C7'	0.020(2)	0.029(2)	0.022(2)	-0.001(2)	0.004(1)	-0.003(2)
C8'	0.016(2)	0.036(2)	0.027(2)	-0.001(2)	0.004(2)	0.004(2)
C9'	0.025(2)	0.019(2)	0.033(2)	-0.005(2)	0.012(2)	-0.003(2)
C10'	0.035(2)	0.026(2)	0.030(2)	0.003(2)	0.014(2)	0.005(2)
C11'	0.036(2)	0.022(2)	0.032(2)	0.004(2)	0.010(2)	0.006(2)
C12'	0.025(2)	0.024(2)	0.029(2)	0.003(2)	0.009(2)	0.001(2)
C15'	0.020(2)	0.022(2)	0.033(2)	-0.002(2)	0.002(2)	-0.003(2)
C16'	0.025(2)	0.027(2)	0.022(2)	0.003(2)	0.005(2)	-0.003(2)
C17'	0.024(2)	0.034(2)	0.027(2)	0.002(2)	0.006(2)	0.008(2)
C18'	0.021(2)	0.026(2)	0.027(2)	0.001(2)	0.000(2)	-0.002(2)
C19'	0.032(2)	0.039(3)	0.056(2)	0.005(2)	0.029(2)	0.003(2)
C20'	0.027(2)	0.053(3)	0.065(3)	-0.015(2)	-0.014(2)	-0.006(3)
C21'	0.027(2)	0.080(4)	0.035(2)	0.014(2)	0.019(2)	0.011(2)
C22'	0.025(2)	0.060(3)	0.032(2)	-0.000(2)	-0.007(2)	-0.005(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 83. Interatomic Distances (Å) for Sb-6 at 208 K

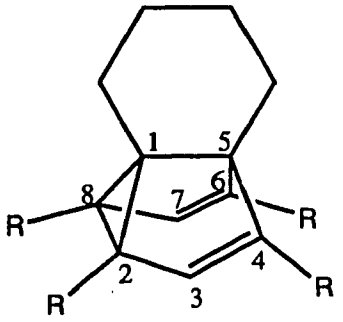
		Unprimed	Primed
O1	C15	1.334(4)	1.333(5)
O1	C19	1.446(4)	1.448(5)
O2	C15	1.209(5)	1.211(5)
O3	C16	1.345(5)	1.338(5)
O3	C20	1.447(5)	1.453(5)
O4	C16	1.193(5)	1.200(5)
O5	C17	1.328(5)	1.326(5)
O5	C21	1.459(5)	1.455(5)
O6	C17	1.203(5)	1.199(4)
O7	C18	1.341(4)	1.335(5)
O7	C22	1.456(5)	1.464(4)
O8	C18	1.192(4)	1.198(5)
C1	C2	1.488(5)	1.483(6)
C1	C5	1.571(5)	1.567(5)
C1	C8	1.525(5)	1.510(5)
C1	C9	1.502(5)	1.510(5)
C2	C3	1.474(5)	1.458(5)
C2	C8	1.644(5)	1.698(5)
C2	C15	1.496(5)	1.492(5)
C3	C4	1.335(5)	1.347(5)
C3	C7	3.065(5)	3.055(5)
C4	C5	1.537(6)	1.516(5)
C4	C6	2.357(5)	2.302(5)
C4	C16	1.483(5)	1.482(5)
C5	C6	1.525(5)	1.525(5)
C5	C12	1.522(6)	1.515(5)
C6	C7	1.349(5)	1.338(5)
C6	C17	1.469(5)	1.479(6)
C7	C8	1.458(5)	1.450(5)
C8	C18	1.498(5)	1.480(5)
C9	C10	1.541(6)	1.527(5)
C10	C11	1.548(6)	1.554(6)
C11	C12	1.531(5)	1.534(6)

Table 84. Angles (°) for Sb-6 at 208 K

			Unprimed	Primed
C15	O1	C19	115.7(3)	116.7(3)
C16	O3	C20	115.2(3)	115.5(3)
C17	O5	C21	115.8(3)	115.2(3)
C18	O7	C22	115.4(3)	117.1(3)
C2	C1	C5	104.7(3)	104.7(3)
C2	C1	C8	66.1(3)	69.1(3)
C2	C1	C9	128.2(3)	127.7(3)
C5	C1	C8	104.0(3)	104.0(3)
C5	C1	C9	116.0(3)	115.1(3)
C8	C1	C9	127.1(3)	126.9(3)
C1	C2	C3	108.0(3)	108.3(3)
C1	C2	C8	58.0(2)	56.2(2)
C1	C2	C15	126.8(3)	127.6(3)
C3	C2	C8	117.9(3)	117.2(3)
C3	C2	C15	115.4(3)	116.1(3)
C8	C2	C15	119.0(3)	118.3(3)
C2	C3	C4	110.9(3)	110.7(3)
C3	C4	C5	110.9(3)	111.0(3)
C3	C4	C16	124.7(4)	124.5(4)
C5	C4	C6	39.5(2)	40.9(2)
C5	C4	C16	124.4(3)	124.5(3)
C1	C5	C4	102.0(3)	102.6(3)
C1	C5	C6	102.6(3)	102.8(3)
C1	C5	C12	111.9(3)	112.1(3)
C4	C5	C6	100.7(3)	98.4(3)
C4	C5	C12	117.5(3)	118.5(3)
C6	C5	C12	119.6(3)	119.8(3)
C4	C6	C5	39.8(2)	40.7(2)
C5	C6	C7	111.4(3)	111.4(3)
C5	C6	C17	122.5(3)	123.0(3)
C7	C6	C17	125.4(3)	125.3(4)
C6	C7	C8	111.2(3)	111.2(3)
C1	C8	C2	55.9(2)	54.7(2)
C1	C8	C7	107.5(3)	108.3(3)
C1	C8	C18	120.6(3)	121.8(3)
C2	C8	C7	120.0(3)	118.4(3)
C2	C8	C18	112.9(3)	113.7(3)
C7	C8	C18	122.3(3)	122.0(3)
C1	C9	C10	108.8(3)	108.7(3)
C9	C10	C11	113.6(3)	114.0(3)
C10	C11	C12	114.3(3)	113.1(3)
C5	C12	C11	109.1(3)	109.3(3)
O1	C15	O2	124.2(3)	123.5(4)
O1	C15	C2	111.6(3)	112.9(3)
O2	C15	C2	123.8(3)	123.4(4)
O3	C16	O4	123.4(4)	123.6(3)
O3	C16	C4	111.2(3)	112.1(3)
O4	C16	C4	125.4(4)	124.0(4)
O5	C17	O6	123.0(3)	124.4(4)
O5	C17	C6	112.7(3)	110.9(3)
O6	C17	C6	124.3(3)	124.7(4)
O7	C18	O8	125.1(4)	124.0(3)
O7	C18	C8	110.1(3)	111.3(3)
O8	C18	C8	124.7(3)	124.7(3)

Table 85. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-6 at **208 K**

	Unprimed			Primed		
Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O1	0.132	0.158	0.177	0.130	0.164	0.210
O2	0.134	0.201	0.236	0.144	0.184	0.276
O3	0.109	0.189	0.244	0.122	0.188	0.244
O4	0.125	0.207	0.280	0.153	0.199	0.246
O5	0.153	0.165	0.276	0.128	0.174	0.285
O6	0.149	0.182	0.324	0.148	0.178	0.300
O7	0.119	0.192	0.236	0.137	0.169	0.234
O8	0.148	0.173	0.262	0.126	0.193	0.228
C1	0.118	0.143	0.162	0.106	0.151	0.155
C2	0.133	0.145	0.162	0.126	0.149	0.189
C3	0.142	0.147	0.173	0.142	0.152	0.155
C4	0.144	0.148	0.157	0.136	0.158	0.179
C5	0.134	0.144	0.157	0.120	0.134	0.148
C6	0.146	0.156	0.159	0.147	0.169	0.194
C7	0.142	0.151	0.180	0.138	0.146	0.174
C8	0.132	0.153	0.177	0.124	0.160	0.192
C9	0.137	0.157	0.171	0.125	0.145	0.196
C10	0.147	0.174	0.201	0.143	0.158	0.207
C11	0.150	0.171	0.193	0.140	0.170	0.202
C12	0.136	0.170	0.170	0.140	0.157	0.182
C15	0.117	0.164	0.186	0.135	0.153	0.186
C16	0.138	0.174	0.192	0.138	0.160	0.172
C17	0.154	0.166	0.179	0.143	0.154	0.199
C18	0.146	0.157	0.182	0.143	0.158	0.174
C19	0.146	0.187	0.218	0.122	0.197	0.259
C20	0.109	0.237	0.269	0.120	0.244	0.278
C21	0.142	0.195	0.278	0.118	0.195	0.294
C22	0.105	0.225	0.244	0.133	0.203	0.248



R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Table 8–86. X-ray Crystal Data for Sb-6 at **236 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	117–118
Crystal size (mm)	0.32 x 0.50 x 0.64
Crystal system	monoclinic
Space group	*P2/n*
a (Å)	41.455(2)
b (Å)	7.405(4)
c (Å)	12.210(3)
β (°)	98.10(2)
Cell volume ($Å^3$)	3710.03(8.46)
Z	8
d_{calc} (g cm^{-3})	1.398
μ(Cu $K\alpha$) (cm^{-1})	8.72
Maximum θ(°)	60
Unique reflections	5505
Observed reflections [$I > 3.0\sigma(I)$]	4174
Number of variables	505
R	0.046
R_w	0.060
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.26
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.26

Table 87. Final Atomic Parameters for Sb-6 at **236 K**

Atom	x	y	z	B(Å^2)
O1	0.55578(4)	0.1534(2)	0.2622(1)	2.43(4)
O2	0.55641(4)	0.4202(3)	0.3494(2)	3.59(4)
O3	0.69219(4)	0.4034(3)	0.3907(2)	3.35(4)
O4	0.70585(4)	0.1170(3)	0.3635(2)	4.28(5)
O5	0.68215(4)	0.0820(3)	0.7589(2)	4.12(5)
O6	0.70735(5)	0.0309(4)	0.6134(2)	5.01(6)
O7	0.56083(4)	0.1229(3)	0.6679(1)	3.37(4)
O8	0.53753(4)	0.0938(3)	0.4918(2)	3.91(5)
C1	0.60570(6)	0.0109(4)	0.4390(2)	2.02(5)
C2	0.59757(6)	0.2019(4)	0.4092(2)	2.10(5)
C3	0.62784(6)	0.2934(4)	0.3913(2)	2.20(5)
C4	0.65339(6)	0.1822(4)	0.4112(2)	2.16(5)
C5	0.64384(6)	0.0072(4)	0.4648(2)	2.05(5)
C6	0.65003(6)	0.0593(4)	0.5868(2)	2.35(5)
C7	0.62349(6)	0.1331(4)	0.6199(2)	2.42(5)
C8	0.59520(6)	0.1202(4)	0.5327(2)	2.37(5)
C9	0.58980(6)	-0.1582(4)	0.3879(2)	2.45(5)
C10	0.60557(7)	-0.2084(4)	0.2864(2)	2.93(6)
C11	0.64337(7)	-0.2062(4)	0.3069(2)	2.77(6)
C12	0.65750(6)	-0.1689(4)	0.4272(2)	2.57(5)
C15	0.56713(6)	0.2705(4)	0.3409(2)	2.39(5)
C16	0.68677(6)	0.2255(4)	0.3880(2)	2.52(5)
C17	0.68283(6)	0.0560(4)	0.6516(2)	2.72(6)
C18	0.56141(6)	0.1111(4)	0.5593(2)	2.47(5)
C19	0.52883(7)	0.2169(4)	0.1818(2)	3.31(6)
C20	0.72358(7)	0.4604(5)	0.3626(3)	4.56(8)
C21	0.71337(7)	0.0767(5)	0.8291(2)	4.36(8)
C22	0.52887(7)	0.1097(5)	0.7040(2)	3.84(7)
O1'	0.44781(4)	0.3560(3)	-0.0504(1)	2.80(4)
O2'	0.44673(5)	0.0944(3)	0.0401(2)	4.14(5)
O3'	0.31000(4)	0.0966(3)	-0.0602(2)	3.49(4)
O4'	0.29683(5)	0.3809(3)	-0.1062(2)	3.89(5)
O5'	0.31789(4)	0.4186(3)	0.3130(2)	4.13(5)
O6'	0.29195(4)	0.4599(4)	0.1422(2)	4.72(5)
O7'	0.43795(4)	0.3723(3)	0.3501(1)	3.30(4)
O8'	0.46211(4)	0.4426(3)	0.2030(2)	3.39(4)
C1'	0.39511(5)	0.4966(4)	0.0738(2)	1.93(5)
C2'	0.40408(6)	0.3079(4)	0.0493(2)	2.43(5)
C3'	0.37474(6)	0.2115(4)	0.0025(2)	2.19(5)
C4'	0.34834(6)	0.3192(4)	-0.0014(2)	2.34(5)
C5'	0.35699(5)	0.4960(4)	0.0592(2)	1.87(5)
C6'	0.34974(6)	0.4378(4)	0.1724(2)	2.81(6)
C7'	0.37644(6)	0.3701(4)	0.2348(2)	2.31(5)
C8'	0.40491(6)	0.3930(4)	0.1802(2)	2.55(5)
C9'	0.41035(6)	0.6674(4)	0.0385(2)	2.43(5)
C10'	0.39492(6)	0.7133(4)	-0.0797(2)	2.81(6)
C11'	0.35715(6)	0.7108(4)	-0.0972(2)	2.74(6)
C12'	0.34251(6)	0.6706(4)	0.0085(2)	2.36(5)
C15'	0.43545(6)	0.2415(4)	0.0156(2)	2.48(5)
C16'	0.31543(6)	0.2736(4)	-0.0592(2)	2.54(5)
C17'	0.31676(6)	0.4394(4)	0.2050(2)	2.73(6)
C18'	0.43813(6)	0.4055(4)	0.2433(2)	2.44(5)
C19'	0.47616(7)	0.2945(5)	-0.0974(3)	3.84(7)
C20'	0.27901(7)	0.0385(5)	-0.1207(3)	4.57(8)
C21'	0.28693(7)	0.4261(5)	0.3545(2)	4.38(8)
C22'	0.46899(7)	0.3859(5)	0.4220(2)	3.58(7)

Table 87 (cont.). Final Atomic Parameters for Sb-6 at **236 K**

Atom	x	y	z	B(Å^2)
H3	0.629	0.422	0.367	2.4
H7	0.623	0.189	0.694	2.6
H9A	0.566	-0.136	0.365	2.6
H9B	0.593	-0.259	0.443	2.6
H10A	0.598	-0.120	0.226	3.1
H10B	0.598	-0.333	0.262	3.1
H11A	0.651	-0.110	0.259	3.0
H11B	0.651	-0.327	0.285	3.0
H12A	0.652	-0.270	0.475	2.8
H12B	0.682	-0.160	0.434	2.8
H19A	0.522	0.119	0.127	3.6
H19B	0.510	0.249	0.221	3.6
H19C	0.536	0.326	0.143	3.6
H20A	0.725	0.595	0.367	4.9
H20B	0.741	0.405	0.416	4.9
H20C	0.726	0.420	0.286	4.9
H21A	0.710	0.097	0.908	4.7
H21B	0.724	-0.044	0.823	4.7
H21C	0.728	0.173	0.806	4.7
H22A	0.531	0.120	0.786	4.2
H22B	0.515	0.209	0.670	4.2
H22C	0.519	-0.009	0.681	4.2
H3'	0.374	0.083	-0.023	2.3
H7'	0.377	0.312	0.309	2.5
H9A'	0.434	0.649	0.041	2.6
H9B'	0.406	0.768	0.089	2.6
H10A'	0.403	0.623	-0.131	3.0
H10B'	0.402	0.837	-0.098	3.0
H11A'	0.350	0.616	-0.153	2.9
H11B'	0.349	0.832	-0.126	2.9
H12A'	0.348	0.772	0.062	2.5
H12B'	0.318	0.658	-0.010	2.5
H19A'	0.483	0.391	-0.146	4.1
H19B'	0.494	0.266	-0.036	4.1
H19C'	0.470	0.184	-0.143	4.1
H20A'	0.277	-0.096	-0.117	5.0
H20B'	0.261	0.095	-0.087	5.0
H20C'	0.278	0.076	-0.200	5.0
H21A'	0.290	0.409	0.437	4.8
H21B'	0.276	0.546	0.336	4.8
H21C'	0.272	0.328	0.319	4.8
H22A'	0.466	0.358	0.500	3.9
H22B'	0.485	0.298	0.398	3.9
H22C'	0.478	0.511	0.418	3.9
H19BA'	0.479	0.161	-0.081	4.1
H19BB'	0.473	0.313	-0.178	4.1
H19BC'	0.496	0.360	-0.063	4.1

The parameters of the hydrogen atoms were not refined.

Table 88. Final Anisotropic Thermal Parameters (U's) for Sb-6 at **236 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0267(8)	0.031(1)	0.0341(9)	0.0049(8)	0.0011(7)	0.0028(8)
O2	0.039(1)	0.033(1)	0.064(1)	0.0132(9)	0.0032(9)	-0.006(1)
O3	0.0280(9)	0.040(1)	0.064(1)	-0.0093(9)	0.0199(8)	0.002(1)
O4	0.0353(9)	0.053(1)	0.081(1)	0.008(1)	0.0310(9)	0.005(1)
O5	0.032(1)	0.095(2)	0.0286(9)	0.013(1)	-0.0007(8)	-0.005(1)
O6	0.029(1)	0.118(2)	0.043(1)	0.004(1)	0.0052(9)	-0.018(1)
O7	0.0326(9)	0.063(1)	0.0360(9)	-0.006(1)	0.0165(7)	-0.004(1)
O8	0.0263(9)	0.082(2)	0.041(1)	-0.009(1)	0.0070(8)	0.002(1)
C1	0.024(1)	0.028(1)	0.026(1)	-0.001(1)	0.006(1)	0.003(1)
C2	0.022(1)	0.027(1)	0.032(1)	0.000(1)	0.007(1)	0.002(1)
C3	0.024(1)	0.027(1)	0.034(1)	-0.002(1)	0.010(1)	-0.001(1)
C4	0.024(1)	0.030(1)	0.029(1)	0.001(1)	0.009(1)	-0.000(1)
C5	0.022(1)	0.027(1)	0.028(1)	0.000(1)	0.004(1)	0.002(1)
C6	0.027(1)	0.033(1)	0.029(1)	-0.002(1)	0.004(1)	-0.000(1)
C7	0.029(1)	0.036(2)	0.028(1)	-0.003(1)	0.007(1)	-0.003(1)
C8	0.027(1)	0.035(1)	0.029(1)	-0.001(1)	0.009(1)	-0.003(1)
C9	0.034(1)	0.026(1)	0.033(1)	-0.003(1)	0.002(1)	0.000(1)
C10	0.043(1)	0.033(2)	0.034(1)	0.003(1)	0.002(1)	-0.003(1)
C11	0.042(1)	0.031(1)	0.033(1)	0.004(1)	0.008(1)	-0.002(1)
C12	0.033(1)	0.030(1)	0.035(1)	0.006(1)	0.006(1)	0.002(1)
C15	0.024(1)	0.032(1)	0.037(1)	-0.000(1)	0.012(1)	0.005(1)
C16	0.025(1)	0.038(2)	0.034(1)	0.002(1)	0.009(1)	0.004(1)
C17	0.028(1)	0.042(2)	0.033(1)	0.000(1)	0.004(1)	-0.005(1)
C18	0.027(1)	0.036(1)	0.033(1)	-0.004(1)	0.010(1)	0.001(1)
C19	0.032(1)	0.044(2)	0.046(2)	0.005(1)	-0.007(1)	0.009(1)
C20	0.034(1)	0.061(2)	0.083(2)	-0.015(2)	0.026(1)	0.007(2)
C21	0.038(2)	0.090(3)	0.034(1)	0.015(2)	-0.008(1)	-0.006(2)
C22	0.039(1)	0.062(2)	0.051(2)	-0.008(2)	0.029(1)	-0.002(2)
O1'	0.0349(9)	0.034(1)	0.0406(9)	0.0062(8)	0.0173(7)	0.0019(9)
O2'	0.040(1)	0.039(1)	0.083(1)	0.016(1)	0.0249(9)	0.016(1)
O3'	0.0286(9)	0.037(1)	0.063(1)	-0.0083(9)	-0.0083(9)	-0.002(1)
O4'	0.038(1)	0.049(1)	0.055(1)	0.006(1)	-0.0131(9)	-0.001(1)
O5'	0.0273(9)	0.095(2)	0.036(1)	0.012(1)	0.0104(8)	0.011(1)
O6'	0.0255(9)	0.111(2)	0.044(1)	0.006(1)	0.0065(8)	0.016(1)
O7'	0.0263(9)	0.065(1)	0.0325(9)	-0.005(1)	-0.0020(8)	0.004(1)
O8'	0.0215(9)	0.064(1)	0.043(1)	-0.002(1)	0.0050(8)	0.001(1)
C1'	0.020(1)	0.029(1)	0.025(1)	-0.000(1)	0.0051(9)	-0.002(1)
C2'	0.021(1)	0.028(1)	0.044(1)	0.001(1)	0.005(1)	-0.003(1)
C3'	0.026(1)	0.029(1)	0.029(1)	-0.003(1)	0.004(1)	-0.000(1)
C4'	0.022(1)	0.031(1)	0.036(1)	-0.000(1)	0.002(1)	-0.002(1)
C5'	0.020(1)	0.026(1)	0.026(1)	0.003(1)	0.0055(9)	-0.003(1)
C6'	0.027(1)	0.045(2)	0.036(1)	0.002(1)	0.008(1)	0.009(1)
C7'	0.026(1)	0.037(2)	0.025(1)	-0.002(1)	0.005(1)	0.002(1)
C8'	0.021(1)	0.042(2)	0.033(1)	-0.003(1)	0.004(1)	0.006(1)
C9'	0.029(1)	0.028(1)	0.037(1)	-0.004(1)	0.012(1)	-0.002(1)
C10'	0.040(1)	0.032(2)	0.038(1)	0.004(1)	0.015(1)	0.005(1)
C11'	0.038(1)	0.032(1)	0.036(1)	0.004(1)	0.011(1)	0.005(1)
C12'	0.029(1)	0.030(1)	0.032(1)	0.005(1)	0.008(1)	0.001(1)
C15'	0.023(1)	0.030(1)	0.042(1)	-0.001(1)	0.003(1)	-0.002(1)
C16'	0.024(1)	0.040(2)	0.032(1)	0.000(1)	0.004(1)	-0.003(1)
C17'	0.026(1)	0.044(2)	0.035(1)	0.003(1)	0.009(1)	0.008(1)
C18'	0.024(1)	0.034(1)	0.033(1)	0.001(1)	0.002(1)	-0.000(1)
C19'	0.042(1)	0.050(2)	0.061(2)	0.010(1)	0.031(1)	0.002(2)
C20'	0.035(2)	0.062(2)	0.068(2)	-0.016(2)	-0.018(2)	-0.009(2)
C21'	0.033(1)	0.095(3)	0.043(1)	0.010(2)	0.020(1)	0.008(2)
C22'	0.031(1)	0.065(2)	0.036(1)	-0.001(2)	-0.009(1)	-0.005(2)

The form of the anisotropic displacement parameter is:
$\exp(-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)])$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 89. Iinteratomic Distances (Å) for Sb-6 at **236 K**

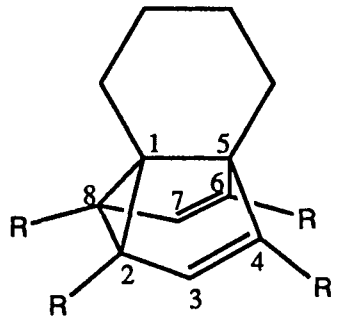
		Unprimed	Primed
O1	C15	1.330(3)	1.322(3)
O1	C19	1.456(3)	1.453(4)
O2	C15	1.204(3)	1.206(3)
O3	C16	1.336(3)	1.330(3)
O3	C20	1.455(4)	1.453(3)
O4	C16	1.195(3)	1.195(3)
O5	C17	1.327(3)	1.322(3)
O5	C21	1.448(3)	1.446(4)
O6	C17	1.192(3)	1.202(3)
O7	C18	1.332(3)	1.328(3)
O7	C22	1.458(3)	1.454(3)
O8	C18	1.201(3)	1.202(3)
C1	C2	1.488(4)	1.487(4)
C1	C5	1.568(3)	1.565(3)
C1	C8	1.516(4)	1.514(3)
C1	C9	1.508(4)	1.504(4)
C2	C3	1.469(3)	1.455(3)
C2	C8	1.641(4)	1.714(4)
C2	C15	1.499(3)	1.501(4)
C3	C4	1.337(3)	1.349(4)
C3	C7	3.062(4)	3.061(3)
C4	C5	1.529(4)	1.522(4)
C4	C6	2.351(4)	2.290(4)
C4	C16	1.486(4)	1.483(3)
C5	C6	1.524(3)	1.519(4)
C5	C12	1.519(4)	1.519(4)
C6	C7	1.342(4)	1.348(3)
C6	C17	1.473(3)	1.477(4)
C7	C8	1.471(3)	1.446(4)
C8	C18	1.483(4)	1.482(3)
C9	C10	1.527(4)	1.531(3)
C10	C11	1.551(4)	1.550(4)
C11	C12	1.528(4)	1.531(4)

Table 90. Angles (°) for Sb-6 at **236 K**

			Unprimed	Primed
C15	O1	C19	115.8(2)	116.4(2)
C16	O3	C20	115.7(2)	115.7(2)
C17	O5	C21	115.9(2)	115.9(2)
C18	O7	C22	116.3(2)	116.9(2)
C2	C1	C5	104.6(2)	104.6(2)
C2	C1	C8	66.2(2)	69.6(2)
C2	C1	C9	128.2(2)	127.2(2)
C5	C1	C8	104.3(2)	103.9(2)
C5	C1	C9	116.0(2)	115.4(2)
C8	C1	C9	126.9(2)	126.9(2)
C1	C2	C3	107.8(2)	108.7(2)
C1	C2	C8	57.7(2)	55.9(2)
C1	C2	C15	127.0(2)	127.9(2)
C3	C2	C8	118.1(2)	116.8(2)
C3	C2	C15	115.5(2)	116.1(2)
C8	C2	C15	118.7(2)	118.2(2)
C2	C3	C4	111.1(2)	110.6(2)
C3	C4	C5	110.7(2)	111.0(2)
C3	C4	C16	124.6(2)	124.7(2)
C5	C4	C6	39.6(1)	41.1(1)
C5	C4	C16	124.7(2)	124.4(2)
C1	C5	C4	102.4(2)	102.8(2)
C1	C5	C6	102.5(2)	103.0(2)
C1	C5	C12	111.3(2)	112.2(2)
C4	C5	C6	100.7(2)	97.8(2)
C4	C5	C12	117.9(2)	118.8(2)
C6	C5	C12	119.6(2)	119.7(2)
C4	C6	C5	39.7(1)	41.2(1)
C5	C6	C7	111.5(2)	111.5(2)
C5	C6	C17	122.4(2)	123.6(2)
C7	C6	C17	125.3(2)	124.6(2)
C6	C7	C8	111.0(2)	110.8(2)
C1	C8	C2	56.0(2)	54.5(2)
C1	C8	C7	107.2(2)	108.6(2)
C1	C8	C18	121.5(2)	122.1(2)
C2	C8	C7	119.7(2)	118.5(2)
C2	C8	C18	113.6(2)	113.7(2)
C7	C8	C18	121.7(2)	121.8(2)
C1	C9	C10	109.0(2)	108.7(2)
C9	C10	C11	113.9(2)	113.9(2)
C10	C11	C12	113.4(2)	113.6(2)
C5	C12	C11	109.7(2)	109.1(2)
O1	C15	O2	124.5(2)	124.1(2)
O1	C15	C2	111.4(2)	112.5(2)
O2	C15	C2	123.8(2)	123.2(2)
O3	C16	O4	123.6(2)	123.6(2)
O3	C16	C4	111.5(2)	111.8(2)
O4	C16	C4	124.7(3)	124.3(3)
O5	C17	O6	123.2(2)	123.9(2)
O5	C17	C6	112.4(2)	111.4(2)
O6	C17	C6	124.4(2)	124.7(2)
O7	C18	O8	124.0(2)	124.4(2)
O7	C18	C8	111.5(2)	111.4(2)
O8	C18	C8	124.5(2)	124.2(2)

Table 91. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-6 at **236 K**

	Unprimed			Primed		
Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O1	0.150	0.184	0.190	0.149	0.184	0.224
O2	0.148	0.217	0.260	0.153	0.202	0.305
O3	0.130	0.210	0.258	0.144	0.203	0.266
O4	0.145	0.230	0.298	0.163	0.221	0.269
O5	0.159	0.182	0.313	0.151	0.188	0.314
O6	0.169	0.197	0.351	0.158	0.200	0.338
O7	0.143	0.207	0.255	0.152	0.190	0.257
O8	0.155	0.202	0.290	0.146	0.208	0.254
C1	0.146	0.161	0.172	0.139	0.158	0.171
C2	0.141	0.163	0.183	0.142	0.166	0.211
C3	0.143	0.163	0.191	0.155	0.170	0.174
C4	0.143	0.174	0.178	0.146	0.175	0.192
C5	0.148	0.160	0.174	0.130	0.158	0.171
C6	0.162	0.171	0.184	0.157	0.178	0.225
C7	0.155	0.170	0.197	0.152	0.164	0.194
C8	0.150	0.176	0.191	0.144	0.175	0.214
C9	0.157	0.176	0.194	0.150	0.168	0.204
C10	0.175	0.186	0.215	0.166	0.174	0.221
C11	0.167	0.184	0.208	0.168	0.177	0.211
C12	0.159	0.183	0.197	0.153	0.172	0.192
C15	0.135	0.175	0.205	0.150	0.172	0.206
C16	0.150	0.179	0.203	0.154	0.177	0.204
C17	0.167	0.178	0.210	0.154	0.176	0.222
C18	0.146	0.187	0.194	0.154	0.184	0.187
C19	0.152	0.213	0.240	0.143	0.223	0.275
C20	0.134	0.261	0.295	0.134	0.263	0.294
C21	0.154	0.215	0.310	0.140	0.221	0.313
C22	0.130	0.242	0.266	0.145	0.221	0.257



R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Table 8–92. X-ray Crystal Data for Sb-6 at **236 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	117–118
Crystal size (mm)	0.21 x 0.25 x 0.33
Crystal system	monoclinic
Space group	*P2/n*
a (Å)	41.451(2)
b (Å)	7.407(1)
c (Å)	12.209(1)
β (°)	98.17(1)
Cell volume ($Å^3$)	3710.32(2.38)
Z	8
d_{calc} (g cm^{-3})	1.398
μ(Cu $K\alpha$) (cm^{-1})	8.72
Maximum θ (°)	60
Unique reflections	5508
Observed reflections [$I > 3.0\sigma(I)$]	3138
Number of variables	505
R	0.051
R_w	0.059
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.24
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.27

Table 93. Final Atomic Parameters for Sb-6 at **236 K**

Atom	x	y	z	B(Å^2)
O1	0.55572(6)	0.1532(4)	0.2623(2)	2.22(6)
O2	0.55643(7)	0.4198(4)	0.3495(3)	3.53(7)
O3	0.69229(7)	0.4030(4)	0.3905(3)	3.35(7)
O4	0.70574(7)	0.1166(5)	0.3638(3)	4.19(8)
O5	0.68215(7)	0.0832(5)	0.7588(2)	3.96(8)
O6	0.70740(7)	0.0316(6)	0.6129(3)	4.97(9)
O7	0.56095(6)	0.1226(5)	0.6684(2)	3.18(7)
O8	0.53755(7)	0.0936(5)	0.4925(2)	3.67(8)
C1	0.60572(9)	0.0101(6)	0.4389(3)	1.87(8)
C2	0.59762(9)	0.2027(6)	0.4093(3)	1.92(8)
C3	0.62792(9)	0.2946(6)	0.3911(3)	2.12(9)
C4	0.65351(9)	0.1828(6)	0.4110(3)	2.01(9)
C5	0.64384(9)	0.0069(6)	0.4647(3)	1.72(8)
C6	0.65015(9)	0.0595(6)	0.5868(3)	2.08(9)
C7	0.6233(1)	0.1328(6)	0.6205(3)	2.32(9)
C8	0.59529(9)	0.1212(6)	0.5333(3)	2.12(9)
C9	0.5897(1)	-0.1575(6)	0.3882(3)	2.38(9)
C10	0.6057(1)	-0.2085(6)	0.2867(3)	2.8(1)
C11	0.6434(1)	-0.2061(7)	0.3071(3)	2.7(1)
C12	0.6578(1)	-0.1694(6)	0.4278(3)	2.29(9)
C15	0.56737(9)	0.2703(6)	0.3409(3)	2.24(9)
C16	0.6865(1)	0.2254(6)	0.3883(3)	2.45(9)
C17	0.6825(1)	0.0555(6)	0.6520(3)	2.8(1)
C18	0.56117(9)	0.1106(6)	0.5590(3)	2.37(9)
C19	0.5290(1)	0.2178(7)	0.1824(4)	3.1(1)
C20	0.7238(1)	0.4590(7)	0.3630(4)	4.3(1)
C21	0.7136(1)	0.0763(8)	0.8295(4)	3.9(1)
C22	0.5290(1)	0.1092(7)	0.7039(4)	3.6(1)
O1'	0.44781(6)	0.3560(4)	-0.0504(2)	2.69(6)
O2'	0.44679(7)	0.0948(5)	0.0401(3)	4.12(8)
O3'	0.30986(7)	0.0964(4)	-0.0602(3)	3.34(7)
O4'	0.29683(7)	0.3807(5)	-0.1063(3)	3.90(8)
O5'	0.31791(7)	0.4195(5)	0.3128(2)	3.98(8)
O6'	0.29217(7)	0.4597(5)	0.1422(2)	4.41(9)
O7'	0.43792(7)	0.3723(5)	0.3503(2)	3.21(7)
O8'	0.46210(6)	0.4431(5)	0.2029(2)	3.24(7)
C1'	0.39519(9)	0.4958(6)	0.0740(3)	1.85(8)
C2'	0.40407(9)	0.3087(6)	0.0490(3)	2.24(9)
C3'	0.37461(9)	0.2124(6)	0.0027(3)	1.94(8)
C4'	0.34825(9)	0.3199(6)	-0.0010(3)	2.24(9)
C5'	0.35690(9)	0.4955(6)	0.0593(3)	1.74(8)
C6'	0.3496(1)	0.4368(6)	0.1723(3)	2.6(1)
C7'	0.37644(9)	0.3701(6)	0.2344(3)	2.04(9)
C8'	0.40502(9)	0.3938(6)	0.1806(3)	2.36(9)
C9'	0.4106(1)	0.6672(6)	0.0384(3)	2.33(9)
C10'	0.3951(1)	0.7126(6)	-0.0793(3)	2.61(9)
C11'	0.3572(1)	0.7102(6)	-0.0976(3)	2.7(1)
C12'	0.34250(9)	0.6704(6)	0.0080(3)	2.19(9)
C15'	0.43526(9)	0.2416(6)	0.0157(4)	2.35(9)
C16'	0.3155(1)	0.2726(6)	-0.0590(3)	2.38(9)
C17'	0.3167(1)	0.4389(6)	0.2050(3)	2.6(1)
C18'	0.4380(1)	0.4061(6)	0.2431(3)	2.21(9)
C19'	0.4762(1)	0.2940(7)	-0.0973(4)	3.7(1)
C20'	0.2792(1)	0.0387(7)	-0.1213(4)	4.3(1)
C21'	0.2866(1)	0.4269(8)	0.3541(4)	4.3(1)
C22'	0.4691(1)	0.3858(7)	0.4228(4)	3.5(1)

Table 93 (cont.). Final Atomic Parameters for Sb-6 at **236 K**

Atom	x	y	z	B(Å^2)
H3	0.629	0.422	0.367	2.4
H7	0.623	0.189	0.694	2.6
H9A	0.566	-0.136	0.365	2.6
H9B	0.593	-0.259	0.443	2.6
H10A	0.598	-0.120	0.226	3.1
H10B	0.598	-0.333	0.262	3.1
H11A	0.651	-0.110	0.259	3.0
H11B	0.651	-0.327	0.285	3.0
H12A	0.652	-0.270	0.475	2.8
H12B	0.682	-0.160	0.434	2.8
H19A	0.522	0.119	0.127	3.6
H19B	0.510	0.249	0.221	3.6
H19C	0.536	0.326	0.143	3.6
H20A	0.725	0.595	0.367	4.9
H20B	0.741	0.405	0.416	4.9
H20C	0.726	0.420	0.286	4.9
H21A	0.710	0.097	0.908	4.7
H21B	0.724	-0.044	0.823	4.7
H21C	0.728	0.173	0.806	4.7
H22A	0.531	0.120	0.786	4.2
H22B	0.515	0.209	0.670	4.2
H22C	0.519	-0.009	0.681	4.2
H3'	0.374	0.083	-0.023	2.3
H7'	0.377	0.312	0.309	2.5
H9A'	0.434	0.649	0.041	2.6
H9B'	0.406	0.768	0.089	2.6
H10A'	0.403	0.623	-0.131	3.0
H10B'	0.402	0.837	-0.098	3.0
H11A'	0.350	0.616	-0.153	2.9
H11B'	0.349	0.832	-0.126	2.9
H12A'	0.348	0.772	0.062	2.5
H12B'	0.318	0.658	-0.010	2.5
H19A'	0.483	0.391	-0.146	4.1
H19B'	0.494	0.266	-0.036	4.1
H19C'	0.470	0.184	-0.143	4.1
H20A'	0.277	-0.096	-0.117	5.0
H20B'	0.261	0.095	-0.087	5.0
H20C'	0.278	0.076	-0.200	5.0
H21A'	0.290	0.409	0.437	4.8
H21B'	0.276	0.546	0.336	4.8
H21C'	0.272	0.328	0.319	4.8
H22A'	0.466	0.358	0.500	3.9
H22B'	0.485	0.298	0.398	3.9
H22C'	0.478	0.511	0.418	3.9
H19BA'	0.479	0.161	-0.081	4.1
H19BB'	0.473	0.313	-0.178	4.1
H19BC'	0.496	0.360	-0.063	4.1

The parameters of the hydrogen atoms were not refined.

Table 94. Final Anisotropic Thermal Parameters (U's) for Sb-6 at **236 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.027(1)	0.026(2)	0.031(1)	0.005(1)	0.001(1)	0.004(1)
O2	0.039(2)	0.030(2)	0.064(2)	0.012(2)	0.004(2)	-0.004(2)
O3	0.030(1)	0.036(2)	0.066(2)	-0.009(1)	0.024(1)	0.002(2)
O4	0.033(2)	0.047(2)	0.086(2)	0.011(2)	0.031(1)	0.004(2)
O5	0.034(2)	0.090(3)	0.026(2)	0.013(2)	-0.000(1)	-0.009(2)
O6	0.027(2)	0.117(3)	0.045(2)	0.004(2)	0.004(1)	-0.021(2)
O7	0.033(2)	0.058(2)	0.034(1)	-0.003(2)	0.017(1)	-0.003(2)
O8	0.026(1)	0.075(3)	0.039(2)	-0.010(2)	0.006(1)	0.002(2)
C1	0.021(2)	0.023(2)	0.028(2)	0.001(2)	0.008(2)	0.002(2)
C2	0.022(2)	0.022(2)	0.030(2)	0.004(2)	0.007(2)	0.005(2)
C3	0.024(2)	0.024(2)	0.034(2)	-0.002(2)	0.012(2)	-0.001(2)
C4	0.028(2)	0.024(2)	0.027(2)	0.000(2)	0.011(2)	-0.001(2)
C5	0.019(2)	0.021(2)	0.026(2)	0.004(2)	0.005(2)	-0.001(2)
C6	0.024(2)	0.032(3)	0.024(2)	-0.000(2)	0.006(2)	0.002(2)
C7	0.031(2)	0.033(3)	0.024(2)	-0.005(2)	0.004(2)	-0.002(2)
C8	0.029(2)	0.030(3)	0.023(2)	0.000(2)	0.011(2)	0.000(2)
C9	0.034(2)	0.026(3)	0.029(2)	-0.003(2)	0.002(2)	0.001(2)
C10	0.046(3)	0.026(3)	0.033(2)	-0.000(2)	0.002(2)	-0.002(2)
C11	0.039(2)	0.036(3)	0.030(2)	0.003(2)	0.009(2)	-0.001(2)
C12	0.031(2)	0.024(2)	0.033(2)	0.004(2)	0.007(2)	0.002(2)
C15	0.022(2)	0.027(2)	0.038(2)	-0.002(2)	0.013(2)	0.003(2)
C16	0.028(2)	0.036(3)	0.030(2)	0.005(2)	0.010(2)	0.005(2)
C17	0.034(2)	0.040(3)	0.031(2)	-0.001(2)	0.006(2)	-0.006(2)
C18	0.026(2)	0.032(3)	0.033(2)	-0.004(2)	0.010(2)	0.001(2)
C19	0.035(2)	0.035(3)	0.046(3)	0.008(2)	-0.006(2)	0.008(2)
C20	0.032(2)	0.058(4)	0.081(3)	-0.018(2)	0.029(2)	0.008(3)
C21	0.034(2)	0.080(4)	0.030(2)	0.009(3)	-0.010(2)	-0.007(3)
C22	0.033(2)	0.065(4)	0.045(2)	-0.012(3)	0.027(2)	-0.001(3)
O1'	0.033(1)	0.029(2)	0.044(2)	0.006(1)	0.018(1)	0.003(1)
O2'	0.042(2)	0.040(2)	0.080(2)	0.016(2)	0.027(1)	0.014(2)
O3'	0.029(2)	0.033(2)	0.060(2)	-0.010(2)	-0.009(1)	-0.003(2)
O4'	0.041(2)	0.048(2)	0.053(2)	0.005(2)	-0.012(2)	0.002(2)
O5'	0.027(2)	0.091(3)	0.035(2)	0.011(2)	0.009(1)	0.011(2)
O6'	0.029(2)	0.098(3)	0.041(2)	0.008(2)	0.008(1)	0.018(2)
O7'	0.026(1)	0.061(2)	0.032(2)	-0.008(2)	-0.003(1)	0.004(2)
O8'	0.020(1)	0.060(2)	0.043(2)	-0.003(2)	0.008(1)	0.001(2)
C1'	0.023(2)	0.024(2)	0.025(2)	-0.000(2)	0.009(2)	-0.003(2)
C2'	0.019(2)	0.025(2)	0.042(2)	0.002(2)	0.007(2)	-0.002(2)
C3'	0.026(2)	0.023(2)	0.026(2)	-0.005(2)	0.006(2)	-0.000(2)
C4'	0.019(2)	0.032(3)	0.034(2)	-0.002(2)	0.003(2)	-0.004(2)
C5'	0.019(2)	0.024(2)	0.023(2)	0.001(2)	0.004(2)	-0.004(2)
C6'	0.029(2)	0.039(3)	0.033(2)	-0.002(2)	0.010(2)	0.005(2)
C7'	0.021(2)	0.033(3)	0.023(2)	-0.001(2)	0.003(2)	0.002(2)
C8'	0.019(2)	0.040(3)	0.029(2)	-0.002(2)	0.002(2)	0.005(2)
C9'	0.029(2)	0.025(2)	0.036(2)	-0.005(2)	0.010(2)	-0.003(2)
C10'	0.039(2)	0.026(3)	0.036(2)	0.008(2)	0.015(2)	0.007(2)
C11'	0.038(2)	0.031(3)	0.036(2)	0.006(2)	0.013(2)	0.005(2)
C12'	0.026(2)	0.024(2)	0.035(2)	0.007(2)	0.011(2)	0.001(2)
C15'	0.020(2)	0.025(3)	0.044(2)	-0.001(2)	0.004(2)	0.000(2)
C16'	0.023(2)	0.033(3)	0.036(2)	0.001(2)	0.008(2)	-0.001(2)
C17'	0.024(2)	0.042(3)	0.030(2)	0.004(2)	0.004(2)	0.011(2)
C18'	0.029(2)	0.026(2)	0.030(2)	-0.000(2)	0.004(2)	0.002(2)
C19'	0.039(2)	0.047(3)	0.062(3)	0.009(2)	0.033(2)	0.008(3)
C20'	0.033(3)	0.054(4)	0.069(3)	-0.015(3)	-0.016(2)	-0.008(3)
C21'	0.034(2)	0.093(4)	0.040(2)	0.015(3)	0.019(2)	0.010(3)
C22'	0.034(2)	0.060(3)	0.035(2)	-0.002(3)	-0.009(2)	-0.006(3)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 95. Interatomic Distances (Å) for Sb-6 at **236 K**

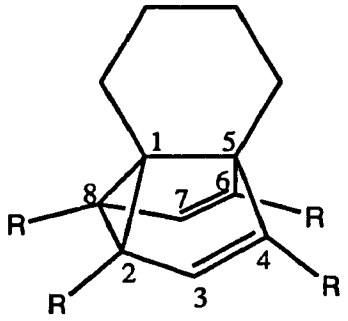
		Unprimed	Primed
O1	C15	1.332(5)	1.326(5)
O1	C19	1.449(5)	1.453(6)
O2	C15	1.206(5)	1.208(5)
O3	C16	1.336(6)	1.326(6)
O3	C20	1.455(6)	1.444(5)
O4	C16	1.200(5)	1.202(5)
O5	C17	1.322(5)	1.319(5)
O5	C21	1.460(5)	1.460(6)
O6	C17	1.210(5)	1.193(5)
O7	C18	1.340(5)	1.333(5)
O7	C22	1.455(5)	1.462(5)
O8	C18	1.187(5)	1.205(5)
C1	C2	1.498(6)	1.477(6)
C1	C5	1.567(5)	1.571(5)
C1	C8	1.528(6)	1.511(5)
C1	C9	1.499(6)	1.511(6)
C2	C3	1.473(6)	1.457(5)
C2	C8	1.646(6)	1.721(6)
C2	C15	1.490(5)	1.495(6)
C3	C4	1.340(6)	1.347(6)
C3	C7	3.076(6)	3.052(5)
C4	C5	1.537(6)	1.512(6)
C4	C6	2.355(6)	2.280(6)
C4	C16	1.469(6)	1.481(5)
C5	C6	1.527(5)	1.518(6)
C5	C12	1.522(6)	1.523(6)
C6	C7	1.352(6)	1,346(5)
C6	C17	1.459(5)	1.476(6)
C7	C8	1.463(5)	1.444(6)
C8	C18	1.494(6)	1.472(5)
C9	C10	1.533(6)	1.525(6)
C10	C11	1.546(6)	1.554(6)
C11	C12	1.533(5)	1.531(6)

Table 96. Angles (°) for Sb-6 at **236 K**

			Unprimed	Primed
C15	O1	C19	115.8(3)	116.6(3)
C16	O3	C20	116.1(4)	116.0(3)
C17	O5	C21	116.4(3)	115.5(3)
C18	O7	C22	115.3(3)	117.1(3)
C2	C1	C5	104.4(3)	104.6(3)
C2	C1	C8	65.9(3)	70.4(3)
C2	C1	C9	128.2(3)	127.0(4)
C5	C1	C8	104.0(3)	104.0(3)
C5	C1	C9	116.4(3)	115.4(3)
C8	C1	C9	127.0(4)	126.5(3)
C1	C2	C3	108.0(3)	108.6(3)
C1	C2	C8	57.9(3)	55.7(2)
C1	C2	C15	126.7(3)	128.2(4)
C3	C2	C8	118.1(3)	116.7(3)
C3	C2	C15	115.4(3)	116.2(4)
C8	C2	C15	118.9(3)	118.0(3)
C2	C3	C4	110.9(4)	110.8(4)
C3	C4	C5	110.7(3)	110.9(3)
C3	C4	C16	124.6(4)	124.1(4)
C5	C4	C6	39.6(2)	41.3(2)
C5	C4	C16	124.7(3)	125.0(4)
C1	C5	C4	102.6(3)	102.9(3)
C1	C5	C6	102.7(3)	103.0(3)
C1	C5	C12	111.6(3)	112.1(3)
C4	C5	C6	100.5(3)	97.6(3)
C4	C5	C12	117.8(3)	118.6(3)
C6	C5	C12	119.2(3)	120.0(3)
C4	C6	C5	39.9(2)	41.1(2)
C5	C6	C7	111.4(3)	111.2(4)
C5	C6	C17	122.9(4)	123.6(3)
C7	C6	C17	125.0(4)	125.0(4)
C6	C7	C8	111.0(3)	111.4(4)
C1	C8	C2	56.2(2)	53.9(2)
C1	C8	C7	107.4(3)	108.3(3)
C1	C8	C18	120.6(3)	122.2(4)
C2	C8	C7	120.2(3)	117.9(3)
C2	C8	C18	113.2(3)	113.8(3)
C7	C8	C18	121.9(3)	122.3(3)
C1	C9	C10	108.8(3)	108.5(3)
C9	C10	C11	114.2(3)	114.5(4)
C10	C11	C12	113.8(4)	113.3(3)
C5	C12	C11	108.9(3)	109.3(3)
O1	C15	O2	123.9(3)	123.3(4)
O1	C15	C2	112.0(3)	112.5(3)
O2	C15	C2	123.8(4)	124.0(4)
O3	C16	O4	122.9(4)	123.4(4)
O3	C16	C4	112.1(4)	112.7(3)
O4	C16	C4	124.9(4)	123.8(4)
O5	C17	O6	122.8(4)	124.3(4)
O5	C17	C6	113.3(4)	111.3(3)
O6	C17	C6	123.9(4)	124.4(4)
O7	C18	O8	124.6(4)	124.2(3)
O7	C18	C8	110.3(3)	111.4(3)
O8	C18	C8	125.1(4)	124.4(4)

Table 97. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-6 at 236 K

	Unprimed			Primed		
Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O1	0.141	0.176	0.183	0.145	0.171	0.228
O2	0.146	0.215	0.258	0.156	0.203	0.302
O3	0.127	0.201	0.266	0.133	0.201	0.262
O4	0.136	0.221	0.303	0.168	0.223	0.265
O5	0.156	0.178	0.308	0.154	0.183	0.307
O6	0.164	0.198	0.350	0.167	0.189	0.322
O7	0.136	0.207	0.243	0.147	0.189	0.254
O8	0.153	0.198	0.277	0.137	0.209	0.247
C1	0.134	0.151	0.174	0.131	0.153	0.173
C2	0.135	0.145	0.183	0.132	0.160	0.205
C3	0.137	0.157	0.192	0.139	0.158	0.172
C4	0.138	0.156	0.182	0.137	0.172	0.192
C5	0.124	0.155	0.161	0.132	0.145	0.166
C6	0.143	0.161	0.181	0.150	0.187	0.205
C7	0.153	0.165	0.193	0.143	0.151	0.185
C8	0.132	0.174	0.181	0.138	0.165	0.208
C9	0.159	0.168	0.191	0.145	0.167	0.200
C10	0.159	0.183	0.218	0.148	0.164	0.224
C11	0.162	0.187	0.203	0.164	0.169	0.218
C12	0.151	0.170	0.188	0.130	0.166	0.197
C15	0.126	0.167	0.203	0.140	0.160	0.210
C16	0.149	0.171	0.204	0.145	0.182	0.191
C17	0.166	0.184	0.208	0.151	0.159	0.221
C18	0.143	0.184	0.189	0.158	0.170	0.174
C19	0.147	0.206	0.236	0.134	0.210	0.281
C20	0.105	0.259	0.294	0.133	0.247	0.290
C21	0.140	0.211	0.291	0.139	0.211	0.315
C22	0.107	0.234	0.267	0.145	0.223	0.249



R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Table 8–98. X-ray Crystal Data for Sb-6 at **265 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	117–118
Crystal size (mm)	0.32 x 0.50 x 0.64
Crystal system	monoclinic
Space group	*P2/n*
a (Å)	41.483(2)
b (Å)	7.437(1)
c (Å)	12.231(1)
β (°)	98.21(1)
Cell volume ($Å^3$)	3734.82(2.73)
Z	8
d_{calc} (g cm^{-3})	1.388
μ(Cu $K\alpha$) (cm^{-1})	8.66
Maximum θ (°)	60
Unique reflections	5551
Observed reflections [$I > 3.0\sigma(I)$]	4113
Number of variables	505
R	0.048
R_w	0.061
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.25
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.27

Table 99. Final Atomic Parameters for Sb-6 at **265 K**

Atom	x	y	z	B(Å^2)
O1	0.55591(4)	0.1551(3)	0.2625(1)	2.86(4)
O2	0.55681(5)	0.4207(3)	0.3499(2)	4.19(5)
O3	0.69229(4)	0.4033(3)	0.3907(2)	3.87(5)
O4	0.70587(5)	0.1180(3)	0.3641(2)	4.94(5)
O5	0.68215(5)	0.0833(4)	0.7586(2)	4.70(5)
O6	0.70739(5)	0.0316(4)	0.6136(2)	5.78(6)
O7	0.56102(4)	0.1239(3)	0.6675(2)	3.88(5)
O8	0.53774(4)	0.0946(3)	0.4921(2)	4.45(5)
C1	0.60588(6)	0.0124(4)	0.4391(2)	2.27(5)
C2	0.59779(6)	0.2030(4)	0.4089(2)	2.39(5)
C3	0.62802(6)	0.2941(4)	0.3920(2)	2.54(5)
C4	0.65355(6)	0.1830(4)	0.4119(2)	2.49(5)
C5	0.64398(6)	0.0085(4)	0.4647(2)	2.37(5)
C6	0.65021(6)	0.0606(4)	0.5869(2)	2.72(6)
C7	0.62365(6)	0.1338(4)	0.6200(2)	2.76(6)
C8	0.59533(6)	0.1204(4)	0.5330(2)	2.70(6)
C9	0.58985(6)	-0.1556(4)	0.3881(2)	2.80(6)
C10	0.60578(7)	-0.2061(4)	0.2867(2)	3.30(6)
C11	0.64352(7)	-0.2041(4)	0.3074(2)	3.22(6)
C12	0.65767(6)	-0.1668(4)	0.4274(2)	2.88(6)
C15	0.56742(6)	0.2716(4)	0.3413(2)	2.75(6)
C16	0.68693(6)	0.2266(4)	0.3888(2)	2.95(6)
C17	0.68287(6)	0.0565(4)	0.6520(2)	3.14(6)
C18	0.56169(6)	0.1119(4)	0.5594(2)	2.85(6)
C19	0.52897(7)	0.2178(4)	0.1831(3)	3.91(7)
C20	0.72365(7)	0.4598(5)	0.3630(3)	5.21(8)
C21	0.71334(8)	0.0772(6)	0.8291(3)	4.98(9)
C22	0.52915(7)	0.1103(5)	0.7038(3)	4.46(7)
O1'	0.44788(4)	0.3547(3)	-0.0500(2)	3.19(4)
O2'	0.44652(5)	0.0939(3)	0.0393(2)	4.75(5)
O3'	0.30993(5)	0.0966(3)	-0.0601(2)	4.10(5)
O4'	0.29691(5)	0.3802(3)	-0.1061(2)	4.52(5)
O5'	0.31801(4)	0.4178(4)	0.3116(2)	4.77(5)
O6'	0.29203(5)	0.4586(4)	0.1418(2)	5.20(6)
O7'	0.43785(4)	0.3720(3)	0.3498(2)	3.78(5)
O8'	0.46204(4)	0.4417(3)	0.2029(2)	3.86(5)
C1'	0.39504(6)	0.4946(4)	0.0738(2)	2.14(5)
C2'	0.40394(6)	0.3071(4)	0.0483(2)	2.79(6)
C3'	0.37473(6)	0.2111(4)	0.0026(2)	2.44(5)
C4'	0.34820(6)	0.3181(4)	-0.0007(2)	2.62(6)
C5'	0.35704(6)	0.4946(4)	0.0591(2)	2.15(5)
C6'	0.34963(6)	0.4358(4)	0.1716(2)	3.17(6)
C7'	0.37652(6)	0.3689(4)	0.2344(2)	2.64(6)
C8'	0.40476(6)	0.3936(4)	0.1804(2)	2.87(6)
C9'	0.41034(6)	0.6651(4)	0.0383(2)	2.77(6)
C10'	0.39483(7)	0.7109(4)	-0.0796(2)	3.20(6)
C11'	0.35718(7)	0.7089(4)	-0.0971(2)	3.13(6)
C12'	0.34252(6)	0.6685(4)	0.0084(2)	2.69(6)
C15'	0.43532(6)	0.2408(4)	0.0154(2)	2.94(6)
C16'	0.31540(6)	0.2731(4)	-0.0588(2)	2.87(6)
C17'	0.31673(6)	0.4381(4)	0.2042(2)	3.15(6)
C18'	0.43797(6)	0.4050(4)	0.2431(2)	2.77(6)
C19'	0.47615(7)	0.2925(5)	-0.0967(3)	4.40(7)
C20'	0.27910(8)	0.0382(5)	-0.1209(3)	5.16(9)
C21'	0.28706(7)	0.4262(6)	0.3537(3)	5.05(9)
C22'	0.46883(7)	0.3854(5)	0.4220(2)	4.14(7)

Table 99 (cont.). Final Atomic Parameters for Sb-6 at **265 K**

Atom	x	y	z	B(Å^2)
H3	0.629	0.422	0.369	2.8
H7	0.623	0.190	0.694	3.0
H9A	0.566	-0.133	0.365	3.1
H9B	0.593	-0.256	0.443	3.1
H10A	0.598	-0.119	0.226	3.6
H10B	0.598	-0.330	0.263	3.6
H11A	0.651	-0.109	0.260	3.5
H11B	0.652	-0.324	0.286	3.5
H12A	0.652	-0.267	0.475	3.2
H12B	0.682	-0.158	0.434	3.2
H19A	0.522	0.121	0.128	4.3
H19B	0.510	0.250	0.222	4.3
H19C	0.536	0.326	0.144	4.3
H20A	0.725	0.594	0.367	5.7
H20B	0.741	0.406	0.417	5.7
H20C	0.726	0.419	0.287	5.7
H21A	0.710	0.099	0.907	5.4
H21B	0.723	-0.044	0.823	5.4
H21C	0.728	0.172	0.806	5.4
H22A	0.532	0.121	0.786	4.9
H22B	0.515	0.209	0.669	4.9
H22C	0.519	-0.008	0.681	4.9
H3'	0.374	0.083	-0.023	2.7
H7'	0.377	0.311	0.308	2.9
H9A'	0.434	0.647	0.040	3.0
H9B'	0.406	0.766	0.089	3.0
H10A'	0.403	0.621	-0.131	3.5
H10B'	0.402	0.834	-0.098	3.5
H11A'	0.350	0.615	-0.153	3.4
H11B'	0.349	0.829	-0.125	3.4
H12A'	0.348	0.769	0.062	3.0
H12B'	0.318	0.655	-0.010	3.0
H19A'	0.484	0.389	-0.144	4.8
H19B'	0.494	0.263	-0.036	4.8
H19C'	0.470	0.182	-0.142	4.8
H20A'	0.277	-0.096	-0.117	5.7
H20B'	0.261	0.094	-0.088	5.7
H20C'	0.278	0.076	-0.200	5.7
H21A'	0.291	0.409	0.436	5.5
H21B'	0.277	0.546	0.336	5.5
H21C'	0.272	0.329	0.319	5.5
H22A'	0.466	0.358	0.500	4.5
H22B'	0.485	0.298	0.398	4.5
H22C'	0.478	0.510	0.418	4.5
H19BA'	0.479	0.161	-0.081	4.8
H19BB'	0.473	0.313	-0.178	4.8
H19BC'	0.496	0.360	-0.063	4.8

The parameters of the hydrogen atoms were not refined.

Table 100. Final Anisotropic Thermal Parameters (U's) for Sb-6 at **265 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0310(9)	0.036(1)	0.0403(9)	0.0054(9)	0.0021(8)	0.0032(9)
O2	0.045(1)	0.037(1)	0.075(1)	0.014(1)	0.003(1)	-0.007(1)
O3	0.0320(9)	0.047(1)	0.073(1)	-0.010(1)	0.0225(8)	0.001(1)
O4	0.041(1)	0.060(1)	0.094(1)	0.011(1)	0.0350(9)	0.006(1)
O5	0.038(1)	0.107(2)	0.032(1)	0.014(1)	-0.0004(8)	-0.007(1)
O6	0.033(1)	0.138(2)	0.048(1)	0.004(1)	0.0056(9)	-0.021(1)
O7	0.038(1)	0.072(2)	0.041(1)	-0.008(1)	0.0176(8)	-0.004(1)
O8	0.031(1)	0.094(2)	0.046(1)	-0.010(1)	0.0086(8)	0.002(1)
C1	0.026(1)	0.031(1)	0.030(1)	-0.001(1)	0.007(1)	0.003(1)
C2	0.026(1)	0.030(1)	0.037(1)	-0.000(1)	0.009(1)	0.002(1)
C3	0.029(1)	0.030(1)	0.039(1)	-0.002(1)	0.011(1)	0.001(1)
C4	0.025(1)	0.036(2)	0.035(1)	0.001(1)	0.009(1)	-0.000(1)
C5	0.025(1)	0.034(1)	0.032(1)	0.002(1)	0.005(1)	0.002(1)
C6	0.032(1)	0.040(2)	0.032(1)	-0.000(1)	0.005(1)	0.001(1)
C7	0.031(1)	0.042(2)	0.033(1)	-0.002(1)	0.008(1)	-0.003(1)
C8	0.032(1)	0.042(2)	0.031(1)	-0.002(1)	0.010(1)	-0.002(1)
C9	0.037(1)	0.028(1)	0.040(1)	-0.005(1)	0.002(1)	0.002(1)
C10	0.048(2)	0.037(2)	0.039(1)	0.003(1)	0.001(1)	-0.003(1)
C11	0.050(2)	0.037(2)	0.037(1)	0.005(1)	0.009(1)	-0.003(1)
C12	0.037(1)	0.034(2)	0.040(1)	0.007(1)	0.006(1)	0.002(1)
C15	0.028(1)	0.036(2)	0.042(1)	-0.001(1)	0.011(1)	0.005(1)
C16	0.029(1)	0.046(2)	0.038(1)	0.002(1)	0.009(1)	0.005(1)
C17	0.033(1)	0.049(2)	0.037(1)	0.002(1)	0.005(1)	-0.005(1)
C18	0.031(1)	0.041(2)	0.038(1)	-0.003(1)	0.012(1)	0.001(1)
C19	0.036(2)	0.053(2)	0.055(2)	0.006(2)	-0.008(1)	0.011(2)
C20	0.039(1)	0.072(2)	0.093(2)	-0.019(2)	0.030(1)	0.007(2)
C21	0.044(2)	0.102(3)	0.039(2)	0.014(2)	-0.009(1)	-0.006(2)
C22	0.042(1)	0.075(2)	0.060(2)	-0.007(2)	0.033(1)	-0.003(2)
O1'	0.040(1)	0.039(1)	0.046(1)	0.0077(9)	0.0204(8)	0.0028(9)
O2'	0.046(1)	0.045(1)	0.095(1)	0.019(1)	0.029(1)	0.016(1)
O3'	0.034(1)	0.044(1)	0.072(1)	-0.011(1)	-0.011(1)	-0.002(1)
O4'	0.043(1)	0.058(1)	0.064(1)	0.007(1)	-0.017(1)	-0.000(1)
O5'	0.031(1)	0.108(2)	0.044(1)	0.013(1)	0.0128(8)	0.013(1)
O6'	0.029(1)	0.119(2)	0.051(1)	0.006(1)	0.0081(9)	0.019(1)
O7'	0.0306(9)	0.073(2)	0.037(1)	-0.005(1)	-0.0038(8)	0.004(1)
O8'	0.0233(9)	0.073(2)	0.050(1)	-0.002(1)	0.0047(8)	0.000(1)
C1'	0.023(1)	0.032(1)	0.027(1)	-0.001(1)	0.004(1)	-0.002(1)
C2'	0.025(1)	0.030(1)	0.051(2)	0.002(1)	0.007(1)	-0.002(1)
C3'	0.028(1)	0.030(1)	0.034(1)	-0.002(1)	0.005(1)	0.000(1)
C4'	0.023(1)	0.035(2)	0.040(1)	0.000(1)	0.001(1)	-0.002(1)
C5'	0.023(1)	0.030(1)	0.030(1)	0.003(1)	0.007(1)	-0.003(1)
C6'	0.030(1)	0.051(2)	0.041(1)	0.002(1)	0.010(1)	0.010(1)
C7'	0.028(1)	0.043(2)	0.030(1)	-0.000(1)	0.005(1)	0.002(1)
C8'	0.025(1)	0.047(2)	0.037(1)	-0.003(1)	0.004(1)	0.005(1)
C9'	0.034(1)	0.030(1)	0.043(1)	-0.004(1)	0.012(1)	-0.002(1)
C10'	0.046(1)	0.037(2)	0.043(1)	0.005(1)	0.018(1)	0.007(1)
C11'	0.044(1)	0.036(2)	0.040(1)	0.004(1)	0.012(1)	0.006(1)
C12'	0.035(1)	0.033(2)	0.036(1)	0.006(1)	0.009(1)	0.000(1)
C15'	0.025(1)	0.035(2)	0.051(2)	-0.000(1)	0.004(1)	-0.003(1)
C16'	0.028(1)	0.046(2)	0.035(1)	0.000(1)	0.005(1)	-0.003(1)
C17'	0.027(1)	0.053(2)	0.040(1)	0.004(1)	0.008(1)	0.011(1)
C18'	0.028(1)	0.041(2)	0.036(1)	0.001(1)	0.001(1)	0.000(1)
C19'	0.048(2)	0.056(2)	0.070(2)	0.010(2)	0.034(1)	0.001(2)
C20'	0.040(2)	0.069(2)	0.079(2)	-0.017(2)	-0.018(2)	-0.011(2)
C21'	0.037(1)	0.111(3)	0.048(2)	0.016(2)	0.021(1)	0.012(2)
C22'	0.036(2)	0.074(2)	0.042(2)	-0.003(2)	-0.010(1)	-0.005(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 101. Interatomic Distances (Å) for Sb-6 at **265 K**

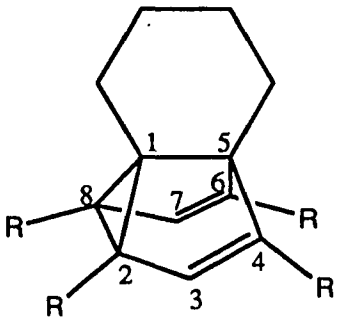
		Unprimed	Primed
O1	C15	1.333(3)	1.322(3)
O1	C19	1.449(3)	1.451(4)
O2	C15	1.203(3)	1.207(4)
O3	C16	1.333(4)	1.332(4)
O3	C20	1.452(4)	1.451(4)
O4	C16	1.195(4)	1.196(3)
O5	C17	1.324(3)	1.316(3)
O5	C21	1.449(3)	1.452(4)
O6	C17	1.194(4)	1.196(3)
O7	C18	1.330(3)	1.329(3)
O7	C22	1.457(4)	1.455(3)
O8	C18	1.203(3)	1.205(3)
C1	C2	1.491(4)	1.487(4)
C1	C5	1.567(3)	1.561(3)
C1	C8	1.516(4)	1.508(4)
C1	C9	1.508(4)	1.510(4)
C2	C3	1.466(4)	1.448(4)
C2	C8	1.653(4)	1.735(4)
C2	C15	1.495(3)	1.500(4)
C3	C4	1.338(4)	1.354(4)
C3	C7	3.062(4)	3.060(4)
C4	C5	1.527(4)	1.522(4)
C4	C6	2.348(4)	2.275(4)
C4	C16	1.488(4)	1.480(3)
C5	C6	1.530(4)	1.517(4)
C5	C12	1.518(4)	1.521(4)
C6	C7	1.342(4)	1.355(4)
C6	C17	1.470(3)	1.475(4)
C7	C8	1.471(3)	1.437(4)
C8	C18	1.478(4)	1.480(3)
C9	C10	1.533(4)	1.531(4)
C10	C11	1.550(4)	1.546(4)
C11	C12	1.526(4)	1.532(4)

Table 102. Angles (°) for Sb-6 at **265 K**

			Unprimed	Primed
C15	O1	C19	116.0(2)	116.4(2)
C16	O3	C20	115.7(2)	115.9(2)
C17	O5	C21	116.0(2)	116.0(2)
C18	O7	C22	116.6(2)	117.2(2)
C2	C1	C5	104.6(2)	104.7(2)
C2	C1	C8	66.7(2)	70.8(2)
C2	C1	C9	127.9(2)	126.9(2)
C5	C1	C8	104.5(2)	103.9(2)
C5	C1	C9	116.1(2)	115.2(2)
C8	C1	C9	126.5(2)	126.5(2)
C1	C2	C3	107.9(2)	108.9(2)
C1	C2	C8	57.4(2)	55.2(2)
C1	C2	C15	127.1(2)	128.0(2)
C3	C2	C8	117.9(2)	116.5(2)
C3	C2	C15	115.7(2)	116.4(2)
C8	C2	C15	118.5(2)	118.0(2)
C2	C3	C4	111.1(2)	110.7(2)
C3	C4	C5	110.8(2)	110.7(2)
C3	C4	C16	124.4(3)	124.7(3)
C5	C4	C6	39.9(1)	41.4(1)
C5	C4	C16	124.8(2)	124.6(2)
C1	C5	C4	102.5(2)	103.0(2)
C1	C5	C6	102.4(2)	103.1(2)
C1	C5	C12	111.4(2)	112.4(2)
C4	C5	C6	100.4(2)	97.0(2)
C4	C5	C12	118.2(2)	118.9(2)
C6	C5	C12	119.5(2)	119.7(2)
C4	C6	C5	39.8(1)	41.6(1)
C5	C6	C7	111.4(2)	111.3(2)
C5	C6	C17	122.5(2)	123.8(2)
C7	C6	C17	125.3(2)	124.7(3)
C6	C7	C8	111.1(2)	110.6(2)
C1	C8	C2	55.9(2)	54.0(2)
C1	C8	C7	107.3(2)	109.1(2)
C1	C8	C18	121.8(2)	122.3(2)
C2	C8	C7	119.4(2)	118.2(2)
C2	C8	C18	113.6(2)	113.4(2)
C7	C8	C18	121.7(2)	121.9(2)
C1	C9	C10	108.8(2)	108.7(2)
C9	C10	C11	114.0(2)	114.1(2)
C10	C11	C12	113.6(2)	113.6(2)
C5	C12	C11	109.6(2)	109.2(2)
O1	C15	O2	124.4(2)	123.8(3)
O1	C15	C2	111.4(2)	112.6(2)
O2	C15	C2	123.8(2)	123.4(3)
O3	C16	O4	123.8(3)	123.6(2)
O3	C16	C4	111.7(2)	111.9(2)
O4	C16	C4	124.3(3)	124.3(3)
O5	C17	O6	123.4(2)	124.0(3)
O5	C17	C6	112.5(2)	111.1(2)
O6	C17	C6	124.1(2)	124.8(3)
O7	C18	O8	123.7(3)	124.2(2)
O7	C18	C8	111.7(2)	111.4(2)
O8	C18	C8	124.6(2)	124.4(2)

Table 103. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-6 at 265 K

	Unprimed			Primed		
Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O1	0.164	0.199	0.205	0.157	0.196	0.241
O2	0.160	0.231	0.283	0.161	0.222	0.325
O3	0.142	0.226	0.275	0.155	0.222	0.287
O4	0.156	0.245	0.321	0.171	0.240	0.291
O5	0.172	0.195	0.333	0.161	0.207	0.335
O6	0.180	0.209	0.379	0.166	0.214	0.352
O7	0.158	0.219	0.273	0.160	0.207	0.274
O8	0.166	0.214	0.309	0.152	0.224	0.271
C1	0.154	0.171	0.183	0.149	0.161	0.182
C2	0.152	0.172	0.195	0.154	0.175	0.227
C3	0.156	0.176	0.202	0.166	0.176	0.185
C4	0.149	0.190	0.190	0.152	0.185	0.205
C5	0.155	0.175	0.187	0.139	0.173	0.181
C6	0.176	0.180	0.200	0.163	0.191	0.239
C7	0.167	0.184	0.208	0.166	0.173	0.207
C8	0.159	0.187	0.207	0.155	0.188	0.223
C9	0.162	0.190	0.211	0.164	0.179	0.215
C10	0.185	0.196	0.229	0.172	0.186	0.239
C11	0.177	0.199	0.227	0.179	0.191	0.225
C12	0.168	0.196	0.207	0.162	0.186	0.203
C15	0.153	0.188	0.213	0.159	0.185	0.228
C16	0.163	0.191	0.222	0.168	0.185	0.217
C17	0.181	0.189	0.226	0.160	0.185	0.245
C18	0.158	0.203	0.206	0.165	0.193	0.202
C19	0.163	0.231	0.262	0.158	0.239	0.291
C20	0.139	0.284	0.313	0.152	0.277	0.311
C21	0.168	0.231	0.328	0.154	0.227	0.342
C22	0.137	0.263	0.286	0.157	0.240	0.274



R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Table 8–104. X-ray Crystal Data for Sb-6 at **294 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	117–118
Crystal size (mm)	0.32 x 0.50 x 0.64
Crystal system	monoclinic
Space group	*P2/n*
a (Å)	41.518(2)
b (Å)	7.463(1)
c (Å)	12.253(1)
β (°)	98.22(1)
Cell volume ($Å^3$)	3757.82(2.00)
Z	8
d_{calc} (g cm^{-3})	1.380
μ(Cu $K\alpha$) (cm^{-1})	8.61
Maximum θ (°)	60
Unique reflections	5591
Observed reflections [$I > 3.0\sigma(I)$]	3982
Number of variables	505
R	0.049
R_w	0.062
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.29
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.23

Table 105. Final Atomic Parameters for Sb-6 at **294 K**

Atom	x	y	z	B(Å^2)
O1	0.55600(4)	0.1569(3)	0.2633(2)	3.22(4)
O2	0.55702(5)	0.4213(3)	0.3500(2)	4.83(5)
O3	0.69246(4)	0.4029(3)	0.3917(2)	4.42(5)
O4	0.70580(5)	0.1190(3)	0.3649(2)	5.60(6)
O5	0.68223(5)	0.0850(4)	0.7579(2)	5.32(6)
O6	0.70750(5)	0.0321(4)	0.6138(2)	6.44(7)
O7	0.56123(5)	0.1244(3)	0.6674(2)	4.43(5)
O8	0.53796(5)	0.0950(4)	0.4924(2)	5.10(6)
C1	0.60603(6)	0.0141(4)	0.4391(2)	2.56(6)
C2	0.59804(6)	0.2036(4)	0.4091(2)	2.74(6)
C3	0.62815(6)	0.2947(4)	0.3920(2)	2.86(6)
C4	0.65362(6)	0.1841(4)	0.4126(2)	2.85(6)
C5	0.64406(6)	0.0098(4)	0.4650(2)	2.57(5)
C6	0.65028(6)	0.0626(4)	0.5863(2)	3.05(6)
C7	0.62377(6)	0.1346(4)	0.6197(2)	3.08(6)
C8	0.59554(6)	0.1208(4)	0.5332(2)	3.13(6)
C9	0.59007(7)	-0.1532(4)	0.3881(2)	3.12(6)
C10	0.60591(8)	-0.2039(4)	0.2872(2)	3.80(7)
C11	0.64362(7)	-0.2019(4)	0.3076(2)	3.58(7)
C12	0.65791(7)	-0.1645(4)	0.4275(2)	3.28(6)
C15	0.56760(6)	0.2720(4)	0.3413(2)	3.11(6)
C16	0.68700(6)	0.2276(4)	0.3897(2)	3.39(6)
C17	0.68287(7)	0.0568(4)	0.6518(2)	3.58(7)
C18	0.56182(7)	0.1124(4)	0.5594(2)	3.32(6)
C19	0.52886(7)	0.2190(5)	0.1841(3)	4.38(8)
C20	0.72383(8)	0.4598(5)	0.3638(3)	5.80(9)
C21	0.71330(8)	0.0789(6)	0.8287(3)	5.6(1)
C22	0.52945(7)	0.1109(5)	0.7037(3)	5.06(8)
O1'	0.44779(4)	0.3530(3)	-0.0501(2)	3.65(4)
O2'	0.44625(5)	0.0931(3)	0.0391(2)	5.45(6)
O3'	0.30991(5)	0.0967(3)	-0.0598(2)	4.60(5)
O4'	0.29712(5)	0.3786(3)	-0.1059(2)	5.16(6)
O5'	0.31803(5)	0.4168(4)	0.3108(2)	5.27(6)
O6'	0.29205(5)	0.4571(4)	0.1411(2)	5.89(7)
O7'	0.43778(5)	0.3717(3)	0.3497(2)	4.28(5)
O8'	0.46185(4)	0.4413(3)	0.2034(2)	4.40(5)
C1'	0.39508(6)	0.4928(4)	0.0734(2)	2.46(5)
C2'	0.40389(6)	0.3067(4)	0.0474(2)	3.22(6)
C3'	0.37466(6)	0.2107(4)	0.0028(2)	2.82(6)
C4'	0.34818(6)	0.3169(4)	-0.0000(2)	2.95(6)
C5'	0.35699(6)	0.4937(4)	0.0587(2)	2.42(5)
C6'	0.34965(7)	0.4338(5)	0.1710(2)	3.66(7)
C7'	0.37641(6)	0.3680(4)	0.2340(2)	2.94(6)
C8'	0.40473(6)	0.3938(4)	0.1803(2)	3.23(6)
C9'	0.41035(6)	0.6627(4)	0.0381(2)	3.14(6)
C10'	0.39486(7)	0.7089(4)	-0.0793(2)	3.69(7)
C11'	0.35713(7)	0.7066(4)	-0.0964(2)	3.56(7)
C12'	0.34255(7)	0.6669(4)	0.0081(2)	3.08(6)
C15'	0.43520(6)	0.2394(4)	0.0148(3)	3.33(6)
C16'	0.31540(6)	0.2716(4)	-0.0582(2)	3.24(6)
C17'	0.31667(7)	0.4369(4)	0.2035(2)	3.62(7)
C18'	0.43784(6)	0.4047(4)	0.2434(2)	3.14(6)
C19'	0.47619(7)	0.2925(5)	-0.0963(3)	5.09(8)
C20'	0.27914(8)	0.0386(6)	-0.1209(3)	5.80(9)
C21'	0.28726(7)	0.4261(6)	0.3532(3)	5.67(9)
C22'	0.46875(7)	0.3842(5)	0.4220(3)	4.69(8)

Table 105 (cont.). Final Atomic Parameters for Sb-6 at **294 K**

Atom	x	y	z	B(Å^2)
H3	0.629	0.422	0.368	3.1
H7	0.623	0.190	0.694	3.3
H9A	0.566	-0.131	0.365	3.4
H9B	0.593	-0.253	0.443	3.4
H10A	0.598	-0.117	0.227	4.1
H10B	0.599	-0.327	0.263	4.1
H11A	0.651	-0.107	0.260	3.9
H11B	0.652	-0.322	0.286	3.9
H12A	0.652	-0.265	0.475	3.5
H12B	0.682	-0.155	0.434	3.5
H19A	0.522	0.122	0.129	4.7
H19B	0.510	0.251	0.224	4.7
H19C	0.536	0.327	0.145	4.7
H20A	0.725	0.594	0.368	6.3
H20B	0.742	0.406	0.417	6.3
H20C	0.726	0.420	0.287	6.3
H21A	0.710	0.102	0.907	6.1
H21B	0.723	-0.042	0.824	6.1
H21C	0.728	0.172	0.805	6.1
H22A	0.532	0.122	0.786	5.5
H22B	0.515	0.209	0.669	5.5
H22C	0.519	-0.008	0.681	5.5
H3'	0.374	0.083	-0.023	3.0
H7'	0.377	0.310	0.308	3.2
H9A'	0.434	0.645	0.040	3.4
H9B'	0.406	0.763	0.089	3.4
H10A'	0.403	0.620	-0.131	4.0
H10B'	0.402	0.831	-0.098	4.0
H11A'	0.350	0.613	-0.152	3.8
H11B'	0.349	0.827	-0.125	3.8
H12A'	0.348	0.767	0.062	3.3
H12B'	0.318	0.654	-0.010	3.3
H19A'	0.484	0.389	-0.144	5.5
H19B'	0.494	0.264	-0.035	5.5
H19C'	0.471	0.183	-0.142	5.5
H20A'	0.277	-0.095	-0.117	6.3
H20B'	0.261	0.094	-0.088	6.3
H20C'	0.278	0.076	-0.200	6.3
H21A'	0.291	0.409	0.435	6.1
H21B'	0.277	0.546	0.335	6.1
H21C'	0.272	0.330	0.319	6.1
H22A'	0.465	0.357	0.499	5.1
H22B'	0.485	0.297	0.398	5.1
H22C'	0.478	0.508	0.419	5.1
H19BA'	0.484	0.177	-0.060	5.5
H19BB'	0.470	0.273	-0.177	5.5
H19BC'	0.494	0.385	-0.083	5.5

The parameters of the hydrogen atoms were not refined.

Table 106. Final Anisotropic Thermal Parameters (U's) for Sb-6 at **294 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.034(1)	0.042(1)	0.045(1)	0.0058(9)	0.0018(8)	0.004(1)
O2	0.053(1)	0.043(1)	0.086(2)	0.017(1)	0.002(1)	-0.008(1)
O3	0.038(1)	0.051(1)	0.084(1)	-0.012(1)	0.0269(9)	0.002(1)
O4	0.047(1)	0.067(2)	0.106(2)	0.012(1)	0.038(1)	0.004(1)
O5	0.042(1)	0.119(2)	0.039(1)	0.017(1)	-0.0007(9)	-0.009(1)
O6	0.037(1)	0.154(3)	0.052(1)	0.008(2)	0.004(1)	-0.024(2)
O7	0.042(1)	0.083(2)	0.048(1)	-0.006(1)	0.0210(8)	-0.004(1)
O8	0.034(1)	0.109(2)	0.052(1)	-0.012(1)	0.0090(9)	0.003(1)
C1	0.027(1)	0.036(2)	0.035(1)	-0.000(1)	0.007(1)	0.003(1)
C2	0.029(1)	0.035(2)	0.042(1)	0.001(1)	0.009(1)	0.005(1)
C3	0.032(1)	0.035(2)	0.044(1)	-0.001(1)	0.010(1)	0.001(1)
C4	0.030(1)	0.039(2)	0.041(1)	-0.000(1)	0.011(1)	0.001(1)
C5	0.027(1)	0.035(2)	0.036(1)	0.001(1)	0.005(1)	0.001(1)
C6	0.035(1)	0.045(2)	0.036(1)	0.000(1)	0.006(1)	0.000(1)
C7	0.035(1)	0.046(2)	0.037(1)	-0.005(1)	0.008(1)	-0.004(1)
C8	0.037(1)	0.047(2)	0.037(1)	-0.004(1)	0.014(1)	-0.003(1)
C9	0.042(2)	0.032(2)	0.043(2)	-0.005(1)	0.003(1)	0.002(1)
C10	0.056(2)	0.043(2)	0.044(2)	0.002(2)	0.002(1)	-0.005(2)
C11	0.054(2)	0.041(2)	0.042(1)	0.007(2)	0.013(1)	-0.003(1)
C12	0.041(1)	0.039(2)	0.045(2)	0.009(1)	0.007(1)	0.001(1)
C15	0.032(1)	0.041(2)	0.047(2)	-0.001(1)	0.012(1)	0.004(1)
C16	0.032(1)	0.053(2)	0.046(2)	0.004(1)	0.014(1)	0.006(2)
C17	0.038(1)	0.056(2)	0.042(2)	0.001(2)	0.005(1)	-0.007(2)
C18	0.036(1)	0.046(2)	0.047(1)	-0.002(1)	0.016(1)	-0.000(1)
C19	0.041(2)	0.062(2)	0.059(2)	0.007(2)	-0.007(2)	0.010(2)
C20	0.044(2)	0.078(3)	0.106(2)	-0.023(2)	0.036(2)	0.007(2)
C21	0.050(2)	0.117(3)	0.043(2)	0.016(2)	-0.008(2)	-0.003(2)
C22	0.049(2)	0.087(3)	0.064(2)	-0.010(2)	0.037(1)	-0.002(2)
O1'	0.045(1)	0.045(1)	0.054(1)	0.008(1)	0.0217(8)	0.002(1)
O2'	0.052(1)	0.050(1)	0.110(2)	0.021(1)	0.032(1)	0.020(1)
O3'	0.039(1)	0.050(1)	0.079(1)	-0.012(1)	-0.013(1)	-0.002(1)
O4'	0.050(1)	0.066(2)	0.073(1)	0.007(1)	-0.018(1)	-0.002(1)
O5'	0.035(1)	0.121(2)	0.047(1)	0.014(1)	0.0129(9)	0.013(1)
O6'	0.032(1)	0.136(2)	0.057(1)	0.008(1)	0.0086(9)	0.020(1)
O7'	0.035(1)	0.084(2)	0.042(1)	-0.007(1)	-0.0039(9)	0.004(1)
O8'	0.0257(9)	0.087(2)	0.055(1)	-0.002(1)	0.0052(9)	0.001(1)
C1'	0.026(1)	0.037(2)	0.031(1)	-0.002(1)	0.007(1)	-0.003(1)
C2'	0.029(1)	0.034(2)	0.060(2)	0.003(1)	0.007(1)	-0.004(1)
C3'	0.033(1)	0.037(2)	0.037(1)	-0.004(1)	0.005(1)	-0.002(1)
C4'	0.025(1)	0.039(2)	0.048(2)	0.000(1)	0.002(1)	-0.002(1)
C5'	0.025(1)	0.037(2)	0.031(1)	0.003(1)	0.007(1)	-0.002(1)
C6'	0.032(1)	0.060(2)	0.049(2)	0.003(1)	0.012(1)	0.013(2)
C7'	0.029(1)	0.049(2)	0.033(1)	-0.001(1)	0.006(1)	0.003(1)
C8'	0.027(1)	0.055(2)	0.040(1)	-0.004(1)	0.003(1)	0.007(1)
C9'	0.037(1)	0.036(2)	0.049(2)	-0.006(1)	0.014(1)	-0.002(1)
C10'	0.053(2)	0.040(2)	0.051(2)	0.007(2)	0.022(1)	0.008(1)
C11'	0.053(2)	0.040(2)	0.045(2)	0.006(2)	0.014(1)	0.007(1)
C12'	0.040(1)	0.037(2)	0.042(1)	0.008(1)	0.010(1)	0.002(1)
C15'	0.028(1)	0.042(2)	0.056(2)	0.001(1)	0.005(1)	-0.003(2)
C16'	0.030(1)	0.052(2)	0.040(1)	0.001(1)	0.004(1)	-0.004(1)
C17'	0.032(1)	0.060(2)	0.047(2)	0.004(1)	0.011(1)	0.011(2)
C18'	0.029(1)	0.046(2)	0.043(1)	0.001(1)	0.001(1)	-0.001(1)
C19'	0.053(2)	0.067(2)	0.081(2)	0.012(2)	0.039(1)	-0.002(2)
C20'	0.044(2)	0.081(3)	0.087(3)	-0.018(2)	-0.019(2)	-0.011(2)
C21'	0.044(2)	0.124(3)	0.053(2)	0.017(2)	0.025(1)	0.012(2)
C22'	0.041(2)	0.084(3)	0.048(2)	-0.005(2)	-0.013(1)	-0.006(2)

The form of the anisotropic displacement parameter is:
$\exp(-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)])$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 107. Interatomic Distances (Å) for Sb-6 at **294 K**

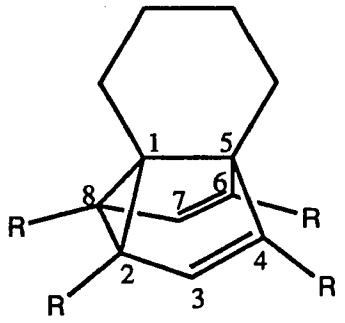
		Unprimed	Primed
O1	C15	1.324(3)	1.321(4)
O1	C19	1.454(3)	1.451(4)
O2	C15	1.208(4)	1.206(4)
O3	C16	1.328(4)	1.325(4)
O3	C20	1.456(4)	1.452(4)
O4	C16	1.194(4)	1.195(4)
O5	C17	1.321(4)	1.316(4)
O5	C21	1.448(4)	1.448(4)
O6	C17	1.197(4)	1.195(3)
O7	C18	1.329(4)	1.327(3)
O7	C22	1.455(4)	1.456(3)
O8	C18	1.200(3)	1.204(3)
C1	C2	1.487(4)	1.482(4)
C1	C5	1.566(3)	1.566(3)
C1	C8	1.515(4)	1.507(4)
C1	C9	1.506(4)	1.508(4)
C2	C3	1.464(4)	1.448(4)
C2	C8	1.658(4)	1.749(4)
C2	C15	1.499(4)	1.500(4)
C3	C4	1.337(4)	1.352(4)
C3	C7	3.064(4)	3.058(4)
C4	C5	1.528(4)	1.522(4)
C4	C6	2.335(4)	2.262(4)
C4	C16	1.489(4)	1.483(4)
C5	C6	1.523(4)	1.519(4)
C5	C12	1.520(4)	1.519(4)
C6	C7	1.340(4)	1.352(4)
C6	C17	1.472(4)	1.480(4)
C7	C8	1.467(4)	1.440(4)
C8	C18	1.482(4)	1.480(4)
C9	C10	1.529(4)	1.530(4)
C10	C11	1.550(4)	1.550(4)
C11	C12	1.530(4)	1.522(4)

Table 108. Angles (°) for Sb-6 at **294 K**

			Unprimed	Primed
C15	O1	C19	116.2(2)	116.7(2)
C16	O3	C20	116.1(2)	116.0(2)
C17	O5	C21	116.3(2)	116.0(2)
C18	O7	C22	116.5(2)	117.4(2)
C2	C1	C5	104.6(2)	104.8(2)
C2	C1	C8	67.0(2)	71.6(2)
C2	C1	C9	128.0(2)	126.8(2)
C5	C1	C8	104.3(2)	103.9(2)
C5	C1	C9	116.0(2)	115.0(2)
C8	C1	C9	126.4(2)	126.2(2)
C1	C2	C3	108.2(2)	109.0(2)
C1	C2	C8	57.3(2)	54.9(2)
C1	C2	C15	127.0(2)	128.4(2)
C3	C2	C8	118.1(2)	116.1(2)
C3	C2	C15	115.6(2)	116.5(3)
C8	C2	C15	118.5(2)	118.0(2)
C2	C3	C4	110.8(3)	110.7(3)
C3	C4	C5	111.0(2)	110.9(2)
C3	C4	C16	124.2(3)	124.5(3)
C5	C4	C6	40.0(1)	41.9(1)
C5	C4	C16	124.8(2)	124.5(2)
C1	C5	C4	102.3(2)	102.8(2)
C1	C5	C6	102.6(2)	103.0(2)
C1	C5	C12	111.7(2)	112.6(2)
C4	C5	C6	99.9(2)	96.2(2)
C4	C5	C12	118.0(2)	119.4(2)
C6	C5	C12	119.8(2)	120.1(2)
C4	C6	C5	40.1(1)	42.0(1)
C5	C6	C7	111.7(2)	111.7(2)
C5	C6	C17	122.6(2)	123.5(2)
C7	C6	C17	125.2(3)	124.6(3)
C6	C7	C8	110.9(2)	110.4(2)
C1	C8	C2	55.7(2)	53.5(2)
C1	C8	C7	107.4(2)	109.3(2)
C1	C8	C18	121.8(2)	122.6(2)
C2	C8	C7	119.2(2)	117.8(2)
C2	C8	C18	113.6(2)	113.6(2)
C7	C8	C18	121.9(2)	121.8(2)
C1	C9	C10	109.1(2)	108.8(2)
C9	C10	C11	114.1(2)	113.9(2)
C10	C11	C12	113.6(2)	113.8(2)
C5	C12	C11	109.6(2)	109.1(2)
O1	C15	O2	124.3(2)	124.2(3)
O1	C15	C2	111.7(2)	112.2(2)
O2	C15	C2	123.6(3)	123.4(3)
O3	C16	O4	123.9(3)	123.8(2)
O3	C16	C4	111.9(2)	112.1(2)
O4	C16	C4	124.0(3)	123.9(3)
O5	C17	O6	123.1(2)	124.3(3)
O5	C17	C6	112.7(2)	111.0(2)
O6	C17	C6	124.2(3)	124.7(3)
O7	C18	O8	123.9(3)	124.1(2)
O7	C18	C8	111.5(2)	111.8(2)
O8	C18	C8	124.7(3)	124.1(3)

Table 109. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-6 at **294 K**

Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O1	0.173	0.211	0.219	0.170	0.213	0.254
O2	0.172	0.248	0.304	0.171	0.235	0.350
O3	0.152	0.238	0.297	0.164	0.236	0.303
O4	0.172	0.262	0.339	0.186	0.256	0.310
O5	0.186	0.208	0.353	0.172	0.214	0.353
O6	0.192	0.217	0.401	0.176	0.228	0.376
O7	0.165	0.237	0.291	0.171	0.219	0.292
O8	0.176	0.227	0.333	0.160	0.234	0.295
C1	0.162	0.181	0.196	0.158	0.175	0.196
C2	0.163	0.181	0.212	0.164	0.186	0.247
C3	0.169	0.188	0.212	0.175	0.192	0.199
C4	0.161	0.198	0.208	0.157	0.196	0.222
C5	0.164	0.186	0.191	0.151	0.177	0.195
C6	0.186	0.191	0.213	0.169	0.204	0.262
C7	0.178	0.190	0.221	0.169	0.182	0.223
C8	0.167	0.203	0.224	0.163	0.194	0.242
C9	0.174	0.201	0.219	0.170	0.194	0.229
C10	0.195	0.216	0.244	0.186	0.193	0.261
C11	0.182	0.212	0.241	0.187	0.203	0.243
C12	0.175	0.211	0.222	0.172	0.198	0.219
C15	0.167	0.201	0.224	0.166	0.204	0.239
C16	0.163	0.211	0.241	0.173	0.198	0.232
C17	0.194	0.198	0.243	0.172	0.202	0.259
C18	0.169	0.214	0.227	0.169	0.209	0.217
C19	0.177	0.250	0.269	0.164	0.264	0.311
C20	0.141	0.298	0.334	0.162	0.297	0.325
C21	0.181	0.244	0.349	0.162	0.244	0.359
C22	0.146	0.279	0.305	0.161	0.259	0.291



R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Table 8–110. X-ray Crystal Data for Sb-6 at **294 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	117–118
Crystal size (mm)	0.21 x 0.25 x 0.33
Crystal system	monoclinic
Space group	*P2/n*
a (Å)	41.518(2)
b (Å)	7.462(1)
c (Å)	12.254(1)
β (°)	98.21(1)
Cell volume ($Å^3$)	3757.56(1.95)
Z	8
d_{calc} (g cm^{-3})	1.380
μ(Cu $K\alpha$) (cm^{-1})	8.61
Maximum θ (°)	60
Unique reflections	5588
Observed reflections [$I > 3.0\sigma(I)$]	3203
Number of variables	505
R	0.048
R_w	0.056
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.27
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.22

Table 111. Final Atomic Parameters for Sb-6 at **294 K**

Atom	x	y	z	B(Å^2)
O1	0.55604(5)	0.1568(4)	0.2629(2)	3.22(6)
O2	0.55702(6)	0.4211(4)	0.3501(2)	4.85(7)
O3	0.69239(6)	0.4025(4)	0.3913(2)	4.44(7)
O4	0.70597(6)	0.1188(4)	0.3652(3)	5.71(8)
O5	0.68226(6)	0.0854(5)	0.7579(2)	5.37(8)
O6	0.70752(6)	0.0314(5)	0.6139(2)	6.47(9)
O7	0.56133(6)	0.1248(4)	0.6679(2)	4.37(7)
O8	0.53808(6)	0.0946(5)	0.4929(2)	5.02(8)
C1	0.60598(8)	0.0136(5)	0.4392(3)	2.56(7)
C2	0.59804(8)	0.2035(5)	0.4092(3)	2.79(8)
C3	0.62824(8)	0.2944(5)	0.3921(3)	2.90(8)
C4	0.65378(8)	0.1842(5)	0.4122(3)	2.81(8)
C5	0.64403(8)	0.0099(5)	0.4647(3)	2.62(8)
C6	0.65046(8)	0.0626(5)	0.5862(3)	3.11(9)
C7	0.62381(8)	0.1347(5)	0.6197(3)	3.04(8)
C8	0.59563(8)	0.1209(5)	0.5338(3)	2.97(8)
C9	0.59021(9)	-0.1532(5)	0.3881(3)	3.05(8)
C10	0.60595(9)	-0.2036(6)	0.2869(3)	3.68(9)
C11	0.64373(9)	-0.2019(6)	0.3075(3)	3.55(9)
C12	0.65791(9)	-0.1649(5)	0.4283(3)	3.30(9)
C15	0.56767(8)	0.2720(5)	0.3412(3)	2.99(8)
C16	0.68694(8)	0.2269(6)	0.3899(3)	3.33(9)
C17	0.68293(9)	0.0569(6)	0.6516(3)	3.60(9)
C18	0.56171(8)	0.1117(6)	0.5596(3)	3.33(9)
C19	0.5289(1)	0.2188(6)	0.1842(3)	4.5(1)
C20	0.72376(9)	0.4593(7)	0.3639(4)	5.8(1)
C21	0.7132(1)	0.0781(7)	0.8288(3)	5.6(1)
C22	0.52944(9)	0.1101(7)	0.7041(3)	5.1(1)
O1'	0.44780(6)	0.3529(4)	-0.0498(2)	3.64(6)
O2'	0.44628(7)	0.0934(4)	0.0395(3)	5.46(8)
O3'	0.30989(6)	0.0961(4)	-0.0593(2)	4.54(7)
O4'	0.29699(6)	0.3785(4)	-0.1056(2)	5.17(8)
O5'	0.31806(6)	0.4171(5)	0.3108(2)	5.37(8)
O6'	0.29202(6)	0.4574(5)	0.1412(2)	5.86(8)
O7'	0.43773(6)	0.3720(4)	0.3495(2)	4.28(7)
O8'	0.46187(6)	0.4423(4)	0.2034(2)	4.51(7)
C1'	0.39513(7)	0.4927(5)	0.0735(3)	2.43(7)
C2'	0.40377(8)	0.3068(5)	0.0473(3)	3.18(9)
C3'	0.37472(8)	0.2112(5)	0.0025(3)	2.70(8)
C4'	0.34817(8)	0.3169(5)	0.0003(3)	2.96(8)
C5'	0.35696(7)	0.4939(5)	0.0582(3)	2.36(7)
C6'	0.34959(8)	0.4330(6)	0.1706(3)	3.70(9)
C7'	0.37648(8)	0.3694(5)	0.2338(3)	2.89(8)
C8'	0.40474(8)	0.3947(6)	0.1810(3)	3.18(9)
C9'	0.41036(8)	0.6621(5)	0.0383(3)	3.11(8)
C10'	0.39497(9)	0.7087(6)	-0.0794(3)	3.60(9)
C11'	0.35717(9)	0.7072(6)	-0.0967(3)	3.59(9)
C12'	0.34259(8)	0.6674(5)	0.0087(3)	2.94(8)
C15'	0.43522(9)	0.2388(5)	0.0150(3)	3.42(9)
C16'	0.31552(8)	0.2712(5)	-0.0585(3)	3.05(9)
C17'	0.31685(8)	0.4372(6)	0.2029(3)	3.70(9)
C18'	0.43800(8)	0.4046(5)	0.2428(3)	3.14(8)
C19'	0.47627(9)	0.2919(7)	-0.0958(3)	5.0(1)
C20'	0.2792(1)	0.0381(7)	-0.1206(4)	5.9(1)
C21'	0.28722(9)	0.4265(7)	0.3532(3)	5.6(1)
C22'	0.46878(9)	0.3842(7)	0.4222(3)	4.6(1)

Table 111 (cont.). Final Atomic Parameters for Sb-6 at **294 K**

Atom	x	y	z	B(Å^2)
H3	0.629	0.422	0.368	3.1
H7	0.623	0.190	0.694	3.3
H9A	0.566	-0.131	0.365	3.4
H9B	0.593	-0.253	0.443	3.4
H10A	0.598	-0.117	0.227	4.1
H10B	0.599	-0.327	0.263	4.1
H11A	0.651	-0.107	0.260	3.9
H11B	0.652	-0.322	0.286	3.9
H12A	0.652	-0.265	0.475	3.5
H12B	0.682	-0.155	0.434	3.5
H19A	0.522	0.122	0.129	4.7
H19B	0.510	0.251	0.224	4.7
H19C	0.536	0.327	0.145	4.7
H20A	0.725	0.594	0.368	6.3
H20B	0.742	0.406	0.417	6.3
H20C	0.726	0.420	0.287	6.3
H21A	0.710	0.102	0.907	6.1
H21B	0.723	-0.042	0.824	6.1
H21C	0.728	0.172	0.805	6.1
H22A	0.532	0.122	0.786	5.5
H22B	0.515	0.209	0.669	5.5
H22C	0.519	-0.008	0.681	5.5
H3'	0.374	0.083	-0.023	3.0
H7'	0.377	0.310	0.308	3.2
H9A'	0.434	0.645	0.040	3.4
H9B'	0.406	0.763	0.089	3.4
H10A'	0.403	0.620	-0.131	4.0
H10B'	0.402	0.831	-0.098	4.0
H11A'	0.350	0.613	-0.152	3.8
H11B'	0.349	0.827	-0.125	3.8
H12A'	0.348	0.767	0.062	3.3
H12B'	0.318	0.654	-0.010	3.3
H19A'	0.484	0.389	-0.144	5.5
H19B'	0.494	0.264	-0.035	5.5
H19C'	0.471	0.183	-0.142	5.5
H20A'	0.277	-0.095	-0.117	6.3
H20B'	0.261	0.094	-0.088	6.3
H20C'	0.278	0.076	-0.200	6.3
H21A'	0.291	0.409	0.435	6.1
H21B'	0.277	0.546	0.335	6.1
H21C'	0.272	0.330	0.319	6.1
H22A'	0.465	0.357	0.499	5.1
H22B'	0.485	0.297	0.398	5.1
H22C'	0.478	0.508	0.419	5.1
H19BA'	0.484	0.177	-0.060	5.5
H19BB'	0.470	0.273	-0.177	5.5
H19BC'	0.494	0.385	-0.083	5.5

The parameters of the hydrogen atoms were not refined.

Table 112. Final Anisotropic Thermal Parameters (U's) for Sb-6 at **294 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.036(1)	0.043(2)	0.042(1)	0.007(1)	0.000(1)	0.006(1)
O2	0.054(2)	0.046(2)	0.082(2)	0.017(1)	0.001(1)	-0.004(2)
O3	0.038(1)	0.053(2)	0.083(2)	-0.012(1)	0.029(1)	-0.001(2)
O4	0.049(1)	0.070(2)	0.107(2)	0.011(2)	0.040(1)	0.003(2)
O5	0.043(1)	0.122(3)	0.036(1)	0.018(2)	-0.002(1)	-0.008(2)
O6	0.038(1)	0.152(3)	0.056(2)	0.009(2)	0.004(1)	-0.023(2)
O7	0.043(1)	0.083(2)	0.045(1)	-0.007(2)	0.021(1)	-0.006(2)
O8	0.033(1)	0.112(3)	0.047(1)	-0.011(2)	0.007(1)	0.004(2)
C1	0.028(2)	0.037(2)	0.033(2)	0.000(2)	0.008(1)	0.002(2)
C2	0.028(2)	0.039(2)	0.040(2)	0.001(2)	0.009(1)	0.002(2)
C3	0.032(2)	0.036(2)	0.043(2)	-0.002(2)	0.011(2)	0.002(2)
C4	0.030(2)	0.038(2)	0.040(2)	0.001(2)	0.010(2)	0.003(2)
C5	0.029(2)	0.037(2)	0.033(2)	0.004(2)	0.004(1)	0.001(2)
C6	0.035(2)	0.050(3)	0.034(2)	0.001(2)	0.007(2)	-0.001(2)
C7	0.038(2)	0.046(2)	0.033(2)	-0.005(2)	0.008(2)	-0.002(2)
C8	0.030(2)	0.049(2)	0.035(2)	-0.003(2)	0.009(1)	-0.005(2)
C9	0.043(2)	0.035(2)	0.037(2)	-0.006(2)	0.003(2)	0.003(2)
C10	0.052(2)	0.043(2)	0.042(2)	0.005(2)	-0.001(2)	-0.001(2)
C11	0.055(2)	0.041(3)	0.039(2)	0.008(2)	0.009(2)	-0.004(2)
C12	0.040(2)	0.040(2)	0.045(2)	0.007(2)	0.005(2)	0.001(2)
C15	0.032(2)	0.037(2)	0.046(2)	-0.003(2)	0.012(2)	0.003(2)
C16	0.032(2)	0.050(3)	0.046(2)	-0.000(2)	0.012(2)	0.004(2)
C17	0.038(2)	0.059(3)	0.040(2)	0.002(2)	0.005(2)	-0.005(2)
C18	0.032(2)	0.051(3)	0.045(2)	-0.002(2)	0.012(2)	0.000(2)
C19	0.041(2)	0.065(3)	0.059(2)	0.008(2)	-0.009(2)	0.006(2)
C20	0.041(2)	0.083(4)	0.102(3)	-0.022(2)	0.032(2)	0.009(3)
C21	0.044(2)	0.123(4)	0.040(2)	0.018(3)	-0.014(2)	-0.004(3)
C22	0.048(2)	0.089(4)	0.067(2)	-0.011(2)	0.037(2)	-0.002(3)
O1'	0.047(1)	0.044(2)	0.051(1)	0.009(1)	0.018(1)	0.001(1)
O2'	0.055(2)	0.049(2)	0.109(2)	0.019(2)	0.030(1)	0.019(2)
O3'	0.039(1)	0.051(2)	0.076(2)	-0.012(1)	-0.014(1)	-0.004(2)
O4'	0.052(2)	0.064(2)	0.072(2)	0.008(2)	-0.019(1)	-0.003(2)
O5'	0.036(1)	0.126(3)	0.045(1)	0.015(2)	0.013(1)	0.014(2)
O6'	0.033(1)	0.139(3)	0.052(2)	0.009(2)	0.008(1)	0.023(2)
O7'	0.033(1)	0.086(2)	0.040(1)	-0.006(2)	-0.005(1)	0.003(2)
O8'	0.027(1)	0.089(2)	0.055(2)	-0.004(2)	0.005(1)	0.002(2)
C1'	0.027(2)	0.037(2)	0.029(2)	0.000(2)	0.006(1)	0.000(2)
C2'	0.025(2)	0.038(2)	0.057(2)	-0.000(2)	0.005(2)	-0.002(2)
C3'	0.032(2)	0.036(2)	0.033(2)	-0.005(2)	0.002(2)	0.002(2)
C4'	0.027(2)	0.041(2)	0.043(2)	0.002(2)	0.001(2)	-0.001(2)
C5'	0.026(2)	0.036(2)	0.029(2)	0.004(2)	0.005(1)	-0.000(2)
C6'	0.032(2)	0.065(3)	0.044(2)	0.003(2)	0.008(2)	0.010(2)
C7'	0.030(2)	0.049(2)	0.031(2)	-0.002(2)	0.004(1)	0.003(2)
C8'	0.023(2)	0.055(3)	0.042(2)	-0.004(2)	0.002(2)	0.007(2)
C9'	0.037(2)	0.037(2)	0.046(2)	-0.008(2)	0.014(2)	-0.002(2)
C10'	0.052(2)	0.040(2)	0.049(2)	0.002(2)	0.020(2)	0.005(2)
C11'	0.053(2)	0.043(2)	0.042(2)	0.006(2)	0.010(2)	0.010(2)
C12'	0.034(2)	0.039(2)	0.040(2)	0.005(2)	0.009(2)	0.001(2)
C15'	0.033(2)	0.043(2)	0.054(2)	-0.003(2)	0.007(2)	0.000(2)
C16'	0.029(2)	0.051(3)	0.036(2)	0.001(2)	0.005(2)	-0.002(2)
C17'	0.033(2)	0.062(3)	0.048(2)	0.004(2)	0.009(2)	0.013(2)
C18'	0.034(2)	0.047(3)	0.037(2)	0.002(2)	0.000(2)	-0.001(2)
C19'	0.058(2)	0.064(3)	0.076(3)	0.014(2)	0.042(2)	0.002(2)
C20'	0.043(2)	0.083(4)	0.089(3)	-0.021(3)	-0.022(2)	-0.009(3)
C21'	0.043(2)	0.123(4)	0.053(2)	0.015(3)	0.026(2)	0.011(3)
C22'	0.039(2)	0.085(4)	0.046(2)	-0.005(2)	-0.013(2)	-0.005(3)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 113. Interatomic Distances (Å) for Sb-6 at **294 K**

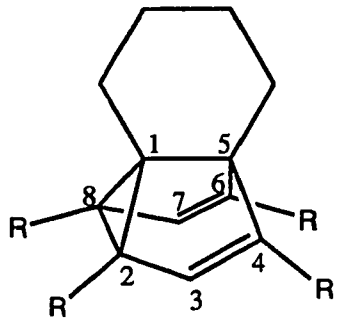
		Unprimed	Primed
O1	C15	1.326(4)	1.322(5)
O1	C19	1.450(4)	1.453(5)
O2	C15	1.208(5)	1.199(5)
O3	C16	1.329(5)	1.327(5)
O3	C20	1.454(5)	1.449(5)
O4	C16	1.198(5)	1.200(5)
O5	C17	1.323(4)	1.325(5)
O5	C21	1.445(4)	1.451(5)
O6	C17	1.195(5)	1.198(4)
O7	C18	1.333(4)	1.331(4)
O7	C22	1.459(5)	1.462(4)
O8	C18	1.191(4)	1.197(4)
C1	C2	1.489(5)	1.479(5)
C1	C5	1.566(4)	1.569(4)
C1	C8	1.520(5)	1.509(5)
C1	C9	1.501(5)	1.504(5)
C2	C3	1.467(5)	1.441(5)
C2	C8	1.663(5)	1.759(5)
C2	C15	1.498(5)	1.506(5)
C3	C4	1.337(5)	1.352(5)
C3	C7	3.062(5)	3.062(5)
C4	C5	1.531(5)	1.519(5)
C4	C6	2.338(5)	2.252(5)
C4	C16	1.476(5)	1.481(5)
C5	C6	1.526(5)	1.522(5)
C5	C12	1.518(5)	1.516(5)
C6	C7	1.346(5)	1.351(5)
C6	C17	1.468(5)	1.470(5)
C7	C8	1.462(4)	1.432(5)
C8	C18	1.488(5)	1.479(4)
C9	C10	1.530(5)	1.531(5)
C10	C11	1.553(5)	1.553(5)
C11	C12	1.539(5)	1.531(5)

Table 114. Angles (°) for Sb-6 at **294 K**

			Unprimed	Primed
C15	O1	C19	116.2(3)	116.4(3)
C16	O3	C20	116.2(3)	116.1(3)
C17	O5	C21	116.4(3)	116.3(3)
C18	O7	C22	115.9(3)	117.2(3)
C2	C1	C5	104.3(3)	104.6(3)
C2	C1	C8	67.1(3)	72.1(3)
C2	C1	C9	128.2(3)	126.9(3)
C5	C1	C8	104.1(3)	104.1(3)
C5	C1	C9	115.9(3)	114.8(3)
C8	C1	C9	126.9(3)	126.0(3)
C1	C2	C3	108.2(3)	109.3(3)
C1	C2	C8	57.4(2)	54.7(2)
C1	C2	C15	126.9(3)	128.3(3)
C3	C2	C8	117.9(3)	116.5(3)
C3	C2	C15	115.6(3)	116.3(3)
C8	C2	C15	118.7(3)	117.7(3)
C2	C3	C4	111.2(3)	110.8(3)
C3	C4	C5	110.5(3)	110.9(3)
C3	C4	C16	124.7(4)	124.2(3)
C5	C4	C6	40.0(2)	42.2(2)
C5	C4	C16	124.8(3)	124.7(3)
C1	C5	C4	102.8(3)	102.8(3)
C1	C5	C6	102.8(3)	102.7(2)
C1	C5	C12	111.8(3)	112.7(3)
C4	C5	C6	99.8(3)	95.6(3)
C4	C5	C12	118.2(3)	120.1(3)
C6	C5	C12	119.1(3)	119.9(3)
C4	C6	C5	40.2(2)	42.2(2)
C5	C6	C7	111.3(3)	111.6(3)
C5	C6	C17	123.0(3)	123.4(3)
C7	C6	C17	125.1(3)	125.0(3)
C6	C7	C8	111.1(3)	110.9(3)
C1	C8	C2	55.6(2)	53.1(2)
C1	C8	C7	107.6(3)	109.1(3)
C1	C8	C18	121.1(3)	122.3(3)
C2	C8	C7	119.2(3)	117.4(3)
C2	C8	C18	113.3(3)	113.0(3)
C7	C8	C18	122.3(3)	122.7(3)
C1	C9	C10	109.3(3)	109.0(3)
C9	C10	C11	113.9(3)	113.9(3)
C10	C11	C12	113.4(3)	113.6(3)
C5	C12	C11	109.1(3)	108.8(3)
O1	C15	O2	124.2(3)	124.3(4)
O1	C15	C2	111.8(3)	111.9(3)
O2	C15	C2	123.6(3)	123.7(4)
O3	C16	O4	123.4(3)	123.6(3)
O3	C16	C4	111.8(3)	112.3(3)
O4	C16	C4	124.6(4)	124.0(4)
O5	C17	O6	123.1(3)	123.4(3)
O5	C17	C6	112.7(3)	111.2(3)
O6	C17	C6	124.2(3)	125.3(3)
O7	C18	O8	124.4(3)	124.3(3)
O7	C18	C8	110.7(3)	110.9(3)
O8	C18	C8	124.8(3)	124.8(3)

Table 115. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-6 at **294 K**

	Unprimed			Primed		
Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O1	0.169	0.213	0.220	0.178	0.214	0.247
O2	0.179	0.251	0.299	0.180	0.237	0.345
O3	0.153	0.238	0.298	0.162	0.238	0.300
O4	0.174	0.266	0.340	0.187	0.251	0.314
O5	0.180	0.208	0.358	0.173	0.210	0.360
O6	0.192	0.226	0.397	0.179	0.215	0.380
O7	0.162	0.233	0.292	0.165	0.218	0.296
O8	0.174	0.216	0.337	0.162	0.235	0.300
C1	0.158	0.184	0.196	0.158	0.175	0.192
C2	0.161	0.194	0.206	0.159	0.195	0.239
C3	0.168	0.193	0.212	0.170	0.180	0.203
C4	0.167	0.189	0.208	0.162	0.202	0.213
C5	0.166	0.182	0.197	0.154	0.170	0.192
C6	0.179	0.190	0.223	0.177	0.200	0.263
C7	0.174	0.190	0.222	0.173	0.173	0.224
C8	0.165	0.186	0.226	0.151	0.196	0.244
C9	0.177	0.191	0.219	0.165	0.198	0.227
C10	0.197	0.204	0.244	0.183	0.201	0.251
C11	0.182	0.207	0.242	0.179	0.214	0.242
C12	0.182	0.213	0.216	0.172	0.197	0.209
C15	0.164	0.196	0.220	0.178	0.210	0.233
C16	0.169	0.213	0.230	0.169	0.189	0.227
C17	0.193	0.198	0.246	0.176	0.201	0.263
C18	0.167	0.216	0.228	0.176	0.202	0.217
C19	0.175	0.260	0.268	0.159	0.254	0.314
C20	0.143	0.303	0.327	0.153	0.301	0.332
C21	0.155	0.246	0.359	0.158	0.247	0.357
C22	0.148	0.280	0.308	0.157	0.256	0.293



R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Table 8–116. X-ray Crystal Data for Sb-6 at **295 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	117–118
Crystal size (mm)	0.32 x 0.50 x 0.64
Crystal system	monoclinic
Space group	*P*2/*n*
a (Å)	41.522(2)
b (Å)	7.467(1)
c (Å)	12.255(1)
β (°)	98.24(1)
Cell volume ($Å^3$)	3760.49(3.87)
Z	8
d_{calc} (g cm^{-3})	1.379
μ(Cu $K\alpha$) (cm^{-1})	8.60
Maximum θ (°)	60
Unique reflections	5596
Observed reflections [$I > 3.0\sigma(I)$]	4664
Number of variables	505
R	0.055
R_w	0.080
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.30
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.33

Table 117. Final Atomic Parameters for Sb-6 at **295 K**

Atom	x	y	z	B(Å^2)
O1	0.55605(4)	0.1571(3)	0.2633(2)	3.60(4)
O2	0.55708(5)	0.4207(3)	0.3503(2)	5.06(5)
O3	0.69252(4)	0.4031(3)	0.3914(2)	4.66(5)
O4	0.70566(5)	0.1197(3)	0.3648(2)	6.00(6)
O5	0.68233(5)	0.0849(4)	0.7577(2)	5.56(6)
O6	0.70750(5)	0.0320(4)	0.6137(2)	6.87(7)
O7	0.56124(4)	0.1252(3)	0.6672(2)	4.76(5)
O8	0.53807(4)	0.0946(4)	0.4929(2)	5.41(6)
C1	0.60608(6)	0.0143(4)	0.4393(2)	2.80(5)
C2	0.59806(6)	0.2037(4)	0.4087(2)	3.06(5)
C3	0.62810(6)	0.2948(4)	0.3922(2)	3.12(5)
C4	0.65384(6)	0.1851(4)	0.4126(2)	3.16(5)
C5	0.64407(6)	0.0096(4)	0.4650(2)	2.89(5)
C6	0.65029(6)	0.0623(4)	0.5866(2)	3.38(6)
C7	0.62375(6)	0.1344(4)	0.6192(2)	3.42(6)
C8	0.59557(6)	0.1212(4)	0.5335(2)	3.33(6)
C9	0.59011(6)	-0.1526(4)	0.3882(2)	3.45(6)
C10	0.60595(7)	-0.2038(4)	0.2874(2)	4.03(6)
C11	0.64363(7)	-0.2022(4)	0.3080(2)	3.90(6)
C12	0.65774(6)	-0.1641(4)	0.4277(2)	3.52(6)
C15	0.56756(6)	0.2724(4)	0.3409(2)	3.37(6)
C16	0.68686(6)	0.2265(4)	0.3899(2)	3.54(6)
C17	0.68292(6)	0.0579(4)	0.6516(2)	3.76(6)
C18	0.56189(6)	0.1136(4)	0.5592(2)	3.47(6)
C19	0.52879(7)	0.2182(5)	0.1847(3)	4.70(7)
C20	0.72382(7)	0.4601(5)	0.3643(3)	6.10(9)
C21	0.71340(8)	0.0790(6)	0.8288(3)	5.84(9)
C22	0.52951(7)	0.1120(5)	0.7032(3)	5.42(8)
O1'	0.44776(4)	0.3527(3)	-0.0499(2)	3.96(4)
O2'	0.44617(5)	0.0934(3)	0.0389(2)	5.74(5)
O3'	0.30989(5)	0.0965(3)	-0.0596(2)	4.89(5)
O4'	0.29713(5)	0.3782(3)	-0.1059(2)	5.53(5)
O5'	0.31805(4)	0.4170(4)	0.3107(2)	5.71(6)
O6'	0.29208(5)	0.4567(4)	0.1409(2)	6.15(6)
O7'	0.43773(4)	0.3725(3)	0.3496(2)	4.59(5)
O8'	0.46184(4)	0.4406(3)	0.2034(2)	4.81(5)
C1'	0.39502(5)	0.4923(3)	0.0735(2)	2.65(5)
C2'	0.40384(6)	0.3054(4)	0.0476(2)	3.38(6)
C3'	0.37471(6)	0.2111(4)	0.0025(2)	2.98(5)
C4'	0.34817(6)	0.3167(4)	0.0007(2)	3.30(6)
C5'	0.35705(6)	0.4930(4)	0.0584(2)	2.73(5)
C6'	0.34950(6)	0.4324(4)	0.1708(2)	3.82(6)
C7'	0.37624(6)	0.3678(4)	0.2335(2)	3.25(6)
C8'	0.40472(6)	0.3928(4)	0.1809(2)	3.49(6)
C9'	0.41022(6)	0.6621(4)	0.0381(2)	3.42(6)
C10'	0.39471(7)	0.7084(4)	-0.0795(2)	3.84(6)
C11'	0.35698(7)	0.7063(4)	-0.0964(2)	3.84(6)
C12'	0.34263(6)	0.6665(4)	0.0084(2)	3.27(5)
C15'	0.43520(6)	0.2394(4)	0.0149(2)	3.47(6)
C16'	0.31540(6)	0.2722(4)	-0.0584(2)	3.42(6)
C17'	0.31692(6)	0.4368(4)	0.2027(2)	3.89(6)
C18'	0.43774(6)	0.4052(4)	0.2431(2)	3.46(6)
C19'	0.47601(7)	0.2916(5)	-0.0964(3)	5.33(8)
C20'	0.27919(8)	0.0386(5)	-0.1199(3)	6.25(9)
C21'	0.28738(7)	0.4260(6)	0.3536(3)	6.02(9)
C22'	0.46870(7)	0.3841(5)	0.4215(3)	4.88(8)

Table 117 (cont.). Final Atomic Parameters for Sb-6 at **295 K**

Atom	x	y	z	B(Å^2)
H3	0.629	0.422	0.368	3.1
H7	0.623	0.190	0.694	3.3
H9A	0.566	-0.131	0.365	3.4
H9B	0.593	-0.253	0.443	3.4
H10A	0.598	-0.117	0.227	4.1
H10B	0.599	-0.327	0.263	4.1
H11A	0.651	-0.107	0.260	3.9
H11B	0.652	-0.322	0.286	3.9
H12A	0.652	-0.265	0.475	3.5
H12B	0.682	-0.155	0.434	3.5
H19A	0.522	0.122	0.129	4.7
H19B	0.510	0.251	0.224	4.7
H19C	0.536	0.327	0.145	4.7
H20A	0.725	0.594	0.368	6.3
H20B	0.742	0.406	0.417	6.3
H20C	0.726	0.420	0.287	6.3
H21A	0.710	0.102	0.907	6.1
H21B	0.723	-0.042	0.824	6.1
H21C	0.728	0.172	0.805	6.1
H22A	0.532	0.122	0.786	5.5
H22B	0.515	0.209	0.669	5.5
H22C	0.519	-0.008	0.681	5.5
H3'	0.374	0.083	-0.023	3.0
H7'	0.377	0.310	0.308	3.2
H9A'	0.434	0.645	0.040	3.4
H9B'	0.406	0.763	0.089	3.4
H10A'	0.403	0.620	-0.131	4.0
H10B'	0.402	0.831	-0.098	4.0
H11A'	0.350	0.613	-0.152	3.8
H11B'	0.349	0.827	-0.125	3.8
H12A'	0.348	0.767	0.062	3.3
H12B'	0.318	0.654	-0.010	3.3
H19A'	0.484	0.389	-0.144	5.5
H19B'	0.494	0.264	-0.035	5.5
H19C'	0.471	0.183	-0.142	5.5
H20A'	0.277	-0.095	-0.117	6.3
H20B'	0.261	0.094	-0.088	6.3
H20C'	0.278	0.076	-0.200	6.3
H21A'	0.291	0.409	0.435	6.1
H21B'	0.277	0.546	0.335	6.1
H21C'	0.272	0.330	0.319	6.1
H22A'	0.465	0.357	0.499	5.1
H22B'	0.485	0.297	0.398	5.1
H22C'	0.478	0.508	0.419	5.1
H19BA'	0.484	0.177	-0.060	5.5
H19BB'	0.470	0.273	-0.177	5.5
H19BC'	0.494	0.385	-0.083	5.5

The parameters of the hydrogen atoms were not refined.

Table 118. Final Anisotropic Thermal Parameters (U's) for Sb-6 at 295 K

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0399(9)	0.046(1)	0.049(1)	0.0063(9)	0.0003(8)	0.0052(9)
O2	0.056(1)	0.044(1)	0.089(1)	0.017(1)	0.001(1)	-0.006(1)
O3	0.0414(9)	0.056(1)	0.084(1)	-0.0117(9)	0.0235(9)	0.002(1)
O4	0.053(1)	0.073(2)	0.110(2)	0.012(1)	0.038(1)	0.005(1)
O5	0.046(1)	0.121(2)	0.043(1)	0.016(1)	-0.0009(9)	-0.008(1)
O6	0.042(1)	0.159(2)	0.058(1)	0.006(1)	0.004(1)	-0.023(2)
O7	0.046(1)	0.089(2)	0.049(1)	-0.007(1)	0.0187(8)	-0.005(1)
O8	0.0350(9)	0.115(2)	0.056(1)	-0.009(1)	0.0082(9)	0.003(1)
C1	0.035(1)	0.038(1)	0.034(1)	-0.002(1)	0.007(1)	0.002(1)
C2	0.030(1)	0.039(1)	0.048(1)	0.001(1)	0.008(1)	0.003(1)
C3	0.036(1)	0.038(1)	0.046(1)	-0.001(1)	0.009(1)	0.002(1)
C4	0.036(1)	0.041(1)	0.044(1)	-0.002(1)	0.009(1)	-0.001(1)
C5	0.035(1)	0.038(1)	0.037(1)	0.001(1)	0.006(1)	0.002(1)
C6	0.038(1)	0.049(2)	0.041(1)	-0.001(1)	0.004(1)	-0.001(1)
C7	0.041(1)	0.051(2)	0.038(1)	-0.003(1)	0.008(1)	-0.003(1)
C8	0.036(1)	0.049(2)	0.043(1)	-0.003(1)	0.010(1)	-0.004(1)
C9	0.047(1)	0.036(1)	0.047(1)	-0.004(1)	0.002(1)	0.005(1)
C10	0.060(2)	0.043(2)	0.048(2)	0.003(1)	0.001(1)	-0.005(1)
C11	0.061(2)	0.041(2)	0.045(1)	0.006(1)	0.008(1)	-0.004(1)
C12	0.046(1)	0.041(1)	0.046(1)	0.009(1)	0.006(1)	0.002(1)
C15	0.035(1)	0.044(1)	0.051(1)	0.001(1)	0.011(1)	0.005(1)
C16	0.033(1)	0.054(2)	0.049(1)	0.003(1)	0.009(1)	0.004(1)
C17	0.038(1)	0.058(2)	0.046(1)	0.000(1)	0.003(1)	-0.005(1)
C18	0.035(1)	0.050(2)	0.049(1)	-0.004(1)	0.012(1)	0.002(1)
C19	0.043(1)	0.067(2)	0.064(2)	0.009(2)	-0.009(1)	0.011(2)
C20	0.050(2)	0.085(2)	0.103(2)	-0.022(2)	0.032(1)	0.007(2)
C21	0.052(2)	0.118(3)	0.047(2)	0.019(2)	-0.009(1)	-0.004(2)
C22	0.053(1)	0.090(2)	0.071(2)	-0.009(2)	0.037(1)	-0.003(2)
O1'	0.048(1)	0.049(1)	0.057(1)	0.0092(9)	0.0200(8)	0.0035(9)
O2'	0.056(1)	0.052(1)	0.115(2)	0.023(1)	0.032(1)	0.020(1)
O3'	0.043(1)	0.054(1)	0.082(1)	-0.010(1)	-0.013(1)	-0.001(1)
O4'	0.055(1)	0.069(1)	0.077(1)	0.008(1)	-0.023(1)	-0.002(1)
O5'	0.039(1)	0.129(2)	0.051(1)	0.014(1)	0.0114(9)	0.013(1)
O6'	0.034(1)	0.140(2)	0.059(1)	0.008(1)	0.0076(9)	0.019(1)
O7'	0.038(1)	0.087(2)	0.046(1)	-0.006(1)	-0.0054(8)	0.005(1)
O8'	0.0312(9)	0.092(2)	0.058(1)	-0.002(1)	0.0026(9)	0.001(1)
C1'	0.032(1)	0.037(1)	0.032(1)	-0.000(1)	0.006(1)	-0.002(1)
C2'	0.028(1)	0.036(1)	0.064(2)	0.003(1)	0.006(1)	-0.003(1)
C3'	0.033(1)	0.038(1)	0.041(1)	-0.002(1)	0.002(1)	-0.001(1)
C4'	0.029(1)	0.043(1)	0.052(1)	-0.001(1)	0.001(1)	-0.002(1)
C5'	0.031(1)	0.039(1)	0.033(1)	0.005(1)	0.005(1)	-0.003(1)
C6'	0.031(1)	0.063(2)	0.051(2)	0.002(1)	0.007(1)	0.013(1)
C7'	0.036(1)	0.051(2)	0.036(1)	-0.002(1)	0.005(1)	0.002(1)
C8'	0.029(1)	0.059(2)	0.044(1)	-0.004(1)	0.001(1)	0.007(1)
C9'	0.044(1)	0.038(1)	0.050(1)	-0.004(1)	0.012(1)	-0.005(1)
C10'	0.056(1)	0.042(2)	0.051(1)	0.007(1)	0.019(1)	0.008(1)
C11'	0.056(2)	0.045(2)	0.046(1)	0.006(1)	0.011(1)	0.008(1)
C12'	0.040(1)	0.040(1)	0.045(1)	0.006(1)	0.006(1)	0.001(1)
C15'	0.030(1)	0.041(1)	0.059(2)	0.001(1)	0.003(1)	-0.005(1)
C16'	0.033(1)	0.053(2)	0.043(1)	0.005(1)	0.002(1)	-0.004(1)
C17'	0.034(1)	0.064(2)	0.050(1)	0.004(1)	0.009(1)	0.011(1)
C18'	0.034(1)	0.049(2)	0.047(1)	0.000(1)	-0.000(1)	-0.001(1)
C19'	0.059(2)	0.069(2)	0.082(2)	0.012(2)	0.037(1)	0.001(2)
C20'	0.055(2)	0.082(2)	0.091(2)	-0.022(2)	-0.024(2)	-0.011(2)
C21'	0.046(2)	0.129(3)	0.058(2)	0.016(2)	0.022(1)	0.009(2)
C22'	0.042(1)	0.087(2)	0.051(2)	-0.003(2)	-0.013(1)	-0.004(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 119. Interatomic Distances (Å) for Sb-6 at **295 K**

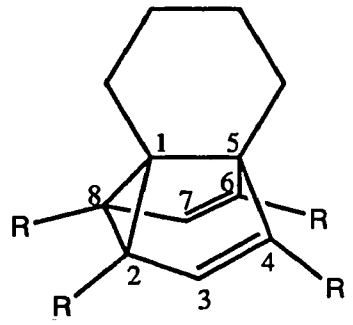
		Unprimed	Primed
O1	C15	1.320(3)	1.318(3)
O1	C19	1.451(3)	1.449(4)
O2	C15	1.201(3)	1.202(3)
O3	C16	1.339(4)	1.332(4)
O3	C20	1.451(4)	1.445(4)
O4	C16	1.187(4)	1.189(3)
O5	C17	1.319(3)	1.326(3)
O5	C21	1.450(3)	1.448(4)
O6	C17	1.197(4)	1.198(3)
O7	C18	1.331(3)	1.328(3)
O7	C22	1.451(4)	1.453(3)
O8	C18	1.195(3)	1.203(3)
C1	C2	1.488(4)	1.488(4)
C1	C5	1.564(3)	1.561(3)
C1	C8	1.518(4)	1.514(4)
C1	C9	1.506(4)	1.508(4)
C2	C3	1.460(4)	1.440(3)
C2	C8	1.665(4)	1.754(4)
C2	C15	1.502(3)	1.500(4)
C3	C4	1.341(4)	1.353(4)
C3	C7	3.058(4)	3.057(4)
C4	C5	1.540(4)	1.515(4)
C4	C6	2.346(4)	2.250(4)
C4	C16	1.471(4)	1.485(3)
C5	C6	1.527(4)	1.524(4)
C5	C12	1.513(4)	1.519(4)
C6	C7	1.338(4)	1.346(3)
C6	C17	1.470(3)	1.461(4)
C7	C8	1.459(3)	1.438(4)
C8	C18	1.478(4)	1.473(3)
C9	C10	1.529(4)	1.532(4)
C10	C11	1.549(4)	1.551(4)
C11	C12	1.526(4)	1.521(4)

Table 120. Angles (°) for Sb-6 at **295 K**

			Unprimed	Primed
C15	O1	C19	116.2(2)	116.6(2)
C16	O3	C20	116.5(2)	116.0(2)
C17	O5	C21	116.5(2)	116.8(2)
C18	O7	C22	116.5(2)	117.4(2)
C2	C1	C5	104.8(2)	104.7(2)
C2	C1	C8	67.3(2)	71.5(2)
C2	C1	C9	127.8(2)	126.9(2)
C5	C1	C8	104.5(2)	104.1(2)
C5	C1	C9	115.9(2)	114.9(2)
C8	C1	C9	126.4(2)	126.3(2)
C1	C2	C15	127.2(2)	127.9(2)
C1	C2	C3	108.2(2)	108.8(2)
C1	C2	C8	57.2(2)	54.9(2)
C3	C2	C8	117.8(2)	116.4(2)
C3	C2	C15	115.7(2)	116.8(2)
C8	C2	C15	118.4(2)	117.9(2)
C2	C3	C4	111.3(2)	111.0(2)
C3	C4	C5	110.3(2)	110.9(2)
C3	C4	C16	125.2(3)	124.4(2)
C5	C4	C6	39.9(1)	42.4(1)
C5	C4	C16	124.5(2)	124.5(2)
C1	C5	C4	102.4(2)	103.1(2)
C1	C5	C6	102.5(2)	103.1(2)
C1	C5	C12	111.7(2)	112.6(2)
C4	C5	C6	99.8(2)	95.5(2)
C4	C5	C12	118.1(2)	119.8(2)
C6	C5	C12	119.9(2)	119.8(2)
C4	C6	C5	40.3(1)	42.1(1)
C5	C6	C7	111.3(2)	111.3(2)
C5	C6	C17	122.5(2)	123.6(2)
C7	C6	C17	125.6(2)	125.1(3)
C6	C7	C8	111.6(2)	111.1(2)
C1	C8	C2	55.5(2)	53.6(2)
C1	C8	C7	107.1(2)	108.7(2)
C1	C8	C18	121.7(2)	122.1(2)
C2	C8	C7	119.1(2)	117.4(2)
C2	C8	C18	113.3(2)	113.5(2)
C7	C8	C18	122.3(2)	122.7(2)
C1	C9	C10	109.1(2)	108.9(2)
C9	C10	C11	114.1(2)	113.8(2)
C10	C11	C12	113.5(2)	113.6(2)
C5	C12	C11	110.0(2)	109.2(2)
O1	C15	O2	124.8(2)	124.1(3)
O1	C15	C2	111.4(2)	112.6(2)
O2	C15	C2	123.4(2)	123.1(3)
O3	C16	O4	123.0(3)	123.7(2)
O3	C16	C4	111.8(2)	111.7(2)
O4	C16	C4	125.0(3)	124.4(3)
O5	C17	O6	123.0(2)	123.3(3)
O5	C17	C6	112.6(2)	111.3(2)
O6	C17	C6	124.3(3)	125.4(3)
O7	C18	O8	123.4(3)	123.7(2)
O7	C18	C8	111.4(2)	111.4(2)
O8	C18	C8	125.1(3)	124.8(3)

Table 121. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-6 at **295 K**

	Unprimed			Primed		
Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O1	0.183	0.224	0.231	0.186	0.220	0.260
O2	0.179	0.253	0.310	0.176	0.246	0.356
O3	0.170	0.248	0.294	0.178	0.240	0.310
O4	0.188	0.272	0.344	0.187	0.262	0.327
O5	0.194	0.219	0.355	0.187	0.221	0.365
O6	0.205	0.233	0.406	0.183	0.234	0.381
O7	0.183	0.237	0.301	0.177	0.232	0.299
O8	0.183	0.237	0.341	0.176	0.243	0.304
C1	0.177	0.190	0.198	0.175	0.181	0.193
C2	0.172	0.194	0.221	0.164	0.192	0.254
C3	0.183	0.195	0.216	0.177	0.198	0.207
C4	0.184	0.202	0.213	0.169	0.207	0.232
C5	0.185	0.188	0.200	0.167	0.182	0.207
C6	0.193	0.205	0.222	0.176	0.208	0.266
C7	0.192	0.202	0.229	0.188	0.190	0.228
C8	0.183	0.204	0.227	0.167	0.204	0.251
C9	0.184	0.206	0.235	0.189	0.199	0.233
C10	0.200	0.218	0.257	0.193	0.202	0.260
C11	0.192	0.218	0.252	0.194	0.217	0.247
C12	0.185	0.216	0.230	0.183	0.213	0.213
C15	0.180	0.202	0.233	0.172	0.200	0.249
C16	0.177	0.215	0.238	0.178	0.206	0.237
C17	0.194	0.213	0.245	0.183	0.209	0.266
C18	0.175	0.224	0.226	0.179	0.220	0.226
C19	0.179	0.261	0.280	0.185	0.265	0.314
C20	0.169	0.308	0.329	0.168	0.302	0.343
C21	0.186	0.250	0.354	0.181	0.250	0.365
C22	0.164	0.287	0.311	0.169	0.264	0.295



R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Table 8–122. X-ray Crystal Data for Sb-6 at **322 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	117–118
Crystal size (mm)	0.21 x 0.25 x 0.33
Crystal system	monoclinic
Space group	*P2/n*
a (Å)	41.558(1)
b (Å)	7.493(1)
c (Å)	12.276(1)
β (°)	98.22(1)
Cell volume ($Å^3$)	3783.39(1.91)
Z	8
d_{calc} (g cm^{-3})	1.371
μ(Cu $K\alpha$) (cm^{-1})	8.55
Maximum θ (°)	60
Unique reflections	5630
Observed reflections [$I > 3.0\sigma(I)$]	3407
Number of variables	505
R	0.048
R_w	0.056
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.24
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.20

Table 123. Final Atomic Parameters for Sb-6 at **322 K**

Atom	x	y	z	B(Å^2)
O1	0.55614(5)	0.1580(3)	0.2637(2)	3.65(5)
O2	0.55739(6)	0.4211(3)	0.3505(2)	5.51(7)
O3	0.69256(5)	0.4024(4)	0.3922(2)	4.99(6)
O4	0.70590(6)	0.1204(4)	0.3654(2)	6.48(7)
O5	0.68238(6)	0.0878(4)	0.7571(2)	5.94(7)
O6	0.70750(6)	0.0322(5)	0.6140(2)	7.36(9)
O7	0.56149(5)	0.1250(4)	0.6676(2)	4.97(6)
O8	0.53820(5)	0.0948(4)	0.4930(2)	5.80(7)
C1	0.60615(7)	0.0151(5)	0.4395(2)	2.86(7)
C2	0.59820(7)	0.2039(5)	0.4091(3)	3.20(7)
C3	0.62837(7)	0.2947(5)	0.3922(3)	3.20(7)
C4	0.65384(7)	0.1853(5)	0.4133(3)	3.19(7)
C5	0.64410(7)	0.0109(5)	0.4652(2)	2.82(7)
C6	0.65045(7)	0.0647(5)	0.5861(3)	3.49(8)
C7	0.62381(8)	0.1353(5)	0.6192(3)	3.56(8)
C8	0.59582(7)	0.1213(5)	0.5340(3)	3.46(7)
C9	0.59023(8)	-0.1510(5)	0.3883(3)	3.61(8)
C10	0.60607(9)	-0.2011(5)	0.2877(3)	4.29(9)
C11	0.64373(8)	-0.1998(5)	0.3083(3)	4.06(8)
C12	0.65804(7)	-0.1628(5)	0.4277(3)	3.63(8)
C15	0.56794(7)	0.2731(5)	0.3411(3)	3.48(7)
C16	0.68708(7)	0.2279(5)	0.3900(3)	3.78(8)
C17	0.68302(8)	0.0584(5)	0.6515(3)	4.01(8)
C18	0.56187(8)	0.1123(5)	0.5591(3)	3.68(8)
C19	0.52903(9)	0.2199(6)	0.1859(3)	5.1(1)
C20	0.72383(9)	0.4597(6)	0.3645(4)	6.4(1)
C21	0.71310(9)	0.0786(7)	0.8287(3)	6.3(1)
C22	0.52986(8)	0.1121(6)	0.7043(3)	5.7(1)
O1'	0.44783(5)	0.3517(3)	-0.0496(2)	4.13(5)
O2'	0.44599(6)	0.0930(4)	0.0386(2)	6.20(7)
O3'	0.30990(5)	0.0967(3)	-0.0588(2)	5.19(6)
O4'	0.29718(6)	0.3771(4)	-0.1053(2)	5.76(7)
O5'	0.31812(5)	0.4158(4)	0.3096(2)	5.99(7)
O6'	0.29203(5)	0.4555(5)	0.1408(2)	6.61(8)
O7'	0.43763(5)	0.3716(4)	0.3495(2)	4.87(6)
O8'	0.46172(5)	0.4407(4)	0.2034(2)	5.05(7)
C1'	0.39509(7)	0.4904(5)	0.0735(2)	2.78(7)
C2'	0.40365(7)	0.3058(5)	0.0468(3)	3.66(8)
C3'	0.37466(7)	0.2109(5)	0.0028(3)	3.08(7)
C4'	0.34811(7)	0.3156(5)	0.0013(3)	3.47(8)
C5'	0.35699(7)	0.4917(5)	0.0585(2)	2.69(7)
C6'	0.34954(7)	0.4309(5)	0.1699(3)	4.03(8)
C7'	0.37642(7)	0.3677(5)	0.2336(2)	3.32(7)
C8'	0.40463(7)	0.3938(5)	0.1809(3)	3.57(8)
C9'	0.41033(7)	0.6596(5)	0.0381(3)	3.49(8)
C10'	0.39490(8)	0.7063(5)	-0.0789(3)	4.15(8)
C11'	0.35707(8)	0.7048(5)	-0.0961(3)	4.03(8)
C12'	0.34274(7)	0.6643(5)	0.0084(3)	3.50(8)
C15'	0.43493(7)	0.2380(5)	0.0142(3)	3.65(8)
C16'	0.31552(7)	0.2713(5)	-0.0578(3)	3.58(8)
C17'	0.31670(7)	0.4346(5)	0.2024(3)	3.99(8)
C18'	0.43784(7)	0.4043(5)	0.2433(3)	3.49(8)
C19'	0.47622(9)	0.2908(6)	-0.0953(3)	5.7(1)
C20'	0.27919(9)	0.0395(6)	-0.1208(4)	6.5(1)
C21'	0.28742(9)	0.4261(7)	0.3530(3)	6.4(1)
C22'	0.46852(8)	0.3835(6)	0.4217(3)	5.2(1)

Table 123 (cont.). Final Atomic Parameters for Sb-6 at **322 K**

Atom	x	y	z	B(Å^2)
H3	0.630	0.422	0.369	3.6
H7	0.623	0.190	0.693	3.9
H9A	0.567	-0.129	0.365	4.0
H9B	0.593	-0.251	0.443	4.0
H10A	0.599	-0.114	0.228	4.8
H10B	0.599	-0.324	0.264	4.8
H11A	0.652	-0.105	0.261	4.5
H11B	0.652	-0.319	0.287	4.5
H12A	0.652	-0.263	0.475	4.1
H12B	0.682	-0.152	0.434	4.1
H19A	0.522	0.123	0.132	5.7
H19B	0.510	0.252	0.226	5.7
H19C	0.536	0.327	0.146	5.7
H20A	0.725	0.593	0.368	7.2
H20B	0.742	0.406	0.417	7.2
H20C	0.726	0.420	0.288	7.2
H21A	0.710	0.103	0.906	7.0
H21B	0.723	-0.043	0.824	7.0
H21C	0.728	0.170	0.805	7.0
H22A	0.532	0.123	0.786	6.3
H22B	0.515	0.210	0.670	6.3
H22C	0.520	-0.006	0.681	6.3
H3'	0.374	0.084	-0.023	3.4
H7'	0.376	0.310	0.307	3.7
H9A'	0.434	0.641	0.040	3.9
H9B'	0.407	0.759	0.089	3.9
H10A'	0.403	0.618	-0.131	4.5
H10B'	0.402	0.829	-0.097	4.5
H11A'	0.349	0.612	-0.152	4.4
H11B'	0.349	0.825	-0.124	4.4
H12A'	0.348	0.764	0.062	3.9
H12B'	0.319	0.652	-0.010	3.9
H19A'	0.484	0.387	-0.142	6.3
H19B'	0.494	0.260	-0.035	6.3
H19C'	0.470	0.182	-0.142	6.3
H20A'	0.277	-0.094	-0.116	7.2
H20B'	0.261	0.096	-0.089	7.2
H20C'	0.278	0.076	-0.199	7.2
H21A'	0.291	0.410	0.434	7.1
H21B'	0.277	0.545	0.334	7.1
H21C'	0.273	0.330	0.319	7.1
H22A'	0.465	0.356	0.499	5.8
H22B'	0.484	0.296	0.397	5.8
H22C'	0.478	0.507	0.418	5.8
H19BA'	0.484	0.175	-0.060	6.1
H19BB'	0.470	0.273	-0.177	6.1
H19BC'	0.494	0.382	-0.082	6.1

The parameters of the hydrogen atoms were not refined.

Table 124. Final Anisotropic Thermal Parameters (U's) for Sb-6 at **322 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.040(1)	0.047(1)	0.050(1)	0.009(1)	0.002(1)	0.007(1)
O2	0.060(1)	0.050(2)	0.096(2)	0.019(1)	0.001(1)	-0.006(2)
O3	0.041(1)	0.057(2)	0.097(2)	-0.010(1)	0.030(1)	0.001(1)
O4	0.055(1)	0.077(2)	0.125(2)	0.014(1)	0.046(1)	0.006(2)
O5	0.049(1)	0.132(3)	0.043(1)	0.020(2)	-0.001(1)	-0.008(2)
O6	0.042(1)	0.172(3)	0.065(2)	0.009(2)	0.004(1)	-0.028(2)
O7	0.048(1)	0.093(2)	0.053(1)	-0.009(1)	0.023(1)	-0.006(1)
O8	0.038(1)	0.125(2)	0.058(1)	-0.013(2)	0.009(1)	0.003(2)
C1	0.033(1)	0.039(2)	0.039(2)	-0.001(2)	0.009(1)	0.003(2)
C2	0.031(2)	0.043(2)	0.048(2)	0.001(2)	0.007(1)	0.004(2)
C3	0.037(2)	0.038(2)	0.048(2)	-0.000(2)	0.013(1)	0.001(2)
C4	0.034(2)	0.043(2)	0.045(2)	-0.000(2)	0.010(1)	0.002(2)
C5	0.035(2)	0.036(2)	0.036(2)	0.002(2)	0.005(1)	0.001(2)
C6	0.039(2)	0.054(2)	0.040(2)	0.001(2)	0.004(1)	-0.001(2)
C7	0.042(2)	0.054(2)	0.040(2)	-0.005(2)	0.007(1)	-0.002(2)
C8	0.037(2)	0.055(2)	0.041(2)	-0.004(2)	0.012(1)	-0.008(2)
C9	0.049(2)	0.043(2)	0.045(2)	-0.005(2)	0.002(2)	0.003(2)
C10	0.062(2)	0.045(2)	0.053(2)	0.004(2)	0.001(2)	-0.006(2)
C11	0.060(2)	0.046(2)	0.049(2)	0.005(2)	0.011(2)	-0.006(2)
C12	0.042(2)	0.044(2)	0.052(2)	0.009(2)	0.006(2)	0.004(2)
C15	0.035(2)	0.045(2)	0.054(2)	-0.000(2)	0.014(1)	0.003(2)
C16	0.038(2)	0.055(2)	0.053(2)	0.003(2)	0.014(1)	0.005(2)
C17	0.041(2)	0.065(3)	0.046(2)	0.001(2)	0.004(2)	-0.010(2)
C18	0.040(2)	0.054(2)	0.048(2)	-0.005(2)	0.015(1)	-0.000(2)
C19	0.048(2)	0.068(3)	0.073(2)	0.007(2)	-0.009(2)	0.013(2)
C20	0.051(2)	0.089(3)	0.112(3)	-0.025(2)	0.039(2)	0.011(3)
C21	0.052(2)	0.132(4)	0.050(2)	0.021(3)	-0.013(2)	-0.005(3)
C22	0.056(2)	0.093(3)	0.078(2)	-0.011(2)	0.043(2)	-0.002(2)
O1'	0.051(1)	0.052(2)	0.059(1)	0.010(1)	0.023(1)	-0.001(1)
O2'	0.061(1)	0.057(2)	0.124(2)	0.026(1)	0.035(1)	0.021(2)
O3'	0.045(1)	0.060(2)	0.085(2)	-0.013(1)	-0.016(1)	-0.002(2)
O4'	0.055(1)	0.074(2)	0.081(2)	0.009(1)	-0.022(1)	-0.004(2)
O5'	0.040(1)	0.137(3)	0.053(1)	0.017(2)	0.014(1)	0.016(2)
O6'	0.035(1)	0.156(3)	0.061(1)	0.008(2)	0.009(1)	0.024(2)
O7'	0.038(1)	0.095(2)	0.048(1)	-0.008(1)	-0.004(1)	0.003(1)
O8'	0.031(1)	0.099(2)	0.062(1)	-0.003(1)	0.007(1)	0.000(2)
C1'	0.031(1)	0.040(2)	0.035(2)	-0.001(2)	0.009(1)	-0.002(2)
C2'	0.029(2)	0.041(2)	0.070(2)	0.004(2)	0.008(2)	-0.002(2)
C3'	0.036(2)	0.038(2)	0.042(2)	-0.001(2)	0.004(1)	-0.003(2)
C4'	0.030(2)	0.047(2)	0.055(2)	-0.001(2)	0.005(1)	-0.003(2)
C5'	0.030(1)	0.040(2)	0.033(1)	0.003(2)	0.006(1)	-0.002(2)
C6'	0.034(2)	0.069(3)	0.051(2)	0.004(2)	0.010(1)	0.014(2)
C7'	0.032(2)	0.056(2)	0.037(2)	-0.001(2)	0.005(1)	-0.000(2)
C8'	0.029(2)	0.061(2)	0.045(2)	-0.003(2)	0.002(1)	0.005(2)
C9'	0.042(2)	0.041(2)	0.052(2)	-0.004(2)	0.014(1)	-0.005(2)
C10'	0.062(2)	0.045(2)	0.055(2)	0.006(2)	0.023(2)	0.008(2)
C11'	0.058(2)	0.045(2)	0.051(2)	0.006(2)	0.013(2)	0.008(2)
C12'	0.045(2)	0.045(2)	0.045(2)	0.006(2)	0.011(1)	0.001(2)
C15'	0.031(2)	0.044(2)	0.063(2)	-0.001(2)	0.006(2)	0.002(2)
C16'	0.031(2)	0.059(2)	0.045(2)	0.002(2)	0.005(1)	-0.005(2)
C17'	0.034(2)	0.068(3)	0.051(2)	0.002(2)	0.011(1)	0.015(2)
C18'	0.037(2)	0.051(2)	0.044(2)	0.001(2)	0.002(1)	-0.003(2)
C19'	0.063(2)	0.077(3)	0.087(2)	0.011(2)	0.042(2)	-0.003(2)
C20'	0.049(2)	0.089(3)	0.099(3)	-0.022(2)	-0.020(2)	-0.015(3)
C21'	0.053(2)	0.139(4)	0.058(2)	0.020(3)	0.029(2)	0.011(3)
C22'	0.046(2)	0.091(3)	0.052(2)	-0.003(2)	-0.016(2)	-0.007(2)

The form of the anisotropic displacement parameter is:
$\exp(-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)])$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 125. Interatomic Distances (Å) for Sb-6 at 322 K

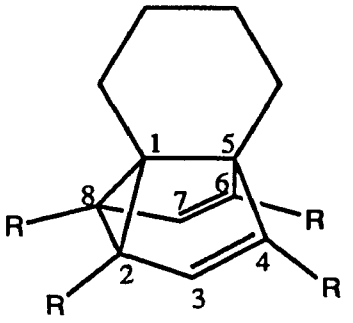
		Unprimed	Primed
O1	C15	1.325(4)	1.322(4)
O1	C19	1.445(4)	1.451(5)
O2	C15	1.204(4)	1.201(4)
O3	C16	1.327(5)	1.328(5)
O3	C20	1.455(5)	1.454(4)
O4	C16	1.191(4)	1.193(4)
O5	C17	1.320(4)	1.316(4)
O5	C21	1.444(4)	1.454(4)
O6	C17	1.192(4)	1.194(4)
O7	C18	1.337(4)	1.329(4)
O7	C22	1.453(4)	1.454(4)
O8	C18	1.190(4)	1.199(4)
C1	C2	1.488(5)	1.477(5)
C1	C5	1.564(4)	1.568(4)
C1	C8	1.519(5)	1.506(4)
C1	C9	1.504(5)	1.509(5)
C2	C3	1.467(4)	1.436(4)
C2	C8	1.670(5)	1.769(5)
C2	C15	1.499(4)	1.502(5)
C3	C4	1.335(4)	1.352(4)
C3	C7	3.063(5)	3.058(4)
C4	C5	1.534(5)	1.516(5)
C4	C6	2.329(5)	2.235(5)
C4	C16	1.485(4)	1.480(4)
C5	C6	1.525(4)	1.514(5)
C5	C12	1.522(5)	1.516(5)
C6	C7	1.341(5)	1.355(4)
C6	C17	1.472(4)	1.476(5)
C7	C8	1.453(4)	1.431(4)
C8	C18	1.488(5)	1.481(4)
C9	C10	1.527(5)	1.528(4)
C10	C11	1.549(5)	1.556(5)
C11	C12	1.527(4)	1.521(5)

Table 126. Angles (°) for Sb-6 at 322 K

			Unprimed	Primed
C15	O1	C19	116.0(3)	116.6(3)
C16	O3	C20	116.2(3)	115.8(3)
C17	O5	C21	116.7(3)	116.4(2)
C18	O7	C22	116.4(2)	117.2(3)
C2	C1	C5	104.5(3)	104.5(2)
C2	C1	C8	67.4(2)	72.7(2)
C2	C1	C9	127.8(2)	126.8(3)
C5	C1	C8	104.1(2)	103.9(2)
C5	C1	C9	116.0(3)	114.8(3)
C8	C1	C9	126.7(3)	125.9(2)
C1	C2	C3	108.3(3)	109.4(3)
C1	C2	C8	57.2(2)	54.4(2)
C1	C2	C15	127.4(3)	128.4(3)
C3	C2	C8	117.8(2)	116.1(3)
C3	C2	C15	115.2(3)	116.3(3)
C8	C2	C15	119.0(3)	117.9(2)
C2	C3	C4	111.0(3)	110.9(3)
C3	C4	C5	110.8(3)	110.8(3)
C3	C4	C16	124.4(3)	124.4(3)
C5	C4	C6	40.3(2)	42.4(2)
C5	C4	C16	124.8(3)	124.6(3)
C1	C5	C4	102.6(2)	103.0(2)
C1	C5	C6	102.7(2)	103.0(2)
C1	C5	C12	111.9(3)	112.5(3)
C4	C5	C6	99.2(3)	95.1(3)
C4	C5	C12	118.0(3)	120.0(2)
C6	C5	C12	120.0(3)	120.3(3)
C4	C6	C5	40.5(2)	42.5(2)
C5	C6	C7	111.3(3)	111.6(3)
C5	C6	C17	122.7(3)	123.7(3)
C7	C6	C17	125.6(3)	124.6(3)
C6	C7	C8	111.4(3)	110.6(3)
C1	C8	C2	55.4(2)	52.9(2)
C1	C8	C7	107.6(3)	109.3(2)
C1	C8	C18	121.0(3)	122.4(3)
C2	C8	C7	119.2(3)	117.3(2)
C2	C8	C18	112.9(2)	113.4(2)
C7	C8	C18	122.7(3)	122.5(3)
C1	C9	C10	109.1(3)	109.0(3)
C9	C10	C11	114.1(3)	114.0(3)
C10	C11	C12	113.8(3)	113.4(3)
C5	C12	C11	109.4(3)	109.6(3)
O1	C15	O2	124.4(3)	123.9(3)
O1	C15	C2	111.7(3)	112.3(3)
O2	C15	C2	123.6(3)	123.7(3)
O3	C16	O4	123.7(3)	123.4(3)
O3	C16	C4	111.7(3)	111.9(3)
O4	C16	C4	124.5(3)	124.5(3)
O5	C17	O6	123.1(3)	124.0(3)
O5	C17	C6	112.6(3)	110.9(3)
O6	C17	C6	124.3(3)	125.1(3)
O7	C18	O8	124.1(3)	124.4(3)
O7	C18	C8	110.4(2)	111.2(3)
O8	C18	C8	125.4(3)	124.5(3)

Table 127. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-6 at **322 K**

	Unprimed			Primed		
Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O1	0.177	0.226	0.237	0.180	0.234	0.265
O2	0.188	0.266	0.322	0.181	0.258	0.369
O3	0.166	0.247	0.318	0.175	0.254	0.319
O4	0.182	0.279	0.368	0.192	0.268	0.332
O5	0.197	0.220	0.372	0.185	0.226	0.377
O6	0.202	0.242	0.425	0.185	0.235	0.402
O7	0.178	0.248	0.309	0.181	0.235	0.311
O8	0.189	0.240	0.357	0.176	0.248	0.315
C1	0.173	0.193	0.205	0.167	0.191	0.203
C2	0.175	0.202	0.224	0.166	0.204	0.264
C3	0.181	0.196	0.225	0.187	0.195	0.210
C4	0.180	0.206	0.216	0.172	0.215	0.237
C5	0.181	0.190	0.196	0.167	0.183	0.202
C6	0.195	0.201	0.233	0.180	0.208	0.278
C7	0.199	0.199	0.237	0.179	0.194	0.237
C8	0.176	0.201	0.246	0.168	0.210	0.251
C9	0.198	0.205	0.236	0.189	0.199	0.239
C10	0.205	0.226	0.264	0.196	0.211	0.273
C11	0.197	0.231	0.249	0.198	0.221	0.254
C12	0.184	0.224	0.232	0.192	0.209	0.229
C15	0.175	0.211	0.238	0.177	0.209	0.252
C16	0.185	0.222	0.246	0.177	0.208	0.248
C17	0.201	0.207	0.263	0.177	0.208	0.278
C18	0.181	0.225	0.237	0.189	0.210	0.230
C19	0.192	0.261	0.297	0.182	0.281	0.324
C20	0.153	0.319	0.346	0.168	0.313	0.345
C21	0.180	0.262	0.374	0.174	0.261	0.381
C22	0.158	0.297	0.322	0.169	0.275	0.304



R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Table 8–128. X-ray Crystal Data for Sb-6 at **335 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	117–118
Crystal size (mm)	0.21 x 0.25 x 0.33
Crystal system	monoclinic
Space group	*P2/n*
a (Å)	41.574(2)
b (Å)	7.509(1)
c (Å)	12.285(1)
β (°)	98.22(1)
Cell volume ($Å^3$)	3796.08(1.87)
Z	8
d_{calc} (g cm^{-3})	1.366
μ(Cu $K\alpha$) (cm^{-1})	8.52
Maximum θ (°)	60
Unique reflections	5649
Observed reflections [$I > 3.0\sigma(I)$]	3082
Number of variables	505
R	0.053
R_w	0.061
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.30
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.19

Table 129. Final Atomic Parameters for Sb-6 at 335 K

Atom	x	y	z	B(Å^2)
O1	0.55612(6)	0.1591(4)	0.2639(2)	3.90(7)
O2	0.55759(8)	0.4210(4)	0.3504(3)	5.87(9)
O3	0.69260(7)	0.4023(4)	0.3921(3)	5.31(8)
O4	0.70597(7)	0.1207(5)	0.3663(3)	7.04(9)
O5	0.68236(8)	0.0883(5)	0.7570(3)	6.45(9)
O6	0.70751(8)	0.0323(6)	0.6139(3)	7.8(1)
O7	0.56155(7)	0.1252(4)	0.6672(2)	5.23(8)
O8	0.53844(7)	0.0959(5)	0.4932(3)	6.24(9)
C1	0.60632(9)	0.0166(5)	0.4394(3)	3.13(9)
C2	0.59838(9)	0.2051(5)	0.4087(3)	3.19(9)
C3	0.62846(9)	0.2943(5)	0.3928(3)	3.40(9)
C4	0.65392(9)	0.1854(5)	0.4139(3)	3.54(9)
C5	0.64416(9)	0.0111(5)	0.4649(3)	3.07(9)
C6	0.6506(1)	0.0646(5)	0.5861(3)	3.7(1)
C7	0.6238(1)	0.1355(6)	0.6188(3)	3.8(1)
C8	0.5958(1)	0.1204(6)	0.5342(3)	3.7(1)
C9	0.5903(1)	-0.1497(5)	0.3879(3)	3.7(1)
C10	0.6063(1)	-0.2008(6)	0.2874(4)	4.6(1)
C11	0.6438(1)	-0.1988(6)	0.3077(3)	4.4(1)
C12	0.6582(1)	-0.1621(6)	0.4278(3)	3.8(1)
C15	0.5681(1)	0.2736(5)	0.3411(3)	3.7(1)
C16	0.6871(1)	0.2283(6)	0.3906(4)	4.3(1)
C17	0.6828(1)	0.0589(6)	0.6522(4)	4.4(1)
C18	0.5621(1)	0.1129(6)	0.5595(4)	4.1(1)
C19	0.5290(1)	0.2208(7)	0.1859(4)	5.4(1)
C20	0.7239(1)	0.4599(7)	0.3646(5)	6.8(1)
C21	0.7129(1)	0.0786(8)	0.8284(4)	6.6(1)
C22	0.5298(1)	0.1117(7)	0.7035(4)	6.0(1)
O1'	0.44789(7)	0.3505(4)	-0.0494(2)	4.44(7)
O2'	0.44576(8)	0.0922(4)	0.0385(3)	6.56(9)
O3'	0.30990(7)	0.0978(4)	-0.0583(3)	5.47(8)
O4'	0.29721(8)	0.3769(4)	-0.1052(3)	6.25(9)
O5'	0.31815(7)	0.4144(5)	0.3094(3)	6.36(9)
O6'	0.29205(7)	0.4545(6)	0.1406(3)	7.0(1)
O7'	0.43764(7)	0.3714(4)	0.3498(2)	5.10(8)
O8'	0.46168(7)	0.4406(4)	0.2032(3)	5.27(8)
C1'	0.39495(9)	0.4892(5)	0.0734(3)	2.91(8)
C2'	0.40363(9)	0.3058(5)	0.0458(4)	3.8(1)
C3'	0.3746(1)	0.2095(5)	0.0031(3)	3.25(9)
C4'	0.34795(9)	0.3149(6)	0.0013(3)	3.6(1)
C5'	0.35708(9)	0.4916(5)	0.0585(3)	2.84(8)
C6'	0.3496(1)	0.4300(6)	0.1700(3)	4.2(1)
C7'	0.3764(1)	0.3668(6)	0.2336(3)	3.6(1)
C8'	0.40468(9)	0.3952(6)	0.1816(3)	3.8(1)
C9'	0.4104(1)	0.6588(5)	0.0381(3)	3.8(1)
C10'	0.3951(1)	0.7050(6)	-0.0783(4)	4.4(1)
C11'	0.3574(1)	0.7053(6)	-0.0963(4)	4.3(1)
C12'	0.3425(1)	0.6637(5)	0.0081(3)	3.8(1)
C15'	0.4350(1)	0.2371(6)	0.0139(4)	3.9(1)
C16'	0.3154(1)	0.2702(6)	-0.0574(3)	3.7(1)
C17'	0.3167(1)	0.4348(6)	0.2023(4)	4.4(1)
C18'	0.4377(1)	0.4048(6)	0.2428(3)	3.9(1)
C19'	0.4763(1)	0.2910(7)	-0.0944(4)	6.1(1)
C20'	0.2793(1)	0.0389(7)	-0.1197(5)	6.9(1)
C21'	0.2873(1)	0.4261(8)	0.3523(4)	6.6(1)
C22'	0.4685(1)	0.3833(7)	0.4222(4)	5.7(1)

Table 129 (cont.). Final Atomic Parameters for Sb-6 at 335 K

Atom	x	y	z	B(Å^2)
H3	0.630	0.421	0.369	3.7
H7	0.623	0.191	0.692	4.2
H9A	0.567	-0.127	0.364	4.1
H9B	0.593	-0.249	0.443	4.1
H10A	0.599	-0.115	0.227	5.0
H10B	0.599	-0.324	0.264	5.0
H11A	0.652	-0.104	0.260	4.9
H11B	0.652	-0.318	0.286	4.9
H12A	0.653	-0.262	0.475	4.1
H12B	0.682	-0.152	0.434	4.1
H19A	0.522	0.124	0.132	5.9
H19B	0.511	0.253	0.226	5.9
H19C	0.536	0.328	0.146	5.9
H20A	0.725	0.593	0.368	7.5
H20B	0.742	0.407	0.418	7.5
H20C	0.726	0.420	0.288	7.5
H21A	0.709	0.103	0.906	7.3
H21B	0.722	-0.043	0.824	7.3
H21C	0.728	0.169	0.805	7.3
H22A	0.532	0.123	0.785	6.6
H22B	0.515	0.209	0.669	6.6
H22C	0.520	-0.006	0.681	6.6
H3'	0.374	0.083	-0.022	3.6
H7'	0.376	0.308	0.307	4.0
H9A'	0.434	0.640	0.040	4.2
H9B'	0.407	0.758	0.089	4.2
H10A'	0.403	0.616	-0.130	4.8
H10B'	0.403	0.826	-0.096	4.8
H11A'	0.350	0.614	-0.153	4.7
H11B'	0.350	0.826	-0.123	4.7
H12A'	0.347	0.763	0.062	4.2
H12B'	0.318	0.650	-0.011	4.2
H19A'	0.484	0.388	-0.141	6.7
H19B'	0.494	0.261	-0.033	6.7
H19C'	0.471	0.183	-0.141	6.7
H20A'	0.278	-0.094	-0.115	7.6
H20B'	0.261	0.095	-0.088	7.6
H20C'	0.278	0.075	-0.198	7.6
H21A'	0.291	0.409	0.434	7.3
H21B'	0.277	0.546	0.335	7.3
H21C'	0.272	0.332	0.318	7.3
H22A'	0.465	0.355	0.499	6.3
H22B'	0.484	0.296	0.398	6.3
H22C'	0.477	0.507	0.419	6.3
H19BA'	0.484	0.175	-0.060	6.7
H19BB'	0.470	0.273	-0.177	6.7
H19BC'	0.494	0.382	-0.082	6.7

The parameters of the hydrogen atoms were not refined.

Table 130. Final Anisotropic Thermal Parameters (U's) for Sb-6 at **335 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.041(2)	0.055(2)	0.051(2)	0.009(1)	0.001(1)	0.005(1)
O2	0.062(2)	0.054(2)	0.103(3)	0.021(2)	-0.000(2)	-0.007(2)
O3	0.046(2)	0.061(2)	0.102(2)	-0.013(1)	0.032(2)	0.000(2)
O4	0.056(2)	0.085(2)	0.136(3)	0.016(2)	0.049(2)	0.005(2)
O5	0.052(2)	0.144(3)	0.047(2)	0.020(2)	0.000(2)	-0.012(2)
O6	0.042(2)	0.185(4)	0.067(2)	0.012(2)	0.001(2)	-0.030(2)
O7	0.052(2)	0.093(2)	0.059(2)	-0.007(2)	0.025(1)	-0.004(2)
O8	0.040(2)	0.138(3)	0.061(2)	-0.012(2)	0.013(2)	0.006(2)
C1	0.035(2)	0.044(2)	0.041(2)	-0.002(2)	0.009(2)	0.002(2)
C2	0.031(2)	0.044(2)	0.048(2)	0.002(2)	0.010(2)	0.003(2)
C3	0.037(2)	0.042(2)	0.052(2)	0.001(2)	0.012(2)	0.002(2)
C4	0.034(2)	0.049(2)	0.052(2)	-0.002(2)	0.011(2)	0.004(2)
C5	0.036(2)	0.045(2)	0.036(2)	0.001(2)	0.006(2)	0.002(2)
C6	0.040(2)	0.059(3)	0.041(2)	0.001(2)	0.005(2)	-0.001(2)
C7	0.042(2)	0.062(3)	0.043(2)	-0.006(2)	0.011(2)	-0.004(2)
C8	0.037(2)	0.060(3)	0.046(2)	-0.007(2)	0.015(2)	-0.008(2)
C9	0.047(2)	0.046(2)	0.047(2)	-0.005(2)	0.002(2)	0.004(2)
C10	0.061(3)	0.053(3)	0.056(3)	0.000(2)	-0.000(2)	-0.006(2)
C11	0.070(3)	0.052(3)	0.045(2)	0.006(2)	0.007(2)	-0.006(2)
C12	0.045(2)	0.048(2)	0.050(2)	0.006(2)	0.007(2)	0.003(2)
C15	0.037(2)	0.048(2)	0.057(3)	0.000(2)	0.011(2)	0.006(2)
C16	0.043(2)	0.066(3)	0.054(3)	0.003(2)	0.013(2)	0.005(2)
C17	0.044(3)	0.069(3)	0.053(3)	0.004(2)	0.002(2)	-0.009(2)
C18	0.043(2)	0.063(3)	0.051(2)	-0.005(2)	0.013(2)	-0.001(2)
C19	0.045(3)	0.078(3)	0.075(3)	0.011(2)	-0.010(3)	0.011(3)
C20	0.048(3)	0.106(4)	0.113(4)	-0.027(3)	0.037(2)	0.005(3)
C21	0.054(3)	0.137(5)	0.055(3)	0.019(3)	-0.012(3)	-0.006(3)
C22	0.062(3)	0.098(4)	0.079(3)	-0.012(3)	0.046(2)	-0.001(3)
O1'	0.056(2)	0.055(2)	0.063(2)	0.010(1)	0.027(1)	0.000(1)
O2'	0.063(2)	0.062(2)	0.131(3)	0.024(2)	0.037(2)	0.023(2)
O3'	0.048(2)	0.062(2)	0.089(2)	-0.012(2)	-0.018(2)	-0.002(2)
O4'	0.058(2)	0.083(2)	0.086(2)	0.011(2)	-0.022(2)	-0.001(2)
O5'	0.042(2)	0.144(3)	0.058(2)	0.018(2)	0.014(1)	0.018(2)
O6'	0.037(2)	0.168(3)	0.062(2)	0.013(2)	0.008(2)	0.027(2)
O7'	0.037(2)	0.105(2)	0.049(2)	-0.008(2)	-0.004(1)	0.003(2)
O8'	0.032(2)	0.106(2)	0.063(2)	-0.004(2)	0.006(1)	0.003(2)
C1'	0.032(2)	0.039(2)	0.040(2)	-0.003(2)	0.007(2)	-0.004(2)
C2'	0.028(2)	0.048(2)	0.068(3)	0.001(2)	0.006(2)	-0.002(2)
C3'	0.041(2)	0.040(2)	0.041(2)	-0.001(2)	0.003(2)	-0.001(2)
C4'	0.031(2)	0.055(3)	0.051(2)	-0.001(2)	0.000(2)	-0.004(2)
C5'	0.030(2)	0.044(2)	0.035(2)	0.003(2)	0.006(2)	-0.004(2)
C6'	0.036(2)	0.076(3)	0.046(2)	0.006(2)	0.008(2)	0.017(2)
C7'	0.038(2)	0.062(3)	0.037(2)	0.000(2)	0.003(2)	0.001(2)
C8'	0.025(2)	0.073(3)	0.046(2)	-0.002(2)	0.001(2)	0.007(2)
C9'	0.041(2)	0.050(2)	0.056(3)	-0.005(2)	0.015(2)	-0.006(2)
C10'	0.056(3)	0.053(3)	0.061(3)	0.006(2)	0.023(2)	0.013(2)
C11'	0.064(3)	0.050(3)	0.052(3)	0.006(2)	0.017(2)	0.008(2)
C12'	0.047(2)	0.048(2)	0.051(2)	0.011(2)	0.013(2)	0.001(2)
C15'	0.033(2)	0.052(3)	0.064(3)	-0.001(2)	0.005(2)	-0.003(2)
C16'	0.036(2)	0.059(3)	0.046(2)	0.001(2)	0.001(2)	-0.004(2)
C17'	0.035(2)	0.081(3)	0.053(3)	0.004(2)	0.008(2)	0.021(2)
C18'	0.041(2)	0.059(3)	0.045(2)	0.002(2)	0.001(2)	-0.001(2)
C19'	0.064(3)	0.082(4)	0.094(3)	0.013(3)	0.043(2)	-0.003(3)
C20'	0.054(3)	0.099(4)	0.098(4)	-0.023(3)	-0.028(3)	-0.016(3)
C21'	0.054(3)	0.141(5)	0.064(3)	0.016(3)	0.033(2)	0.012(3)
C22'	0.046(3)	0.104(4)	0.062(3)	-0.002(3)	-0.016(3)	-0.005(3)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 131. Interatomic Distances (Å) for Sb-6 at **335 K**

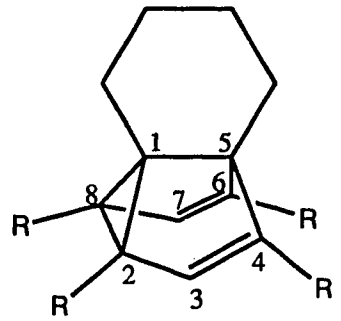
		Unprimed	Primed
O1	C15	1.322(5)	1.317(5)
O1	C19	1.448(5)	1.444(6)
O2	C15	1.202(5)	1.198(5)
O3	C16	1.326(5)	1.314(5)
O3	C20	1.458(6)	1.451(6)
O4	C16	1.193(6)	1.197(5)
O5	C17	1.309(5)	1.318(5)
O5	C21	1.437(6)	1.455(6)
O6	C17	1.205(6)	1.195(5)
O7	C18	1.329(5)	1.339(5)
O7	C22	1.454(6)	1.456(5)
O8	C18	1.191(5)	1.199(5)
C1	C2	1.489(5)	1.476(6)
C1	C5	1.560(5)	1.559(5)
C1	C8	1.516(6)	1.509(5)
C1	C9	1.511(5)	1.517(6)
C2	C3	1.457(6)	1.440(5)
C2	C8	1.685(6)	1.793(6)
C2	C15	1.498(5)	1.506(6)
C3	C4	1.334(5)	1.359(6)
C3	C7	3.054(6)	3.059(6)
C4	C5	1.530(6)	1.524(6)
C4	C6	2.324(6)	2.237(6)
C4	C16	1.485(6)	1.478(5)
C5	C6	1.528(5)	1.519(6)
C5	C12	1.522(6)	1.520(5)
C6	C7	1.346(6)	1.352(5)
C6	C17	1.466(6)	1.477(6)
C7	C8	1.449(5)	1.432(6)
C8	C18	1.480(6)	1.470(5)
C9	C10	1.533(6)	1.521(6)
C10	C11	1.543(7)	1.552(6)
C11	C12	1.536(6)	1.533(6)

Table 132. Angles (Å) for Sb-6 at **335 K**

			Unprimed	Primed
C15	O1	C19	116.4(3)	116.7(3)
C16	O3	C20	116.5(4)	116.3(3)
C17	O5	C21	117.1(4)	116.0(3)
C18	O7	C22	116.5(3)	117.6(3)
C2	C1	C5	104.9(3)	105.1(3)
C2	C1	C8	68.2(3)	73.9(3)
C2	C1	C9	127.7(3)	126.2(4)
C5	C1	C8	104.6(3)	104.3(3)
C5	C1	C9	115.7(3)	114.8(3)
C8	C1	C9	126.1(4)	125.0(3)
C1	C2	C3	107.9(3)	109.4(3)
C1	C2	C8	56.7(2)	53.9(2)
C1	C2	C15	127.2(3)	129.0(4)
C3	C2	C8	117.6(3)	115.8(3)
C3	C2	C15	115.9(3)	116.4(4)
C8	C2	C15	118.7(3)	117.7(3)
C2	C3	C4	111.3(4)	110.6(3)
C3	C4	C5	110.8(3)	110.5(3)
C3	C4	C16	124.3(4)	124.2(4)
C5	C4	C6	40.5(2)	42.6(2)
C5	C4	C16	125.0(3)	125.0(3)
C1	C5	C4	102.4(3)	103.0(3)
C1	C5	C6	102.6(3)	103.0(3)
C1	C5	C12	112.4(3)	113.2(3)
C4	C5	C6	98.9(3)	94.7(3)
C4	C5	C12	118.2(3)	119.6(3)
C6	C5	C12	119.7(3)	120.4(3)
C4	C6	C5	40.6(2)	42.8(2)
C5	C6	C7	111.0(3)	111.8(4)
C5	C6	C17	123.4(4)	123.4(3)
C7	C6	C17	125.1(4)	124.8(4)
C6	C7	C8	111.5(4)	110.5(4)
C1	C8	C2	55.1(2)	52.2(2)
C1	C8	C7	107.6(3)	109.2(3)
C1	C8	C18	121.8(3)	122.7(4)
C2	C8	C7	118.6(3)	116.5(3)
C2	C8	C18	113.1(3)	113.0(3)
C7	C8	C18	122.6(4)	123.1(4)
C1	C9	C10	109.2(3)	108.8(3)
C9	C10	C11	114.3(3)	114.4(4)
C10	C11	C12	113.7(4)	113.6(3)
C5	C12	C11	109.2(3)	109.3(3)
O1	C15	O2	124.3(4)	124.6(4)
O1	C15	C2	112.0(3)	111.9(3)
O2	C15	C2	123.4(4)	123.4(4)
O3	C16	O4	123.7(4)	123.9(4)
O3	C16	C4	111.9(4)	112.0(3)
O4	C16	C4	124.2(4)	123.9(4)
O5	C17	O6	123.0(4)	124.0(4)
O5	C17	C6	113.5(4)	110.8(3)
O6	C17	C6	123.4(4)	125.2(4)
O7	C18	O8	123.8(4)	124.0(4)
O7	C18	C8	111.0(3)	111.0(4)
O8	C18	C8	125.1(4)	125.0(4)

Table 133. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-6 at **335 K**

	Unprimed			Primed		
Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O1	0.187	0.232	0.244	0.185	0.238	0.278
O2	0.192	0.273	0.335	0.196	0.258	0.380
O3	0.171	0.256	0.327	0.182	0.258	0.329
O4	0.184	0.296	0.383	0.198	0.288	0.339
O5	0.209	0.227	0.387	0.191	0.234	0.388
O6	0.202	0.246	0.441	0.190	0.238	0.418
O7	0.186	0.263	0.309	0.179	0.236	0.326
O8	0.189	0.248	0.374	0.178	0.251	0.325
C1	0.179	0.204	0.213	0.175	0.189	0.210
C2	0.170	0.205	0.224	0.168	0.219	0.262
C3	0.184	0.205	0.231	0.194	0.203	0.211
C4	0.178	0.217	0.236	0.172	0.223	0.240
C5	0.187	0.191	0.213	0.166	0.186	0.214
C6	0.199	0.202	0.244	0.187	0.197	0.291
C7	0.191	0.212	0.254	0.189	0.200	0.248
C8	0.173	0.212	0.257	0.157	0.212	0.274
C9	0.202	0.209	0.238	0.190	0.214	0.250
C10	0.216	0.237	0.265	0.197	0.220	0.280
C11	0.202	0.232	0.270	0.205	0.224	0.267
C12	0.201	0.221	0.233	0.185	0.221	0.246
C15	0.188	0.213	0.247	0.182	0.226	0.255
C16	0.199	0.232	0.261	0.185	0.218	0.246
C17	0.206	0.224	0.273	0.187	0.205	0.303
C18	0.192	0.230	0.254	0.197	0.221	0.244
C19	0.186	0.282	0.300	0.187	0.293	0.332
C20	0.160	0.338	0.347	0.162	0.330	0.357
C21	0.191	0.268	0.378	0.171	0.276	0.382
C22	0.163	0.305	0.330	0.177	0.287	0.323



R = $COOCH_3$

1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-6)

Table 8–134. X-ray Crystal Data for the Polymorph of Sb-6 at **295 K**

Formula	$C_{20}H_{22}O_8$
Formula weight	390.39
Melting point (°C)	123–124
Crystal size (mm)	0.13 x 0.55 x 0.84
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.798(1)
b (Å)	7.681(1)
c (Å)	22.872(1)
β (°)	95.86(1)
Cell volume (Å^3)	1887(1)
Z	4
d_{calc} (g cm^{-3})	1.374
μ(Cu $K\alpha$) (cm^{-1})	8.57
Maximum θ (°)	75
Unique reflections	3898
Observed reflections	3343
[$I > 3.0\sigma(I)$]	
Number of variables	349
R	0.054
R_w	0.082
$(\Delta\rho)_{max}$ (e Å^{-3})	0.29
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.27

Table 135. Final Atomic Parameters for the Polymorph of Sb-6 at 295 K

Atom	x	y	z	B(Å^2)
C1	0.5084(1)	0.3277(2)	0.39000(6)	2.62(3)
C2	0.5412(2)	0.1429(2)	0.38015(8)	3.31(3)
C3	0.4380(1)	0.0512(2)	0.35233(7)	2.75(3)
C4	0.3390(2)	0.1605(3)	0.34103(9)	3.66(3)
C5	0.3667(1)	0.3395(2)	0.36758(7)	2.83(3)
C6	0.3037(2)	0.2966(3)	0.42220(8)	3.58(3)
C7	0.3872(2)	0.2350(2)	0.46597(7)	3.13(3)
C8	0.5111(2)	0.2435(3)	0.44979(8)	4.09(4)
C9	0.5853(2)	0.4844(2)	0.37683(8)	3.28(3)
C10	0.5651(2)	0.5286(3)	0.31133(8)	4.15(4)
C11	0.4285(2)	0.5210(3)	0.28529(8)	4.19(4)
C12	0.3350(2)	0.5019(2)	0.33094(8)	3.48(3)
C13	0.6704(1)	0.0808(2)	0.37345(7)	3.10(3)
C14	0.2213(2)	0.1081(3)	0.30660(8)	3.73(4)
C15	0.1705(2)	0.3163(3)	0.43059(9)	3.99(4)
C16	0.6151(2)	0.2335(3)	0.49760(7)	3.30(3)
O1A	0.6896(2)	-0.0808(3)	0.39579(9)	2.86(4)
O2A	0.7467(2)	0.1413(4)	0.3515(1)	4.09(5)
O3A	0.1978(2)	-0.0617(4)	0.3150(1)	3.62(5)
O4A	0.1620(2)	0.1989(4)	0.2707(1)	3.91(5)
O5A	0.1076(2)	0.4045(4)	0.3832(1)	3.63(5)
O6A	0.1250(2)	0.2716(4)	0.4746(1)	3.89(5)
O7A	0.7318(2)	0.2518(4)	0.4767(1)	3.38(5)
O8A	0.5944(2)	0.2124(3)	0.54958(9)	3.36(5)
C17A	0.8022(3)	-0.1694(5)	0.3868(2)	3.97(7)
C18A	0.1007(4)	-0.1541(6)	0.2792(2)	5.5(1)
C19A	-0.0270(3)	0.4014(6)	0.3887(2)	4.89(9)
C20A	0.8323(3)	0.2295(6)	0.5213(2)	3.77(7)
O1B	0.6818(4)	-0.0876(7)	0.3796(2)	3.32(8)*
O2B	0.7463(4)	0.1866(6)	0.3510(2)	2.42(6)*
O3B	0.1669(5)	-0.0238(8)	0.3286(2)	4.3(1)*
O4B	0.1811(6)	0.2037(9)	0.2616(3)	4.8(1)*
O5B	0.1091(6)	0.4214(9)	0.3980(3)	4.3(1)*
O6B	0.1141(6)	0.2168(9)	0.4604(3)	4.8(1)*
O7B	0.7231(4)	0.2088(6)	0.4803(2)	2.97(7)*
O8B	0.6021(6)	0.2587(9)	0.5463(3)	5.0(1)*
C17B	0.8197(9)	-0.137(1)	0.3739(4)	5.2(2)*
C18B	0.0695(8)	-0.099(1)	0.2892(4)	4.2(1)*
C19B	-0.0204(7)	0.448(1)	0.4023(3)	3.5(1)*
C20B	0.8177(8)	0.202(1)	0.5310(4)	4.2(1)*
O1C	0.6991(5)	-0.0647(7)	0.4089(2)	3.37(8)*
O2C	0.7381(4)	0.1639(6)	0.3408(2)	2.59(7)*
O3C	0.2193(5)	-0.0749(7)	0.2980(2)	3.53(8)*
O4C	0.1364(6)	0.187(1)	0.2925(3)	5.4(1)*
O5C	0.1042(5)	0.3657(7)	0.3851(2)	4.66(9)*
O6C	0.1399(7)	0.329(1)	0.4824(3)	5.8(1)*
O7C	0.7146(5)	0.2642(7)	0.4827(2)	3.34(8)*
O8C	0.6044(5)	0.1743(7)	0.5446(2)	3.91(9)*
C17C	0.8217(7)	-0.1328(9)	0.3950(3)	3.2(1)*
C18C	0.090(1)	-0.116(1)	0.2671(4)	5.0(2)*
C19C	-0.0190(6)	0.4528(9)	0.3842(3)	3.0(1)*
C20C	0.8355(7)	0.181(1)	0.5189(3)	3.5(1)*

Table 135 (cont'd). Final Atomic Parameters for the Polymorph of Sb-6 at **295 K**

Atom	x	y	z	B(Å^2)
H3	0.437	-0.076	0.343	3.5
H7	0.364	0.189	0.504	3.5
H9A	0.678	0.473	0.383	4
H9B	0.560	0.595	0.395	4
H10A	0.613	0.444	0.290	4.5
H10B	0.596	0.649	0.306	4.5
H11A	0.419	0.418	0.257	4.5
H11B	0.409	0.630	0.262	4.5
H12A	0.340	0.606	0.357	4
H12B	0.249	0.491	0.311	4
H17AA	0.804	-0.288	0.406	4.5
H17AB	0.808	-0.183	0.344	4.5
H17AC	0.874	-0.100	0.405	4.5
H18AA	0.094	-0.277	0.294	6
H18AB	0.015	-0.095	0.289	6
H18AC	0.106	-0.146	0.239	6
H19AA	-0.074	0.461	0.355	5
H19AB	-0.055	0.275	0.389	5
H19AC	-0.043	0.457	0.426	5
H20AA	0.911	0.257	0.505	4.5
H20AB	0.823	0.313	0.556	4.5
H20AC	0.829	0.110	0.536	4.5
H17BA	0.818	-0.271	0.375	4.5
H17BB	0.826	-0.113	0.328	4.5
H17BC	0.875	-0.082	0.397	4.5
H18BA	0.032	-0.199	0.308	4.5
H18BB	0.004	-0.007	0.279	4.5
H18BC	0.104	-0.138	0.252	4.5
H19BA	-0.058	0.535	0.378	4
H19BB	-0.064	0.330	0.396	4
H19BC	-0.033	0.477	0.447	4
H20BA	0.905	0.168	0.518	4.5
H20BB	0.819	0.293	0.556	4.5
H20BC	0.795	0.083	0.553	4.5
H17CA	0.841	-0.237	0.420	4
H17CB	0.816	-0.167	0.352	4
H17CC	0.887	-0.042	0.403	4
H18CA	0.109	-0.260	0.260	4.5
H18CB	0.035	-0.100	0.288	4.5
H18CC	0.096	-0.072	0.226	4.5
H19CA	-0.053	0.468	0.342	4
H19CB	-0.078	0.378	0.404	4
H19CC	-0.007	0.566	0.404	4
H20CA	0.908	0.217	0.492	4
H20CB	0.852	0.230	0.556	4
H20CC	0.836	0.051	0.518	4

Standard deviations are in parentheses.

The starred atoms were refined isotropically.

Table 136. General Temperature Factors (U's) for the Polymorph of Sb-6 at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
C1	0.0328(6)	0.0337(7)	0.0329(6)	-0.0002(6)	0.0035(5)	0.0000(6)
C2	0.0306(7)	0.0353(8)	0.0595(9)	0.0007(6)	0.0025(7)	-0.0040(7)
C3	0.0326(7)	0.0360(7)	0.0359(6)	-0.0001(6)	0.0031(6)	0.0002(6)
C4	0.0361(7)	0.0408(8)	0.060(1)	-0.0029(7)	-0.0077(7)	0.0051(8)
C5	0.0333(7)	0.0373(7)	0.0368(7)	0.0028(6)	0.0039(6)	0.0018(6)
C6	0.0345(7)	0.0509(9)	0.0514(8)	0.0044(7)	0.0095(6)	0.0100(8)
C7	0.0379(7)	0.0455(9)	0.0364(7)	0.0024(7)	0.0077(6)	0.0023(7)
C8	0.0375(8)	0.075(1)	0.0420(8)	-0.0088(8)	-0.0017(7)	0.0196(8)
C9	0.0413(8)	0.0368(8)	0.0468(8)	-0.0054(7)	0.0056(7)	0.0006(7)
C10	0.057(1)	0.053(1)	0.0499(9)	-0.0045(9)	0.0144(8)	0.0124(8)
C11	0.062(1)	0.054(1)	0.0431(8)	-0.0026(9)	0.0040(8)	0.0108(8)
C12	0.0455(8)	0.0401(8)	0.0459(8)	0.0067(7)	0.0019(7)	0.0066(7)
C13	0.0295(7)	0.0418(8)	0.0458(8)	0.0012(6)	0.0010(6)	-0.0057(7)
C14	0.0320(7)	0.053(1)	0.0544(9)	0.0018(7)	-0.0049(7)	-0.0025(8)
C15	0.0365(7)	0.054(1)	0.063(1)	0.0051(8)	0.0103(7)	0.0080(9)
C16	0.0403(7)	0.0482(9)	0.0362(7)	-0.0021(7)	0.0017(6)	0.0026(7)
O1A	0.0326(9)	0.041(1)	0.0349(9)	0.0109(9)	0.0000(8)	-0.0059(9)
O2A	0.049(1)	0.045(1)	0.063(1)	0.005(1)	0.016(1)	0.015(1)
O3A	0.034(1)	0.050(1)	0.052(1)	-0.011(1)	-0.005(1)	-0.007(1)
O4A	0.041(1)	0.063(2)	0.041(1)	0.001(1)	-0.013(1)	0.015(1)
O5A	0.0224(8)	0.060(1)	0.056(1)	0.0149(9)	0.0047(9)	0.010(1)
O6A	0.0264(9)	0.069(2)	0.055(1)	0.001(1)	0.0174(8)	0.003(1)
O7A	0.0266(9)	0.065(1)	0.037(1)	-0.006(1)	0.0023(8)	0.004(1)
O8A	0.052(1)	0.051(1)	0.0245(9)	0.002(1)	0.0040(9)	0.0050(9)
C17A	0.026(1)	0.039(2)	0.087(2)	0.007(1)	0.013(1)	-0.002(2)
C18A	0.048(2)	0.052(2)	0.102(3)	-0.005(2)	-0.035(2)	-0.009(2)
C19A	0.029(1)	0.052(2)	0.104(3)	0.003(2)	0.006(2)	0.003(2)
C20A	0.032(1)	0.065(2)	0.044(2)	0.004(2)	-0.007(1)	0.003(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 137. Interatomic Distances (Å) for the Polymorph of Sb-6 at **295 K**

C1	C2	1.485(2)
C1	C5	1.566(2)
C1	C8	1.510(2)
C1	C9	1.510(2)
C2	C3	1.414(2)
C2	C8	1.829(3)
C2	C13	1.497(2)
C3	C4	1.362(2)
C3	C7	3.056
C4	C5	1.520(3)
C4	C6	2.197
C4	C14	1.481(2)
C5	C6	1.519(2)
C5	C12	1.522(2)
C6	C7	1.362(2)
C6	C15	1.478(3)
C7	C8	1.425(2)
C8	C16	1.487(2)
C9	C10	1.530(3)
C10	C11	1.534(3)
C11	C12	1.532(3)
C13	O1A	1.350(3)
C13	O2A	1.110(3)
C14	O3A	1.346(3)
C14	O4A	1.210(3)
C15	O5A	1.394(3)
C15	O6A	1.215(3)
C16	O7A	1.400(3)
C16	O8A	1.243(3)
O1A	C17A	1.426(4)
O3A	C18A	1.448(5)
O5A	C19A	1.472(4)
O7A	C20A	1.420(4)
C13	O1B	1.305(5)
C13	O2B	1.297(4)
C14	O3B	1.298(6)
C14	O4B	1.303(7)
C15	O5B	1.244(7)
C15	O6B	1.226(7)
C16	O7B	1.283(5)
C16	O8B	1.153(7)
O1B	C17B	1.554(11)
O3B	C18B	1.436(10)
O5B	C19B	1.426(10)
O7B	C20B	1.467(9)
C13	O1C	1.397(5)
C13	O2C	1.269(5)
C14	O3C	1.419(6)
C14	O4C	1.118(7)
C15	O5C	1.260(5)
C15	O6C	1.267(8)
C16	O7C	1.183(5)
C16	O8C	1.184(6)
O1C	C17C	1.488(9)
O3C	C18C	1.533(11)
O5C	C19C	1.486(8)
O7C	C20C	1.604(8)

Table 138. Angles in (°) for the Polymorph of Sb-6 at **295 K**

C2	C1	C5	104.2(1)
C2	C1	C8	75.3(1)
C2	C1	C9	125.9(1)
C5	C1	C8	104.4(1)
C5	C1	C9	115.3(1)
C8	C1	C9	124.2(1)
C1	C2	C3	110.8(1)
C1	C2	C8	53.0(1)
C1	C2	C13	124.0(1)
C3	C2	C8	113.6(1)
C3	C2	C13	119.7(2)
C8	C2	C13	118.3(1)
C2	C3	C4	110.2(2)
C3	C4	C5	111.3(1)
C3	C4	C14	123.2(2)
C5	C4	C6	43.7(1)
C5	C4	C14	125.6(2)
C1	C5	C4	102.9(1)
C1	C5	C6	102.9(1)
C1	C5	C12	112.7(1)
C4	C5	C6	92.6(1)
C6	C5	C12	122.4(2)
C4	C6	C5	43.7(1)
C5	C6	C7	111.2(2)
C5	C6	C15	127.5(2)
C7	C6	C15	121.4(2)
C6	C7	C8	111.2(2)
C1	C8	C2	51.7(1)
C1	C8	C7	108.8(1)
C1	C8	C16	129.1(2)
C2	C8	C7	117.5(1)
C2	C8	C16	115.5(1)
C7	C8	C16	117.7(2)
C1	C9	C10	110.2(1)
C9	C10	C11	114.0(2)
C10	C11	C12	114.4(2)
C5	C12	C11	109.1(2)
C2	C13	O1A	111.3(2)
C2	C13	O2A	130.9(2)
O1A	C13	O2A	117.6(2)
C4	C14	O3A	110.6(2)
C4	C14	O4A	124.8(2)
O3A	C14	O4A	124.1(2)
C6	C15	O5A	110.6(2)
C6	C15	O6A	124.1(2)
O5A	C15	O6A	125.2(2)
C8	C16	O7A	112.5(2)
C8	C16	O8A	120.9(2)
O7A	C16	O8A	126.6(2)
C13	O1A	C17A	119.0(2)
C14	O3A	C18A	122.0(3)
C15	O5A	C19A	109.4(3)
C16	O7A	C20A	113.1(2)

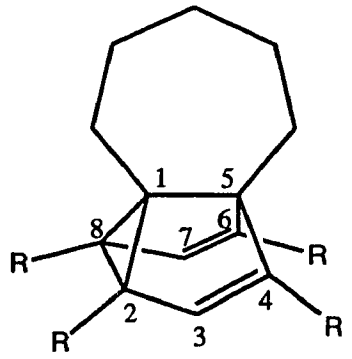
Table 138 (cont'd). Angles in (°) for the Polymorph of Sb-6 at **295 K**

C2	C13	O1B	112.5(3)
C2	C13	O2B	118.3(2)
O1B	C13	O2B	127.4(3)
C4	C14	O3B	113.9(3)
C4	C14	O4B	117.7(3)
O3B	C14	O4B	128.2(4)
C6	C15	O5B	117.1(4)
C6	C15	O6B	123.6(3)
O5B	C15	O6B	118.2(5)
C8	C16	O7B	115.0(2)
C8	C16	O8B	122.9(4)
O7B	C16	O8B	121.8(4)
C13	O1B	C17B	108.1(5)
C14	O3B	C18B	113.9(5)
C15	O5B	C19B	121.3(6)
C16	O7B	C20B	110.0(5)
C2	C13	O1C	110.5(2)
C2	C13	O2C	119.9(2)
O1C	C13	O2C	129.6(3)
C4	C14	O3C	110.1(2)
C4	C14	O4C	129.9(4)
O3C	C14	O4C	119.6(4)
C6	C15	O5C	113.7(3)
C6	C15	O6C	118.7(4)
O5C	C15	O6C	124.6(4)
C8	C16	O7C	114.7(3)
C8	C16	O8C	123.4(3)
O7C	C16	O8C	120.9(4)
C13	O1C	C17C	107.9(4)
C14	O3C	C18C	105.6(5)
C15	O5C	C19C	125.4(5)
C16	O7C	C20C	119.2(5)

Table 139. Root-Mean-Square Amplitudes of Thermal Vibration (A) for the Popymorph of SB-6 at **295 K**

Atom	Min.	Int'med.	Max.
C1	0.181	0.181	0.184
C2	0.175	0.186	0.246
C3	0.180	0.190	0.190
C4	0.178	0.199	0.260
C5	0.178	0.190	0.199
C6	0.180	0.203	0.249
C7	0.181	0.198	0.217
C8	0.181	0.189	0.295
C9	0.182	0.212	0.217
C10	0.183	0.244	0.254
C11	0.191	0.241	0.255
C12	0.181	0.221	0.225
C13	0.171	0.194	0.225
C14	0.172	0.228	0.245
C15	0.185	0.222	0.261
C16	0.188	0.201	0.223
O1A	0.157	0.179	0.228
O2A	0.191	0.208	0.275
O3A	0.157	0.233	0.242
O4A	0.148	0.229	0.272
O5A	0.131	0.225	0.265
O6A	0.140	0.241	0.265
O7A	0.160	0.190	0.258
O8A	0.154	0.225	0.231
C17A	0.147	0.205	0.296
C18A	0.161	0.233	0.361
C19A	0.169	0.230	0.323
C20A	0.162	0.227	0.255

8.5 SB-7



R = $COOCH_3$

1,5-Cycloheptano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-7)

Table 8–140. X-ray Crystal Data for Sb-7 at **115 K**

Formula	$C_{21}H_{24}O_8$
Formula weight	404.42
Melting point (°C)	99–100
Crystal size (mm)	0.16 x 0.24 x 0.50
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.118(1)
b (Å)	8.482(2)
c (Å)	20.453(1)
β (°)	90.20(1)
Cell volume (Å^3)	1928.65(0.37)
Z	4
d_{calc} (g cm^{-3})	1.395
μ(Cu $K\alpha$) (cm^{-1})	8.57
Maximum θ (°)	60
Unique reflections	2865
Observed reflections [$I > 3.0\sigma(I)$]	2513
Number of variables	262
R	0.041
R_w	0.059
$(\Delta\rho)_{max}$ (e Å^{-3})	0.32
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.25

Table 141. Final Atomic Parameters for Sb-7 at **115 K**

Atom	x	y	z	B(Å^2)
O1	0.4109(1)	0.4713(2)	0.68047(7)	1.41(3)
O2	0.4171(1)	0.6928(2)	0.74083(7)	1.66(3)
O3	0.9002(1)	0.5471(2)	0.64346(6)	1.38(3)
O4	0.9248(1)	0.7302(2)	0.56497(7)	1.72(3)
O5	0.7990(1)	0.9332(2)	0.45771(7)	1.45(3)
O6	0.7651(1)	0.6839(2)	0.42605(7)	1.59(3)
O7	0.3164(1)	0.6741(2)	0.50277(6)	1.30(3)
O8	0.2775(1)	0.7217(2)	0.60913(7)	1.47(3)
C1	0.5421(2)	0.8366(2)	0.61517(9)	1.09(4)
C2	0.5340(2)	0.6734(2)	0.64240(9)	1.10(4)
C3	0.6557(2)	0.6071(2)	0.64523(9)	1.17(4)
C4	0.7358(2)	0.7064(2)	0.61851(9)	1.12(4)
C5	0.6731(2)	0.8487(2)	0.58708(9)	1.16(4)
C6	0.6576(2)	0.7863(2)	0.51699(9)	1.18(4)
C7	0.5561(2)	0.7017(2)	0.51171(9)	1.16(4)
C8	0.4811(2)	0.7173(2)	0.57003(9)	1.21(4)
C9	0.4761(2)	0.9779(2)	0.6423(1)	1.41(4)
C10	0.5339(2)	1.0439(3)	0.7051(1)	1.67(4)
C11	0.6441(2)	1.1470(3)	0.6942(1)	1.83(4)
C12	0.7533(2)	1.0618(3)	0.6660(1)	1.65(4)
C13	0.7370(2)	1.0066(2)	0.5952(1)	1.35(4)
C15	0.4460(2)	0.6189(2)	0.69339(9)	1.19(4)
C16	0.8626(2)	0.6663(2)	0.60565(9)	1.26(4)
C17	0.7462(2)	0.7919(2)	0.46308(9)	1.14(4)
C18	0.3478(2)	0.7051(2)	0.5650(1)	1.19(4)
C19	0.3217(2)	0.4065(3)	0.7242(1)	1.86(4)
C20	1.0207(2)	0.4902(3)	0.6294(1)	1.56(4)
C21	0.8899(2)	0.9445(3)	0.4074(1)	1.95(4)
C22	0.1877(2)	0.6575(3)	0.4909(1)	1.56(4)
H3	0.677	0.503	0.665	1.9
H7	0.534	0.635	0.473	1.9
H9A	0.476	1.061	0.608	2.1
H9B	0.392	0.945	0.652	2.1
H10A	0.472	1.109	0.728	2.5
H10B	0.559	0.954	0.733	2.5
H11A	0.621	1.233	0.663	2.7
H11B	0.667	1.196	0.737	2.7
H12A	0.824	1.136	0.668	2.4
H12B	0.770	0.968	0.694	2.4
H13A	0.819	0.996	0.575	2.0
H13B	0.690	1.088	0.571	2.0
H19A	0.295	0.301	0.708	2.8
H19B	0.358	0.393	0.769	2.8
H19C	0.251	0.478	0.727	2.8
H20A	1.041	0.402	0.660	2.6
H20B	1.024	0.451	0.583	2.6
H20C	1.080	0.578	0.635	2.6
H21A	0.925	1.053	0.406	2.8
H21B	0.852	0.922	0.363	2.8
H21C	0.955	0.866	0.415	2.8
H22A	0.171	0.669	0.443	2.2
H22B	0.160	0.552	0.506	2.2
H22C	0.145	0.743	0.515	2.2

The parameters of the hydrogen atoms were not refined.

Table 142. Final Anisotropic Thermal Parameters (U's) for Sb-7 at 115 K

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0161(6)	0.0183(7)	0.0192(7)	-0.0037(6)	0.0022(6)	0.0020(6)
O2	0.0216(7)	0.0231(7)	0.0182(7)	-0.0010(6)	0.0022(6)	-0.0016(6)
O3	0.0120(6)	0.0232(7)	0.0172(6)	0.0039(6)	-0.0012(5)	0.0042(6)
O4	0.0149(7)	0.0257(8)	0.0245(7)	-0.0007(6)	0.0010(6)	0.0052(7)
O5	0.0184(6)	0.0180(7)	0.0188(7)	-0.0022(6)	0.0039(6)	0.0016(6)
O6	0.0197(7)	0.0206(7)	0.0202(7)	-0.0023(6)	0.0016(6)	-0.0022(6)
O7	0.0122(6)	0.0214(7)	0.0158(6)	-0.0026(6)	-0.0050(5)	0.0001(6)
O8	0.0141(6)	0.0233(7)	0.0184(7)	0.0008(6)	-0.0004(6)	-0.0009(6)
C1	0.0137(9)	0.0157(9)	0.0121(9)	0.0007(8)	-0.0029(8)	-0.0002(8)
C2	0.0133(9)	0.0146(9)	0.0138(9)	-0.0003(8)	-0.0019(8)	-0.0012(8)
C3	0.0147(9)	0.017(1)	0.0127(9)	0.0002(8)	-0.0028(8)	-0.0009(8)
C4	0.0146(9)	0.017(1)	0.0107(9)	-0.0010(8)	-0.0035(8)	-0.0016(8)
C5	0.0143(9)	0.0159(9)	0.0137(9)	0.0007(8)	-0.0016(8)	0.0011(8)
C6	0.0145(9)	0.0140(9)	0.0163(9)	0.0023(8)	-0.0040(8)	0.0029(8)
C7	0.0149(9)	0.0135(9)	0.0155(9)	0.0011(8)	-0.0030(8)	0.0018(8)
C8	0.0151(9)	0.016(1)	0.0152(9)	-0.0002(8)	-0.0036(8)	0.0002(8)
C9	0.0179(9)	0.016(1)	0.0193(9)	0.0025(8)	-0.0016(8)	-0.0019(9)
C10	0.025(1)	0.019(1)	0.020(1)	-0.0013(9)	-0.0010(9)	-0.0038(9)
C11	0.029(1)	0.020(1)	0.021(1)	-0.0034(9)	-0.0024(9)	-0.0039(9)
C12	0.023(1)	0.019(1)	0.021(1)	-0.0049(9)	-0.0059(9)	-0.0008(9)
C13	0.0166(9)	0.017(1)	0.0178(9)	-0.0026(8)	-0.0018(8)	0.0008(9)
C15	0.0119(8)	0.018(1)	0.0156(9)	0.0020(8)	-0.0042(8)	0.0014(8)
C16	0.0164(9)	0.019(1)	0.0123(9)	-0.0034(8)	-0.0036(8)	-0.0016(8)
C17	0.0127(9)	0.016(1)	0.0142(9)	0.0008(8)	-0.0045(8)	0.0018(8)
C18	0.0169(9)	0.0116(9)	0.0168(9)	-0.0018(8)	-0.0013(8)	0.0015(8)
C19	0.022(1)	0.026(1)	0.023(1)	-0.007(1)	0.0042(9)	0.004(1)
C20	0.0112(9)	0.027(1)	0.021(1)	0.0065(9)	0.0002(8)	0.0018(9)
C21	0.024(1)	0.025(1)	0.026(1)	-0.0051(9)	0.0101(9)	0.002(1)
C22	0.0107(9)	0.026(1)	0.023(1)	-0.0035(8)	-0.0056(8)	0.0009(9)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 143. Interatomic Distances (Å) for Sb-7 at **115 K**

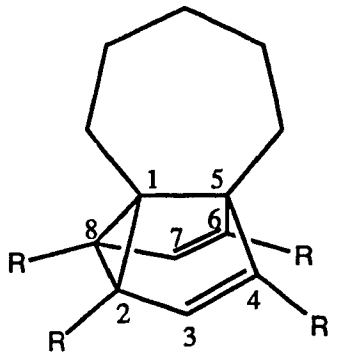
O1	C15	1.337(2)	C2	C8	1.634(3)
O1	C19	1.446(2)	C2	C15	1.505(3)
O2	C15	1.200(2)	C3	C4	1.343(3)
O3	C16	1.339(2)	C3	C7	3.051(3)
O3	C20	1.454(2)	C4	C5	1.534(3)
O4	C16	1.212(2)	C4	C6	2.348(3)
O5	C17	1.339(2)	C4	C16	1.474(3)
O5	C21	1.448(3)	C5	C6	1.537(3)
O6	C17	1.208(2)	C5	C13	1.525(3)
O7	C18	1.345(2)	C6	C7	1.342(3)
O7	C22	1.457(2)	C6	C17	1.482(3)
O8	C18	1.204(2)	C7	C8	1.463(3)
C1	C2	1.495(3)	C8	C18	1.489(3)
C1	C5	1.571(3)	C9	C10	1.540(3)
C1	C8	1.527(3)	C10	C11	1.522(3)
C1	C9	1.511(3)	C11	C12	1.528(3)
C2	C3	1.467(3)	C12	C13	1.532(3)

Table 144. Angles (°) for Sb-7 at **115 K**

C15	O1	C19	115.7(2)	C7	C6	C17	121.2(2)
C16	O3	C20	115.0(1)	C6	C7	C8	111.6(2)
C17	O5	C21	115.1(2)	C5	C13	C12	115.2(2)
C18	O7	C22	115.3(1)	C1	C8	C2	56.3(1)
C2	C1	C5	104.7(2)	C1	C8	C7	107.5(2)
C2	C1	C8	65.4(1)	C1	C8	C18	121.8(2)
C2	C1	C9	124.6(2)	C2	C8	C7	120.9(2)
C5	C1	C8	103.4(1)	C2	C8	C18	113.7(2)
C5	C1	C9	122.3(2)	C7	C8	C18	120.5(2)
C8	C1	C9	122.2(2)	C1	C9	C10	113.1(2)
C1	C2	C3	108.2(2)	C9	C10	C11	114.9(2)
C1	C2	C8	58.2(1)	C10	C11	C12	115.1(2)
C1	C2	C15	125.6(2)	C11	C12	C13	114.2(2)
C3	C2	C8	116.9(2)	O1	C15	O2	124.7(2)
C3	C2	C15	117.2(2)	O1	C15	C2	109.9(2)
C8	C2	C15	117.7(2)	O2	C15	C2	125.2(2)
C2	C3	C4	110.9(2)	O3	C16	O4	123.8(2)
C3	C4	C5	111.3(2)	O3	C16	C4	111.6(2)
C3	C4	C16	124.3(2)	O4	C16	C4	124.6(2)
C5	C4	C16	122.7(2)	O5	C17	O6	123.4(2)
C1	C5	C4	102.5(1)	O5	C17	C6	112.5(2)
C1	C5	C6	102.6(1)	O6	C17	C6	124.0(2)
C1	C5	C13	116.7(2)	O7	C18	O8	124.4(2)
C4	C5	C6	99.7(2)	O7	C18	C8	109.5(2)
C4	C5	C13	115.7(2)	O8	C18	C8	126.1(2)
C6	C5	C13	117.0(2)				
C5	C6	C7	110.5(2)	C5	C4	C6	40.2(1)
C5	C6	C17	127.6(2)	C4	C6	C5	40.1(1)

Table 145. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-7 at **115 K**

Atom	Min.	Int'med.	Max.
O1	0.110	0.143	0.146
O2	0.130	0.146	0.157
O3	0.099	0.128	0.161
O4	0.121	0.142	0.174
O5	0.115	0.140	0.150
O6	0.133	0.136	0.156
O7	0.092	0.136	0.150
O8	0.118	0.135	0.153
C1	0.099	0.123	0.128
C2	0.106	0.120	0.126
C3	0.103	0.127	0.133
C4	0.091	0.129	0.133
C5	0.109	0.125	0.128
C6	0.094	0.128	0.141
C7	0.103	0.122	0.135
C8	0.107	0.125	0.138
C9	0.120	0.131	0.148
C10	0.123	0.152	0.159
C11	0.124	0.156	0.173
C12	0.114	0.144	0.170
C13	0.118	0.130	0.144
C15	0.092	0.136	0.136
C16	0.096	0.131	0.146
C17	0.092	0.127	0.136
C18	0.104	0.124	0.138
C19	0.115	0.163	0.176
C20	0.094	0.145	0.172
C21	0.112	0.162	0.188
C22	0.089	0.153	0.167



R = $COOCH_3$

1,5-Cycloheptano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-7)

Table 8–146. X-ray Crystal Data for Sb-7 at **127 K**

Formula	$C_{21}H_{24}O_8$
Formula weight	404.42
Melting point (°C)	99–100
Crystal size (mm)	0.16 x 0.24 x 0.50
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.121(1)
b (Å)	8.498(5)
c (Å)	20.467(1)
β (°)	90.22(1)
Cell volume (Å^3)	1934.22(1.22)
Z	4
d_{calc} (g cm^{-3})	1.389
μ(Cu $K\alpha$) (cm^{-1})	8.54
Maximum θ (°)	60
Unique reflections	2868
Observed reflections [$I > 3.0\sigma(I)$]	2363
Number of variables	262
R	0.050
R_w	0.071
$(\Delta\rho)_{max}$ (e Å^{-3})	0.27
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.31

Table 147. Final Atomic Parameters for Sb-7 at 127 K

Atom	x	y	z	B(Å^2)
O1	0.4110(2)	0.4715(2)	0.68042(9)	1.82(4)
O2	0.4175(2)	0.6933(3)	0.74070(9)	2.08(4)
O3	0.9001(2)	0.5473(3)	0.64357(9)	1.79(4)
O4	0.9248(2)	0.7300(3)	0.56513(9)	2.16(4)
O5	0.7991(2)	0.9332(2)	0.45794(9)	1.85(4)
O6	0.7650(2)	0.6836(3)	0.42591(9)	2.03(4)
O7	0.3163(2)	0.6737(2)	0.50278(9)	1.68(4)
O8	0.2780(2)	0.7225(3)	0.60909(9)	1.83(4)
C1	0.5418(2)	0.8372(3)	0.6152(1)	1.44(5)
C2	0.5340(2)	0.6728(4)	0.6425(1)	1.44(5)
C3	0.6561(2)	0.6074(4)	0.6452(1)	1.54(5)
C4	0.7357(2)	0.7058(3)	0.6186(1)	1.37(5)
C5	0.6730(2)	0.8491(3)	0.5870(1)	1.32(5)
C6	0.6572(2)	0.7856(3)	0.5170(1)	1.40(5)
C7	0.5563(2)	0.7019(4)	0.5117(1)	1.52(5)
C8	0.4814(2)	0.7175(3)	0.5701(1)	1.48(5)
C9	0.4765(2)	0.9779(4)	0.6421(1)	1.69(5)
C10	0.5343(3)	1.0440(4)	0.7048(1)	2.06(6)
C11	0.6442(3)	1.1464(4)	0.6937(2)	2.30(6)
C12	0.7533(3)	1.0619(4)	0.6661(1)	2.04(6)
C13	0.7373(2)	1.0063(3)	0.5951(1)	1.63(5)
C15	0.4462(2)	0.6192(4)	0.6935(1)	1.51(5)
C16	0.8626(2)	0.6656(4)	0.6054(1)	1.64(5)
C17	0.7462(2)	0.7912(4)	0.4631(1)	1.60(5)
C18	0.3476(2)	0.7061(3)	0.5647(1)	1.47(5)
C19	0.3223(3)	0.4068(4)	0.7242(2)	2.28(6)
C20	1.0206(3)	0.4903(4)	0.6294(2)	2.05(6)
C21	0.8900(3)	0.9441(4)	0.4073(2)	2.30(6)
C22	0.1881(2)	0.6582(4)	0.4909(1)	1.86(6)
H3	0.677	0.503	0.664	1.6
H7	0.534	0.636	0.473	1.7
H9A	0.393	0.946	0.652	1.9
H9B	0.477	1.061	0.608	1.9
H10A	0.558	0.955	0.733	2.2
H10B	0.473	1.110	0.727	2.2
H11A	0.668	1.193	0.736	2.5
H11B	0.621	1.232	0.662	2.5
H12A	0.771	0.969	0.694	2.2
H12B	0.823	1.136	0.668	2.2
H13A	0.690	1.088	0.571	1.8
H13B	0.819	0.997	0.575	1.8
H19A	0.291	0.304	0.707	2.5
H19B	0.358	0.389	0.769	2.5
H19C	0.252	0.482	0.729	2.5
H20A	1.041	0.403	0.660	2.3
H20B	1.024	0.451	0.584	2.3
H20C	1.080	0.578	0.635	2.3
H21A	0.924	1.053	0.407	2.5
H21B	0.955	0.866	0.416	2.5
H21C	0.852	0.921	0.364	2.5
H22A	0.170	0.677	0.444	2.1
H22B	0.161	0.549	0.503	2.1
H22C	0.143	0.736	0.518	2.1

The parameters of the hydrogen atoms were not refined.

Table 148. Final Anisotropic Thermal Parameters (U's) for Sb-7 at **127 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0187(9)	0.029(1)	0.022(1)	-0.0055(9)	0.0060(8)	0.0007(9)
O2	0.025(1)	0.035(1)	0.019(1)	-0.0007(9)	0.0065(8)	-0.0023(9)
O3	0.0137(9)	0.035(1)	0.0194(9)	0.0053(9)	0.0016(8)	0.0064(9)
O4	0.018(1)	0.037(1)	0.028(1)	-0.0019(9)	0.0048(9)	0.010(1)
O5	0.0211(9)	0.030(1)	0.0191(9)	-0.0032(9)	0.0084(8)	0.0030(9)
O6	0.023(1)	0.033(1)	0.020(1)	-0.0015(9)	0.0057(8)	-0.0037(9)
O7	0.0138(9)	0.032(1)	0.0174(9)	-0.0012(8)	-0.0014(8)	0.0003(9)
O8	0.0178(9)	0.033(1)	0.0183(9)	0.0014(9)	0.0028(8)	-0.0010(9)
C1	0.014(1)	0.026(1)	0.014(1)	0.001(1)	0.001(1)	0.000(1)
C2	0.016(1)	0.025(1)	0.014(1)	-0.000(1)	0.001(1)	0.001(1)
C3	0.016(1)	0.030(2)	0.012(1)	0.002(1)	0.001(1)	-0.002(1)
C4	0.016(1)	0.022(1)	0.014(1)	0.002(1)	0.001(1)	-0.001(1)
C5	0.017(1)	0.018(1)	0.016(1)	-0.001(1)	0.001(1)	0.002(1)
C6	0.016(1)	0.022(1)	0.015(1)	0.004(1)	0.001(1)	0.004(1)
C7	0.017(1)	0.027(2)	0.014(1)	0.002(1)	0.001(1)	0.003(1)
C8	0.016(1)	0.025(2)	0.015(1)	0.001(1)	0.001(1)	-0.003(1)
C9	0.018(1)	0.026(2)	0.021(1)	0.000(1)	0.002(1)	-0.002(1)
C10	0.028(1)	0.028(2)	0.022(1)	0.001(1)	0.002(1)	-0.005(1)
C11	0.033(2)	0.030(2)	0.024(2)	-0.003(1)	-0.002(1)	-0.003(1)
C12	0.027(1)	0.028(2)	0.022(1)	-0.007(1)	-0.002(1)	-0.003(1)
C13	0.019(1)	0.021(1)	0.022(1)	-0.002(1)	0.001(1)	0.001(1)
C15	0.013(1)	0.027(2)	0.017(1)	0.001(1)	-0.000(1)	0.002(1)
C16	0.017(1)	0.030(2)	0.016(1)	-0.003(1)	-0.002(1)	-0.000(1)
C17	0.013(1)	0.032(2)	0.016(1)	0.001(1)	-0.001(1)	0.004(1)
C18	0.019(1)	0.022(1)	0.015(1)	-0.001(1)	0.002(1)	0.002(1)
C19	0.025(1)	0.035(2)	0.027(2)	-0.009(1)	0.008(1)	0.006(1)
C20	0.013(1)	0.038(2)	0.027(2)	0.008(1)	0.004(1)	0.001(1)
C21	0.028(1)	0.033(2)	0.026(1)	-0.006(1)	0.015(1)	0.005(1)
C22	0.013(1)	0.035(2)	0.023(1)	-0.005(1)	-0.002(1)	0.002(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 149. Interatomic Distances (Å) for Sb-7 at **127 K**

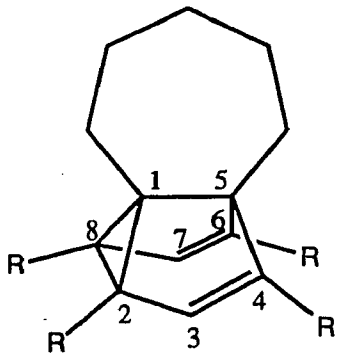
O1	C15	1.341(4)	C2	C8	1.636(4)
O1	C19	1.443(4)	C2	C15	1.503(4)
O2	C15	1.198(3)	C3	C4	1.335(4)
O3	C16	1.338(4)	C3	C7	3.053(4)
O3	C20	1.454(3)	C4	C5	1.544(4)
O4	C16	1.210(3)	C4	C6	2.351(4)
O5	C17	1.346(4)	C4	C16	1.478(4)
O5	C21	1.454(4)	C5	C6	1.539(4)
O6	C17	1.208(4)	C5	C13	1.524(4)
O7	C18	1.342(3)	C6	C7	1.333(4)
O7	C22	1.451(3)	C6	C17	1.487(4)
O8	C18	1.203(3)	C7	C8	1.465(4)
C1	C2	1.507(4)	C8	C18	1.495(4)
C1	C5	1.575(4)	C9	C10	1.539(4)
C1	C8	1.529(4)	C10	C11	1.519(4)
C1	C9	1.504(4)	C11	C12	1.521(4)
C2	C3	1.469(4)	C12	C13	1.537(4)

Table 150. Angles (°) for Sb-7 at **127 K**

C15	O1	C19	115.6(2)	C7	C6	C17	121.3(2)
C16	O3	C20	114.8(2)	C6	C7	C8	111.4(2)
C17	O5	C21	114.7(2)	C1	C8	C2	56.7(2)
C18	O7	C22	115.3(2)	C1	C8	C7	107.7(2)
C2	C1	C5	104.5(2)	C1	C8	C18	121.5(2)
C2	C1	C8	65.2(2)	C2	C8	C7	121.0(2)
C2	C1	C9	124.9(2)	C2	C8	C18	113.8(2)
C5	C1	C8	103.0(2)	C7	C8	C18	120.2(2)
C5	C1	C9	122.2(2)	C1	C9	C10	113.3(2)
C8	C1	C9	122.6(2)	C9	C10	C11	114.7(2)
C1	C2	C3	108.1(2)	C10	C11	C12	115.4(3)
C1	C2	C8	58.0(2)	C11	C12	C13	114.0(2)
C1	C2	C15	125.3(2)	C5	C13	C12	115.2(2)
C3	C2	C8	116.7(2)	O1	C15	O2	125.1(3)
C3	C2	C15	117.5(2)	O1	C15	C2	109.6(2)
C8	C2	C15	118.0(2)	O2	C15	C2	125.2(3)
C2	C3	C4	111.2(3)	O3	C16	O4	124.0(2)
C3	C4	C5	111.5(2)	O3	C16	C4	111.3(2)
C3	C4	C16	124.3(3)	O4	C16	C4	124.6(3)
C5	C4	C16	122.4(2)	O5	C17	O6	123.5(2)
C1	C5	C4	102.3(2)	O5	C17	C6	112.3(2)
C1	C5	C6	102.5(2)	O6	C17	C6	124.1(3)
C1	C5	C13	116.8(2)	O7	C18	O8	124.9(2)
C4	C5	C6	99.4(2)	O7	C18	C8	109.6(2)
C4	C5	C13	115.8(2)	O8	C18	C8	125.5(2)
C6	C5	C13	117.4(2)				
C5	C6	C7	110.9(2)	C5	C4	C6	40.2(1)
C5	C6	C17	127.3(2)	C4	C6	C5	40.4(1)

Table 151. Root-Mean-Square Amplitudes of Thermal Vibration (Å)
Sb-7 at **127 K**

Atom	Min.	Int'med.	Max.
O1	0.112	0.158	0.178
O2	0.121	0.169	0.189
O3	0.112	0.131	0.196
O4	0.119	0.158	0.208
O5	0.103	0.169	0.177
O6	0.126	0.162	0.188
O7	0.115	0.134	0.180
O8	0.123	0.144	0.183
C1	0.114	0.123	0.162
C2	0.115	0.128	0.158
C3	0.109	0.128	0.174
C4	0.117	0.124	0.152
C5	0.117	0.131	0.139
C6	0.113	0.123	0.159
C7	0.117	0.128	0.167
C8	0.118	0.129	0.160
C9	0.129	0.147	0.162
C10	0.137	0.169	0.176
C11	0.148	0.174	0.187
C12	0.134	0.158	0.186
C13	0.132	0.147	0.152
C15	0.113	0.129	0.167
C16	0.118	0.133	0.175
C17	0.112	0.124	0.181
C18	0.117	0.139	0.151
C19	0.112	0.183	0.201
C20	0.099	0.165	0.202
C21	0.096	0.189	0.207
C22	0.107	0.150	0.191



R = $COOCH_3$

1,5-Cycloheptano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-7)

Table 8–152. X-ray Crystal Data for Sb-7 at **153 K**

Formula	$C_{21}H_{24}O_8$
Formula weight	404.42
Melting point (°C)	99–100
Crystal size (mm)	0.16 x 0.24 x 0.50
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.128(1)
b (Å)	8.513(6)
c (Å)	20.502(1)
β (°)	90.29(1)
Cell volume ($Å^3$)	1942.27(1.38)
Z	4
d_{calc} (g cm^{-3})	1.383
μ(Cu $K\alpha$) (cm^{-1})	8.50
Maximum θ (°)	60
Unique reflections	2881
Observed reflections [$I > 3.0\sigma(I)$]	2358
Number of variables	262
R	0.048
R_w	0.068
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.27
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.29

Table 153. Final Atomic Parameters for Sb-7 at 153 K

Atom	x	y	z	B(Å^2)
O1	0.4117(2)	0.4725(2)	0.68055(9)	2.08(4)
O2	0.4181(2)	0.6939(3)	0.74053(9)	2.42(4)
O3	0.9002(2)	0.5472(2)	0.64356(9)	1.98(4)
O4	0.9251(2)	0.7301(3)	0.56557(9)	2.57(4)
O5	0.7990(2)	0.9321(2)	0.45814(9)	2.12(4)
O6	0.7645(2)	0.6839(2)	0.42611(9)	2.36(4)
O7	0.3165(2)	0.6741(2)	0.50287(9)	1.93(4)
O8	0.2783(2)	0.7226(2)	0.60898(9)	2.13(4)
C1	0.5423(2)	0.8368(3)	0.6151(1)	1.61(5)
C2	0.5342(2)	0.6730(3)	0.6424(1)	1.59(5)
C3	0.6563(2)	0.6077(3)	0.6452(1)	1.69(5)
C4	0.7358(2)	0.7065(3)	0.6186(1)	1.55(5)
C5	0.6734(2)	0.8490(3)	0.5869(1)	1.47(5)
C6	0.6571(2)	0.7850(3)	0.5171(1)	1.58(5)
C7	0.5563(2)	0.7021(3)	0.5116(1)	1.65(5)
C8	0.4815(2)	0.7180(3)	0.5700(1)	1.67(5)
C9	0.4772(2)	0.9773(3)	0.6422(1)	1.95(5)
C10	0.5347(3)	1.0438(4)	0.7044(1)	2.34(6)
C11	0.6449(3)	1.1460(4)	0.6935(1)	2.63(6)
C12	0.7539(3)	1.0607(4)	0.6657(1)	2.34(6)
C13	0.7374(2)	1.0053(3)	0.5949(1)	1.85(5)
C15	0.4466(2)	0.6201(3)	0.6934(1)	1.73(5)
C16	0.8626(2)	0.6660(3)	0.6056(1)	1.79(5)
C17	0.7460(2)	0.7911(3)	0.4633(1)	1.68(5)
C18	0.3478(2)	0.7059(3)	0.5647(1)	1.67(5)
C19	0.3234(3)	0.4079(4)	0.7244(1)	2.60(6)
C20	1.0204(2)	0.4913(4)	0.6301(2)	2.36(6)
C21	0.8895(3)	0.9439(4)	0.4075(2)	2.72(6)
C22	0.1882(2)	0.6582(4)	0.4910(1)	2.14(6)
H3	0.678	0.502	0.665	1.8
H7	0.534	0.637	0.473	1.8
H9A	0.393	0.945	0.652	2.1
H9B	0.476	1.061	0.608	2.1
H10A	0.559	0.954	0.733	2.5
H10B	0.473	1.109	0.727	2.5
H11A	0.669	1.193	0.736	2.9
H11B	0.622	1.232	0.662	2.9
H12A	0.771	0.967	0.694	2.5
H12B	0.824	1.134	0.667	2.5
H13A	0.690	1.087	0.571	2.0
H13B	0.819	0.995	0.575	2.0
H19A	0.286	0.313	0.704	2.8
H19B	0.363	0.378	0.766	2.8
H19C	0.260	0.488	0.733	2.8
H20A	1.041	0.403	0.661	2.6
H20B	1.024	0.453	0.584	2.6
H20C	1.079	0.579	0.636	2.6
H21A	0.924	1.052	0.407	3.0
H21B	0.955	0.866	0.416	3.0
H21C	0.852	0.921	0.364	3.0
H22A	0.173	0.652	0.443	2.4
H22B	0.158	0.560	0.512	2.4
H22C	0.145	0.751	0.510	2.4

The parameters of the hydrogen atoms were not refined.

Table 154. Final Anisotropic Thermal Parameters (U's) for Sb-7 at **153 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0224(9)	0.031(1)	0.0259(9)	-0.0051(8)	0.0069(8)	0.0020(9)
O2	0.031(1)	0.038(1)	0.023(1)	-0.0009(9)	0.0083(8)	-0.0029(9)
O3	0.0173(8)	0.035(1)	0.0227(9)	0.0056(8)	0.0020(7)	0.0068(9)
O4	0.0211(9)	0.042(1)	0.035(1)	-0.0020(9)	0.0062(9)	0.013(1)
O5	0.0263(9)	0.031(1)	0.0232(9)	-0.0041(9)	0.0099(8)	0.0033(9)
O6	0.028(1)	0.034(1)	0.028(1)	-0.0026(9)	0.0083(8)	-0.0047(9)
O7	0.0167(8)	0.035(1)	0.0212(9)	-0.0029(8)	-0.0018(7)	-0.0000(9)
O8	0.0188(9)	0.038(1)	0.0242(9)	0.0003(9)	0.0033(8)	-0.0020(9)
C1	0.017(1)	0.028(1)	0.016(1)	0.000(1)	0.001(1)	0.001(1)
C2	0.019(1)	0.026(1)	0.016(1)	0.000(1)	0.002(1)	0.001(1)
C3	0.018(1)	0.028(1)	0.017(1)	0.001(1)	0.001(1)	-0.001(1)
C4	0.017(1)	0.023(1)	0.019(1)	0.001(1)	0.000(1)	0.000(1)
C5	0.018(1)	0.019(1)	0.018(1)	-0.001(1)	0.001(1)	0.003(1)
C6	0.020(1)	0.023(1)	0.017(1)	0.004(1)	0.001(1)	0.004(1)
C7	0.018(1)	0.027(1)	0.018(1)	0.002(1)	0.001(1)	0.003(1)
C8	0.018(1)	0.027(1)	0.019(1)	0.000(1)	0.000(1)	-0.002(1)
C9	0.023(1)	0.026(1)	0.024(1)	0.002(1)	0.004(1)	-0.001(1)
C10	0.034(1)	0.028(2)	0.026(1)	0.002(1)	0.003(1)	-0.005(1)
C11	0.040(2)	0.032(2)	0.028(2)	-0.005(1)	-0.001(1)	-0.005(1)
C12	0.033(1)	0.030(2)	0.025(1)	-0.007(1)	-0.002(1)	-0.003(1)
C13	0.025(1)	0.021(1)	0.025(1)	-0.004(1)	0.000(1)	0.002(1)
C15	0.015(1)	0.028(1)	0.022(1)	-0.000(1)	-0.000(1)	0.002(1)
C16	0.019(1)	0.030(1)	0.019(1)	-0.002(1)	-0.002(1)	0.001(1)
C17	0.015(1)	0.030(1)	0.019(1)	0.002(1)	0.000(1)	0.003(1)
C18	0.020(1)	0.024(1)	0.019(1)	-0.002(1)	0.002(1)	0.002(1)
C19	0.030(1)	0.037(2)	0.032(2)	-0.010(1)	0.010(1)	0.006(1)
C20	0.015(1)	0.041(2)	0.034(2)	0.009(1)	0.003(1)	0.004(1)
C21	0.034(1)	0.036(2)	0.033(2)	-0.008(1)	0.018(1)	0.005(1)
C22	0.015(1)	0.038(2)	0.028(1)	-0.006(1)	-0.003(1)	0.002(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 155. Interatomic Distances (Å) for Sb-7 at **153 K**

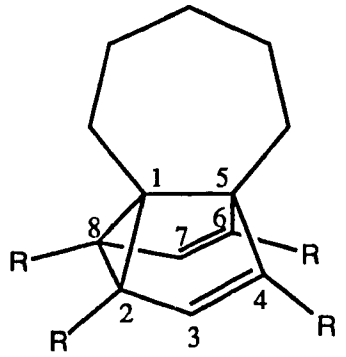
O1	C15	1.341(3)	C2	C8	1.639(4)
O1	C19	1.445(3)	C2	C15	1.502(4)
O2	C15	1.197(3)	C3	C4	1.340(4)
O3	C16	1.341(3)	C3	C7	3.059(4)
O3	C20	1.448(3)	C4	C5	1.541(4)
O4	C16	1.209(3)	C4	C6	2.351(4)
O5	C17	1.342(3)	C4	C16	1.478(4)
O5	C21	1.453(3)	C5	C6	1.540(4)
O6	C17	1.208(3)	C5	C13	1.518(4)
O7	C18	1.341(3)	C6	C7	1.330(4)
O7	C22	1.454(3)	C6	C17	1.487(4)
O8	C18	1.204(3)	C7	C8	1.469(4)
C1	C2	1.506(4)	C8	C18	1.495(4)
C1	C5	1.575(4)	C9	C10	1.532(4)
C1	C8	1.525(4)	C10	C11	1.520(4)
C1	C9	1.506(4)	C11	C12	1.526(4)
C2	C3	1.468(4)	C12	C13	1.537(4)

Table 156. Angles (°) for Sb-7 at **153 K**

C15	O1	C19	115.6(2)	C5	C6	C7	111.2(2)
C16	O3	C20	115.0(2)	C5	C6	C17	127.0(2)
C17	O5	C21	115.1(2)	C7	C6	C17	121.3(2)
C18	O7	C22	115.3(2)	C6	C7	C8	111.3(2)
C2	C1	C5	104.7(2)	C1	C8	C2	56.7(2)
C2	C1	C8	65.4(2)	C1	C8	C7	107.7(2)
C2	C1	C9	124.6(2)	C1	C8	C18	121.9(2)
C5	C1	C8	103.3(2)	C2	C8	C7	121.0(2)
C5	C1	C9	122.1(2)	C2	C8	C18	113.7(2)
C8	C1	C9	122.5(2)	C7	C8	C18	120.1(2)
C1	C2	C3	108.0(2)	C1	C9	C10	113.6(2)
C1	C2	C8	57.8(2)	C9	C10	C11	115.0(2)
C1	C2	C15	125.3(2)	C10	C11	C12	115.2(3)
C3	C2	C8	116.8(2)	C11	C12	C13	114.0(2)
C3	C2	C15	117.6(2)	C5	C13	C12	115.1(2)
C8	C2	C15	118.0(2)	O1	C15	O2	125.0(2)
C2	C3	C4	111.1(2)	O1	C15	C2	109.5(2)
C3	C4	C5	111.6(2)	O2	C15	C2	125.4(3)
C3	C4	C16	124.1(2)	O3	C16	O4	123.8(2)
C5	C4	C16	122.4(2)	O3	C16	C4	111.5(2)
C5	C4	C6	40.3(1)	O4	C16	C4	124.8(3)
C1	C5	C4	102.1(2)	O5	C17	O6	123.4(2)
C1	C5	C6	102.3(2)	O5	C17	C6	112.6(2)
C1	C5	C13	117.0(2)	O6	C17	C6	124.0(3)
C4	C5	C6	99.4(2)	O7	C18	O8	124.9(2)
C4	C5	C13	115.7(2)	O7	C18	C8	109.6(2)
C6	C5	C13	117.6(2)	O8	C18	C8	125.4(2)
C4	C6	C5	40.3(1)				

Table 157. Root-Mean-Square Amplitudes of Thermal Vibration (Å)
Sb-7 at **153 K**

Atom	Min.	Int'med.	Max.
O1	0.124	0.174	0.183
O2	0.133	0.186	0.199
O3	0.125	0.141	0.200
O4	0.129	0.171	0.228
O5	0.115	0.179	0.187
O6	0.140	0.173	0.201
O7	0.125	0.148	0.189
O8	0.131	0.159	0.195
C1	0.124	0.133	0.169
C2	0.122	0.140	0.162
C3	0.128	0.137	0.169
C4	0.129	0.139	0.151
C5	0.123	0.138	0.147
C6	0.124	0.134	0.164
C7	0.130	0.134	0.167
C8	0.133	0.136	0.165
C9	0.139	0.164	0.167
C10	0.146	0.180	0.187
C11	0.155	0.183	0.206
C12	0.144	0.171	0.197
C13	0.134	0.158	0.166
C15	0.122	0.148	0.170
C16	0.131	0.142	0.175
C17	0.121	0.135	0.176
C18	0.128	0.147	0.159
C19	0.122	0.199	0.210
C20	0.110	0.179	0.213
C21	0.110	0.198	0.228
C22	0.114	0.167	0.201



R = $COOCH_3$

1,5-Cycloheptano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-7)

Table 8–158. X-ray Crystal Data for Sb-7 at **181 K**

Formula	$C_{21}H_{24}O_8$
Formula weight	404.42
Melting point (°C)	99–100
Crystal size (mm)	0.16 x 0.24 x 0.50
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.133(1)
b (Å)	8.533(6)
c (Å)	20.538(13)
β (°)	90.39(1)
Cell volume (Å^3)	1950.98(1.42)
Z	4
d_{calc} (g cm^{-3})	1.377
μ(Cu $K\alpha$) (cm^{-1})	8.46
Maximum θ(°)	60
Unique reflections	2889
Observed reflections	2325
[$I > 3.0\sigma(I)$]	
Number of variables	262
R	0.053
R_w	0.075
$(\Delta\rho)_{max}$ (e Å^{-3})	0.26
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.33

Table 159. Final Atomic Parameters for Sb-7 at **181 K**

Atom	x	y	z	B(Å^2)
O1	0.4125(2)	0.4737(3)	0.6807(1)	2.44(4)
O2	0.4190(2)	0.6950(3)	0.7402(1)	2.78(5)
O3	0.9001(2)	0.5474(3)	0.6437(1)	2.36(4)
O4	0.9253(2)	0.7302(3)	0.5662(1)	3.01(5)
O5	0.7990(2)	0.9307(3)	0.4584(1)	2.49(4)
O6	0.7641(2)	0.6838(3)	0.4263(1)	2.76(5)
O7	0.3166(2)	0.6746(3)	0.5030(1)	2.20(4)
O8	0.2789(2)	0.7231(3)	0.6089(1)	2.45(5)
C1	0.5426(3)	0.8363(4)	0.6148(1)	1.77(6)
C2	0.5347(3)	0.6741(4)	0.6424(1)	1.80(6)
C3	0.6564(3)	0.6086(4)	0.6452(1)	1.99(6)
C4	0.7360(3)	0.7065(4)	0.6185(1)	1.75(6)
C5	0.6736(3)	0.8482(4)	0.5869(1)	1.74(6)
C6	0.6573(3)	0.7851(4)	0.5173(1)	1.79(6)
C7	0.5564(3)	0.7013(4)	0.5118(1)	1.92(6)
C8	0.4818(3)	0.7183(4)	0.5701(1)	1.89(6)
C9	0.4777(3)	0.9773(4)	0.6417(2)	2.28(6)
C10	0.5355(3)	1.0433(4)	0.7039(2)	2.69(7)
C11	0.6455(3)	1.1461(4)	0.6930(2)	3.16(8)
C12	0.7542(3)	1.0602(4)	0.6655(2)	2.71(7)
C13	0.7377(3)	1.0049(4)	0.5948(2)	2.10(6)
C15	0.4474(3)	0.6210(4)	0.6933(2)	2.00(6)
C16	0.8629(3)	0.6664(4)	0.6057(2)	2.09(6)
C17	0.7457(3)	0.7904(4)	0.4635(1)	1.98(6)
C18	0.3480(3)	0.7068(4)	0.5645(1)	1.87(6)
C19	0.3247(3)	0.4095(5)	0.7244(2)	3.17(7)
C20	1.0205(3)	0.4922(5)	0.6304(2)	2.77(7)
C21	0.8891(3)	0.9433(5)	0.4079(2)	3.17(7)
C22	0.1884(3)	0.6590(4)	0.4910(2)	2.47(7)
H3	0.677	0.504	0.664	2.0
H7	0.534	0.637	0.473	2.1
H9A	0.393	0.945	0.652	2.5
H9B	0.477	1.060	0.608	2.5
H10A	0.559	0.955	0.733	2.9
H10B	0.474	1.109	0.727	2.9
H11A	0.670	1.192	0.736	3.5
H11B	0.623	1.231	0.662	3.5
H12A	0.771	0.967	0.693	3.0
H12B	0.824	1.134	0.667	3.0
H13A	0.690	1.086	0.571	2.3
H13B	0.819	0.995	0.575	2.3
H19A	0.280	0.323	0.702	3.4
H19B	0.366	0.366	0.764	3.4
H19C	0.267	0.493	0.738	3.4
H20A	1.041	0.404	0.661	3.1
H20B	1.025	0.454	0.584	3.1
H20C	1.079	0.580	0.637	3.1
H21A	0.923	1.052	0.408	3.4
H21B	0.955	0.866	0.416	3.4
H21C	0.851	0.921	0.364	3.4
H22A	0.172	0.664	0.443	2.8
H22B	0.161	0.554	0.508	2.8
H22C	0.145	0.744	0.514	2.8

The parameters of the hydrogen atoms were not refined.

Table 160. Final Anisotropic Thermal Parameters (U's) for Sb-7 at **181 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.027(1)	0.035(1)	0.031(1)	-0.006(1)	0.0092(9)	0.002(1)
O2	0.038(1)	0.041(1)	0.026(1)	-0.002(1)	0.010(1)	-0.004(1)
O3	0.020(1)	0.043(1)	0.026(1)	0.007(1)	0.0020(9)	0.009(1)
O4	0.024(1)	0.048(1)	0.042(1)	-0.002(1)	0.007(1)	0.016(1)
O5	0.030(1)	0.037(1)	0.028(1)	-0.005(1)	0.0124(9)	0.003(1)
O6	0.034(1)	0.039(1)	0.032(1)	-0.004(1)	0.011(1)	-0.006(1)
O7	0.0183(9)	0.041(1)	0.024(1)	-0.004(1)	-0.0014(8)	-0.000(1)
O8	0.022(1)	0.043(1)	0.028(1)	0.001(1)	0.0046(9)	-0.002(1)
C1	0.019(1)	0.029(2)	0.019(1)	0.000(1)	0.002(1)	0.000(1)
C2	0.021(1)	0.029(2)	0.019(1)	-0.000(1)	0.002(1)	0.004(1)
C3	0.021(1)	0.034(2)	0.020(1)	0.001(1)	0.002(1)	0.002(1)
C4	0.021(1)	0.025(2)	0.020(1)	0.001(1)	0.001(1)	-0.001(1)
C5	0.021(1)	0.024(2)	0.021(1)	-0.001(1)	0.001(1)	0.002(1)
C6	0.022(1)	0.026(2)	0.020(1)	0.003(1)	0.003(1)	0.004(1)
C7	0.023(1)	0.030(2)	0.020(1)	0.002(1)	0.002(1)	0.001(1)
C8	0.019(1)	0.030(2)	0.022(1)	0.001(1)	0.002(1)	-0.001(1)
C9	0.028(2)	0.030(2)	0.028(2)	0.002(1)	0.004(1)	-0.002(1)
C10	0.040(2)	0.032(2)	0.031(2)	0.001(2)	0.005(1)	-0.006(2)
C11	0.049(2)	0.039(2)	0.032(2)	-0.004(2)	-0.001(2)	-0.006(2)
C12	0.038(2)	0.034(2)	0.031(2)	-0.008(2)	-0.001(1)	-0.005(2)
C13	0.028(1)	0.025(2)	0.027(2)	-0.004(1)	0.001(1)	0.002(1)
C15	0.018(1)	0.033(2)	0.025(1)	-0.001(1)	0.001(1)	0.003(1)
C16	0.021(1)	0.035(2)	0.023(1)	-0.003(1)	-0.002(1)	0.002(1)
C17	0.019(1)	0.035(2)	0.022(1)	0.000(1)	0.002(1)	0.003(1)
C18	0.023(1)	0.026(2)	0.022(1)	-0.002(1)	0.002(1)	0.000(1)
C19	0.034(2)	0.049(2)	0.038(2)	-0.012(2)	0.011(1)	0.009(2)
C20	0.019(1)	0.049(2)	0.037(2)	0.011(1)	0.004(1)	0.006(2)
C21	0.040(2)	0.041(2)	0.039(2)	-0.007(2)	0.022(1)	0.006(2)
C22	0.018(1)	0.043(2)	0.032(2)	-0.006(1)	-0.003(1)	0.002(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 161. Interatomic Distances (Å) for Sb-7 at **181 K**

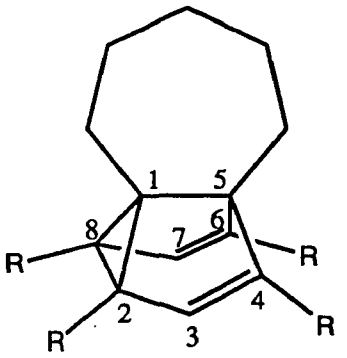
O1	C15	1.340(4)	C2	C8	1.638(4)
O1	C19	1.440(4)	C2	C15	1.502(4)
O2	C15	1.196(4)	C3	C4	1.338(4)
O3	C16	1.344(4)	C3	C7	3.055(4)
O3	C20	1.449(4)	C4	C5	1.537(4)
O4	C16	1.203(4)	C4	C16	1.479(4)
O5	C17	1.340(4)	C5	C6	1.537(4)
O5	C21	1.452(4)	C5	C13	1.524(4)
O6	C17	1.206(4)	C6	C7	1.336(4)
O7	C18	1.337(4)	C6	C17	1.485(4)
O7	C22	1.452(3)	C7	C8	1.469(4)
O8	C18	1.205(4)	C8	C18	1.496(4)
C1	C2	1.498(4)	C9	C10	1.534(5)
C1	C5	1.574(4)	C10	C11	1.524(5)
C1	C8	1.519(4)	C11	C12	1.528(5)
C1	C9	1.510(4)	C12	C13	1.537(5)
C2	C3	1.466(4)	C4	C6	2.350(4)

Table 162. Angles (°) for Sb-7 at **181 K**

C15	O1	C19	115.7(2)	C7	C6	C17	121.0(3)
C16	O3	C20	114.7(2)	C6	C7	C8	111.0(3)
C17	O5	C21	115.5(3)	C1	C8	C2	56.5(2)
C18	O7	C22	115.4(2)	C1	C8	C7	107.8(2)
C2	C1	C5	104.7(2)	C1	C8	C18	121.9(3)
C2	C1	C8	65.7(2)	C2	C8	C7	121.0(2)
C2	C1	C9	124.6(3)	C2	C8	C18	113.9(2)
C5	C1	C8	103.5(2)	C7	C8	C18	120.0(3)
C5	C1	C9	121.9(3)	C1	C9	C10	113.5(3)
C8	C1	C9	122.5(2)	C9	C10	C11	114.9(3)
C1	C2	C3	108.1(2)	C10	C11	C12	114.7(3)
C1	C2	C8	57.8(2)	C11	C12	C13	114.0(3)
C1	C2	C15	125.6(3)	C5	C13	C12	115.0(3)
C3	C2	C8	116.7(2)	O1	C15	O2	125.0(3)
C3	C2	C15	117.3(3)	O1	C15	C2	109.7(3)
C8	C2	C15	118.1(2)	O2	C15	C2	125.2(3)
C2	C3	C4	111.1(3)	O3	C16	O4	123.8(3)
C3	C4	C5	111.4(2)	O3	C16	C4	111.2(2)
C3	C4	C16	124.4(3)	O4	C16	C4	124.9(3)
C5	C4	C16	122.4(3)	O5	C17	O6	123.2(3)
C1	C5	C4	102.3(2)	O5	C17	C6	112.4(3)
C1	C5	C6	102.3(2)	O6	C17	C6	124.3(3)
C1	C5	C13	116.9(2)	O7	C18	O8	125.1(3)
C4	C5	C6	99.7(2)	O7	C18	C8	109.8(2)
C4	C5	C13	115.8(2)	O8	C18	C8	125.1(3)
C6	C5	C13	117.3(2)				
C5	C6	C7	111.1(3)	C5	C4	C6	40.1(1)
C5	C6	C17	127.3(3)	C4	C6	C5	40.1(2)

Table 163. Root-Mean-Square Amplitudes of Thermal Vibration (Å)
Sb-7 at **181 K**

Atom	Min.	Int'med.	Max.
O1	0.131	0.189	0.199
O2	0.141	0.198	0.216
O3	0.135	0.150	0.221
O4	0.140	0.182	0.249
O5	0.123	0.196	0.204
O6	0.148	0.186	0.220
O7	0.132	0.157	0.203
O8	0.139	0.174	0.209
C1	0.130	0.146	0.170
C2	0.131	0.146	0.173
C3	0.137	0.148	0.187
C4	0.138	0.147	0.160
C5	0.137	0.146	0.160
C6	0.134	0.144	0.171
C7	0.136	0.152	0.176
C8	0.135	0.153	0.174
C9	0.151	0.178	0.180
C10	0.157	0.190	0.204
C11	0.169	0.203	0.224
C12	0.156	0.185	0.211
C13	0.145	0.167	0.176
C15	0.134	0.156	0.184
C16	0.140	0.154	0.191
C17	0.135	0.147	0.189
C18	0.143	0.154	0.164
C19	0.131	0.217	0.237
C20	0.124	0.186	0.235
C21	0.121	0.210	0.248
C22	0.126	0.180	0.214



R = $COOCH_3$

1,5-Cycloheptano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-7)

Table 8–164. X-ray Crystal Data for Sb-7 at **208 K**

Formula	$C_{21}H_{24}O_8$
Formula weight	404.42
Melting point (°C)	99–100
Crystal size (mm)	0.16 x 0.24 x 0.50
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.138(1)
b (Å)	8.557(6)
c (Å)	20.582(10)
β (°)	90.53(1)
Cell volume (Å^3)	1961.61(1.30)
Z	4
d_{calc} (g cm^{-3})	1.369
μ(Cu $K\alpha$) (cm^{-1})	8.412
Maximum θ(°)	60
Unique reflections	2906
Observed reflections [$I > 3.0\sigma(I)$]	2329
Number of variables	262
R	0.038
R_w	0.051
$(\Delta\rho)_{max}$ (e Å^{-3})	0.23
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.22

Table 165. Final Atomic Parameters for Sb-7 at 208 K

Atom	x	y	z	B(Å^2)
O1	0.4137(1)	0.4750(2)	0.68083(7)	2.67(3)
O2	0.4196(1)	0.6958(2)	0.73972(7)	3.12(3)
O3	0.9003(1)	0.5480(2)	0.64362(7)	2.57(3)
O4	0.9257(1)	0.7307(2)	0.56669(8)	3.35(4)
O5	0.7987(1)	0.9294(2)	0.45846(7)	2.71(3)
O6	0.7634(1)	0.6834(2)	0.42677(7)	3.08(3)
O7	0.3164(1)	0.6754(2)	0.50313(7)	2.38(3)
O8	0.2795(1)	0.7234(2)	0.60865(7)	2.76(3)
C1	0.5431(2)	0.8362(2)	0.6148(1)	1.88(4)
C2	0.5353(2)	0.6743(3)	0.6422(1)	1.95(4)
C3	0.6566(2)	0.6089(3)	0.6450(1)	2.02(4)
C4	0.7363(2)	0.7062(2)	0.6183(1)	2.02(4)
C5	0.6739(2)	0.8480(2)	0.5867(1)	1.91(4)
C6	0.6574(2)	0.7845(2)	0.5174(1)	1.92(4)
C7	0.5563(2)	0.7023(2)	0.5119(1)	2.00(4)
C8	0.4818(2)	0.7182(3)	0.5699(1)	2.04(4)
C9	0.4784(2)	0.9769(3)	0.6416(1)	2.50(4)
C10	0.5363(2)	1.0436(3)	0.7035(1)	3.04(5)
C11	0.6469(2)	1.1449(3)	0.6925(1)	3.45(5)
C12	0.7551(2)	1.0593(3)	0.6649(1)	3.05(5)
C13	0.7380(2)	1.0042(3)	0.5946(1)	2.40(4)
C15	0.4483(2)	0.6219(3)	0.6931(1)	2.16(4)
C16	0.8628(2)	0.6671(3)	0.6061(1)	2.24(4)
C17	0.7455(2)	0.7901(3)	0.4638(1)	2.08(4)
C18	0.3484(2)	0.7065(2)	0.5646(1)	2.07(4)
C19	0.3263(2)	0.4108(3)	0.7248(1)	3.49(5)
C20	1.0209(2)	0.4925(3)	0.6310(1)	3.09(5)
C21	0.8880(2)	0.9419(3)	0.4083(1)	3.64(5)
C22	0.1883(2)	0.6590(3)	0.4913(1)	2.79(5)
H3	0.677	0.505	0.664	2.2
H7	0.534	0.638	0.473	2.2
H9A	0.394	0.946	0.652	2.7
H9B	0.478	1.060	0.608	2.7
H10A	0.560	0.954	0.732	3.3
H10B	0.475	1.109	0.726	3.3
H11A	0.671	1.192	0.735	3.8
H11B	0.624	1.230	0.662	3.8
H12A	0.772	0.966	0.693	3.3
H12B	0.826	1.131	0.667	3.3
H13A	0.690	1.085	0.571	2.6
H13B	0.819	0.995	0.575	2.6
H19A	0.294	0.314	0.706	3.8
H19B	0.368	0.387	0.767	3.8
H19C	0.262	0.489	0.732	3.8
H20A	1.041	0.404	0.661	3.4
H20B	1.026	0.455	0.585	3.4
H20C	1.079	0.580	0.638	3.4
H21A	0.922	1.050	0.408	4.0
H21B	0.954	0.865	0.417	4.0
H21C	0.850	0.920	0.365	4.0
H22A	0.172	0.655	0.444	3.0
H22B	0.159	0.562	0.512	3.0
H22C	0.145	0.751	0.510	3.0

The parameters of the hydrogen atoms were not refined.

Table 166. Final Anisotropic Thermal Parameters (U's) for Sb-7 at **208 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0335(7)	0.0306(8)	0.0375(8)	-0.0061(7)	0.0105(7)	0.0024(7)
O2	0.0474(9)	0.0412(9)	0.0302(8)	-0.0028(8)	0.0116(7)	-0.0036(8)
O3	0.0247(7)	0.0413(9)	0.0317(8)	0.0084(7)	0.0026(6)	0.0085(7)
O4	0.0285(8)	0.0473(9)	0.052(1)	0.0013(7)	0.0086(7)	0.0186(8)
O5	0.0377(8)	0.0310(8)	0.0344(8)	-0.0046(7)	0.0132(6)	0.0046(7)
O6	0.0420(8)	0.0377(9)	0.0377(8)	-0.0044(8)	0.0127(7)	-0.0074(8)
O7	0.0238(7)	0.0366(8)	0.0301(7)	-0.0038(7)	-0.0023(6)	0.0000(7)
O8	0.0266(7)	0.0454(9)	0.0331(8)	0.0005(7)	0.0045(6)	-0.0020(8)
C1	0.025(1)	0.023(1)	0.024(1)	0.0015(9)	0.0010(8)	0.0013(9)
C2	0.025(1)	0.024(1)	0.025(1)	-0.0003(9)	0.0021(8)	0.0019(9)
C3	0.026(1)	0.025(1)	0.026(1)	0.0001(9)	0.0018(9)	0.0009(9)
C4	0.026(1)	0.025(1)	0.026(1)	-0.0008(9)	-0.0010(9)	0.0011(9)
C5	0.0237(9)	0.024(1)	0.025(1)	-0.0015(9)	0.0015(8)	0.0022(9)
C6	0.026(1)	0.022(1)	0.025(1)	0.0019(9)	0.0008(9)	0.0035(9)
C7	0.027(1)	0.026(1)	0.023(1)	0.0017(9)	0.0014(9)	0.0020(9)
C8	0.024(1)	0.027(1)	0.026(1)	-0.0008(9)	0.0015(9)	0.0000(9)
C9	0.035(1)	0.027(1)	0.034(1)	0.004(1)	0.004(1)	-0.001(1)
C10	0.049(1)	0.030(1)	0.037(1)	0.000(1)	0.003(1)	-0.008(1)
C11	0.059(2)	0.033(1)	0.039(1)	-0.006(1)	-0.002(1)	-0.008(1)
C12	0.045(1)	0.034(1)	0.038(1)	-0.010(1)	-0.005(1)	-0.004(1)
C13	0.035(1)	0.024(1)	0.032(1)	-0.006(1)	0.0009(9)	0.003(1)
C15	0.024(1)	0.029(1)	0.028(1)	0.0012(9)	0.0002(9)	0.003(1)
C16	0.026(1)	0.031(1)	0.028(1)	-0.0015(9)	-0.0012(9)	0.002(1)
C17	0.024(1)	0.028(1)	0.027(1)	0.0012(9)	0.0004(9)	0.0034(9)
C18	0.028(1)	0.024(1)	0.027(1)	-0.0016(9)	0.0015(9)	0.0017(9)
C19	0.042(1)	0.046(1)	0.045(1)	-0.014(1)	0.013(1)	0.008(1)
C20	0.023(1)	0.050(1)	0.045(1)	0.011(1)	0.004(1)	0.007(1)
C21	0.046(1)	0.045(1)	0.047(1)	-0.007(1)	0.024(1)	0.005(1)
C22	0.024(1)	0.042(1)	0.040(1)	-0.007(1)	-0.005(1)	0.002(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 167. Interatomic Distances (Å) for Sb-7 at **208 K**

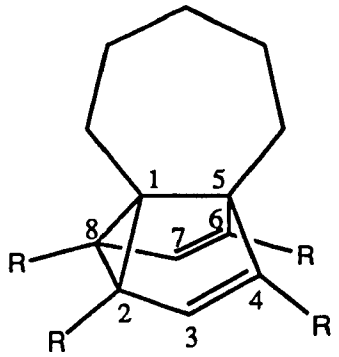
O1	C15	1.338(3)	C2	C8	1.642(3)
O1	C19	1.443(3)	C2	C15	1.502(3)
O2	C15	1.195(3)	C3	C4	1.338(3)
O3	C16	1.344(3)	C3	C7	3.055(3)
O3	C20	1.451(3)	C4	C5	1.539(3)
O4	C16	1.206(3)	C4	C16	1.473(3)
O5	C17	1.336(3)	C5	C6	1.536(3)
O5	C21	1.445(3)	C5	C13	1.524(3)
O6	C17	1.207(3)	C6	C7	1.332(3)
O7	C18	1.339(2)	C6	C17	1.484(3)
O7	C22	1.452(2)	C7	C8	1.465(3)
O8	C18	1.201(3)	C8	C18	1.493(3)
C1	C2	1.498(3)	C9	C10	1.533(3)
C1	C5	1.575(3)	C10	C11	1.524(3)
C1	C8	1.526(3)	C11	C12	1.525(3)
C1	C9	1.511(3)	C12	C13	1.533(3)
C2	C3	1.463(3)	C4	C6	2.345(3)

Table 168. Angles (°) for Sb-7 at **208 K**

C15	O1	C19	115.7(2)	C7	C6	C17	121.2(2)
C16	O3	C20	115.4(2)	C6	C7	C8	111.5(2)
C17	O5	C21	115.7(2)	C1	C8	C2	56.3(1)
C18	O7	C22	115.4(2)	C1	C8	C7	107.5(2)
C2	C1	C5	104.7(2)	C1	C8	C18	121.8(2)
C2	C1	C8	65.8(1)	C2	C8	C7	120.9(2)
C2	C1	C9	124.7(2)	C2	C8	C18	113.7(2)
C5	C1	C8	103.3(2)	C7	C8	C18	120.4(2)
C5	C1	C9	121.9(2)	C1	C9	C10	113.8(2)
C8	C1	C9	122.5(2)	C9	C10	C11	115.0(2)
C1	C2	C3	108.2(2)	C10	C11	C12	115.1(2)
C1	C2	C8	57.9(1)	C11	C12	C13	114.1(2)
C1	C2	C15	125.3(2)	C5	C13	C12	115.1(2)
C3	C2	C8	116.8(2)	O1	C15	O2	124.7(2)
C3	C2	C15	117.4(2)	O1	C15	C2	109.6(2)
C8	C2	C15	118.0(2)	O2	C15	C2	125.5(2)
C2	C3	C4	111.2(2)	O3	C16	O4	123.4(2)
C3	C4	C5	111.4(2)	O3	C16	C4	111.5(2)
C3	C4	C16	124.6(2)	O4	C16	C4	125.1(2)
C5	C4	C16	122.4(2)	O5	C17	O6	123.2(2)
C1	C5	C4	102.1(2)	O5	C17	C6	112.7(2)
C1	C5	C6	102.4(2)	O6	C17	C6	124.0(2)
C1	C5	C13	116.8(2)	O7	C18	O8	124.8(2)
C4	C5	C6	99.4(2)	O7	C18	C8	109.7(2)
C4	C5	C13	115.9(2)	O8	C18	C8	125.5(2)
C6	C5	C13	117.4(2)				
C5	C6	C7	111.0(2)	C5	C4	C6	40.2(1)
C5	C6	C17	127.3(2)	C4	C6	C5	40.4(1)

Table 169. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-7 at **208 K**

Atom	Min.	Int'med.	Max.
O1	0.145	0.186	0.215
O2	0.156	0.200	0.233
O3	0.145	0.166	0.222
O4	0.155	0.184	0.264
O5	0.139	0.186	0.221
O6	0.162	0.187	0.237
O7	0.148	0.176	0.194
O8	0.156	0.187	0.214
C1	0.148	0.152	0.162
C2	0.148	0.158	0.165
C3	0.154	0.159	0.166
C4	0.155	0.158	0.167
C5	0.144	0.158	0.163
C6	0.140	0.158	0.168
C7	0.149	0.158	0.170
C8	0.153	0.164	0.166
C9	0.156	0.181	0.195
C10	0.156	0.204	0.223
C11	0.160	0.211	0.246
C12	0.157	0.200	0.226
C13	0.145	0.181	0.193
C15	0.154	0.162	0.179
C16	0.159	0.165	0.180
C17	0.153	0.157	0.176
C18	0.150	0.166	0.169
C19	0.145	0.231	0.242
C20	0.135	0.201	0.242
C21	0.141	0.220	0.265
C22	0.143	0.196	0.217



R = $COOCH_3$

1,5-Cycloheptano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-7)

Table 8–170. X-ray Crystal Data for Sb-7 at **236 K**

Formula	$C_{21}H_{24}O_8$
Formula weight	404.42
Melting point (°C)	99–100
Crystal size (mm)	0.16 x 0.24 x 0.50
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.142(1)
b (Å)	8.580(4)
c (Å)	20.633(1)
β (°)	90.72(1)
Cell volume (Å^3)	1972.21(0.92)
Z	4
d_{calc} (g cm^{-3})	1.362
μ(Cu $K\alpha$) (cm^{-1})	8.37
Maximum θ (°)	60
Unique reflections	2926
Observed reflections	2296
[$I > 3.0\sigma(I)$]	
Number of variables	262
R	0.039
R_w	0.052
$(\Delta\rho)_{max}$ (e Å^{-3})	0.21
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.20

Table 171. Final Atomic Parameters for Sb-7 at **236 K**

Atom	x	y	z	B(Å^2)
O1	0.4152(1)	0.4763(2)	0.68105(8)	3.01(3)
O2	0.4205(2)	0.6971(2)	0.73931(8)	3.61(4)
O3	0.9005(1)	0.5486(2)	0.64365(7)	2.96(3)
O4	0.9260(1)	0.7312(2)	0.56731(8)	3.95(4)
O5	0.7985(1)	0.9280(2)	0.45888(7)	3.12(3)
O6	0.7628(2)	0.6831(2)	0.42719(8)	3.66(4)
O7	0.3163(1)	0.6760(2)	0.50326(7)	2.71(3)
O8	0.2800(1)	0.7241(2)	0.60839(8)	3.18(3)
C1	0.5437(2)	0.8358(3)	0.6146(1)	2.11(4)
C2	0.5360(2)	0.6751(3)	0.6423(1)	2.31(4)
C3	0.6570(2)	0.6095(3)	0.6449(1)	2.28(4)
C4	0.7365(2)	0.7064(3)	0.6180(1)	2.28(4)
C5	0.6741(2)	0.8477(3)	0.5867(1)	2.16(4)
C6	0.6576(2)	0.7840(3)	0.5178(1)	2.26(4)
C7	0.5561(2)	0.7024(3)	0.5122(1)	2.30(4)
C8	0.4820(2)	0.7188(3)	0.5698(1)	2.36(4)
C9	0.4796(2)	0.9769(3)	0.6412(1)	2.90(5)
C10	0.5377(2)	1.0432(3)	0.7031(1)	3.50(5)
C11	0.6480(3)	1.1441(3)	0.6920(1)	3.96(6)
C12	0.7558(2)	1.0586(3)	0.6645(1)	3.54(5)
C13	0.7386(2)	1.0036(3)	0.5945(1)	2.80(5)
C15	0.4495(2)	0.6230(3)	0.6929(1)	2.45(4)
C16	0.8633(2)	0.6678(3)	0.6064(1)	2.57(4)
C17	0.7452(2)	0.7891(3)	0.4639(1)	2.44(4)
C18	0.3487(2)	0.7072(3)	0.5646(1)	2.35(4)
C19	0.3280(2)	0.4114(3)	0.7248(1)	4.07(6)
C20	1.0214(2)	0.4940(3)	0.6317(1)	3.63(5)
C21	0.8874(2)	0.9407(3)	0.4085(1)	4.16(6)
C22	0.1881(2)	0.6592(3)	0.4914(1)	3.25(5)
H3	0.678	0.506	0.664	2.5
H7	0.534	0.638	0.473	2.5
H9A	0.395	0.946	0.651	3.2
H9B	0.479	1.060	0.607	3.2
H10A	0.562	0.954	0.732	3.8
H10B	0.476	1.109	0.725	3.8
H11A	0.673	1.190	0.735	4.3
H11B	0.625	1.229	0.661	4.3
H12A	0.773	0.965	0.692	3.9
H12B	0.826	1.131	0.666	3.9
H13A	0.691	1.085	0.571	3.0
H13B	0.819	0.994	0.575	3.0
H19A	0.294	0.314	0.706	4.4
H19B	0.368	0.387	0.767	4.4
H19C	0.262	0.489	0.732	4.4
H20A	1.041	0.405	0.662	4.0
H20B	1.027	0.458	0.586	4.0
H20C	1.079	0.581	0.639	4.0
H21A	0.922	1.049	0.409	4.5
H21B	0.953	0.864	0.417	4.5
H21C	0.849	0.919	0.366	4.5
H22A	0.169	0.686	0.445	3.5
H22B	0.164	0.549	0.500	3.5
H22C	0.143	0.730	0.521	3.5

The parameters of the hydrogen atoms were not refined.

Table 172. Final Anisotropic Thermal Parameters (U's) for Sb-7 at **236 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0391(8)	0.0333(8)	0.0421(8)	-0.0074(7)	0.0126(7)	0.0031(7)
O2	0.055(1)	0.046(1)	0.0359(8)	-0.0037(9)	0.0145(8)	-0.0036(8)
O3	0.0284(7)	0.0455(9)	0.0388(8)	0.0090(7)	0.0039(7)	0.0098(8)
O4	0.0325(8)	0.054(1)	0.064(1)	0.0005(8)	0.0103(8)	0.0229(9)
O5	0.0438(8)	0.0345(8)	0.0409(8)	-0.0046(8)	0.0165(7)	0.0045(8)
O6	0.0516(9)	0.0421(9)	0.0458(9)	-0.0049(8)	0.0174(8)	-0.0090(8)
O7	0.0277(7)	0.0404(9)	0.0349(8)	-0.0043(7)	-0.0020(7)	0.0011(7)
O8	0.0307(8)	0.052(1)	0.0386(8)	-0.0002(8)	0.0056(7)	-0.0012(8)
C1	0.027(1)	0.027(1)	0.027(1)	0.0016(9)	0.0019(9)	0.000(1)
C2	0.029(1)	0.028(1)	0.030(1)	-0.001(1)	0.0015(9)	0.001(1)
C3	0.030(1)	0.028(1)	0.029(1)	0.001(1)	0.0019(9)	0.002(1)
C4	0.027(1)	0.028(1)	0.031(1)	0.0000(9)	0.0003(9)	0.002(1)
C5	0.028(1)	0.025(1)	0.029(1)	-0.0016(9)	0.0023(9)	0.003(1)
C6	0.030(1)	0.026(1)	0.030(1)	0.0016(9)	0.0026(9)	0.004(1)
C7	0.031(1)	0.028(1)	0.028(1)	0.001(1)	0.0014(9)	0.002(1)
C8	0.028(1)	0.031(1)	0.031(1)	-0.0004(9)	0.0017(9)	-0.002(1)
C9	0.040(1)	0.029(1)	0.041(1)	0.006(1)	0.004(1)	-0.001(1)
C10	0.056(1)	0.035(1)	0.043(1)	0.001(1)	0.005(1)	-0.010(1)
C11	0.070(2)	0.035(1)	0.046(1)	-0.006(1)	-0.002(1)	-0.011(1)
C12	0.051(1)	0.038(1)	0.045(1)	-0.013(1)	-0.005(1)	-0.004(1)
C13	0.039(1)	0.028(1)	0.039(1)	-0.007(1)	0.001(1)	0.003(1)
C15	0.028(1)	0.033(1)	0.032(1)	0.002(1)	0.0023(9)	0.004(1)
C16	0.032(1)	0.033(1)	0.033(1)	-0.004(1)	-0.001(1)	0.004(1)
C17	0.028(1)	0.032(1)	0.033(1)	-0.000(1)	0.0010(9)	0.005(1)
C18	0.031(1)	0.027(1)	0.031(1)	-0.0022(9)	0.0027(9)	0.001(1)
C19	0.049(1)	0.052(2)	0.054(1)	-0.015(1)	0.017(1)	0.011(1)
C20	0.027(1)	0.057(2)	0.054(1)	0.015(1)	0.005(1)	0.009(1)
C21	0.054(1)	0.050(2)	0.055(1)	-0.007(1)	0.030(1)	0.006(1)
C22	0.027(1)	0.046(1)	0.050(1)	-0.009(1)	-0.005(1)	0.002(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 173. Interatomic Distances (Å) for Sb-7 at **236 K**

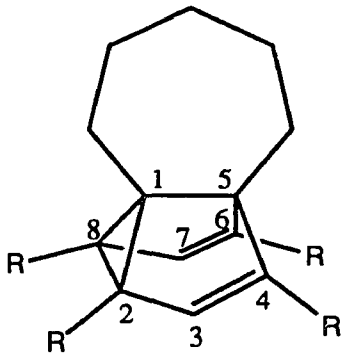
O1	C15	1.337(3)	C2	C8	1.648(3)
O1	C19	1.445(3)	C2	C15	1.498(3)
O2	C15	1.197(3)	C3	C4	1.340(3)
O3	C16	1.341(3)	C3	C7	3.052(3)
O3	C20	1.449(3)	C4	C5	1.537(3)
O4	C16	1.204(3)	C4	C6	2.335(3)
O5	C17	1.336(3)	C4	C16	1.474(3)
O5	C21	1.448(3)	C5	C6	1.532(3)
O6	C17	1.202(3)	C5	C13	1.526(3)
O7	C18	1.338(3)	C6	C7	1.334(3)
O7	C22	1.453(3)	C6	C17	1.488(3)
O8	C18	1.200(3)	C7	C8	1.461(3)
C1	C2	1.495(3)	C8	C18	1.491(3)
C1	C5	1.574(3)	C9	C10	1.534(3)
C1	C8	1.523(3)	C10	C11	1.522(4)
C1	C9	1.512(3)	C11	C12	1.523(4)
C2	C3	1.462(3)	C12	C13	1.529(3)

Table 174. Angles (°) for Sb-7 at **236 K**

C15	O1	C19	116.1(2)	C7	C6	C17	121.0(2)
C16	O3	C20	115.5(2)	C6	C7	C8	111.5(2)
C17	O5	C21	115.6(2)	C1	C8	C2	56.1(1)
C18	O7	C22	115.6(2)	C1	C8	C7	107.6(2)
C2	C1	C5	104.9(2)	C1	C8	C18	121.9(2)
C2	C1	C8	66.2(1)	C2	C8	C7	120.8(2)
C2	C1	C9	124.7(2)	C2	C8	C18	113.7(2)
C5	C1	C8	103.4(2)	C7	C8	C18	120.5(2)
C5	C1	C9	121.6(2)	C1	C9	C10	113.7(2)
C8	C1	C9	122.5(2)	C9	C10	C11	114.8(2)
C1	C2	C3	108.2(2)	C10	C11	C12	115.1(2)
C1	C2	C8	57.7(1)	C11	C12	C13	114.2(2)
C1	C2	C15	125.6(2)	C5	C13	C12	115.1(2)
C3	C2	C8	116.5(2)	O1	C15	O2	124.5(2)
C3	C2	C15	117.4(2)	O1	C15	C2	109.8(2)
C8	C2	C15	118.0(2)	O2	C15	C2	125.5(2)
C2	C3	C4	111.1(2)	O3	C16	O4	123.4(2)
C3	C4	C5	111.5(2)	O3	C16	C4	111.6(2)
C3	C4	C16	124.6(2)	O4	C16	C4	125.0(2)
C5	C4	C16	122.6(2)	O5	C17	O6	123.3(2)
C1	C5	C4	102.1(2)	O5	C17	C6	112.4(2)
C1	C5	C6	102.4(2)	O6	C17	C6	124.2(2)
C1	C5	C13	117.0(2)	O7	C18	O8	124.7(2)
C4	C5	C6	99.1(2)	O7	C18	C8	109.7(2)
C4	C5	C13	115.9(2)	O8	C18	C8	125.5(2)
C6	C5	C13	117.6(2)				
C5	C6	C7	111.1(2)	C5	C4	C6	40.4(1)
C5	C6	C17	127.5(2)	C4	C6	C5	40.6(1)

Table 175. Root-Mean-Square Amplitudes of Thermal Vibration in (Å) for Sb-7 at **236 K**

Atom	Min.	Int'med.	Max.
O1	0.151	0.196	0.230
O2	0.168	0.213	0.253
O3	0.156	0.180	0.236
O4	0.165	0.198	0.289
O5	0.150	0.195	0.241
O6	0.173	0.200	0.262
O7	0.161	0.187	0.205
O8	0.168	0.202	0.227
C1	0.157	0.162	0.171
C2	0.164	0.172	0.176
C3	0.161	0.168	0.179
C4	0.164	0.164	0.180
C5	0.150	0.168	0.177
C6	0.154	0.167	0.185
C7	0.163	0.169	0.179
C8	0.165	0.171	0.182
C9	0.161	0.197	0.213
C10	0.166	0.220	0.239
C11	0.165	0.229	0.266
C12	0.165	0.216	0.245
C13	0.156	0.198	0.207
C15	0.166	0.169	0.192
C16	0.167	0.175	0.197
C17	0.164	0.169	0.193
C18	0.158	0.175	0.183
C19	0.152	0.252	0.261
C20	0.145	0.217	0.264
C21	0.147	0.230	0.289
C22	0.152	0.214	0.233



R = $COOCH_3$

1,5-Cycloheptano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-7)

Table 8–176. X-ray Crystal Data for Sb-7 at **265 K**

Formula	$C_{21}H_{24}O_8$
Formula weight	404.42
Melting point (°C)	99–100
Crystal size (mm)	0.16 x 0.24 x 0.50
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.144(1)
b (Å)	8.612(2)
c (Å)	20.694(1)
β (°)	91.03(1)
Cell volume ($Å^3$)	1985.73(0.37)
Z	4
d_{calc} (g cm^{-3})	1.353
μ(Cu $K\alpha$) (cm^{-1})	8.31
Maximum θ (°)	60
Unique reflections	2944
Observed reflections [$I > 3.0\sigma(I)$]	2225
Number of variables	262
R	0.039
R_w	0.051
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.16
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.20

Table 177. Final Atomic Parameters for Sb-7 at **265 K**

Atom	x	y	z	B(Å^2)
O1	0.4172(1)	0.4777(2)	0.68132(8)	3.61(4)
O2	0.4220(2)	0.6983(2)	0.73867(8)	4.26(4)
O3	0.9010(1)	0.5496(2)	0.64378(8)	3.53(3)
O4	0.9269(1)	0.7317(2)	0.56808(9)	4.74(4)
O5	0.7982(1)	0.9261(2)	0.45921(8)	3.66(3)
O6	0.7617(2)	0.6826(2)	0.42777(8)	4.43(4)
O7	0.3158(1)	0.6765(2)	0.50319(7)	3.21(3)
O8	0.2808(1)	0.7246(2)	0.60789(8)	3.83(4)
C1	0.5445(2)	0.8356(3)	0.6144(1)	2.51(4)
C2	0.5371(2)	0.6760(3)	0.6423(1)	2.64(4)
C3	0.6575(2)	0.6102(3)	0.6448(1)	2.64(4)
C4	0.7373(2)	0.7067(3)	0.6178(1)	2.76(5)
C5	0.6745(2)	0.8475(3)	0.5865(1)	2.56(4)
C6	0.6579(2)	0.7831(3)	0.5181(1)	2.66(4)
C7	0.5559(2)	0.7028(3)	0.5124(1)	2.72(5)
C8	0.4823(2)	0.7197(3)	0.5694(1)	2.83(5)
C9	0.4809(2)	0.9763(3)	0.6408(1)	3.41(5)
C10	0.5396(2)	1.0428(3)	0.7023(1)	4.19(6)
C11	0.6498(3)	1.1432(3)	0.6914(1)	4.74(7)
C12	0.7572(2)	1.0574(3)	0.6642(1)	4.25(6)
C13	0.7391(2)	1.0028(3)	0.5944(1)	3.27(5)
C15	0.4512(2)	0.6241(3)	0.6927(1)	2.93(5)
C16	0.8639(2)	0.6685(3)	0.6068(1)	3.08(5)
C17	0.7449(2)	0.7884(3)	0.4645(1)	2.92(5)
C18	0.3490(2)	0.7076(3)	0.5642(1)	2.77(5)
C19	0.3311(2)	0.4135(3)	0.7251(1)	4.71(6)
C20	1.0223(2)	0.4960(3)	0.6329(1)	4.20(6)
C21	0.8857(2)	0.9394(4)	0.4090(1)	4.96(6)
C22	0.1878(2)	0.6598(3)	0.4914(1)	3.80(5)
H3	0.678	0.507	0.664	2.9
H7	0.533	0.639	0.474	3.0
H9A	0.397	0.946	0.651	3.7
H9B	0.480	1.059	0.607	3.7
H10A	0.564	0.954	0.731	4.6
H10B	0.478	1.107	0.725	4.6
H11A	0.675	1.190	0.734	5.2
H11B	0.627	1.228	0.660	5.2
H12A	0.774	0.965	0.692	4.7
H12B	0.828	1.129	0.666	4.7
H13A	0.691	1.083	0.571	3.6
H13B	0.820	0.993	0.575	3.6
H19A	0.297	0.315	0.707	5.2
H19B	0.371	0.390	0.768	5.2
H19C	0.265	0.490	0.732	5.2
H20A	1.041	0.408	0.663	4.6
H20B	1.029	0.461	0.587	4.6
H20C	1.080	0.583	0.641	4.6
H21A	0.920	1.047	0.409	5.4
H21B	0.951	0.862	0.417	5.4
H21C	0.846	0.918	0.366	5.4
H22A	0.170	0.668	0.444	4.2
H22B	0.161	0.556	0.507	4.2
H22C	0.144	0.744	0.515	4.2

The parameters of the hydrogen atoms were not refined.

Table 178. Final Anisotropic Thermal Parameters (U's) for Sb-7 at **265 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0484(9)	0.0382(9)	0.0512(9)	-0.0072(8)	0.0160(8)	0.0030(8)
O2	0.065(1)	0.055(1)	0.0423(9)	-0.0048(9)	0.0173(8)	-0.0050(9)
O3	0.0338(8)	0.055(1)	0.0455(9)	0.0108(8)	0.0044(7)	0.0120(8)
O4	0.0375(9)	0.065(1)	0.078(1)	0.0022(9)	0.0113(9)	0.030(1)
O5	0.0513(9)	0.0402(9)	0.0484(9)	-0.0042(8)	0.0192(7)	0.0065(8)
O6	0.063(1)	0.051(1)	0.055(1)	-0.0079(9)	0.0222(8)	-0.0108(9)
O7	0.0335(8)	0.0475(9)	0.0409(8)	-0.0054(7)	-0.0016(7)	0.0022(8)
O8	0.0352(8)	0.063(1)	0.0473(9)	0.0008(8)	0.0072(7)	-0.0022(9)
C1	0.034(1)	0.029(1)	0.032(1)	0.001(1)	0.0023(9)	0.002(1)
C2	0.034(1)	0.032(1)	0.034(1)	0.000(1)	0.003(1)	0.004(1)
C3	0.035(1)	0.033(1)	0.033(1)	0.000(1)	0.003(1)	0.004(1)
C4	0.032(1)	0.034(1)	0.039(1)	-0.001(1)	-0.000(1)	0.003(1)
C5	0.033(1)	0.030(1)	0.035(1)	-0.001(1)	0.002(1)	0.003(1)
C6	0.033(1)	0.032(1)	0.036(1)	0.001(1)	0.005(1)	0.004(1)
C7	0.037(1)	0.035(1)	0.032(1)	0.002(1)	0.002(1)	0.002(1)
C8	0.032(1)	0.039(1)	0.036(1)	-0.001(1)	0.003(1)	-0.004(1)
C9	0.047(1)	0.034(1)	0.049(1)	0.007(1)	0.004(1)	-0.002(1)
C10	0.068(2)	0.041(1)	0.050(1)	0.003(1)	0.005(1)	-0.012(1)
C11	0.083(2)	0.042(1)	0.054(2)	-0.009(1)	-0.002(1)	-0.013(1)
C12	0.063(2)	0.046(1)	0.052(1)	-0.016(1)	-0.006(1)	-0.005(1)
C13	0.048(1)	0.032(1)	0.044(1)	-0.009(1)	0.000(1)	0.004(1)
C15	0.033(1)	0.039(1)	0.039(1)	0.002(1)	0.003(1)	0.004(1)
C16	0.035(1)	0.038(1)	0.043(1)	-0.002(1)	-0.000(1)	0.005(1)
C17	0.034(1)	0.036(1)	0.040(1)	0.002(1)	0.003(1)	0.004(1)
C18	0.036(1)	0.031(1)	0.039(1)	-0.001(1)	0.004(1)	0.001(1)
C19	0.060(2)	0.056(2)	0.063(2)	-0.015(1)	0.019(1)	0.014(1)
C20	0.033(1)	0.065(2)	0.062(2)	0.017(1)	0.006(1)	0.013(1)
C21	0.065(2)	0.059(2)	0.066(2)	-0.009(1)	0.035(1)	0.006(2)
C22	0.034(1)	0.055(2)	0.055(1)	-0.010(1)	-0.007(1)	0.005(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 179. Interatomic Distances (Å) for Sb-7 at **265 K**

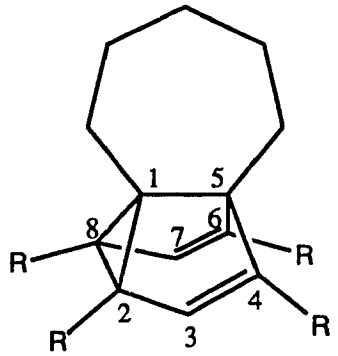
O1	C15	1.337(3)	C2	C8	1.660(3)
O1	C19	1.442(3)	C2	C15	1.497(3)
O2	C15	1.195(3)	C3	C4	1.345(3)
O3	C16	1.339(3)	C3	C7	3.051(3)
O3	C20	1.449(3)	C4	C5	1.538(3)
O4	C16	1.205(3)	C4	C6	2.325(3)
O5	C17	1.332(3)	C4	C16	1.471(3)
O5	C21	1.442(3)	C5	C6	1.529(3)
O6	C17	1.203(3)	C5	C13	1.526(3)
O7	C18	1.337(3)	C6	C7	1.334(3)
O7	C22	1.450(3)	C6	C17	1.486(3)
O8	C18	1.200(3)	C7	C8	1.457(3)
C1	C2	1.494(3)	C8	C18	1.491(3)
C1	C5	1.572(3)	C9	C10	1.531(4)
C1	C8	1.523(3)	C10	C11	1.523(4)
C1	C9	1.511(3)	C11	C12	1.523(4)
C2	C3	1.457(3)	C12	C13	1.529(4)

Table 180. Angles (°) for Sb-7 at **265 K**

C15	O1	C19	116.1(2)	C7	C6	C17	121.1(2)
C16	O3	C20	115.7(2)	C6	C7	C8	111.6(2)
C17	O5	C21	116.0(2)	C1	C8	C2	55.8(1)
C18	O7	C22	115.7(2)	C1	C8	C7	107.6(2)
C2	C1	C5	105.1(2)	C1	C8	C18	122.1(2)
C2	C1	C8	66.8(1)	C2	C8	C7	120.6(2)
C2	C1	C9	124.6(2)	C2	C8	C18	113.6(2)
C5	C1	C8	103.4(2)	C7	C8	C18	120.6(2)
C5	C1	C9	121.5(2)	C1	C9	C10	113.9(2)
C8	C1	C9	122.4(2)	C9	C10	C11	115.0(2)
C1	C2	C3	108.3(2)	C10	C11	C12	114.9(2)
C1	C2	C8	57.5(1)	C11	C12	C13	114.0(2)
C1	C2	C15	125.8(2)	C5	C13	C12	115.1(2)
C3	C2	C8	116.3(2)	O1	C15	O2	124.4(2)
C3	C2	C15	117.3(2)	O1	C15	C2	109.9(2)
C8	C2	C15	118.1(2)	O2	C15	C2	125.6(2)
C2	C3	C4	111.1(2)	O3	C16	O4	123.2(2)
C3	C4	C5	111.3(2)	O3	C16	C4	111.7(2)
C3	C4	C16	124.7(2)	O4	C16	C4	125.0(2)
C5	C4	C16	122.8(2)	O5	C17	O6	123.2(2)
C1	C5	C4	102.1(2)	O5	C17	C6	112.7(2)
C1	C5	C6	102.7(2)	O6	C17	C6	124.0(2)
C1	C5	C13	117.0(2)	O7	C18	O8	124.6(2)
C4	C5	C6	98.6(2)	O7	C18	C8	109.9(2)
C4	C5	C13	115.8(2)	O8	C18	C8	125.5(2)
C6	C5	C13	117.8(2)				
C5	C6	C7	111.0(2)	C5	C4	C6	40.5(1)
C5	C6	C17	127.6(2)	C4	C6	C5	40.8(1)

Table 181. Root-Mean-Square Amplitudes of Thermal Vibration (Å)
Sb-7 at **265 K**

Atom	Min.	Int'med.	Max.
O1	0.169	0.209	0.255
O2	0.182	0.231	0.275
O3	0.171	0.196	0.258
O4	0.182	0.209	0.321
O5	0.163	0.211	0.261
O6	0.191	0.217	0.292
O7	0.177	0.201	0.224
O8	0.179	0.223	0.252
C1	0.168	0.178	0.188
C2	0.170	0.183	0.195
C3	0.167	0.185	0.195
C4	0.179	0.181	0.200
C5	0.166	0.181	0.192
C6	0.168	0.179	0.202
C7	0.176	0.184	0.197
C8	0.175	0.186	0.206
C9	0.173	0.218	0.228
C10	0.178	0.242	0.263
C11	0.181	0.249	0.292
C12	0.183	0.234	0.271
C13	0.167	0.211	0.229
C15	0.179	0.186	0.210
C16	0.184	0.191	0.216
C17	0.182	0.185	0.209
C18	0.174	0.185	0.202
C19	0.168	0.268	0.281
C20	0.161	0.229	0.285
C21	0.165	0.250	0.314
C22	0.170	0.223	0.256



R = $COOCH_3$

1,5-Cycloheptano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-7)

Table 8–182. X-ray Crystal Data for Sb-7 at **294 K**

Formula	$C_{21}H_{24}O_8$
Formula weight	404.42
Melting point (°C)	99–100
Crystal size (mm)	0.16 x 0.24 x 0.50
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.141(1)
b (Å)	8.647(1)
c (Å)	20.763(1)
β (°)	91.53(1)
Cell volume (Å^3)	1999.57(0.21)
Z	4
d_{calc} (g cm^{-3})	1.343
μ(Cu $K\alpha$) (cm^{-1})	8.26
Maximum θ (°)	60
Unique reflections	2966
Observed reflections	2137
[$I > 3.0\sigma(I)$]	
Number of variables	262
R	0.042
R_w	0.053
$(\Delta\rho)_{max}$ (e Å-3)	0.17
$(\Delta\rho)_{min}$ (e Å-3)	-0.16

Table 183. Final Atomic Parameters for Sb-7 at **294 K**

Atom	x	y	z	B(Å^2)
O1	0.4205(2)	0.4794(2)	0.68173(9)	4.25(4)
O2	0.4244(2)	0.7006(2)	0.73785(9)	5.00(5)
O3	0.9023(2)	0.5508(2)	0.64392(8)	4.15(4)
O4	0.9282(2)	0.7326(3)	0.5689(1)	5.79(5)
O5	0.7972(2)	0.9236(2)	0.45969(8)	4.29(4)
O6	0.7606(2)	0.6817(2)	0.42845(9)	5.33(5)
O7	0.3153(1)	0.6771(2)	0.50298(8)	3.79(4)
O8	0.2823(2)	0.7253(2)	0.60740(9)	4.41(4)
C1	0.5457(2)	0.8352(3)	0.6142(1)	2.93(5)
C2	0.5393(2)	0.6770(3)	0.6427(1)	3.11(5)
C3	0.6593(2)	0.6111(3)	0.6446(1)	3.08(5)
C4	0.7382(2)	0.7067(3)	0.6176(1)	3.28(5)
C5	0.6754(2)	0.8473(3)	0.5864(1)	3.01(5)
C6	0.6585(2)	0.7817(3)	0.5184(1)	3.16(5)
C7	0.5560(2)	0.7032(3)	0.5123(1)	3.12(5)
C8	0.4830(2)	0.7210(3)	0.5688(1)	3.41(5)
C9	0.4828(2)	0.9762(3)	0.6404(1)	3.96(6)
C10	0.5420(3)	1.0424(3)	0.7014(1)	4.81(7)
C11	0.6526(3)	1.1421(4)	0.6905(2)	5.50(8)
C12	0.7595(3)	1.0568(4)	0.6637(1)	4.90(7)
C13	0.7403(2)	1.0019(3)	0.5942(1)	3.89(6)
C15	0.4540(2)	0.6258(3)	0.6927(1)	3.37(5)
C16	0.8654(2)	0.6693(3)	0.6075(1)	3.71(6)
C17	0.7446(2)	0.7868(3)	0.4652(1)	3.49(6)
C18	0.3494(2)	0.7091(3)	0.5636(1)	3.35(5)
C19	0.3351(3)	0.4151(4)	0.7253(2)	5.60(8)
C20	1.0241(2)	0.4988(4)	0.6346(1)	5.03(7)
C21	0.8840(3)	0.9369(4)	0.4093(2)	5.82(8)
C22	0.1869(2)	0.6607(4)	0.4913(1)	4.47(6)
H3	0.680	0.508	0.663	3.4
H7	0.532	0.640	0.474	3.4
H9A	0.398	0.947	0.650	4.3
H9B	0.482	1.058	0.607	4.3
H10A	0.567	0.954	0.730	5.3
H10B	0.481	1.107	0.724	5.3
H11A	0.678	1.189	0.733	6.0
H11B	0.629	1.226	0.660	6.0
H12A	0.776	0.964	0.691	5.4
H12B	0.830	1.128	0.665	5.4
H13A	0.692	1.082	0.570	4.3
H13B	0.821	0.992	0.574	4.3
H19A	0.300	0.320	0.706	6.1
H19B	0.377	0.390	0.767	6.1
H19C	0.271	0.493	0.733	6.1
H20A	1.043	0.410	0.664	5.5
H20B	1.033	0.465	0.589	5.5
H20C	1.081	0.586	0.644	5.5
H21A	0.918	1.044	0.409	6.4
H21B	0.950	0.860	0.417	6.4
H21C	0.844	0.915	0.367	6.4
H22A	0.168	0.669	0.444	4.9
H22B	0.160	0.558	0.507	4.9
H22C	0.144	0.745	0.514	4.9

The parameters of the hydrogen atoms were not refined.

Table 184. Final Anisotropic Thermal Parameters (U's) for Sb-7 at **294 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.057(1)	0.046(1)	0.059(1)	-0.0079(9)	0.0190(9)	0.0034(9)
O2	0.077(1)	0.063(1)	0.051(1)	-0.006(1)	0.0219(9)	-0.007(1)
O3	0.0402(9)	0.064(1)	0.054(1)	0.0129(9)	0.0056(8)	0.015(1)
O4	0.046(1)	0.076(1)	0.099(1)	0.004(1)	0.015(1)	0.036(1)
O5	0.060(1)	0.048(1)	0.057(1)	-0.0046(9)	0.0218(9)	0.0067(9)
O6	0.076(1)	0.060(1)	0.068(1)	-0.008(1)	0.028(1)	-0.013(1)
O7	0.0401(9)	0.055(1)	0.048(1)	-0.0056(9)	-0.0019(8)	0.0005(9)
O8	0.0401(9)	0.072(1)	0.056(1)	0.001(1)	0.0081(9)	-0.000(1)
C1	0.038(1)	0.033(1)	0.040(1)	0.003(1)	0.003(1)	0.001(1)
C2	0.041(1)	0.038(1)	0.040(1)	0.001(1)	0.007(1)	0.005(1)
C3	0.039(1)	0.037(1)	0.040(1)	0.002(1)	0.002(1)	0.004(1)
C4	0.038(1)	0.038(1)	0.050(1)	0.001(1)	0.003(1)	0.005(1)
C5	0.036(1)	0.036(1)	0.042(1)	-0.002(1)	0.002(1)	0.003(1)
C6	0.041(1)	0.038(1)	0.041(1)	0.003(1)	0.007(1)	0.006(1)
C7	0.042(1)	0.040(1)	0.036(1)	0.001(1)	0.003(1)	0.002(1)
C8	0.035(1)	0.048(2)	0.047(1)	-0.003(1)	0.003(1)	-0.005(1)
C9	0.054(1)	0.042(1)	0.055(2)	0.010(1)	0.006(1)	-0.003(1)
C10	0.078(2)	0.047(2)	0.058(2)	0.003(2)	0.006(2)	-0.015(1)
C11	0.096(2)	0.050(2)	0.063(2)	-0.010(2)	-0.004(2)	-0.015(2)
C12	0.073(2)	0.053(2)	0.060(2)	-0.013(2)	-0.007(2)	-0.005(2)
C13	0.053(1)	0.040(1)	0.055(2)	-0.010(1)	0.001(1)	0.005(1)
C15	0.041(1)	0.044(1)	0.044(1)	0.002(1)	0.004(1)	0.004(1)
C16	0.040(1)	0.046(2)	0.055(2)	-0.004(1)	0.002(1)	0.008(1)
C17	0.041(1)	0.043(1)	0.049(1)	0.002(1)	0.005(1)	0.004(1)
C18	0.042(1)	0.039(1)	0.046(1)	-0.002(1)	0.004(1)	0.001(1)
C19	0.069(2)	0.068(2)	0.076(2)	-0.017(2)	0.022(2)	0.016(2)
C20	0.040(1)	0.081(2)	0.070(2)	0.021(1)	0.007(1)	0.016(2)
C21	0.073(2)	0.070(2)	0.081(2)	-0.009(2)	0.040(1)	0.010(2)
C22	0.039(1)	0.065(2)	0.065(2)	-0.012(1)	-0.008(1)	0.004(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 185. Interatomic Distances (Å) for Sb-7 at **294 K**

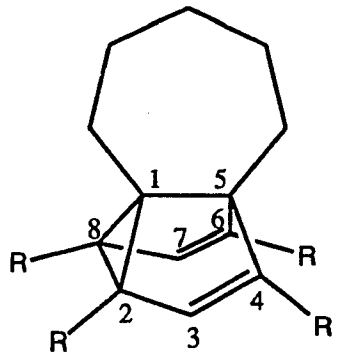
O1	C15	1.338(3)	C2	C8	1.685(3)
O1	C19	1.442(4)	C2	C15	1.493(3)
O2	C15	1.193(3)	C3	C4	1.340(3)
O3	C16	1.332(3)	C3	C7	3.055(3)
O3	C20	1.448(3)	C4	C5	1.537(3)
O4	C16	1.209(3)	C4	C6	2.313(3)
O5	C17	1.326(3)	C4	C16	1.473(3)
O5	C21	1.449(4)	C5	C6	1.529(3)
O6	C17	1.204(3)	C5	C13	1.526(4)
O7	C18	1.334(3)	C6	C7	1.332(3)
O7	C22	1.452(3)	C6	C17	1.482(3)
O8	C18	1.201(3)	C7	C8	1.455(3)
C1	C2	1.493(3)	C8	C18	1.493(3)
C1	C5	1.575(3)	C9	C10	1.523(4)
C1	C8	1.523(3)	C10	C11	1.525(4)
C1	C9	1.514(4)	C11	C12	1.519(4)
C2	C3	1.453(3)	C12	C13	1.528(4)

Table 186. Angles (°) for Sb-7 at **294 K**

C15	O1	C19	116.4(2)	C7	C6	C17	120.9(2)
C16	O3	C20	116.1(2)	C6	C7	C8	111.4(2)
C17	O5	C21	116.0(2)	C1	C8	C2	55.2(1)
C18	O7	C22	115.6(2)	C1	C8	C7	108.1(2)
C2	C1	C5	105.1(2)	C1	C8	C18	122.0(2)
C2	C1	C8	67.9(2)	C2	C8	C7	120.5(2)
C2	C1	C9	124.7(2)	C2	C8	C18	113.4(2)
C5	C1	C8	103.1(2)	C7	C8	C18	120.8(2)
C5	C1	C9	121.1(2)	C1	C9	C10	114.0(2)
C8	C1	C9	122.4(2)	C9	C10	C11	115.0(2)
C1	C2	C3	108.5(2)	C10	C11	C12	115.1(3)
C1	C2	C8	56.9(2)	C11	C12	C13	113.9(2)
C1	C2	C15	125.8(2)	C5	C13	C12	115.2(2)
C3	C2	C8	115.7(2)	O1	C15	O2	124.4(2)
C3	C2	C15	117.9(2)	O1	C15	C2	110.0(2)
C8	C2	C15	118.1(2)	O2	C15	C2	125.5(2)
C2	C3	C4	111.2(2)	O3	C16	O4	123.3(2)
C3	C4	C5	111.5(2)	O3	C16	C4	111.8(2)
C3	C4	C16	124.7(2)	O4	C16	C4	124.8(2)
C5	C4	C16	122.8(2)	O5	C17	O6	123.0(2)
C1	C5	C4	101.8(2)	O5	C17	C6	112.8(2)
C1	C5	C6	102.9(2)	O6	C17	C6	124.1(2)
C1	C5	C13	117.2(2)	O7	C18	O8	124.9(2)
C4	C5	C6	98.0(2)	O7	C18	C8	109.9(2)
C4	C5	C13	116.0(2)	O8	C18	C8	125.2(2)
C6	C5	C13	118.0(2)				
C5	C6	C7	111.2(2)	C5	C4	C6	40.9(1)
C5	C6	C17	127.7(2)	C4	C6	C5	41.2(1)

Table 187. Root-Mean-Square Amplitudes of Thermal Vibration (Å)
Sb-7 at **294 K**

Atom	Min.	Int'med.	Max.
O1	0.186	0.227	0.275
O2	0.197	0.246	0.301
O3	0.185	0.211	0.281
O4	0.202	0.229	0.356
O5	0.181	0.228	0.279
O6	0.207	0.239	0.321
O7	0.194	0.221	0.240
O8	0.193	0.241	0.269
C1	0.178	0.194	0.204
C2	0.181	0.194	0.219
C3	0.185	0.197	0.210
C4	0.190	0.193	0.227
C5	0.182	0.195	0.208
C6	0.183	0.192	0.224
C7	0.187	0.201	0.208
C8	0.185	0.207	0.229
C9	0.186	0.235	0.246
C10	0.190	0.262	0.280
C11	0.194	0.270	0.314
C12	0.206	0.249	0.285
C13	0.184	0.233	0.245
C15	0.196	0.201	0.222
C16	0.192	0.211	0.244
C17	0.199	0.202	0.229
C18	0.194	0.205	0.218
C19	0.188	0.291	0.305
C20	0.177	0.246	0.316
C21	0.179	0.274	0.338
C22	0.182	0.247	0.275



R = $COOCH_3$

1,5-Cycloheptano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-7)

Table 8–188. X-ray Crystal Data for Sb-7 at **294 K**

Formula	$C_{21}H_{24}O_8$
Formula weight	404.42
Melting point (°C)	99–100
Crystal size (mm)	0.26 x 0.28 x 0.48
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.142(1)
b (Å)	8.649(1)
c (Å)	20.763(1)
β (°)	91.53(1)
Cell volume (Å^3)	2000.14(0.25)
Z	4
d_{calc} (g cm^{-3})	1.343
μ(Cu $K\alpha$) (cm^{-1})	8.25
Maximum θ (°)	60
Unique reflections	2933
Observed reflections [$I > 3.0\sigma(I)$]	2167
Number of variables	262
R	0.050
R_w	0.064
$(\Delta\rho)_{max}$ (e Å^{-3})	0.20
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.29

Table 189. Final Atomic Parameters for Sb-7 at **294 K**

Atom	x	y	z	B(Å^2)
O1	0.4207(2)	0.4796(2)	0.6818(1)	4.30(5)
O2	0.4241(2)	0.7005(3)	0.7379(1)	5.04(5)
O3	0.9023(2)	0.5510(3)	0.64394(9)	4.20(5)
O4	0.9282(2)	0.7323(3)	0.5689(1)	5.75(6)
O5	0.7971(2)	0.9239(3)	0.4596(1)	4.34(5)
O6	0.7604(2)	0.6815(3)	0.4282(1)	5.36(5)
O7	0.3155(2)	0.6771(2)	0.50288(9)	3.81(4)
O8	0.2819(2)	0.7253(3)	0.6071(1)	4.39(5)
C1	0.5457(2)	0.8356(3)	0.6141(1)	2.88(5)
C2	0.5393(2)	0.6767(3)	0.6421(1)	3.15(6)
C3	0.6589(2)	0.6108(3)	0.6445(1)	3.08(6)
C4	0.7382(2)	0.7066(3)	0.6174(1)	3.36(6)
C5	0.6754(2)	0.8475(3)	0.5864(1)	2.98(6)
C6	0.6585(2)	0.7815(3)	0.5185(1)	3.16(6)
C7	0.5561(2)	0.7030(3)	0.5126(1)	3.16(6)
C8	0.4829(2)	0.7215(4)	0.5688(1)	3.35(6)
C9	0.4823(3)	0.9758(4)	0.6401(2)	3.93(7)
C10	0.5416(3)	1.0428(4)	0.7014(2)	4.81(8)
C11	0.6519(3)	1.1424(4)	0.6907(2)	5.61(9)
C12	0.7595(3)	1.0568(4)	0.6638(2)	4.91(8)
C13	0.7403(3)	1.0013(4)	0.5943(1)	3.81(6)
C15	0.4538(2)	0.6259(4)	0.6925(1)	3.36(6)
C16	0.8652(2)	0.6695(4)	0.6071(1)	3.72(6)
C17	0.7449(2)	0.7867(4)	0.4650(1)	3.50(6)
C18	0.3501(2)	0.7094(3)	0.5640(1)	3.46(6)
C19	0.3350(3)	0.4155(5)	0.7253(2)	5.65(9)
C20	1.0241(3)	0.4983(4)	0.6344(2)	4.99(8)
C21	0.8840(3)	0.9368(5)	0.4091(2)	5.89(9)
C22	0.1867(3)	0.6601(4)	0.4915(2)	4.56(7)
H3	0.680	0.508	0.663	3.4
H7	0.532	0.640	0.474	3.4
H9A	0.398	0.947	0.650	4.3
H9B	0.482	1.058	0.607	4.3
H10A	0.567	0.954	0.730	5.3
H10B	0.481	1.107	0.724	5.3
H11A	0.678	1.189	0.733	6.0
H11B	0.629	1.226	0.660	6.0
H12A	0.776	0.964	0.691	5.4
H12B	0.830	1.128	0.665	5.4
H13A	0.692	1.082	0.570	4.3
H13B	0.821	0.992	0.574	4.3
H19A	0.300	0.320	0.706	6.1
H19B	0.377	0.390	0.767	6.1
H19C	0.271	0.493	0.733	6.1
H20A	1.043	0.410	0.664	5.5
H20B	1.033	0.465	0.589	5.5
H20C	1.081	0.586	0.644	5.5
H21A	0.918	1.044	0.409	6.4
H21B	0.950	0.860	0.417	6.4
H21C	0.844	0.915	0.367	6.4
H22A	0.168	0.669	0.444	4.9
H22B	0.160	0.558	0.507	4.9
H22C	0.144	0.745	0.514	4.9

The parameters of the hydrogen atoms were not refined.

Table 190. Final Anisotropic Thermal Parameters (U's) for Sb-7 at **294 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.050(1)	0.054(1)	0.060(1)	-0.007(1)	0.0147(9)	0.003(1)
O2	0.073(1)	0.072(2)	0.048(1)	-0.007(1)	0.016(1)	-0.006(1)
O3	0.036(1)	0.072(1)	0.052(1)	0.0155(9)	0.0020(9)	0.015(1)
O4	0.039(1)	0.085(2)	0.094(2)	0.004(1)	0.011(1)	0.035(1)
O5	0.056(1)	0.054(1)	0.056(1)	-0.005(1)	0.018(1)	0.005(1)
O6	0.071(1)	0.066(1)	0.067(1)	-0.010(1)	0.024(1)	-0.015(1)
O7	0.0333(9)	0.061(1)	0.050(1)	-0.0072(9)	-0.0055(9)	0.002(1)
O8	0.035(1)	0.077(2)	0.054(1)	0.001(1)	0.0042(9)	-0.002(1)
C1	0.035(1)	0.038(1)	0.035(1)	0.002(1)	-0.002(1)	0.003(1)
C2	0.034(1)	0.044(2)	0.041(1)	0.002(1)	0.003(1)	0.003(1)
C3	0.036(1)	0.039(2)	0.041(1)	0.001(1)	-0.002(1)	0.002(1)
C4	0.035(1)	0.045(2)	0.048(2)	0.000(1)	-0.002(1)	0.002(1)
C5	0.035(1)	0.041(2)	0.038(1)	-0.001(1)	-0.002(1)	0.003(1)
C6	0.036(1)	0.041(2)	0.043(1)	0.003(1)	0.003(1)	0.004(1)
C7	0.036(1)	0.045(2)	0.039(1)	0.000(1)	-0.000(1)	0.004(1)
C8	0.032(1)	0.050(2)	0.045(1)	-0.002(1)	0.000(1)	-0.002(1)
C9	0.050(2)	0.043(2)	0.056(2)	0.009(1)	0.001(1)	-0.003(2)
C10	0.072(2)	0.050(2)	0.061(2)	0.002(2)	0.001(2)	-0.016(2)
C11	0.093(3)	0.058(2)	0.061(2)	-0.009(2)	-0.007(2)	-0.015(2)
C12	0.067(2)	0.057(2)	0.061(2)	-0.017(2)	-0.013(2)	-0.007(2)
C13	0.051(2)	0.043(2)	0.051(2)	-0.010(1)	-0.004(1)	0.003(1)
C15	0.036(1)	0.049(2)	0.043(1)	0.001(1)	-0.001(1)	0.004(1)
C16	0.034(1)	0.056(2)	0.052(2)	-0.002(1)	0.001(1)	0.005(2)
C17	0.036(1)	0.048(2)	0.049(2)	0.002(1)	0.001(1)	0.004(1)
C18	0.035(1)	0.048(2)	0.048(2)	-0.000(1)	0.002(1)	0.002(1)
C19	0.064(2)	0.074(2)	0.077(2)	-0.017(2)	0.021(2)	0.012(2)
C20	0.037(1)	0.086(2)	0.068(2)	0.023(2)	0.005(1)	0.015(2)
C21	0.068(2)	0.078(2)	0.080(2)	-0.008(2)	0.037(2)	0.012(2)
C22	0.034(1)	0.071(2)	0.068(2)	-0.013(1)	-0.012(1)	0.008(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 191. Interatomic Distances (Å) for Sb-7 at **294 K**

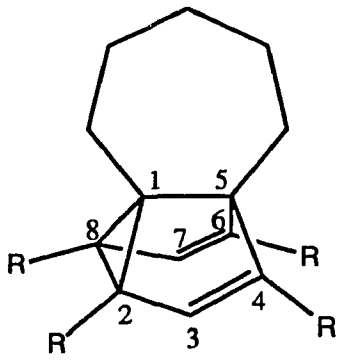
O1	C15	1.335(4)	C2	C8	1.677(4)
O1	C19	1.442(4)	C2	C15	1.500(4)
O2	C15	1.195(4)	C3	C4	1.345(4)
O3	C16	1.338(4)	C3	C7	3.046(4)
O3	C20	1.450(4)	C4	C5	1.538(4)
O4	C16	1.203(4)	C4	C6	2.309(4)
O5	C17	1.328(4)	C4	C16	1.472(4)
O5	C21	1.449(4)	C5	C6	1.529(4)
O6	C17	1.202(4)	C5	C13	1.521(4)
O7	C18	1.346(3)	C6	C7	1.331(4)
O7	C22	1.456(3)	C6	C17	1.490(4)
O8	C18	1.196(3)	C7	C8	1.449(4)
C1	C2	1.496(4)	C8	C18	1.485(4)
C1	C5	1.572(4)	C9	C10	1.532(4)
C1	C8	1.521(4)	C10	C11	1.523(5)
C1	C9	1.511(4)	C11	C12	1.528(5)
C2	C3	1.449(4)	C12	C13	1.531(4)

Table 192. Angles (°) for Sb-7 at **294 K**

C15	O1	C19	116.3(2)	C7	C6	C17	121.1(2)
C16	O3	C20	116.0(2)	C6	C7	C8	111.7(2)
C17	O5	C21	115.6(2)	C1	C8	C2	55.5(2)
C18	O7	C22	115.5(2)	C1	C8	C7	108.0(2)
C2	C1	C5	104.9(2)	C1	C8	C18	121.9(2)
C2	C1	C8	67.6(2)	C2	C8	C7	120.0(2)
C2	C1	C9	124.7(2)	C2	C8	C18	113.1(2)
C5	C1	C8	103.2(2)	C7	C8	C18	121.3(2)
C5	C1	C9	121.5(2)	C1	C9	C10	113.9(2)
C8	C1	C9	122.0(2)	C9	C10	C11	115.2(3)
C1	C2	C3	108.7(2)	C10	C11	C12	115.1(3)
C1	C2	C8	56.9(2)	C11	C12	C13	114.0(3)
C1	C2	C15	125.4(2)	C5	C13	C12	115.4(2)
C3	C2	C8	116.3(2)	O1	C15	O2	124.3(3)
C3	C2	C15	117.5(2)	O1	C15	C2	109.8(2)
C8	C2	C15	118.2(2)	O3	C16	C4	111.5(2)
C2	C3	C4	110.9(2)	O3	C16	O4	123.1(3)
C3	C4	C5	111.5(2)	O4	C16	C4	125.3(3)
C3	C4	C16	124.8(3)	O5	C17	O6	123.5(3)
C5	C4	C16	122.7(2)	O5	C17	C6	112.5(2)
C1	C5	C4	102.0(2)	O6	C17	C6	123.9(3)
C1	C5	C6	102.8(2)	O7	C18	O8	123.9(2)
C1	C5	C13	117.2(2)	O7	C18	C8	109.7(2)
C4	C5	C6	97.7(2)	O8	C18	C8	126.4(3)
C4	C5	C13	116.0(2)	O2	C15	C2	125.8(3)
C6	C5	C13	118.1(2)				
C5	C6	C7	111.0(2)	C5	C4	C6	41.0(1)
C5	C6	C17	127.7(2)	C4	C6	C5	41.3(1)

Table 193. Root-Mean-Square Amplitudes of Thermal Vibration (Å)
Sb-7 at **294 K**

Atom	Min.	Int'med.	Max.
O1	0.192	0.240	0.262
O2	0.202	0.257	0.291
O3	0.171	0.216	0.289
O4	0.193	0.234	0.355
O5	0.191	0.238	0.268
O6	0.212	0.242	0.316
O7	0.173	0.225	0.253
O8	0.187	0.233	0.279
C1	0.176	0.196	0.200
C2	0.184	0.198	0.217
C3	0.185	0.199	0.207
C4	0.184	0.211	0.222
C5	0.180	0.193	0.209
C6	0.186	0.195	0.218
C7	0.188	0.195	0.216
C8	0.178	0.210	0.227
C9	0.193	0.233	0.240
C10	0.196	0.265	0.272
C11	0.204	0.273	0.311
C12	0.191	0.258	0.289
C13	0.190	0.218	0.247
C15	0.188	0.204	0.225
C16	0.183	0.220	0.244
C17	0.190	0.210	0.230
C18	0.187	0.214	0.225
C19	0.195	0.293	0.301
C20	0.166	0.247	0.318
C21	0.181	0.285	0.331
C22	0.164	0.248	0.291



R = $COOCH_3$

1,5-Cycloheptano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-7)

Table 8–194. X-ray Crystal Data for Sb-7 at **295 K**

Formula	$C_{21}H_{24}O_8$
Formula weight	404.42
Melting point (°C)	99–100
Crystal size (mm)	0.17 x 0.20 x 0.47
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.140(1)
b (Å)	8.654(1)
c (Å)	20.770(2)
β (°)	91.65(1)
Cell volume ($Å^3$)	2001.56(0.40)
Z	4
d_{calc} (g cm^{-3})	1.342
μ(Cu $K\alpha$) (cm^{-1})	8.25
Maximum θ (°)	60
Unique reflections	2965
Observed reflections [$I > 3.0\sigma(I)$]	2179
Number of variables	262
R	0.040
R_w	0.052
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.20
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.18

Table 195. Final Atomic Parameters for Sb-7 at 295 K

Atom	x	y	z	B(Å^2)
O1	0.4213(2)	0.4797(2)	0.68182(8)	4.38(4)
O2	0.4247(2)	0.7010(2)	0.73782(8)	5.12(4)
O3	0.9027(1)	0.5512(2)	0.64389(8)	4.21(4)
O4	0.9284(2)	0.7329(2)	0.56907(9)	5.87(5)
O5	0.7971(2)	0.9234(2)	0.45968(8)	4.43(4)
O6	0.7603(2)	0.6811(2)	0.42844(9)	5.50(4)
O7	0.3152(1)	0.6773(2)	0.50298(8)	3.83(4)
O8	0.2824(1)	0.7254(2)	0.60717(8)	4.56(4)
C1	0.5460(2)	0.8358(3)	0.6140(1)	2.94(4)
C2	0.5398(2)	0.6771(3)	0.6423(1)	3.25(5)
C3	0.6593(2)	0.6113(3)	0.6446(1)	3.17(5)
C4	0.7387(2)	0.7068(3)	0.6175(1)	3.40(5)
C5	0.6755(2)	0.8474(3)	0.5865(1)	3.02(5)
C6	0.6587(2)	0.7813(3)	0.5185(1)	3.20(5)
C7	0.5561(2)	0.7033(3)	0.5126(1)	3.23(5)
C8	0.4830(2)	0.7211(3)	0.5689(1)	3.46(5)
C9	0.4828(2)	0.9759(3)	0.6402(1)	4.03(5)
C10	0.5425(3)	1.0423(3)	0.7014(1)	4.93(6)
C11	0.6526(3)	1.1425(3)	0.6906(1)	5.65(7)
C12	0.7598(3)	1.0569(3)	0.6636(1)	4.96(6)
C13	0.7407(2)	1.0014(3)	0.5943(1)	3.93(5)
C15	0.4545(2)	0.6259(3)	0.6926(1)	3.50(5)
C16	0.8657(2)	0.6690(3)	0.6074(1)	3.83(5)
C17	0.7444(2)	0.7866(3)	0.4651(1)	3.62(5)
C18	0.3496(2)	0.7090(3)	0.5638(1)	3.39(5)
C19	0.3360(3)	0.4156(4)	0.7253(1)	5.76(7)
C20	1.0247(2)	0.4993(4)	0.6345(1)	5.23(7)
C21	0.8834(3)	0.9366(4)	0.4094(1)	5.91(7)
C22	0.1867(2)	0.6609(3)	0.4912(1)	4.52(6)
H3	0.680	0.508	0.664	3.5
H7	0.532	0.640	0.474	3.6
H9A	0.399	0.946	0.650	4.4
H9B	0.481	1.058	0.606	4.4
H10A	0.568	0.954	0.730	5.4
H10B	0.482	1.107	0.724	5.4
H11A	0.678	1.190	0.733	6.3
H11B	0.629	1.226	0.659	6.3
H12A	0.777	0.965	0.692	5.5
H12B	0.831	1.128	0.665	5.5
H13A	0.693	1.081	0.570	4.3
H13B	0.821	0.991	0.575	4.3
H19A	0.300	0.320	0.706	6.4
H19B	0.377	0.390	0.767	6.4
H19C	0.271	0.493	0.733	6.4
H20A	1.043	0.411	0.664	5.8
H20B	1.033	0.465	0.589	5.8
H20C	1.082	0.586	0.644	5.8
H21A	0.918	1.044	0.409	6.5
H21B	0.950	0.860	0.417	6.5
H21C	0.843	0.915	0.367	6.5
H22A	0.168	0.669	0.444	5.0
H22B	0.160	0.558	0.507	5.0
H22C	0.144	0.745	0.514	5.0

The parameters of the hydrogen atoms were not refined.

Table 196. Final Anisotropic Thermal Parameters (U's) for Sb-7 at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0590(9)	0.047(1)	0.061(1)	-0.0071(8)	0.0201(8)	0.0053(9)
O2	0.082(1)	0.064(1)	0.0496(9)	-0.006(1)	0.0217(9)	-0.0058(9)
O3	0.0402(8)	0.066(1)	0.0546(9)	0.0134(8)	0.0065(7)	0.0155(9)
O4	0.047(1)	0.080(1)	0.097(1)	0.004(1)	0.015(1)	0.037(1)
O5	0.062(1)	0.049(1)	0.0587(9)	-0.0048(9)	0.0232(8)	0.0076(9)
O6	0.080(1)	0.061(1)	0.069(1)	-0.009(1)	0.0306(9)	-0.014(1)
O7	0.0391(8)	0.056(1)	0.0508(9)	-0.0056(8)	-0.0007(7)	0.0009(8)
O8	0.0420(9)	0.077(1)	0.054(1)	0.0007(9)	0.0084(8)	-0.002(1)
C1	0.041(1)	0.033(1)	0.038(1)	0.003(1)	0.003(1)	0.002(1)
C2	0.042(1)	0.040(1)	0.041(1)	0.002(1)	0.006(1)	0.005(1)
C3	0.041(1)	0.037(1)	0.042(1)	0.001(1)	0.003(1)	0.004(1)
C4	0.039(1)	0.039(1)	0.051(1)	0.001(1)	0.002(1)	0.004(1)
C5	0.038(1)	0.035(1)	0.042(1)	-0.002(1)	0.002(1)	0.005(1)
C6	0.041(1)	0.040(1)	0.042(1)	0.001(1)	0.006(1)	0.004(1)
C7	0.044(1)	0.041(1)	0.038(1)	0.002(1)	0.004(1)	0.002(1)
C8	0.038(1)	0.047(1)	0.047(1)	-0.001(1)	0.002(1)	-0.006(1)
C9	0.056(1)	0.042(1)	0.056(1)	0.011(1)	0.006(1)	-0.002(1)
C10	0.080(2)	0.049(2)	0.059(2)	0.002(1)	0.008(1)	-0.014(1)
C11	0.098(2)	0.052(2)	0.064(2)	-0.009(2)	-0.002(2)	-0.015(1)
C12	0.074(2)	0.052(2)	0.062(2)	-0.017(1)	-0.007(1)	-0.005(1)
C13	0.056(1)	0.039(1)	0.054(1)	-0.009(1)	-0.000(1)	0.005(1)
C15	0.042(1)	0.046(1)	0.045(1)	0.002(1)	0.004(1)	0.006(1)
C16	0.042(1)	0.050(1)	0.054(1)	-0.003(1)	0.003(1)	0.009(1)
C17	0.043(1)	0.045(1)	0.051(1)	0.002(1)	0.006(1)	0.006(1)
C18	0.043(1)	0.040(1)	0.046(1)	-0.002(1)	0.005(1)	0.002(1)
C19	0.073(2)	0.069(2)	0.078(2)	-0.017(2)	0.026(1)	0.016(2)
C20	0.042(1)	0.086(2)	0.071(2)	0.023(1)	0.008(1)	0.017(2)
C21	0.076(2)	0.072(2)	0.079(2)	-0.007(2)	0.040(1)	0.012(2)
C22	0.039(1)	0.066(2)	0.066(2)	-0.010(1)	-0.008(1)	0.006(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 197. Interatomic Distances (Å) for Sb-7 at **295 K**

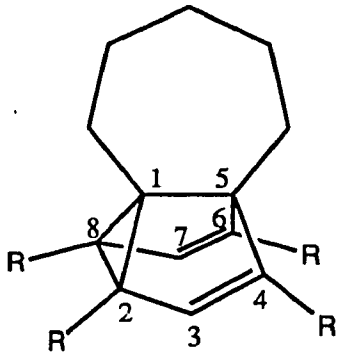
O1	C15	1.335(3)	C2	C8	1.678(3)
O1	C19	1.441(3)	C2	C15	1.499(3)
O2	C15	1.197(3)	C3	C4	1.345(3)
O3	C16	1.329(3)	C3	C7	3.048(3)
O3	C20	1.450(3)	C4	C5	1.538(3)
O4	C16	1.208(3)	C4	C6	2.309(3)
O5	C17	1.328(3)	C4	C16	1.473(3)
O5	C21	1.445(3)	C5	C6	1.529(3)
O6	C17	1.205(3)	C5	C13	1.525(3)
O7	C18	1.337(3)	C6	C7	1.330(3)
O7	C22	1.453(3)	C6	C17	1.485(3)
O8	C18	1.197(3)	C7	C8	1.454(3)
C1	C2	1.496(3)	C8	C18	1.490(3)
C1	C5	1.571(3)	C9	C10	1.531(4)
C1	C8	1.522(3)	C10	C11	1.524(4)
C1	C9	1.512(3)	C11	C12	1.525(4)
C2	C3	1.448(3)	C12	C13	1.528(4)

Table 198. Angles (°) for Sb-7 at **295 K**

C15	O1	C19	116.4(2)	C7	C6	C17	121.0(2)
C16	O3	C20	116.0(2)	C6	C7	C8	111.8(2)
C17	O5	C21	115.9(2)	C1	C8	C2	55.5(1)
C18	O7	C22	115.7(2)	C1	C8	C7	107.8(2)
C2	C1	C5	104.8(2)	C1	C8	C18	122.1(2)
C2	C1	C8	67.5(2)	C2	C8	C7	120.2(2)
C2	C1	C9	124.5(2)	C2	C8	C18	113.5(2)
C5	C1	C8	103.3(2)	C7	C8	C18	121.0(2)
C5	C1	C9	121.5(2)	C1	C9	C10	113.9(2)
C8	C1	C9	122.2(2)	C9	C10	C11	115.0(2)
C1	C2	C3	108.7(2)	C10	C11	C12	114.8(2)
C1	C2	C8	57.0(1)	C11	C12	C13	114.2(2)
C1	C2	C15	125.7(2)	C5	C13	C12	115.3(2)
C3	C2	C8	116.1(2)	O1	C15	O2	124.4(2)
C3	C2	C15	117.5(2)	O1	C15	C2	109.9(2)
C8	C2	C15	118.1(2)	O2	C15	C2	125.6(2)
C2	C3	C4	111.1(2)	O3	C16	O4	123.5(2)
C3	C4	C5	111.3(2)	O3	C16	C4	111.9(2)
C3	C4	C16	124.7(2)	O4	C16	C4	124.6(2)
C5	C4	C16	123.0(2)	O5	C17	O6	123.2(2)
C1	C5	C4	102.1(2)	O5	C17	C6	112.7(2)
C1	C5	C6	102.8(2)	O6	C17	C6	124.0(2)
C1	C5	C13	117.2(2)	O7	C18	O8	124.5(2)
C4	C5	C6	97.7(2)	O7	C18	C8	109.9(2)
C4	C5	C13	115.9(2)	O8	C18	C8	125.6(2)
C6	C5	C13	118.1(2)				
C5	C6	C7	111.0(2)	C5	C4	C6	41.0(1)
C5	C6	C17	127.8(2)	C4	C6	C5	41.3(1)

Table 199. Root-Mean-Square Amplitudes of Thermal Vibration (Å)
Sb-7 at **295 K**

Atom	Min.	Int'med.	Max.
O1	0.186	0.232	0.279
O2	0.198	0.250	0.305
O3	0.185	0.212	0.284
O4	0.203	0.231	0.359
O5	0.182	0.232	0.285
O6	0.207	0.241	0.328
O7	0.193	0.225	0.240
O8	0.196	0.239	0.278
C1	0.179	0.193	0.207
C2	0.187	0.198	0.222
C3	0.187	0.201	0.213
C4	0.194	0.198	0.229
C5	0.177	0.197	0.211
C6	0.186	0.199	0.218
C7	0.190	0.202	0.214
C8	0.193	0.203	0.230
C9	0.187	0.234	0.251
C10	0.194	0.261	0.285
C11	0.200	0.273	0.316
C12	0.200	0.253	0.291
C13	0.185	0.230	0.249
C15	0.199	0.204	0.228
C16	0.198	0.213	0.247
C17	0.199	0.205	0.237
C18	0.194	0.208	0.220
C19	0.187	0.292	0.314
C20	0.179	0.248	0.325
C21	0.183	0.277	0.339
C22	0.186	0.246	0.277



R = $COOCH_3$

1,5-Cycloheptano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-7)

Table 8–200. X-ray Crystal Data for Sb-7 at **308 K**

Formula	$C_{21}H_{24}O_8$
Formula weight	404.42
Melting point (°C)	99–100
Crystal size (mm)	0.16 x 0.20 x 0.80
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.135(1)
b (Å)	8.670(1)
c (Å)	20.796(1)
β (°)	91.96(1)
Cell volume ($Å^3$)	2006.55(0.47)
Z	4
d_{calc} (g cm^{-3})	1.339
μ(Cu $K\alpha$) (cm^{-1})	8.23
Maximum θ (°)	60
Unique reflections	2977
Observed reflections [$I > 3.0\sigma(I)$]	1965
Number of variables	262
R	0.042
R_w	0.054
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.15
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.15

Table 201. Final Atomic Parameters for Sb-7 at **308 K**

Atom	x	y	z	B(Å^2)
O1	0.4235(2)	0.4803(2)	0.6821(1)	4.74(5)
O2	0.4261(2)	0.7023(3)	0.7373(1)	5.49(5)
O3	0.9038(2)	0.5518(2)	0.64407(9)	4.58(5)
O4	0.9291(2)	0.7337(3)	0.5695(1)	6.49(6)
O5	0.7964(2)	0.9223(2)	0.45980(9)	4.85(5)
O6	0.7595(2)	0.6804(3)	0.4287(1)	6.05(5)
O7	0.3148(2)	0.6771(2)	0.50288(9)	4.14(4)
O8	0.2830(2)	0.7260(3)	0.6066(1)	4.95(5)
C1	0.5465(2)	0.8355(3)	0.6135(1)	3.29(6)
C2	0.5412(2)	0.6772(3)	0.6424(1)	3.53(6)
C3	0.6604(2)	0.6120(3)	0.6444(1)	3.46(6)
C4	0.7392(2)	0.7063(3)	0.6169(1)	3.68(6)
C5	0.6762(2)	0.8473(3)	0.5863(1)	3.32(6)
C6	0.6592(2)	0.7805(3)	0.5187(1)	3.52(6)
C7	0.5560(2)	0.7034(3)	0.5125(1)	3.51(6)
C8	0.4830(2)	0.7211(4)	0.5685(1)	3.94(7)
C9	0.4840(3)	0.9753(3)	0.6399(1)	4.27(7)
C10	0.5438(3)	1.0421(4)	0.7009(2)	5.35(8)
C11	0.6540(3)	1.1415(4)	0.6902(2)	6.15(9)
C12	0.7613(3)	1.0570(4)	0.6633(2)	5.45(8)
C13	0.7416(3)	1.0019(4)	0.5939(1)	4.28(7)
C15	0.4561(2)	0.6262(3)	0.6924(1)	3.83(6)
C16	0.8661(3)	0.6699(4)	0.6079(1)	4.20(7)
C17	0.7442(3)	0.7857(4)	0.4654(1)	3.99(7)
C18	0.3503(2)	0.7087(3)	0.5632(1)	3.73(6)
C19	0.3387(3)	0.4155(4)	0.7255(2)	6.32(9)
C20	1.0261(3)	0.5009(5)	0.6357(2)	5.69(8)
C21	0.8826(3)	0.9357(4)	0.4093(2)	6.48(9)
C22	0.1866(3)	0.6605(4)	0.4909(2)	4.83(7)
H3	0.682	0.510	0.664	3.8
H7	0.532	0.641	0.474	3.8
H9A	0.400	0.945	0.650	4.7
H9B	0.482	1.057	0.606	4.7
H10A	0.569	0.954	0.730	5.9
H10B	0.483	1.107	0.723	5.9
H11A	0.680	1.187	0.733	6.7
H11B	0.630	1.226	0.660	6.7
H12A	0.779	0.965	0.691	6.0
H12B	0.832	1.128	0.665	6.0
H13A	0.693	1.082	0.570	4.7
H13B	0.822	0.992	0.574	4.7
H19A	0.301	0.321	0.706	6.9
H19B	0.381	0.387	0.767	6.9
H19C	0.275	0.493	0.734	6.9
H20A	1.044	0.412	0.665	6.2
H20B	1.036	0.468	0.590	6.2
H20C	1.083	0.588	0.646	6.2
H21A	0.916	1.043	0.409	7.1
H21B	0.949	0.860	0.417	7.1
H21C	0.842	0.914	0.367	7.1
H22A	0.168	0.669	0.444	5.3
H22B	0.160	0.557	0.507	5.3
H22C	0.143	0.744	0.514	5.3

The parameters of the hydrogen atoms were not refined.

Table 202. Final Anisotropic Thermal Parameters (U's) for Sb-7 at **308 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.066(1)	0.050(1)	0.066(1)	-0.007(1)	0.024(1)	0.007(1)
O2	0.090(1)	0.066(1)	0.054(1)	-0.008(1)	0.023(1)	-0.007(1)
O3	0.046(1)	0.069(1)	0.060(1)	0.014(1)	0.0064(9)	0.018(1)
O4	0.051(1)	0.085(2)	0.111(2)	0.003(1)	0.017(1)	0.041(1)
O5	0.069(1)	0.051(1)	0.065(1)	-0.006(1)	0.024(1)	0.007(1)
O6	0.090(1)	0.064(1)	0.078(1)	-0.009(1)	0.036(1)	-0.015(1)
O7	0.044(1)	0.058(1)	0.055(1)	-0.006(1)	-0.0018(9)	0.000(1)
O8	0.045(1)	0.081(2)	0.062(1)	0.001(1)	0.009(1)	-0.002(1)
C1	0.044(1)	0.037(1)	0.044(1)	0.003(1)	0.003(1)	0.001(1)
C2	0.045(1)	0.043(2)	0.046(1)	0.001(1)	0.007(1)	0.004(1)
C3	0.046(2)	0.040(2)	0.046(1)	0.003(1)	0.003(1)	0.007(1)
C4	0.042(1)	0.041(2)	0.057(2)	0.001(1)	0.004(1)	0.007(1)
C5	0.040(1)	0.039(2)	0.047(1)	-0.003(1)	-0.000(1)	0.005(1)
C6	0.046(1)	0.041(2)	0.048(2)	0.001(1)	0.008(1)	0.003(1)
C7	0.048(1)	0.043(2)	0.042(1)	0.000(1)	0.004(1)	0.001(1)
C8	0.041(1)	0.056(2)	0.053(2)	-0.001(1)	0.002(1)	-0.008(2)
C9	0.059(2)	0.043(2)	0.061(2)	0.009(2)	0.007(1)	-0.001(2)
C10	0.084(2)	0.053(2)	0.066(2)	0.002(2)	0.007(2)	-0.014(2)
C11	0.108(3)	0.056(2)	0.069(2)	-0.010(2)	-0.003(2)	-0.015(2)
C12	0.079(2)	0.059(2)	0.069(2)	-0.018(2)	-0.007(2)	-0.004(2)
C13	0.061(2)	0.041(2)	0.061(2)	-0.012(1)	0.002(2)	0.006(2)
C15	0.048(2)	0.047(2)	0.051(2)	0.001(1)	0.005(1)	0.007(1)
C16	0.045(2)	0.053(2)	0.062(2)	-0.005(1)	0.003(1)	0.008(2)
C17	0.046(2)	0.048(2)	0.057(2)	0.002(1)	0.006(1)	0.007(2)
C18	0.043(1)	0.045(2)	0.053(2)	0.000(1)	0.004(1)	-0.000(1)
C19	0.084(2)	0.073(2)	0.085(2)	-0.018(2)	0.030(2)	0.014(2)
C20	0.048(2)	0.090(2)	0.079(2)	0.023(2)	0.009(2)	0.019(2)
C21	0.084(2)	0.075(2)	0.090(2)	-0.008(2)	0.048(2)	0.015(2)
C22	0.045(2)	0.064(2)	0.073(2)	-0.011(2)	-0.011(2)	0.005(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 203. Interatomic Distances (Å) for Sb-7 at **308 K**

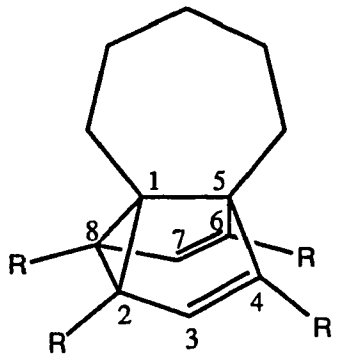
O1	C15	1.332(4)	C2	C8	1.691(4)
O1	C19	1.442(4)	C2	C15	1.497(4)
O2	C15	1.199(4)	C3	C4	1.342(4)
O3	C16	1.330(4)	C3	C7	3.048(4)
O3	C20	1.448(4)	C4	C5	1.537(4)
O4	C16	1.214(4)	C4	C6	2.291(4)
O5	C17	1.326(4)	C4	C16	1.465(4)
O5	C21	1.451(4)	C5	C6	1.526(4)
O6	C17	1.206(4)	C5	C13	1.531(4)
O7	C18	1.331(3)	C6	C7	1.332(4)
O7	C22	1.447(3)	C6	C17	1.484(4)
O8	C18	1.202(3)	C7	C8	1.450(4)
C1	C2	1.500(4)	C8	C18	1.482(4)
C1	C5	1.572(4)	C9	C10	1.527(4)
C1	C8	1.522(4)	C10	C11	1.522(5)
C1	C9	1.509(4)	C11	C12	1.524(5)
C2	C3	1.443(4)	C12	C13	1.530(5)

Table 204. Angles (°) for Sb-7 at **308 K**

C15	O1	C19	116.8(2)	C7	C6	C17	120.9(2)
C16	O3	C20	116.5(2)	C6	C7	C8	112.0(2)
C17	O5	C21	115.9(2)	C1	C8	C2	55.4(2)
C18	O7	C22	116.2(2)	C1	C8	C7	107.5(2)
C2	C1	C5	104.6(2)	C1	C8	C18	122.3(2)
C2	C1	C8	68.0(2)	C2	C8	C7	119.9(2)
C2	C1	C9	124.3(2)	C2	C8	C18	113.6(2)
C5	C1	C8	103.5(2)	C7	C8	C18	121.2(2)
C5	C1	C9	121.3(2)	C1	C9	C10	114.3(2)
C8	C1	C9	122.4(2)	C9	C10	C11	115.2(3)
C1	C2	C3	108.8(2)	C10	C11	C12	115.3(3)
C1	C2	C8	56.6(2)	C11	C12	C13	114.1(3)
C1	C2	C15	125.6(2)	C5	C13	C12	115.0(3)
C3	C2	C8	116.0(2)	O1	C15	O2	124.5(3)
C3	C2	C15	117.9(2)	O1	C15	C2	110.1(2)
C8	C2	C15	117.8(2)	O2	C15	C2	125.3(3)
C2	C3	C4	111.3(2)	O3	C16	O4	122.9(3)
C3	C4	C5	111.4(2)	O3	C16	C4	112.4(2)
C3	C4	C16	124.8(3)	O4	C16	C4	124.6(3)
C5	C4	C16	123.2(2)	O5	C17	O6	123.4(3)
C1	C5	C4	102.3(2)	O5	C17	C6	112.6(2)
C1	C5	C6	102.7(2)	O6	C17	C6	123.9(3)
C1	C5	C13	117.4(2)	O7	C18	O8	124.1(2)
C4	C5	C6	96.9(2)	O7	C18	C8	110.4(2)
C4	C5	C13	116.4(2)	O8	C18	C8	125.5(3)
C6	C5	C13	118.0(2)				
C5	C6	C7	111.0(2)	C5	C4	C6	41.4(1)
C5	C6	C17	128.0(2)	C4	C6	C5	41.7(1)

Table 205. Root-Mean-Square Amplitudes of Thermal Vibration (Å)
Sb-7 at **308 K**

Atom	Min.	Int'med.	Max.
O1	0.191	0.239	0.294
O2	0.209	0.252	0.319
O3	0.196	0.220	0.295
O4	0.212	0.243	0.378
O5	0.196	0.240	0.297
O6	0.215	0.250	0.348
O7	0.202	0.235	0.248
O8	0.206	0.254	0.285
C1	0.190	0.207	0.214
C2	0.197	0.207	0.229
C3	0.186	0.212	0.228
C4	0.196	0.204	0.245
C5	0.189	0.200	0.224
C6	0.196	0.204	0.232
C7	0.202	0.209	0.221
C8	0.201	0.216	0.250
C9	0.196	0.241	0.257
C10	0.210	0.273	0.292
C11	0.211	0.282	0.332
C12	0.213	0.265	0.303
C13	0.185	0.246	0.261
C15	0.202	0.217	0.240
C16	0.204	0.227	0.258
C17	0.210	0.213	0.249
C18	0.207	0.212	0.232
C19	0.199	0.299	0.334
C20	0.193	0.259	0.334
C21	0.184	0.286	0.361
C22	0.193	0.250	0.289



R = $COOCH_3$

1,5-Cycloheptano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-7)

Table 8–206. X-ray Crystal Data for Sb-7 at **315 K**

Formula	$C_{21}H_{24}O_8$
Formula weight	404.42
Melting point (°C)	99–100
Crystal size (mm)	0.16 x 0.20 x 0.80
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.131(1)
b (Å)	8.684(1)
c (Å)	20.820(1)
β (°)	92.25(1)
Cell volume ($Å^3$)	2010.95(0.31)
Z	4
d_{calc} (g cm^{-3})	1.336
μ(Cu $K\alpha$) (cm^{-1})	8.21
Maximum θ(°)	60
Unique reflections	2983
Observed reflections [$I > 3.0\sigma(I)$]	1904
Number of variables	262
R	0.045
R_w	0.055
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.20
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.20

Table 207. Final Atomic Parameters for Sb-7 at **315 K**

Atom	x	y	z	B(Å^2)
O1	0.4251(2)	0.4811(3)	0.6822(1)	5.05(5)
O2	0.4276(2)	0.7029(3)	0.7370(1)	5.79(6)
O3	0.9047(2)	0.5523(3)	0.6443(1)	4.84(5)
O4	0.9302(2)	0.7343(3)	0.5699(1)	6.96(7)
O5	0.7959(2)	0.9214(3)	0.4599(1)	5.16(5)
O6	0.7594(2)	0.6802(3)	0.4289(1)	6.49(6)
O7	0.3144(2)	0.6772(2)	0.5026(1)	4.39(5)
O8	0.2839(2)	0.7259(3)	0.6064(1)	5.27(6)
C1	0.5474(3)	0.8356(3)	0.6135(1)	3.50(6)
C2	0.5425(3)	0.6778(4)	0.6425(1)	3.78(7)
C3	0.6615(3)	0.6121(3)	0.6444(1)	3.65(6)
C4	0.7401(3)	0.7066(4)	0.6169(1)	3.96(7)
C5	0.6770(3)	0.8470(3)	0.5862(1)	3.59(6)
C6	0.6593(3)	0.7796(3)	0.5187(1)	3.75(6)
C7	0.5560(3)	0.7034(4)	0.5125(1)	3.71(7)
C8	0.4831(3)	0.7216(4)	0.5681(1)	4.16(7)
C9	0.4851(3)	0.9756(4)	0.6397(2)	4.61(7)
C10	0.5451(3)	1.0418(4)	0.7005(2)	5.71(9)
C11	0.6557(4)	1.1422(4)	0.6897(2)	6.4(1)
C12	0.7626(3)	1.0567(4)	0.6632(2)	5.68(9)
C13	0.7423(3)	1.0013(4)	0.5939(2)	4.54(7)
C15	0.4576(3)	0.6271(4)	0.6925(1)	4.06(7)
C16	0.8673(3)	0.6705(4)	0.6081(2)	4.41(7)
C17	0.7440(3)	0.7849(4)	0.4656(2)	4.28(7)
C18	0.3505(3)	0.7089(4)	0.5628(1)	3.98(7)
C19	0.3415(3)	0.4162(5)	0.7259(2)	6.55(9)
C20	1.0267(3)	0.5026(5)	0.6360(2)	6.05(9)
C21	0.8816(3)	0.9352(5)	0.4095(2)	6.71(9)
C22	0.1862(3)	0.6607(4)	0.4909(2)	5.13(8)
H3	0.683	0.510	0.664	4.0
H7	0.531	0.641	0.474	4.1
H9A	0.401	0.946	0.649	5.0
H9B	0.483	1.057	0.606	5.0
H10A	0.570	0.954	0.729	6.3
H10B	0.485	1.106	0.722	6.3
H11A	0.682	1.189	0.732	7.1
H11B	0.632	1.226	0.659	7.1
H12A	0.780	0.965	0.691	6.2
H12B	0.834	1.127	0.665	6.2
H13A	0.694	1.081	0.570	5.0
H13B	0.822	0.991	0.574	5.0
H19A	0.302	0.323	0.706	7.2
H19B	0.386	0.386	0.767	7.2
H19C	0.279	0.494	0.735	7.2
H20A	1.045	0.414	0.665	6.6
H20B	1.036	0.470	0.590	6.6
H20C	1.083	0.589	0.647	6.6
H21A	0.915	1.042	0.410	7.3
H21B	0.948	0.860	0.417	7.3
H21C	0.840	0.913	0.367	7.3
H22A	0.167	0.669	0.444	5.6
H22B	0.160	0.558	0.507	5.6
H22C	0.144	0.744	0.514	5.6

The parameters of the hydrogen atoms were not refined.

Table 208. Final Anisotropic Thermal Parameters (U's) for Sb-7 at **315 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.071(1)	0.052(1)	0.071(1)	-0.006(1)	0.025(1)	0.007(1)
O2	0.095(2)	0.070(2)	0.057(1)	-0.008(1)	0.024(1)	-0.008(1)
O3	0.048(1)	0.072(1)	0.064(1)	0.014(1)	0.006(1)	0.019(1)
O4	0.053(1)	0.092(2)	0.121(2)	0.004(1)	0.018(1)	0.044(2)
O5	0.074(1)	0.054(1)	0.070(1)	-0.004(1)	0.027(1)	0.008(1)
O6	0.098(2)	0.067(2)	0.084(1)	-0.011(1)	0.041(1)	-0.015(1)
O7	0.047(1)	0.060(1)	0.059(1)	-0.007(1)	-0.001(1)	0.001(1)
O8	0.050(1)	0.085(2)	0.066(1)	-0.000(1)	0.009(1)	-0.004(1)
C1	0.047(2)	0.040(2)	0.047(2)	0.003(1)	0.003(1)	0.001(1)
C2	0.048(2)	0.045(2)	0.051(2)	0.004(1)	0.009(1)	0.005(2)
C3	0.049(2)	0.043(2)	0.047(2)	0.001(1)	0.002(1)	0.006(1)
C4	0.047(2)	0.045(2)	0.059(2)	0.002(1)	0.006(1)	0.005(2)
C5	0.045(2)	0.041(2)	0.050(2)	-0.004(1)	0.001(1)	0.005(1)
C6	0.048(2)	0.043(2)	0.052(2)	0.003(1)	0.009(1)	0.002(2)
C7	0.049(2)	0.048(2)	0.044(2)	0.001(1)	0.006(1)	0.002(2)
C8	0.043(2)	0.058(2)	0.057(2)	0.001(2)	0.003(1)	-0.007(2)
C9	0.066(2)	0.046(2)	0.063(2)	0.011(2)	0.008(2)	0.000(2)
C10	0.092(2)	0.057(2)	0.069(2)	0.004(2)	0.010(2)	-0.015(2)
C11	0.115(3)	0.057(2)	0.072(2)	-0.007(2)	-0.003(2)	-0.016(2)
C12	0.084(2)	0.061(2)	0.070(2)	-0.019(2)	-0.009(2)	-0.006(2)
C13	0.065(2)	0.045(2)	0.063(2)	-0.012(2)	0.001(2)	0.008(2)
C15	0.051(2)	0.050(2)	0.053(2)	0.004(2)	0.004(1)	0.010(2)
C16	0.047(2)	0.056(2)	0.065(2)	-0.003(2)	0.005(2)	0.009(2)
C17	0.051(2)	0.051(2)	0.061(2)	-0.000(2)	0.009(1)	0.005(2)
C18	0.051(2)	0.045(2)	0.055(2)	-0.001(1)	0.005(1)	-0.002(2)
C19	0.085(2)	0.076(2)	0.090(2)	-0.019(2)	0.032(2)	0.015(2)
C20	0.051(2)	0.097(3)	0.082(2)	0.026(2)	0.009(2)	0.022(2)
C21	0.088(2)	0.077(2)	0.093(2)	-0.010(2)	0.048(2)	0.011(2)
C22	0.051(2)	0.068(2)	0.076(2)	-0.013(2)	-0.010(2)	0.006(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 209. Interatomic Distances (Å) for Sb-7 at **315 K**

O1	C15	1.333(4)	C2	C8	1.702(4)
O1	C19	1.442(4)	C2	C15	1.501(4)
O2	C15	1.195(4)	C3	C4	1.344(4)
O3	C16	1.330(4)	C3	C7	3.048(4)
O3	C20	1.442(4)	C4	C5	1.534(4)
O4	C16	1.214(4)	C4	C6	2.289(4)
O5	C17	1.326(4)	C4	C16	1.469(4)
O5	C21	1.450(4)	C5	C6	1.528(4)
O6	C17	1.205(4)	C5	C13	1.530(4)
O7	C18	1.330(4)	C6	C7	1.328(4)
O7	C22	1.445(4)	C6	C17	1.481(4)
O8	C18	1.204(4)	C7	C8	1.448(4)
C1	C2	1.498(4)	C8	C18	1.480(4)
C1	C5	1.574(4)	C9	C10	1.521(5)
C1	C8	1.526(4)	C10	C11	1.532(5)
C1	C9	1.512(4)	C11	C12	1.525(5)
C2	C3	1.441(4)	C12	C13	1.528(5)

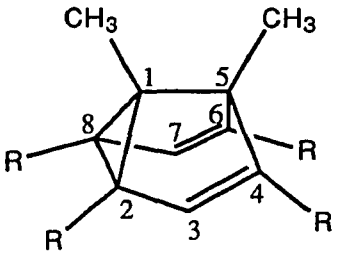
Table 210. Angles (°) for Sb-7 at **315 K**

C15	O1	C19	116.6(2)	C7	C6	C17	121.1(3)
C16	O3	C20	116.0(2)	C6	C7	C8	112.2(3)
C17	O5	C21	116.1(3)	C1	C8	C2	55.0(2)
C18	O7	C22	116.1(2)	C1	C8	C7	107.6(2)
C2	C1	C5	104.5(2)	C1	C8	C18	122.4(3)
C2	C1	C8	68.5(2)	C2	C8	C7	119.5(2)
C2	C1	C9	124.5(3)	C2	C8	C18	113.7(2)
C5	C1	C8	103.4(2)	C7	C8	C18	121.4(3)
C5	C1	C9	121.2(2)	C1	C9	C10	114.3(3)
C8	C1	C9	122.3(2)	C9	C10	C11	115.0(3)
C1	C2	C3	109.0(2)	C10	C11	C12	114.8(3)
C1	C2	C8	56.5(2)	C11	C12	C13	114.0(3)
C1	C2	C15	125.6(3)	C5	C13	C12	115.3(3)
C3	C2	C8	115.9(2)	O1	C15	O2	124.6(3)
C3	C2	C15	117.9(3)	O1	C15	C2	110.0(2)
C8	C2	C15	117.7(2)	O2	C15	C2	125.4(3)
C2	C3	C4	111.1(3)	O3	C16	O4	123.2(3)
C3	C4	C5	111.6(2)	O3	C16	C4	112.1(3)
C3	C4	C16	124.7(3)	O4	C16	C4	124.6(3)
C5	C4	C16	123.1(3)	O5	C17	O6	123.0(3)
C1	C5	C4	102.2(2)	O5	C17	C6	112.8(3)
C1	C5	C6	102.8(2)	O6	C17	C6	124.1(3)
C1	C5	C13	117.1(2)	O7	C18	O8	124.3(3)
C4	C5	C6	96.8(2)	O7	C18	C8	110.5(2)
C4	C5	C13	116.4(2)	O8	C18	C8	125.2(3)
C6	C5	C13	118.4(2)				
C5	C6	C7	111.1(2)	C5	C4	C6	41.5(1)
C5	C6	C17	127.7(2)	C4	C6	C5	41.7(1)

Table 211. Root-Mean-Square Amplitudes of Thermal Vibration (Å)
Sb-7 at **315 K**

Atom	Min.	Int'med.	Max.
O1	0.201	0.243	0.304
O2	0.216	0.259	0.326
O3	0.201	0.228	0.303
O4	0.217	0.251	0.393
O5	0.203	0.245	0.308
O6	0.224	0.253	0.364
O7	0.211	0.242	0.253
O8	0.217	0.261	0.292
C1	0.196	0.213	0.222
C2	0.206	0.206	0.243
C3	0.197	0.221	0.226
C4	0.207	0.214	0.248
C5	0.194	0.215	0.230
C6	0.203	0.209	0.240
C7	0.204	0.218	0.228
C8	0.206	0.225	0.255
C9	0.202	0.247	0.271
C10	0.213	0.280	0.306
C11	0.214	0.286	0.342
C12	0.213	0.271	0.312
C13	0.193	0.249	0.271
C15	0.203	0.224	0.251
C16	0.210	0.230	0.266
C17	0.214	0.227	0.256
C18	0.211	0.222	0.239
C19	0.202	0.304	0.340
C20	0.198	0.263	0.348
C21	0.196	0.288	0.366
C22	0.205	0.256	0.296

8.6 SB-ME$_2$



R = $COOCH_3$

1,5-Dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-Me$_2$)

Table 8–212. X-ray Crystal Data for Sb-Me$_2$ at **20 K**

Formula	$C_{18}H_{20}O_8$
Formula weight	364.36
Melting point (°C)	102-103
Crystal size (mm)	0.25 x 0.38 x 0.63
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.490(2)
b (Å)	10.749(4)
c (Å)	24.296(8)
Cell volume (Å^3)	1694.93
Z	4
d_{calc} (g cm^{-3})	1.428
μ(Mo $K\alpha$) (cm^{-1})	1.06
Maximum θ(°)	25
Unique reflections	2162
Observed reflections [$F > 6.0\sigma(F)$]	1753
Number of variables	235
R	0.036
R_w	0.043
$(\Delta\rho)_{max}$ (e Å^{-3})	0.3
$(\Delta\rho)_{min}$ (e Å^{-3})	

Table 213. Final Atomic Parameters for Sb-Me_2 at **20 K**

Atom	x	y	z	B(Å^2)
O1	0.2986(3)	0.9752(2)	0.3939(1)	1.11(7)
O2	0.1257(3)	0.8951(2)	0.3211(1)	1.33(7)
O3	0.3124(3)	0.4337(2)	0.4867(1)	1.07(7)
O4	0.0845(3)	0.4118(2)	0.4172(1)	1.14(7)
O5	0.7144(3)	0.3616(2)	0.3104(1)	1.03(7)
O6	0.5790(3)	0.3295(2)	0.3950(1)	1.11(7)
O7	0.7426(3)	0.8069(2)	0.2528(1)	1.00(7)
O8	0.6029(3)	0.9543(2)	0.3073(1)	1.17(7)
C1	0.5692(4)	0.7476(2)	0.3952(1)	0.91(9)
C2	0.3631(4)	0.7653(2)	0.3686(1)	0.97(9)
C3	0.2319(4)	0.6597(2)	0.3835(1)	0.96(9)
C4	0.3338(4)	0.5764(2)	0.4139(1)	1.00(9)
C5	0.5658(4)	0.6065(2)	0.4146(1)	0.89(9)
C6	0.6301(4)	0.5368(3)	0.3620(1)	1.06(9)
C7	0.6224(4)	0.6108(2)	0.3175(1)	0.92(9)
C8	0.5742(4)	0.7392(2)	0.3325(1)	0.91(9)
C9	0.6873(4)	0.8439(2)	0.4272(1)	1.05(9)
C10	0.6898(4)	0.5787(2)	0.4662(1)	1.03(9)
C11	0.2534(4)	0.8857(2)	0.3574(1)	1.06(9)
C12	0.2320(4)	0.4645(2)	0.4379(1)	0.96(9)
C13	0.6390(4)	0.3991(3)	0.3592(1)	0.96(9)
C14	0.6387(4)	0.8460(2)	0.2972(1)	0.91(9)
C15	0.2006(5)	1.0942(3)	0.3828(1)	1.48(10)
C16	0.2094(4)	0.3332(2)	0.5157(1)	1.34(10)
C17	0.7222(4)	0.2272(2)	0.3021(1)	1.26(9)
C18	0.8191(4)	0.9055(3)	0.2173(1)	1.16(9)
H3	0.085	0.650	0.372	0.25
H7	0.647	0.581	0.279	0.25
H9A	0.691	0.924	0.406	0.25
H9B	0.619	0.858	0.463	0.25
H9C	0.831	0.814	0.433	0.25
H10A	0.674	0.488	0.475	0.25
H10B	0.838	0.598	0.459	0.25
H10C	0.639	0.630	0.498	0.25
H15A	0.267	1.162	0.405	0.25
H15B	0.218	1.113	0.343	0.25
H15C	0.050	1.091	0.392	0.25
H16A	0.287	0.319	0.550	0.25
H16B	0.067	0.362	0.525	0.25
H16C	0.204	0.255	0.493	0.25
H17A	0.800	0.209	0.268	0.25
H17B	0.794	0.187	0.334	0.25
H17C	0.579	0.193	0.299	0.25
H18A	0.847	0.867	0.181	0.25
H18B	0.715	0.973	0.212	0.25
H18C	0.950	0.942	0.232	0.25

The parameters of the hydrogen atoms were not refined.

Table 214. Final Anisotrcpic Thermal Parameters (U's) for Sb-Me_2 at **20 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0117(7)	0.0133(6)	0.0176(6)	0.0034(6)	-0.0005(6)	-0.0004(6)
O2	0.0130(9)	0.0173(7)	0.0202(7)	0.0008(7)	-0.0047(7)	0.0007(7)
O3	0.0114(8)	0.0152(6)	0.0138(5)	-0.0032(6)	0.0007(6)	0.0020(5)
O4	0.0091(7)	0.0165(7)	0.0176(6)	-0.0021(7)	0.0007(6)	0.0002(6)
O5	0.0143(7)	0.0088(5)	0.0158(6)	0.0019(6)	0.0019(6)	-0.0004(5)
O6	0.0118(7)	0.0137(6)	0.0166(6)	-0.0003(6)	-0.0011(6)	0.0024(5)
O7	0.0105(7)	0.0131(6)	0.0144(5)	-0.0008(6)	0.0022(6)	0.0021(5)
O8	0.0120(9)	0.0128(6)	0.0196(6)	0.0002(7)	0.0012(7)	0.0011(6)
C1	0.0096(8)	0.0114(7)	0.0134(7)	0.0009(7)	0.0001(7)	0.0023(7)
C2	0.0087(9)	0.0120(8)	0.0161(7)	-0.0005(8)	0.0006(8)	-0.0013(7)
C3	0.0101(8)	0.0122(8)	0.0144(7)	-0.0012(8)	0.0018(8)	-0.0015(7)
C4	0.0098(9)	0.0149(8)	0.0135(7)	-0.0001(8)	0.0004(7)	-0.0004(7)
C5	0.0087(8)	0.0099(7)	0.0154(7)	-0.0008(8)	0.0005(7)	0.0007(6)
C6	0.0054(9)	0.0156(8)	0.0192(7)	-0.0020(8)	-0.0006(7)	-0.0018(7)
C7	0.0054(8)	0.0147(8)	0.0150(7)	-0.0019(7)	0.0013(7)	-0.0008(7)
C8	0.0067(9)	0.0137(8)	0.0142(7)	0.0003(8)	0.0003(7)	-0.0011(7)
C9	0.0120(1)	0.0122(8)	0.0157(8)	0.0000(9)	-0.0024(8)	-0.0005(7)
C10	0.010(1)	0.0145(9)	0.0146(8)	0.0001(8)	0.0005(8)	0.0013(7)
C11	0.0111(9)	0.0136(8)	0.0154(8)	-0.0014(8)	0.0044(8)	0.0019(7)
C12	0.0100(9)	0.0123(8)	0.0144(7)	0.0023(8)	0.0023(7)	-0.0010(7)
C13	0.0040(8)	0.0154(7)	0.0171(7)	0.0014(8)	-0.0037(7)	-0.0004(7)
C14	0.0066(9)	0.0144(8)	0.0136(7)	-0.0023(8)	-0.0021(8)	-0.0011(7)
C15	0.018(1)	0.0131(9)	0.026(1)	0.006(1)	-0.002(1)	-0.0017(9)
C16	0.017(1)	0.0166(9)	0.0176(8)	-0.0026(9)	0.0038(9)	0.0038(7)
C17	0.0146(1)	0.0100(8)	0.0231(9)	0.0014(9)	0.000(1)	-0.0024(7)
C18	0.0117(9)	0.0149(8)	0.0174(8)	-0.0015(9)	0.0010(8)	0.0030(7)

The form of the anisotropic displacement parameter is:
exp[-2PI2(h2a2U(1,1) + k2b2U(2,2) + l2c2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3))] where a,b, and c are reciprocal lattice constants.

Table 215. Interatomic Distances (Å) for Sb-Me_2 at **20 K**

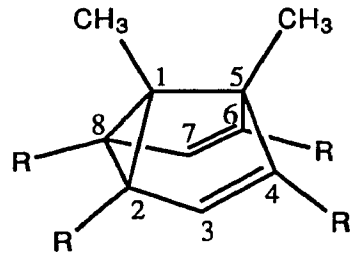
O1	C11	1.341(3)	C1	C9	1.504(4)
O1	C15	1.454(3)	C2	C3	1.464(4)
O2	C11	1.214(3)	C2	C8	1.651(3)
O3	C12	1.337(3)	C2	C11	1.502(4)
O3	C16	1.453(3)	C3	C4	1.336(4)
O4	C12	1.221(3)	C3	C7	3.045
O5	C13	1.345(3)	C4	C5	1.540(4)
O5	C17	1.460(3)	C4	C6	2.339(4)
O6	C13	1.212(3)	C4	C12	1.491(4)
O7	C14	1.340(3)	C5	C6	1.539(4)
O7	C18	1.454(3)	C5	C10	1.519(4)
O8	C14	1.212(3)	C6	C7	1.343(4)
C1	C2	1.498(4)	C6	C13	1.483(4)
C1	C5	1.588(4)	C7	C8	1.461(4)
C1	C8	1.526(3)	C8	C14	1.493(4)

Table 216. Angles (°) for Sb-Me_2 at **20 K**

C11	O1	C15	114.4(2)	C4	C5	C10	119.1(2)
C12	O3	C16	115.8(2)	C6	C5	C10	116.5(2)
C13	O5	C17	115.5(2)	C4	C6	C5	40.6(2)
C14	O7	C18	114.9(2)	C5	C6	C7	111.7(2)
C2	C1	C5	103.7(2)	C5	C6	C13	122.3(2)
C2	C1	C8	66.2(2)	C7	C6	C13	123.8(3)
C2	C1	C9	126.2(2)	C6	C7	C8	111.5(2)
C5	C1	C8	103.9(2)	C1	C8	C2	56.1(2)
C5	C1	C9	120.7(2)	C1	C8	C7	108.0(2)
C8	C1	C9	123.1(2)	C1	C8	C14	122.3(2)
C1	C2	C3	108.3(2)	C2	C8	C14	114.0(2)
C1	C2	C8	57.8(2)	C2	C8	C7	118.1(2)
C1	C2	C11	127.7(2)	C7	C8	C14	121.5(2)
C3	C2	C8	118.8(2)	O2	C11	C2	121.8(2)
C3	C2	C11	115.9(2)	O1	C11	C2	113.2(2)
C8	C2	C11	116.3(2)	O3	C12	O4	123.8(2)
C2	C3	C4	111.6(2)	O3	C12	C4	111.9(2)
C3	C4	C5	110.4(2)	O4	C12	C4	124.1(2)
C3	C4	C12	122.5(2)	O5	C13	O6	124.4(3)
C5	C4	C6	40.6(2)	O5	C13	C6	110.7(2)
C5	C4	C12	126.8(2)	O6	C13	C6	124.8(3)
C1	C5	C4	102.2(2)	O7	C14	O8	124.1(2)
C1	C5	C6	102.4(2)	O1	C11	O2	124.7(2)
C1	C5	C10	115.2(2)	O8	C14	C8	124.6(2)
C4	C5	C6	98.8(2)	O7	C14	C8	111.3(2)

Table 217. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-Me2 at **20 K**

Atom	Min.	Int'med.	Max.
O1	0.095	0.126	0.134
O2	0.103	0.132	0.150
O3	0.095	0.118	0.133
O4	0.092	0.131	0.133
O5	0.090	0.117	0.131
O6	0.107	0.112	0.135
O7	0.094	0.113	0.128
O8	0.109	0.112	0.141
C1	0.095	0.102	0.122
C2	0.093	0.108	0.129
C3	0.096	0.107	0.126
C4	0.099	0.116	0.123
C5	0.091	0.101	0.125
C6	0.070	0.124	0.141
C7	0.070	0.119	0.127
C8	0.082	0.113	0.123
C9	0.104	0.110	0.130
C10	0.099	0.115	0.126
C11	0.087	0.119	0.135
C12	0.088	0.117	0.124
C13	0.054	0.124	0.135
C14	0.073	0.118	0.124
C15	0.097	0.143	0.163
C16	0.101	0.139	0.147
C17	0.096	0.122	0.154
C18	0.102	0.119	0.139



R = $COOCH_3$

1,5-Dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-Me_2)

Table 8–218. X-ray Crystal Data for Sb-Me_2 at **115 K**

Formula	$C_{18}H_{20}O_8$
Formula weight	364.36
Melting point (°C)	102-103
Crystal size (mm)	0.23 x 0.25 x 0.37
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.510(2)
b (Å)	10.763(1)
c (Å)	24.331(3)
Cell volume (Å^3)	1704.75(0.69)
Z	4
d_{calc} (g cm^{-3})	1.420
μ(Cu $K\alpha$) (cm^{-1})	9.08
Maximum θ(°)	75
Unique reflections	2044
Observed reflections [$I > 3.0\sigma(I)$]	1938
Number of variables	235
R	0.035
R_w	0.049
$(\Delta\rho)_{max}$ (e Å^{-3})	0.26
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.20

Table 219. Final Atomic Parameters for Sb-Me_2 at **115 K**

Atom	x	y	z	B(A^2)
O1	0.2961(3)	0.9725(1)	0.39491(6)	1.94(3)
O2	0.1322(3)	0.8950(2)	0.32092(7)	2.61(3)
O3	0.3094(3)	0.4356(1)	0.48649(5)	1.76(3)
O4	0.0875(3)	0.4108(2)	0.41636(6)	1.96(3)
O5	0.7137(3)	0.3615(1)	0.31074(6)	1.68(2)
O6	0.5800(3)	0.3298(1)	0.39521(6)	1.79(3)
O7	0.7428(2)	0.8071(1)	0.25351(5)	1.52(2)
O8	0.6078(3)	0.9526(1)	0.30912(6)	2.17(3)
C1	0.5686(3)	0.7459(2)	0.39547(7)	1.28(3)
C2	0.3652(3)	0.7644(2)	0.36879(8)	1.58(3)
C3	0.2322(3)	0.6590(2)	0.38319(7)	1.41(3)
C4	0.3359(3)	0.5751(2)	0.41322(7)	1.39(3)
C5	0.5648(3)	0.6058(2)	0.41458(7)	1.24(3)
C6	0.6292(3)	0.5363(2)	0.36235(7)	1.43(3)
C7	0.6236(3)	0.6104(2)	0.31757(7)	1.32(3)
C8	0.5776(3)	0.7378(2)	0.33294(7)	1.38(3)
C9	0.6865(4)	0.8414(2)	0.42797(8)	1.66(3)
C10	0.6885(3)	0.5768(2)	0.46612(7)	1.62(3)
C11	0.2547(4)	0.8845(2)	0.35775(8)	1.68(3)
C12	0.2319(3)	0.4637(2)	0.43695(7)	1.47(3)
C13	0.6390(3)	0.3989(2)	0.35943(7)	1.39(3)
C14	0.6417(3)	0.8451(2)	0.29851(8)	1.47(3)
C15	0.1970(5)	1.0905(2)	0.3847(1)	2.83(4)
C16	0.2062(4)	0.3363(2)	0.51578(8)	2.11(4)
C17	0.7234(4)	0.2284(2)	0.30272(9)	1.99(4)
C18	0.8175(3)	0.9067(2)	0.21887(8)	1.79(3)
H3	0.085	0.651	0.372	1.7
H7	0.648	0.582	0.279	1.6
H9A	0.672	0.925	0.410	2.0
H9B	0.631	0.845	0.466	2.0
H9C	0.835	0.818	0.429	2.0
H10A	0.677	0.486	0.475	1.9
H10B	0.836	0.598	0.460	1.9
H10C	0.634	0.627	0.498	1.9
H15A	0.236	1.151	0.414	3.4
H15B	0.242	1.124	0.348	3.4
H15C	0.045	1.079	0.385	3.4
H16A	0.275	0.323	0.552	2.5
H16B	0.059	0.360	0.522	2.5
H16C	0.213	0.258	0.494	2.5
H17A	0.781	0.210	0.265	2.4
H17B	0.814	0.191	0.331	2.4
H17C	0.582	0.192	0.306	2.4
H18A	0.891	0.871	0.186	2.1
H18B	0.699	0.958	0.206	2.1
H18C	0.915	0.960	0.240	2.1

The parameters of the hydrogen atoms were not refined.

Table 220. Final Anisotropic Thermal Parameters (U's) for SB-Me_2 at **115 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0324(8)	0.0196(6)	0.0218(6)	0.0099(6)	-0.0010(6)	-0.0030(6)
O2	0.0403(9)	0.0255(7)	0.0333(7)	0.0059(7)	-0.0153(7)	0.0013(7)
O3	0.0328(8)	0.0194(6)	0.0147(5)	-0.0071(7)	0.0028(6)	0.0035(5)
O4	0.0270(7)	0.0241(7)	0.0235(6)	-0.0071(7)	0.0000(6)	0.0013(6)
O5	0.0332(7)	0.0105(5)	0.0201(6)	0.0003(6)	0.0029(6)	-0.0015(5)
O6	0.0315(7)	0.0161(6)	0.0205(6)	0.0006(6)	-0.0002(6)	0.0046(5)
O7	0.0263(7)	0.0159(6)	0.0155(5)	-0.0002(6)	0.0036(6)	0.0034(5)
O8	0.0431(9)	0.0127(6)	0.0267(6)	0.0010(7)	0.0096(7)	0.0017(6)
C1	0.0220(8)	0.0140(7)	0.0126(7)	-0.0005(7)	0.0002(7)	0.0004(7)
C2	0.0251(9)	0.0164(8)	0.0184(7)	0.0001(8)	-0.0010(8)	0.0007(7)
C3	0.0221(8)	0.0178(8)	0.0139(7)	-0.0008(8)	0.0025(8)	-0.0011(7)
C4	0.0215(9)	0.0167(8)	0.0145(7)	-0.0015(8)	0.0009(7)	-0.0002(7)
C5	0.0221(9)	0.0133(7)	0.0116(7)	-0.0007(8)	-0.0010(7)	0.0000(7)
C6	0.0253(9)	0.0137(8)	0.0155(7)	-0.0001(8)	-0.0010(7)	-0.0014(7)
C7	0.0214(8)	0.0137(8)	0.0150(7)	-0.0009(7)	0.0006(7)	0.0008(7)
C8	0.0250(9)	0.0146(8)	0.0129(7)	-0.0004(8)	0.0025(7)	0.0006(7)
C9	0.028(1)	0.0163(8)	0.0192(8)	-0.0013(9)	-0.0030(8)	-0.0040(7)
C10	0.028(1)	0.0192(9)	0.0146(8)	0.0005(8)	-0.0032(8)	0.0029(7)
C11	0.026(1)	0.0180(8)	0.0197(8)	0.0002(8)	0.0007(8)	0.0021(7)
C12	0.0234(9)	0.0166(8)	0.0159(7)	0.0007(8)	0.0037(8)	-0.0005(7)
C13	0.0220(8)	0.0151(7)	0.0157(7)	0.0008(8)	-0.0028(7)	0.0004(7)
C14	0.0241(9)	0.0150(8)	0.0167(7)	-0.0013(8)	-0.0002(8)	0.0020(7)
C15	0.047(1)	0.0233(9)	0.037(1)	0.017(1)	-0.004(1)	-0.0052(9)
C16	0.038(1)	0.0219(9)	0.0201(9)	-0.0099(9)	0.0047(9)	0.0058(7)
C17	0.036(1)	0.0110(8)	0.0284(9)	0.0046(9)	-0.002(1)	-0.0039(7)
C18	0.025(1)	0.0235(8)	0.0191(8)	-0.0019(9)	0.0030(8)	0.0099(7)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 221. Interatomic Distances (Å) for Sb-Me_2 at **115 K**

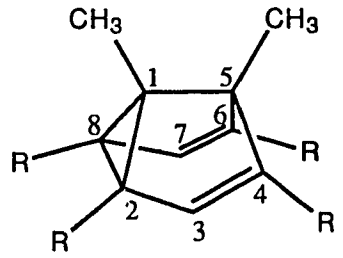
O1	C11	1.337(2)	C1	C9	1.507(3)
O1	C15	1.447(3)	C2	C3	1.469(3)
O2	C11	1.204(3)	C2	C8	1.660(3)
O3	C12	1.341(2)	C2	C11	1.504(3)
O3	C16	1.450(3)	C3	C4	1.344(3)
O4	C12	1.208(3)	C3	C7	3.052(3)
O5	C13	1.342(2)	C4	C5	1.526(3)
O5	C17	1.447(2)	C4	C6	2.313(3)
O6	C13	1.208(2)	C4	C12	1.494(3)
O7	C14	1.341(2)	C5	C6	1.533(3)
O7	C18	1.448(2)	C5	C10	1.523(3)
O8	C14	1.205(2)	C6	C7	1.351(3)
C1	C2	1.488(3)	C6	C13	1.482(3)
C1	C5	1.578(3)	C7	C8	1.452(3)
C1	C8	1.525(2)	C8	C14	1.487(3)

Table 222. Angles (°) for Sb-Me_2 at **115 K**

C11	O1	C15	114.6(2)	C4	C5	C10	119.3(2)
C12	O3	C16	115.7(2)	C6	C5	C10	116.0(2)
C13	O5	C17	115.5(2)	C4	C6	C5	40.8(1)
C14	O7	C18	114.4(1)	C5	C6	C7	111.9(2)
C2	C1	C5	104.0(2)	C5	C6	C13	122.6(2)
C2	C1	C8	66.8(1)	C7	C6	C13	123.5(2)
C2	C1	C9	126.2(2)	C6	C7	C8	110.8(2)
C5	C1	C8	103.9(1)	C1	C8	C2	55.5(1)
C5	C1	C9	120.3(2)	C1	C8	C7	108.6(2)
C8	C1	C9	122.9(2)	C1	C8	C14	121.9(2)
C1	C2	C3	108.5(2)	C2	C8	C7	118.1(2)
C1	C2	C8	57.6(1)	C2	C8	C14	113.3(2)
C1	C2	C11	128.2(2)	C7	C8	C14	122.0(2)
C3	C2	C8	118.9(2)	O1	C11	O2	124.8(2)
C3	C2	C11	115.1(2)	O1	C11	C2	113.0(2)
C8	C2	C11	117.0(2)	O2	C11	C2	122.0(2)
C2	C3	C4	110.6(2)	O3	C12	O4	124.0(2)
C3	C4	C5	110.9(2)	O3	C12	C4	111.0(2)
C3	C4	C12	121.5(2)	O4	C12	C4	124.8(2)
C5	C4	C12	127.4(2)	O5	C13	O6	124.5(2)
C5	C4	C6	41.0(1)	O5	C13	C6	110.9(2)
C1	C5	C4	102.4(2)	O6	C13	C6	124.5(2)
C1	C5	C6	102.6(1)	O7	C14	O8	123.9(2)
C1	C5	C10	115.5(2)	O7	C14	C8	111.1(2)
C4	C5	C6	98.3(1)	O8	C14	C8	125.0(2)

Table 223. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for $Sb-Me_2$ at **115 K**

Atom	Min.	Int'med.	Max.
O1	0.117	0.148	0.195
O2	0.134	0.167	0.230
O3	0.105	0.141	0.190
O4	0.135	0.154	0.181
O5	0.101	0.141	0.184
O6	0.115	0.153	0.178
O7	0.108	0.136	0.166
O8	0.112	0.150	0.218
C1	0.112	0.119	0.148
C2	0.127	0.136	0.159
C3	0.114	0.133	0.152
C4	0.120	0.128	0.148
C5	0.107	0.115	0.149
C6	0.114	0.127	0.159
C7	0.115	0.124	0.147
C8	0.111	0.122	0.160
C9	0.114	0.147	0.169
C10	0.112	0.143	0.169
C11	0.129	0.145	0.163
C12	0.119	0.130	0.158
C13	0.119	0.124	0.152
C14	0.117	0.134	0.156
C15	0.119	0.189	0.240
C16	0.106	0.161	0.208
C17	0.098	0.169	0.194
C18	0.101	0.162	0.177



R = $COOCH_3$

1,5-Dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-Me_2)

Table 8–224. X-ray Crystal Data for Sb-Me_2 at **127 K**

Formula	$C_{18}H_{20}O_8$
Formula weight	364.36
Melting point (°C)	102-103
Crystal size (mm)	0.23 x 0.25 x 0.37
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.514(2)
b (Å)	10.767(1)
c (Å)	24.346(2)
Cell volume (Å^3)	1707.46(0.54)
Z	4
d_{calc} (g cm^{-3})	1.417
μ(Cu $K\alpha$) (cm^{-1})	9.07
Maximum θ(°)	75
Unique reflections	2045
Observed reflections [$I > 3.0\sigma(I)$]	1899
Number of variables	235
R	0.037
R_w	0.048
$(\Delta\rho)_{max}$ (e Å^{-3})	0.28
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.24

Table 225. Final Atomic Parameters for Sb-Me_2 at **127 K**

Atom	x	y	z	B(A^2)
O1	0.2955(3)	0.9718(2)	0.39516(6)	2.20(3)
O2	0.1336(3)	0.8951(2)	0.32097(8)	3.00(4)
O3	0.3084(3)	0.4360(2)	0.48631(6)	1.99(3)
O4	0.0879(3)	0.4104(2)	0.41606(7)	2.26(3)
O5	0.7132(3)	0.3617(1)	0.31096(6)	1.89(3)
O6	0.5806(3)	0.3297(1)	0.39525(6)	2.03(3)
O7	0.7430(3)	0.8070(1)	0.25380(6)	1.69(3)
O8	0.6090(3)	0.9522(2)	0.30968(7)	2.52(3)
C1	0.5685(4)	0.7459(2)	0.39566(8)	1.45(3)
C2	0.3652(4)	0.7642(2)	0.36906(9)	1.76(4)
C3	0.2323(4)	0.6588(2)	0.38328(8)	1.58(3)
C4	0.3359(4)	0.5746(2)	0.41304(8)	1.60(4)
C5	0.5642(4)	0.6055(2)	0.41469(8)	1.43(3)
C6	0.6292(4)	0.5361(2)	0.36238(8)	1.68(4)
C7	0.6239(4)	0.6103(2)	0.31780(8)	1.46(3)
C8	0.5788(4)	0.7373(2)	0.33325(8)	1.61(4)
C9	0.6861(4)	0.8409(2)	0.42807(9)	1.87(4)
C10	0.6880(4)	0.5764(2)	0.46613(8)	1.82(4)
C11	0.2549(4)	0.8842(2)	0.35788(9)	1.90(4)
C12	0.2316(4)	0.4637(2)	0.43670(8)	1.63(4)
C13	0.6386(4)	0.3991(2)	0.35955(8)	1.56(3)
C14	0.6434(4)	0.8450(2)	0.29869(9)	1.70(4)
C15	0.1968(5)	1.0901(3)	0.3852(1)	3.26(5)
C16	0.2050(5)	0.3370(2)	0.5156(1)	2.44(4)
C17	0.7230(5)	0.2286(2)	0.3030(1)	2.29(4)
C18	0.8175(4)	0.9068(2)	0.21917(9)	2.03(4)
H3	0.085	0.651	0.372	1.7
H7	0.648	0.582	0.279	1.6
H9A	0.672	0.924	0.410	2.1
H9B	0.630	0.845	0.466	2.1
H9C	0.834	0.817	0.429	2.1
H10A	0.676	0.486	0.475	2.0
H10B	0.835	0.598	0.460	2.0
H10C	0.634	0.626	0.498	2.0
H15A	0.235	1.150	0.415	3.6
H15B	0.242	1.123	0.349	3.6
H15C	0.044	1.079	0.385	3.6
H16A	0.274	0.324	0.552	2.7
H16B	0.058	0.360	0.522	2.7
H16C	0.212	0.259	0.494	2.7
H17A	0.780	0.210	0.266	2.5
H17B	0.814	0.191	0.332	2.5
H17C	0.582	0.193	0.306	2.5
H18A	0.890	0.871	0.187	2.2
H18B	0.699	0.958	0.206	2.2
H18C	0.915	0.960	0.241	2.2

The parameters of the hydrogen atoms were not refined.

Table 226. Final Anisotropic Thermal Parameters (U's) for Sb-Me_2 at **127 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0370(9)	0.0236(7)	0.0230(7)	0.0110(7)	-0.0014(7)	-0.0027(6)
O2	0.046(1)	0.0296(8)	0.0382(9)	0.0076(9)	-0.0183(9)	0.0005(8)
O3	0.0367(9)	0.0231(7)	0.0157(6)	-0.0077(7)	0.0041(7)	0.0038(6)
O4	0.0303(8)	0.0289(8)	0.0266(7)	-0.0087(8)	-0.0003(7)	0.0022(7)
O5	0.0372(9)	0.0128(6)	0.0219(7)	0.0005(7)	0.0026(7)	-0.0014(6)
O6	0.0363(9)	0.0183(7)	0.0225(7)	0.0011(7)	-0.0001(7)	0.0052(6)
O7	0.0290(8)	0.0183(6)	0.0170(6)	-0.0011(7)	0.0039(6)	0.0030(6)
O8	0.049(1)	0.0161(7)	0.0306(8)	0.0009(8)	0.0110(8)	0.0025(6)
C1	0.024(1)	0.0164(8)	0.0143(8)	-0.0003(8)	0.0020(8)	0.0008(8)
C2	0.027(1)	0.0185(9)	0.0209(9)	0.0005(9)	-0.0021(9)	0.0015(8)
C3	0.024(1)	0.0211(9)	0.0145(8)	-0.0010(9)	0.0021(9)	-0.0003(7)
C4	0.025(1)	0.0198(9)	0.0160(8)	-0.0012(9)	0.0020(8)	-0.0001(8)
C5	0.026(1)	0.0148(8)	0.0137(8)	0.0007(9)	-0.0006(8)	0.0011(7)
C6	0.031(1)	0.0161(9)	0.0165(8)	0.0008(9)	-0.0016(9)	-0.0019(7)
C7	0.023(1)	0.0153(8)	0.0169(8)	0.0002(8)	0.0006(8)	-0.0003(8)
C8	0.030(1)	0.0172(9)	0.0142(8)	-0.0010(9)	0.0034(8)	-0.0000(8)
C9	0.029(1)	0.0206(9)	0.0214(9)	-0.002(1)	-0.003(1)	-0.0048(8)
C10	0.032(1)	0.021(1)	0.0161(8)	0.001(1)	-0.0033(9)	0.0030(8)
C11	0.029(1)	0.021(1)	0.0220(9)	0.001(1)	-0.0005(9)	0.0032(8)
C12	0.025(1)	0.0199(9)	0.0167(8)	0.0003(9)	0.0036(8)	0.0006(8)
C13	0.025(1)	0.0176(8)	0.0173(8)	0.0014(9)	-0.0040(8)	-0.0001(8)
C14	0.028(1)	0.0173(9)	0.0188(8)	-0.0015(9)	0.0001(9)	0.0022(8)
C15	0.053(2)	0.028(1)	0.043(1)	0.019(1)	-0.003(1)	-0.006(1)
C16	0.043(1)	0.026(1)	0.023(1)	-0.010(1)	0.007(1)	0.0058(9)
C17	0.044(1)	0.0129(9)	0.031(1)	0.006(1)	-0.001(1)	-0.0043(8)
C18	0.028(1)	0.027(1)	0.0223(9)	-0.001(1)	0.004(1)	0.0106(9)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 227. Interatomic Distances (Å) for Sb-Me_2 at **127 K**

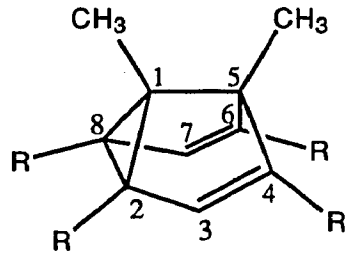
O1	C11	1.336(3)	C1	C9	1.502(3)
O1	C15	1.447(3)	C2	C3	1.468(3)
O2	C11	1.202(3)	C2	C8	1.667(3)
O3	C12	1.341(3)	C2	C11	1.503(3)
O3	C16	1.449(3)	C3	C4	1.342(3)
O4	C12	1.207(3)	C3	C7	3.053(3)
O5	C13	1.340(3)	C4	C5	1.524(3)
O5	C17	1.449(3)	C4	C6	2.312(3)
O6	C13	1.207(3)	C4	C12	1.490(3)
O7	C14	1.335(3)	C5	C6	1.536(3)
O7	C18	1.449(3)	C5	C10	1.522(3)
O8	C14	1.206(3)	C6	C7	1.349(3)
C1	C2	1.487(3)	C6	C13	1.478(3)
C1	C5	1.582(3)	C7	C8	1.448(3)
C1	C8	1.524(3)	C8	C14	1.493(3)

Table 228. Angles (°) for Sb-Me_2 at **127 K**

C11	O1	C15	114.8(2)	C4	C5	C10	119.6(2)
C12	O3	C16	115.7(2)	C6	C5	C10	115.8(2)
C13	O5	C17	115.6(2)	C4	C6	C5	40.7(1)
C14	O7	C18	114.3(2)	C5	C6	C7	111.8(2)
C2	C1	C5	103.8(2)	C5	C6	C13	122.4(2)
C2	C1	C8	67.2(2)	C7	C6	C13	123.7(2)
C2	C1	C9	126.4(2)	C6	C7	C8	110.9(2)
C5	C1	C8	103.6(2)	C1	C8	C2	55.3(1)
C5	C1	C9	120.4(2)	C1	C8	C7	109.0(2)
C8	C1	C9	122.9(2)	C1	C8	C14	121.8(2)
C1	C2	C3	108.7(2)	C2	C8	C7	117.9(2)
C1	C2	C8	57.4(1)	C2	C8	C14	113.3(2)
C1	C2	C11	128.2(2)	C7	C8	C14	122.0(2)
C3	C2	C8	118.8(2)	O1	C11	O2	124.7(2)
C3	C2	C11	115.1(2)	O1	C11	C2	112.9(2)
C8	C2	C11	116.9(2)	O2	C11	C2	122.2(2)
C2	C3	C4	110.6(2)	O3	C12	O4	123.9(2)
C3	C4	C5	110.9(2)	O3	C12	C4	110.9(2)
C3	C4	C12	121.4(2)	O4	C12	C4	125.0(2)
C5	C4	C6	41.1(1)	O5	C13	O6	124.3(2)
C5	C4	C12	127.5(2)	O5	C13	C6	110.8(2)
C1	C5	C4	102.6(2)	O6	C13	C6	124.8(2)
C1	C5	C6	102.5(2)	O7	C14	O8	124.4(2)
C1	C5	C10	115.4(2)	O7	C14	C8	111.1(2)
C4	C5	C6	98.1(2)	O8	C14	C8	124.5(2)

Table 229. Root-Mean-Square Amplitudes of Thermal Vibration (Å)
$Sb-Me_2$ at **127 K**

Atom	Min.	Int'med.	Max.
O1	0.130	0.152	0.209
O2	0.142	0.178	0.249
O3	0.110	0.152	0.201
O4	0.143	0.163	0.196
O5	0.112	0.147	0.194
O6	0.121	0.161	0.191
O7	0.117	0.143	0.174
O8	0.125	0.161	0.233
C1	0.117	0.129	0.157
C2	0.133	0.146	0.167
C3	0.118	0.144	0.158
C4	0.125	0.140	0.161
C5	0.114	0.124	0.160
C6	0.120	0.134	0.177
C7	0.123	0.130	0.153
C8	0.116	0.131	0.174
C9	0.124	0.160	0.174
C10	0.119	0.151	0.180
C11	0.135	0.158	0.170
C12	0.124	0.141	0.163
C13	0.124	0.132	0.163
C14	0.125	0.142	0.169
C15	0.130	0.205	0.255
C16	0.118	0.173	0.221
C17	0.105	0.177	0.212
C18	0.115	0.167	0.190



R = $COOCH_3$

1,5-Dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-Me_2)

Table 8–230. X-ray Crystal Data for Sb-Me_2 at **153 K**

Formula	$C_{18}H_{20}O_8$
Formula weight	364.36
Melting point (°C)	102-103
Crystal size (mm)	0.23 x 0.25 x 0.37
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.524(2)
b (Å)	10.779(1)
c (Å)	24.393(2)
Cell volume ($Å^3$)	1715.50(0.45)
Z	4
d_{calc} (g cm^{-3})	1.411
μ(Cu $K\alpha$) (cm^{-1})	9.03
Maximum θ (°)	75
Unique reflections	2068
Observed reflections [$I > 3.0\sigma(I)$]	1878
Number of variables	235
R	0.037
R_w	0.049
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.23
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.24

Table 231. Final Atomic Parameters for Sb-Me_2 at **153 K**

Atom	x	y	z	B(A^2)
O1	0.2945(3)	0.9712(2)	0.39547(7)	2.64(3)
O2	0.1361(4)	0.8950(2)	0.32105(9)	3.76(4)
O3	0.3060(3)	0.4367(2)	0.48597(6)	2.38(3)
O4	0.0894(3)	0.4102(2)	0.41530(7)	2.74(3)
O5	0.7122(3)	0.3619(1)	0.31128(6)	2.24(3)
O6	0.5812(3)	0.3297(2)	0.39558(7)	2.42(3)
O7	0.7439(3)	0.8072(2)	0.25429(6)	2.00(3)
O8	0.6116(4)	0.9515(2)	0.31048(7)	2.97(4)
C1	0.5676(4)	0.7454(2)	0.39581(8)	1.64(3)
C2	0.3656(4)	0.7640(2)	0.3693(1)	2.18(4)
C3	0.2329(4)	0.6588(2)	0.38325(8)	1.85(4)
C4	0.3363(4)	0.5741(2)	0.41255(9)	1.91(4)
C5	0.5637(4)	0.6051(2)	0.41475(8)	1.62(4)
C6	0.6278(4)	0.5357(2)	0.36258(9)	2.03(4)
C7	0.6239(4)	0.6103(2)	0.31822(9)	1.70(4)
C8	0.5801(4)	0.7369(2)	0.33361(8)	1.95(4)
C9	0.6850(4)	0.8402(2)	0.4283(1)	2.23(4)
C10	0.6871(4)	0.5757(2)	0.46606(9)	2.17(4)
C11	0.2553(4)	0.8841(2)	0.3581(1)	2.29(4)
C12	0.2316(4)	0.4635(2)	0.43624(9)	1.92(4)
C13	0.6380(4)	0.3989(2)	0.35984(9)	1.83(4)
C14	0.6450(4)	0.8447(2)	0.29925(9)	1.99(4)
C15	0.1959(6)	1.0893(3)	0.3856(1)	3.92(6)
C16	0.2029(5)	0.3381(2)	0.5153(1)	2.94(5)
C17	0.7235(5)	0.2291(2)	0.3033(1)	2.79(5)
C18	0.8179(4)	0.9069(2)	0.2198(1)	2.46(4)
H3	0.086	0.651	0.372	2.0
H7	0.648	0.582	0.280	1.9
H9A	0.671	0.923	0.411	2.4
H9B	0.629	0.844	0.466	2.4
H9C	0.833	0.816	0.430	2.4
H10A	0.675	0.485	0.475	2.4
H10B	0.834	0.597	0.460	2.4
H10C	0.633	0.625	0.498	2.4
H15A	0.233	1.149	0.415	4.3
H15B	0.242	1.123	0.349	4.3
H15C	0.044	1.078	0.385	4.3
H16A	0.270	0.326	0.552	3.2
H16B	0.056	0.361	0.521	3.2
H16C	0.211	0.260	0.494	3.2
H17A	0.780	0.211	0.266	3.1
H17B	0.815	0.192	0.332	3.1
H17C	0.583	0.193	0.306	3.1
H18A	0.890	0.871	0.187	2.7
H18B	0.700	0.959	0.207	2.7
H18C	0.916	0.960	0.241	2.7

The parameters of the hydrogen atoms were not refined.

Table 232. Final Anisotropic Thermal Parameters (U's) for Sb-Me_2 at **153 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.044(1)	0.0290(8)	0.0277(8)	0.0138(8)	-0.0010(8)	-0.0036(7)
O2	0.057(1)	0.037(1)	0.048(1)	0.010(1)	-0.024(1)	0.0001(9)
O3	0.043(1)	0.0285(7)	0.0194(6)	-0.0094(8)	0.0047(7)	0.0041(6)
O4	0.0363(9)	0.0358(9)	0.0321(8)	-0.0107(9)	-0.0010(8)	0.0036(8)
O5	0.043(1)	0.0163(6)	0.0259(7)	0.0006(8)	0.0039(8)	-0.0013(6)
O6	0.043(1)	0.0209(7)	0.0279(7)	0.0018(8)	0.0007(8)	0.0062(7)
O7	0.0325(8)	0.0228(7)	0.0208(6)	-0.0010(7)	0.0048(7)	0.0046(6)
O8	0.058(1)	0.0188(7)	0.0364(8)	0.0014(9)	0.0145(9)	0.0036(7)
C1	0.026(1)	0.0201(9)	0.0165(8)	-0.0005(9)	0.0011(9)	0.0000(8)
C2	0.032(1)	0.022(1)	0.029(1)	0.002(1)	-0.003(1)	0.0025(9)
C3	0.026(1)	0.026(1)	0.0182(8)	-0.0007(9)	0.0021(9)	-0.0000(8)
C4	0.028(1)	0.024(1)	0.0207(9)	-0.001(1)	0.0016(9)	0.0016(8)
C5	0.027(1)	0.0192(9)	0.0152(8)	-0.0003(9)	-0.0009(8)	0.0009(8)
C6	0.037(1)	0.0204(9)	0.0197(9)	0.002(1)	-0.003(1)	-0.0017(8)
C7	0.027(1)	0.0174(9)	0.0198(8)	-0.0002(9)	0.0015(9)	-0.0001(8)
C8	0.036(1)	0.0202(9)	0.0182(8)	-0.002(1)	0.0041(9)	0.0005(8)
C9	0.034(1)	0.024(1)	0.027(1)	-0.002(1)	-0.003(1)	-0.0060(9)
C10	0.037(1)	0.027(1)	0.0186(9)	0.001(1)	-0.004(1)	0.0041(8)
C11	0.034(1)	0.025(1)	0.028(1)	0.003(1)	-0.001(1)	0.0031(9)
C12	0.028(1)	0.024(1)	0.0212(9)	0.001(1)	0.0038(9)	0.0002(8)
C13	0.029(1)	0.0200(9)	0.0209(8)	0.0007(9)	-0.0039(9)	0.0009(8)
C14	0.033(1)	0.0199(9)	0.0228(9)	-0.002(1)	0.000(1)	0.0031(8)
C15	0.063(2)	0.035(1)	0.052(2)	0.025(1)	-0.004(2)	-0.006(1)
C16	0.052(2)	0.030(1)	0.029(1)	-0.013(1)	0.010(1)	0.008(1)
C17	0.051(2)	0.018(1)	0.038(1)	0.008(1)	-0.002(1)	-0.0042(9)
C18	0.032(1)	0.033(1)	0.028(1)	-0.001(1)	0.005(1)	0.0131(9)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 233. Interatomic Distances (Å) for Sb-Me_2 at **153 K**

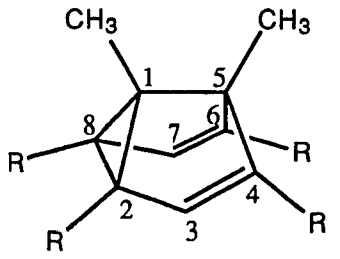
O1	C11	1.333(3)	C1	C9	1.503(3)
O1	C15	1.447(4)	C2	C3	1.466(3)
O2	C11	1.198(3)	C2	C8	1.674(4)
O3	C12	1.338(3)	C2	C11	1.506(3)
O3	C16	1.447(3)	C3	C4	1.342(3)
O4	C12	1.205(3)	C3	C7	3.049(3)
O5	C13	1.340(3)	C4	C5	1.521(4)
O5	C17	1.446(3)	C4	C6	2.296(4)
O6	C13	1.205(3)	C4	C12	1.491(3)
O7	C14	1.335(3)	C5	C6	1.534(3)
O7	C18	1.448(3)	C5	C10	1.522(3)
O8	C14	1.204(3)	C6	C7	1.349(3)
C1	C2	1.481(3)	C6	C13	1.478(3)
C1	C5	1.582(3)	C7	C8	1.443(3)
C1	C8	1.522(3)	C8	C14	1.494(3)

Table 234. Angles (°) for Sb-Me_2 at **153 K**

C11	O1	C15	114.9(2)	C4	C5	C10	120.0(2)
C12	O3	C16	115.9(2)	C6	C5	C10	115.9(2)
C13	O5	C17	115.5(2)	C4	C6	C5	41.1(1)
C14	O7	C18	114.5(2)	C5	C6	C7	111.7(2)
C2	C1	C5	104.0(2)	C5	C6	C13	122.4(2)
C2	C1	C8	67.8(2)	C7	C6	C13	124.0(2)
C2	C1	C9	126.2(2)	C6	C7	C8	111.0(2)
C5	C1	C8	103.6(2)	C1	C8	C2	55.0(1)
C5	C1	C9	120.3(2)	C1	C8	C7	109.1(2)
C8	C1	C9	122.6(2)	C1	C8	C14	121.8(2)
C1	C2	C3	108.7(2)	C2	C8	C7	117.7(2)
C1	C2	C8	57.3(1)	C2	C8	C14	113.2(2)
C1	C2	C11	128.3(2)	C7	C8	C14	122.2(2)
C3	C2	C8	118.7(2)	O1	C11	O2	124.8(2)
C3	C2	C11	115.1(2)	O1	C11	C2	112.9(2)
C8	C2	C11	117.0(2)	O2	C11	C2	122.1(2)
C2	C3	C4	110.6(2)	O3	C12	O4	124.1(2)
C3	C4	C5	111.1(2)	O3	C12	C4	111.0(2)
C3	C4	C12	121.4(2)	O4	C12	C4	124.8(2)
C5	C4	C6	41.5(1)	O5	C13	O6	124.5(2)
C5	C4	C12	127.5(2)	O5	C13	C6	110.7(2)
C1	C5	C4	102.4(2)	O6	C13	C6	124.8(2)
C1	C5	C6	102.7(2)	O7	C14	O8	124.3(2)
C1	C5	C10	115.5(2)	O7	C14	C8	111.3(2)
C4	C5	C6	97.5(2)	O8	C14	C8	124.4(2)

Table 235. Root-Mean-Square Amplitudes of Thermal Vibration (Å)
$Se-Me_2$ at **153 K**

Atom	Min.	Int'med.	Max.
O1	0.141	0.168	0.228
O2	0.157	0.198	0.280
O3	0.124	0.166	0.218
O4	0.157	0.179	0.218
O5	0.127	0.159	0.209
O6	0.131	0.177	0.208
O7	0.126	0.161	0.185
O8	0.134	0.172	0.256
C1	0.128	0.142	0.161
C2	0.143	0.169	0.184
C3	0.133	0.159	0.165
C4	0.140	0.156	0.169
C5	0.122	0.139	0.165
C6	0.135	0.146	0.194
C7	0.132	0.140	0.166
C8	0.131	0.142	0.192
C9	0.135	0.176	0.188
C10	0.127	0.169	0.194
C11	0.150	0.173	0.186
C12	0.140	0.154	0.173
C13	0.136	0.144	0.174
C14	0.133	0.157	0.183
C15	0.141	0.224	0.281
C16	0.121	0.194	0.243
C17	0.124	0.194	0.230
C18	0.126	0.181	0.211



R = $COOCH_3$

1,5-Dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-Me_2)

Table 8–236. X-ray Crystal Data for Sb-Me_2 at **181 K**

Formula	$C_{18}H_{20}O_8$
Formula weight	364.36
Melting point (°C)	102-103
Crystal size (mm)	0.23 x 0.25 x 0.37
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.540(1)
b (Å)	10.790(1)
c (Å)	24.442(2)
Cell volume ($Å^3$)	1724.72(0.34)
Z	4
d_{calc} (g cm^{-3})	1.403
μ(Cu $K\alpha$) (cm^{-1})	8.98
Maximum θ (°)	75
Unique reflections	2068
Observed reflections [$I > 3.0\sigma(I)$]	1878
Number of variables	235
R	0.037
R_w	0.049
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.23
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.24

Table 237. Final Atomic Parameters for Sb-Me_2 at **181 K**

Atom	x	y	z	B(A^2)
O1	0.2937(3)	0.9707(2)	0.39574(7)	3.02(3)
O2	0.1380(4)	0.8951(2)	0.32111(9)	4.49(5)
O3	0.3041(3)	0.4374(2)	0.48559(6)	2.72(3)
O4	0.0908(3)	0.4098(2)	0.41474(8)	3.21(4)
O5	0.7109(3)	0.3622(1)	0.31167(7)	2.52(3)
O6	0.5815(3)	0.3299(2)	0.39585(7)	2.74(3)
O7	0.7442(3)	0.8072(2)	0.25473(6)	2.25(3)
O8	0.6139(4)	0.9508(2)	0.31108(8)	3.46(4)
C1	0.5671(4)	0.7451(2)	0.39581(8)	1.81(4)
C2	0.3650(4)	0.7639(2)	0.3696(1)	2.48(4)
C3	0.2333(4)	0.6590(2)	0.38330(9)	2.05(4)
C4	0.3366(4)	0.5739(2)	0.41214(9)	2.15(4)
C5	0.5628(4)	0.6051(2)	0.41483(8)	1.79(4)
C6	0.6256(4)	0.5355(2)	0.36281(9)	2.27(4)
C7	0.6244(4)	0.6104(2)	0.31854(9)	1.91(4)
C8	0.5824(4)	0.7365(2)	0.33377(8)	2.14(4)
C9	0.6841(4)	0.8396(2)	0.4287(1)	2.51(4)
C10	0.6858(4)	0.5752(2)	0.46605(9)	2.40(4)
C11	0.2560(4)	0.8839(2)	0.3584(1)	2.65(5)
C12	0.2317(4)	0.4636(2)	0.43585(9)	2.21(4)
C13	0.6370(4)	0.3989(2)	0.36005(9)	2.08(4)
C14	0.6464(4)	0.8440(2)	0.29964(9)	2.26(4)
C15	0.1955(6)	1.0886(3)	0.3857(1)	4.53(7)
C16	0.2014(5)	0.3389(3)	0.5148(1)	3.32(5)
C17	0.7234(5)	0.2296(2)	0.3038(1)	3.12(5)
C18	0.8176(4)	0.9067(2)	0.2204(1)	2.75(4)
H3	0.086	0.652	0.373	2.2
H7	0.649	0.582	0.280	2.1
H9A	0.671	0.923	0.411	2.8
H9B	0.627	0.843	0.467	2.8
H9C	0.832	0.815	0.430	2.8
H10A	0.673	0.485	0.475	2.6
H10B	0.833	0.596	0.460	2.6
H10C	0.632	0.625	0.497	2.6
H15A	0.232	1.148	0.416	5.0
H15B	0.243	1.122	0.350	5.0
H15C	0.044	1.077	0.385	5.0
H16A	0.268	0.327	0.551	3.6
H16B	0.054	0.361	0.520	3.6
H16C	0.211	0.260	0.493	3.6
H17A	0.780	0.212	0.267	3.4
H17B	0.815	0.193	0.332	3.4
H17C	0.584	0.193	0.307	3.4
H18A	0.889	0.871	0.188	3.0
H18B	0.699	0.958	0.208	3.0
H18C	0.915	0.959	0.242	3.0

The parameters of the hydrogen atoms were not refined.

Table 238. Final Anisotropic Thermal Parameters (U's) for Sb-Me_2 at **181 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.049(1)	0.0340(8)	0.0320(8)	0.0167(8)	-0.0002(8)	-0.0045(7)
O2	0.068(1)	0.042(1)	0.060(1)	0.013(1)	-0.033(1)	0.000(1)
O3	0.048(1)	0.0322(8)	0.0232(7)	-0.0119(9)	0.0058(8)	0.0044(7)
O4	0.041(1)	0.0411(9)	0.0398(9)	-0.0150(9)	-0.0027(9)	0.0044(9)
O5	0.047(1)	0.0183(6)	0.0305(7)	0.0016(8)	0.0042(8)	-0.0017(6)
O6	0.048(1)	0.0232(7)	0.0326(8)	0.0021(8)	0.0025(9)	0.0069(7)
O7	0.0347(9)	0.0259(7)	0.0249(7)	-0.0020(7)	0.0051(7)	0.0059(6)
O8	0.066(1)	0.0216(7)	0.0435(9)	0.0017(9)	0.019(1)	0.0039(7)
C1	0.028(1)	0.0203(8)	0.0206(8)	0.0001(9)	0.0008(9)	0.0004(8)
C2	0.033(1)	0.024(1)	0.037(1)	0.001(1)	-0.006(1)	0.003(1)
C3	0.028(1)	0.028(1)	0.0217(9)	-0.001(1)	0.0019(9)	-0.0002(8)
C4	0.030(1)	0.027(1)	0.0247(9)	-0.002(1)	0.0024(9)	0.0012(8)
C5	0.028(1)	0.0212(9)	0.0184(8)	-0.0014(9)	-0.0003(8)	0.0014(8)
C6	0.042(1)	0.0214(9)	0.0233(9)	0.001(1)	-0.004(1)	-0.0010(8)
C7	0.030(1)	0.0204(9)	0.0223(9)	0.0001(9)	0.0007(9)	0.0009(8)
C8	0.039(1)	0.0211(9)	0.0208(9)	-0.002(1)	0.006(1)	0.0006(8)
C9	0.037(1)	0.027(1)	0.031(1)	-0.003(1)	-0.003(1)	-0.0067(9)
C10	0.037(1)	0.031(1)	0.0229(9)	-0.000(1)	-0.005(1)	0.0041(9)
C11	0.038(1)	0.030(1)	0.033(1)	0.003(1)	-0.002(1)	0.004(1)
C12	0.032(1)	0.025(1)	0.0268(9)	0.001(1)	0.004(1)	-0.0003(8)
C13	0.032(1)	0.0209(9)	0.0257(9)	0.0018(9)	-0.0035(9)	0.0008(8)
C14	0.036(1)	0.0218(9)	0.028(1)	-0.002(1)	0.001(1)	0.0045(9)
C15	0.070(2)	0.042(1)	0.060(2)	0.031(1)	-0.006(2)	-0.008(1)
C16	0.056(2)	0.035(1)	0.035(1)	-0.016(1)	0.012(1)	0.009(1)
C17	0.055(2)	0.0184(9)	0.045(1)	0.009(1)	-0.001(1)	-0.005(1)
C18	0.035(1)	0.038(1)	0.032(1)	-0.002(1)	0.005(1)	0.015(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 239. Interatomic Distances (Å) for Sb-Me_2 at **181 K**

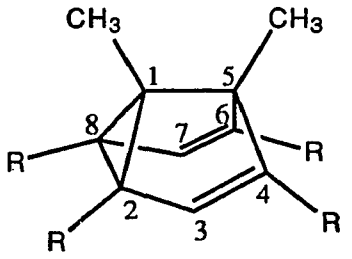
O1	C11	1.331(3)	C1	C9	1.507(3)
O1	C15	1.447(4)	C2	C3	1.462(3)
O2	C11	1.200(4)	C2	C8	1.696(4)
O3	C12	1.335(3)	C2	C11	1.504(4)
O3	C16	1.446(3)	C3	C4	1.340(3)
O4	C12	1.205(3)	C3	C7	3.053(3)
O5	C13	1.338(3)	C4	C5	1.519(3)
O5	C17	1.445(3)	C4	C6	2.279(4)
O6	C13	1.205(3)	C4	C12	1.491(3)
O7	C14	1.331(3)	C5	C6	1.533(3)
O7	C18	1.444(3)	C5	C10	1.522(3)
O8	C14	1.205(3)	C6	C7	1.351(3)
C1	C2	1.482(4)	C6	C13	1.477(3)
C1	C5	1.581(3)	C7	C8	1.437(3)
C1	C8	1.523(3)	C8	C14	1.489(3)

Table 240. Angles (°) for Sb-Me_2 at **181 K**

C11	O1	C15	114.8(2)	C4	C5	C10	120.2(2)
C12	O3	C16	116.2(2)	C6	C5	C10	115.9(2)
C13	O5	C17	115.6(2)	C4	C6	C5	41.4(1)
C14	O7	C18	114.7(2)	C5	C6	C7	111.7(2)
C2	C1	C5	104.0(2)	C5	C6	C13	122.7(2)
C2	C1	C8	68.7(2)	C7	C6	C13	124.1(2)
C2	C1	C9	126.2(2)	C6	C7	C8	111.1(2)
C5	C1	C8	103.7(2)	C1	C8	C2	54.5(1)
C5	C1	C9	119.9(2)	C1	C8	C7	109.2(2)
C8	C1	C9	122.6(2)	C1	C8	C14	121.9(2)
C1	C2	C3	108.7(2)	C2	C8	C7	117.3(2)
C1	C2	C8	56.8(1)	C2	C8	C14	112.9(2)
C1	C2	C11	128.3(2)	C7	C8	C14	122.6(2)
C3	C2	C8	118.5(2)	O1	C11	O2	124.7(2)
C3	C2	C11	115.4(2)	O1	C11	C2	113.1(2)
C8	C2	C11	116.9(2)	O2	C11	C2	122.0(2)
C2	C3	C4	110.7(2)	O3	C12	O4	124.0(2)
C3	C4	C5	111.2(2)	O3	C12	C4	111.1(2)
C3	C4	C12	121.3(2)	O4	C12	C4	124.8(2)
C5	C4	C6	41.9(1)	O5	C13	O6	124.5(2)
C5	C4	C12	127.5(2)	O5	C13	C6	110.8(2)
C1	C5	C4	102.5(2)	O6	C13	C6	124.7(2)
C1	C5	C6	102.7(2)	O7	C14	O8	124.1(2)
C1	C5	C10	115.8(2)	O7	C14	C8	111.4(2)
C4	C5	C6	96.7(2)	O8	C14	C8	124.4(2)

Table 241. Root-Mean-Square Amplitudes of Thermal Vibration (Å)
$Sb\text{-}Me_2$ at **181 K**

Atom	Min.	Int'med.	Max.
O1	0.148	0.182	0.245
O2	0.159	0.214	0.315
O3	0.133	0.176	0.234
O4	0.161	0.196	0.240
O5	0.134	0.173	0.219
O6	0.140	0.188	0.222
O7	0.134	0.175	0.192
O8	0.144	0.182	0.278
C1	0.142	0.144	0.167
C2	0.151	0.174	0.203
C3	0.146	0.165	0.171
C4	0.151	0.165	0.178
C5	0.133	0.147	0.169
C6	0.145	0.152	0.206
C7	0.142	0.150	0.173
C8	0.136	0.147	0.203
C9	0.145	0.189	0.197
C10	0.142	0.179	0.198
C11	0.160	0.189	0.199
C12	0.154	0.160	0.187
C13	0.142	0.157	0.184
C14	0.138	0.175	0.190
C15	0.148	0.239	0.305
C16	0.126	0.210	0.257
C17	0.126	0.213	0.239
C18	0.133	0.191	0.225



R = $COOCH_3$

1,5-Dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-Me_2)

Table 8–242. X-ray Crystal Data for Sb-Me_2 at **208 K**

Formula	$C_{18}H_{20}O_8$
Formula weight	364.36
Melting point (°C)	102-103
Crystal size (mm)	0.23 x 0.25 x 0.37
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.557(1)
b (Å)	10.801(1)
c (Å)	24.490(2)
Cell volume (Å^3)	1734.33(0.30)
Z	4
d_{calc} (g cm^{-3})	1.395
μ(Cu $K\alpha$) (cm^{-1})	8.93
Maximum θ(°)	75
Unique reflections	2079
Observed reflections	1848
[$I > 3.0\sigma(I)$]	
Number of variables	235
R	0.038
R_w	0.050
$(\Delta\rho)_{max}$ (e Å^{-3})	0.22
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.22

Table 243. Final Atomic Parameters for Sb-Me_2 at **208 K**

Atom	x	y	z	B($Å^2$)
O1	0.2936(3)	0.9703(2)	0.39574(7)	3.46(4)
O2	0.1403(4)	0.8949(2)	0.3212(1)	5.29(5)
O3	0.3018(3)	0.4383(2)	0.48513(7)	3.12(4)
O4	0.0921(3)	0.4094(2)	0.41416(8)	3.74(4)
O5	0.7097(3)	0.3624(2)	0.31208(7)	2.91(3)
O6	0.5823(4)	0.3299(2)	0.39613(7)	3.18(4)
O7	0.7445(3)	0.8072(2)	0.25526(6)	2.60(3)
O8	0.6159(4)	0.9502(2)	0.31176(8)	3.98(4)
C1	0.5664(4)	0.7450(2)	0.39598(9)	2.06(4)
C2	0.3646(4)	0.7638(2)	0.3700(1)	2.84(5)
C3	0.2341(4)	0.6592(2)	0.38322(9)	2.33(4)
C4	0.3371(4)	0.5736(2)	0.41172(9)	2.43(4)
C5	0.5619(4)	0.6050(2)	0.41490(9)	2.02(4)
C6	0.6234(5)	0.5354(2)	0.36300(9)	2.66(5)
C7	0.6241(4)	0.6104(2)	0.31888(9)	2.11(4)
C8	0.5844(5)	0.7361(2)	0.33403(9)	2.49(4)
C9	0.6823(5)	0.8393(2)	0.4287(1)	2.87(5)
C10	0.6844(4)	0.5748(2)	0.46601(9)	2.70(5)
C11	0.2569(5)	0.8839(2)	0.3585(1)	3.06(5)
C12	0.2318(4)	0.4635(2)	0.4354(1)	2.53(4)
C13	0.6364(4)	0.3990(2)	0.36042(9)	2.37(4)
C14	0.6480(4)	0.8437(2)	0.30014(9)	2.56(4)
C15	0.1958(6)	1.0882(3)	0.3858(2)	5.30(8)
C16	0.1993(6)	0.3398(3)	0.5144(1)	3.91(6)
C17	0.7236(5)	0.2300(2)	0.3042(1)	3.63(6)
C18	0.8176(5)	0.9068(3)	0.2210(1)	3.24(5)
H3	0.087	0.652	0.373	2.6
H7	0.649	0.582	0.281	2.3
H9A	0.669	0.922	0.411	3.2
H9B	0.625	0.843	0.467	3.2
H9C	0.829	0.815	0.430	3.2
H10A	0.672	0.485	0.474	3.0
H10B	0.831	0.596	0.460	3.0
H10C	0.631	0.624	0.497	3.0
H15A	0.232	1.147	0.416	5.8
H15B	0.243	1.122	0.350	5.8
H15C	0.045	1.077	0.385	5.8
H16A	0.264	0.329	0.551	4.3
H16B	0.052	0.362	0.519	4.3
H16C	0.211	0.261	0.493	4.3
H17A	0.780	0.212	0.267	4.0
H17B	0.816	0.194	0.333	4.0
H17C	0.585	0.192	0.308	4.0
H18A	0.888	0.871	0.188	3.6
H18B	0.700	0.959	0.209	3.6
H18C	0.916	0.959	0.242	3.6

The parameters of the hydrogen atoms were not refined.

Table 244. Final Anisotropic Thermal Parameters (U's) for Sb-Me_2 at **208 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.054(1)	0.0401(9)	0.0371(8)	0.0213(9)	0.0005(9)	-0.0039(8)
O2	0.078(1)	0.051(1)	0.072(1)	0.018(1)	-0.040(1)	-0.001(1)
O3	0.055(1)	0.0366(8)	0.0274(7)	-0.0135(9)	0.0072(8)	0.0047(7)
O4	0.047(1)	0.049(1)	0.046(1)	-0.019(1)	-0.003(1)	0.0048(9)
O5	0.054(1)	0.0210(7)	0.0360(8)	0.0012(8)	0.0050(9)	-0.0017(6)
O6	0.055(1)	0.0270(8)	0.0384(8)	0.0017(9)	0.003(1)	0.0082(7)
O7	0.0397(9)	0.0295(7)	0.0296(7)	-0.0008(8)	0.0065(8)	0.0068(7)
O8	0.075(1)	0.0239(8)	0.052(1)	0.001(1)	0.024(1)	0.0052(8)
C1	0.030(1)	0.0242(9)	0.0237(9)	0.000(1)	0.002(1)	0.0003(9)
C2	0.038(1)	0.027(1)	0.043(1)	0.001(1)	-0.008(1)	0.004(1)
C3	0.030(1)	0.033(1)	0.0259(9)	-0.003(1)	0.002(1)	-0.0007(9)
C4	0.032(1)	0.031(1)	0.029(1)	-0.002(1)	0.002(1)	0.0030(9)
C5	0.030(1)	0.0237(9)	0.0228(9)	-0.000(1)	-0.0004(9)	0.0022(8)
C6	0.049(1)	0.025(1)	0.027(1)	0.002(1)	-0.004(1)	-0.0012(9)
C7	0.032(1)	0.0219(9)	0.0258(9)	0.000(1)	0.0015(9)	0.0004(8)
C8	0.045(1)	0.023(1)	0.026(1)	-0.004(1)	0.004(1)	-0.0000(9)
C9	0.043(1)	0.029(1)	0.037(1)	-0.003(1)	-0.005(1)	-0.007(1)
C10	0.040(1)	0.035(1)	0.027(1)	0.001(1)	-0.004(1)	0.0051(9)
C11	0.044(1)	0.033(1)	0.040(1)	0.005(1)	-0.004(1)	0.004(1)
C12	0.036(1)	0.029(1)	0.032(1)	0.000(1)	0.007(1)	-0.0001(9)
C13	0.035(1)	0.0243(9)	0.030(1)	0.001(1)	-0.005(1)	0.0004(9)
C14	0.039(1)	0.025(1)	0.033(1)	-0.003(1)	0.001(1)	0.0053(9)
C15	0.083(2)	0.048(1)	0.071(2)	0.037(2)	-0.006(2)	-0.011(2)
C16	0.066(2)	0.039(1)	0.043(1)	-0.017(1)	0.015(1)	0.010(1)
C17	0.061(2)	0.022(1)	0.054(1)	0.011(1)	0.000(2)	-0.006(1)
C18	0.041(1)	0.043(1)	0.039(1)	-0.001(1)	0.006(1)	0.018(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 245. Interatomic Distances (Å) for Sb-Me_2 at **208 K**

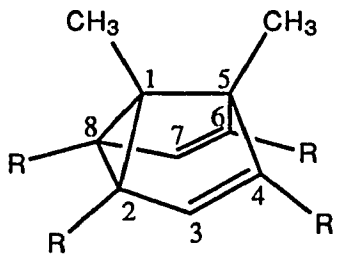
O1	C11	1.327(3)	C1	C9	1.503(3)
O1	C15	1.446(4)	C2	C3	1.454(4)
O2	C11	1.198(4)	C2	C8	1.715(4)
O3	C12	1.331(3)	C2	C11	1.504(4)
O3	C16	1.447(4)	C3	C4	1.341(3)
O4	C12	1.205(3)	C3	C7	3.049(3)
O5	C13	1.338(3)	C4	C5	1.515(4)
O5	C17	1.446(3)	C4	C6	2.263(4)
O6	C13	1.203(3)	C4	C12	1.491(4)
O7	C14	1.328(3)	C5	C6	1.531(3)
O7	C18	1.446(3)	C5	C10	1.522(3)
O8	C14	1.203(3)	C6	C7	1.351(3)
C1	C2	1.483(4)	C6	C13	1.477(3)
C1	C5	1.582(3)	C7	C8	1.431(3)
C1	C8	1.525(3)	C8	C14	1.487(3)

Table 246. Angles (°) for Sb-Me_2 at **208 K**

C11	O1	C15	115.0(2)	C4	C5	C10	120.5(2)
C12	O3	C16	116.4(2)	C6	C5	C10	116.0(2)
C13	O5	C17	115.6(2)	C4	C6	C5	41.8(1)
C14	O7	C18	114.7(2)	C5	C6	C7	111.7(2)
C2	C1	C5	103.9(2)	C5	C6	C13	122.7(2)
C2	C1	C8	69.5(2)	C7	C6	C13	124.3(2)
C2	C1	C9	126.0(2)	C6	C7	C8	111.2(2)
C5	C1	C8	103.4(2)	C1	C8	C2	54.1(2)
C5	C1	C9	120.1(2)	C1	C8	C7	109.4(2)
C8	C1	C9	122.4(2)	C1	C8	C14	121.8(2)
C1	C2	C3	108.9(2)	C2	C8	C7	116.8(2)
C1	C2	C8	56.4(2)	C2	C8	C14	112.7(2)
C1	C2	C11	128.1(2)	C7	C8	C14	123.0(2)
C3	C2	C8	118.3(2)	O1	C11	O2	124.8(3)
C3	C2	C11	115.8(2)	O1	C11	C2	113.1(2)
C8	C2	C11	116.7(2)	O2	C11	C2	121.9(2)
C2	C3	C4	110.9(2)	O3	C12	O4	123.9(2)
C3	C4	C5	111.2(2)	O3	C12	C4	111.1(2)
C3	C4	C12	121.3(2)	O4	C12	C4	124.9(2)
C5	C4	C6	42.3(1)	O5	C13	O6	124.4(2)
C5	C4	C12	127.5(2)	O5	C13	C6	110.7(2)
C1	C5	C4	102.6(2)	O6	C13	C6	124.8(2)
C1	C5	C6	102.8(2)	O7	C14	O8	124.2(2)
C1	C5	C10	115.8(2)	O7	C14	C8	111.3(2)
C4	C5	C6	95.9(2)	O8	C14	C8	124.4(2)

Table 247. Root-Mean-Square Amplitudes of Thermal Vibration (Å) $Sb\text{-}Me_2$ at **208 K**

Atom	Min.	Int'med.	Max.
O1	0.154	0.195	0.264
O2	0.166	0.234	0.344
O3	0.143	0.189	0.250
O4	0.169	0.212	0.262
O5	0.144	0.187	0.234
O6	0.151	0.204	0.237
O7	0.146	0.185	0.208
O8	0.151	0.196	0.300
C1	0.153	0.156	0.175
C2	0.159	0.183	0.221
C3	0.158	0.170	0.186
C4	0.161	0.182	0.182
C5	0.145	0.159	0.174
C6	0.156	0.163	0.224
C7	0.148	0.160	0.181
C8	0.150	0.160	0.216
C9	0.154	0.199	0.213
C10	0.153	0.194	0.204
C11	0.169	0.202	0.216
C12	0.164	0.170	0.201
C13	0.155	0.167	0.195
C14	0.148	0.188	0.200
C15	0.153	0.262	0.330
C16	0.140	0.227	0.278
C17	0.136	0.235	0.254
C18	0.145	0.205	0.245



R = $COOCH_3$

1,5-Dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-Me_2)

Table 8–248. X-ray Crystal Data for Sb-Me_2 at **236 K**

Formula	$C_{18}H_{20}O_8$
Formula weight	364.36
Melting point (°C)	102-103
Crystal size (mm)	0.23 x 0.25 x 0.37
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.577(1)
b (Å)	10.812(2)
c (Å)	24.539(1)
Cell volume ($Å^3$)	1744.79(0.25)
Z	4
d_{calc} (g cm^{-3})	1.387
μ(Cu $K\alpha$) (cm^{-1})	8.88
Maximum θ (°)	75
Unique reflections	2090
Observed reflections	1822
[$I > 3.0\sigma(I)$]	
Number of variables	235
R	0.039
R_w	0.051
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.21
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.24

Table 249. Final Atomic Parameters for Sb-Me_2 at **236 K**

Atom	x	y	z	B(A^2)
O1	0.2932(4)	0.9699(2)	0.39584(8)	3.93(4)
O2	0.1426(4)	0.8947(2)	0.3212(1)	6.21(6)
O3	0.3005(4)	0.4389(2)	0.48469(7)	3.54(4)
O4	0.0936(4)	0.4092(2)	0.41358(9)	4.34(4)
O5	0.7081(4)	0.3626(2)	0.31258(7)	3.30(4)
O6	0.5828(4)	0.3302(2)	0.39650(8)	3.66(4)
O7	0.7448(3)	0.8072(2)	0.25567(7)	2.94(3)
O8	0.6180(4)	0.9495(2)	0.31218(9)	4.68(5)
C1	0.5661(4)	0.7447(2)	0.39611(9)	2.27(4)
C2	0.3645(5)	0.7640(3)	0.3704(1)	3.34(5)
C3	0.2349(4)	0.6595(2)	0.38323(9)	2.62(4)
C4	0.3375(4)	0.5732(2)	0.4114(1)	2.76(5)
C5	0.5616(4)	0.6051(2)	0.41515(9)	2.29(4)
C6	0.6214(5)	0.5355(2)	0.3632(1)	2.93(5)
C7	0.6243(4)	0.6103(2)	0.31927(9)	2.39(4)
C8	0.5861(5)	0.7357(2)	0.3344(1)	2.82(5)
C9	0.6817(5)	0.8388(2)	0.4291(1)	3.30(5)
C10	0.6830(5)	0.5747(3)	0.4660(1)	3.13(5)
C11	0.2575(5)	0.8838(3)	0.3587(1)	3.44(5)
C12	0.2320(5)	0.4636(2)	0.4349(1)	2.86(5)
C13	0.6359(4)	0.3992(2)	0.3608(1)	2.72(4)
C14	0.6497(5)	0.8432(2)	0.3006(1)	2.94(5)
C15	0.1960(7)	1.0879(3)	0.3860(2)	5.97(9)
C16	0.1980(6)	0.3405(3)	0.5139(1)	4.55(7)
C17	0.7231(6)	0.2303(2)	0.3047(1)	4.13(6)
C18	0.8176(5)	0.9063(3)	0.2214(1)	3.69(5)
H3	0.089	0.653	0.373	2.9
H7	0.650	0.582	0.281	2.6
H9A	0.669	0.922	0.412	3.6
H9B	0.625	0.842	0.467	3.6
H9C	0.828	0.815	0.431	3.6
H10A	0.670	0.485	0.474	3.4
H10B	0.829	0.595	0.460	3.4
H10C	0.630	0.624	0.497	3.4
H15A	0.232	1.147	0.416	6.6
H15B	0.244	1.122	0.350	6.6
H15C	0.045	1.076	0.385	6.6
H16A	0.262	0.330	0.551	5.0
H16B	0.051	0.362	0.518	5.0
H16C	0.210	0.262	0.493	5.0
H17A	0.778	0.213	0.268	4.5
H17B	0.816	0.194	0.333	4.5
H17C	0.585	0.192	0.308	4.5
H18A	0.887	0.871	0.189	4.1
H18B	0.700	0.959	0.210	4.1
H18C	0.916	0.958	0.242	4.1

The parameters of the hydrogen atoms were not refined.

Table 250. Final Anisotropic Thermal Parameters (U's) for Sb-Me_2 at **236 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.061(1)	0.0449(9)	0.0437(9)	0.022(1)	0.001(1)	-0.0050(8)
O2	0.091(2)	0.061(1)	0.085(1)	0.023(1)	-0.048(1)	-0.001(1)
O3	0.061(1)	0.0416(9)	0.0320(8)	-0.016(1)	0.0090(9)	0.0052(8)
O4	0.053(1)	0.058(1)	0.054(1)	-0.023(1)	-0.004(1)	0.006(1)
O5	0.059(1)	0.0248(7)	0.0412(9)	0.0017(9)	0.006(1)	-0.0021(7)
O6	0.064(1)	0.0297(8)	0.0453(9)	0.003(1)	0.005(1)	0.0086(8)
O7	0.044(1)	0.0344(8)	0.0339(8)	-0.0007(9)	0.0067(9)	0.0078(7)
O8	0.090(2)	0.0271(8)	0.061(1)	0.003(1)	0.028(1)	0.0059(9)
C1	0.032(1)	0.0268(9)	0.0273(9)	0.000(1)	0.001(1)	0.0004(9)
C2	0.043(1)	0.033(1)	0.052(1)	0.002(1)	-0.011(1)	0.004(1)
C3	0.033(1)	0.037(1)	0.030(1)	-0.001(1)	0.001(1)	-0.000(1)
C4	0.037(1)	0.034(1)	0.034(1)	-0.004(1)	0.002(1)	0.003(1)
C5	0.036(1)	0.026(1)	0.0255(9)	0.000(1)	-0.001(1)	0.0008(9)
C6	0.053(2)	0.027(1)	0.030(1)	0.003(1)	-0.006(1)	-0.002(1)
C7	0.036(1)	0.026(1)	0.029(1)	0.000(1)	0.003(1)	0.0001(9)
C8	0.050(1)	0.027(1)	0.030(1)	-0.005(1)	0.005(1)	-0.0001(9)
C9	0.049(2)	0.034(1)	0.043(1)	-0.004(1)	-0.005(1)	-0.009(1)
C10	0.045(2)	0.042(1)	0.032(1)	0.000(1)	-0.005(1)	0.006(1)
C11	0.047(2)	0.037(1)	0.047(1)	0.008(1)	-0.002(1)	0.005(1)
C12	0.040(1)	0.033(1)	0.036(1)	-0.003(1)	0.008(1)	0.001(1)
C13	0.040(1)	0.027(1)	0.036(1)	0.002(1)	-0.004(1)	0.003(1)
C14	0.046(2)	0.028(1)	0.037(1)	-0.003(1)	0.002(1)	0.005(1)
C15	0.091(3)	0.054(2)	0.082(2)	0.039(2)	-0.003(2)	-0.008(2)
C16	0.077(2)	0.047(1)	0.049(1)	-0.019(2)	0.018(2)	0.011(1)
C17	0.071(2)	0.026(1)	0.060(2)	0.013(1)	0.001(2)	-0.007(1)
C18	0.046(2)	0.050(1)	0.044(1)	-0.001(1)	0.008(1)	0.021(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 251. Interatomic istances (Å) for Sb-Me_2 at **236 K**

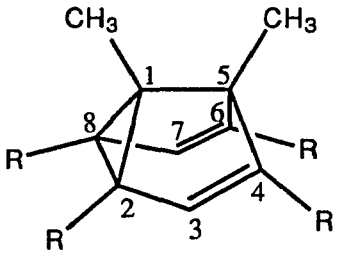
O1	C11	1.324(3)	C1	C9	1.506(4)
O1	C15	1.447(4)	C2	C3	1.449(4)
O2	C11	1.197(4)	C2	C8	1.731(4)
O3	C12	1.329(3)	C2	C11	1.502(4)
O3	C16	1.449(4)	C3	C4	1.343(4)
O4	C12	1.204(4)	C3	C7	3.051(4)
O5	C13	1.335(3)	C4	C5	1.516(4)
O5	C17	1.448(3)	C4	C6	2.247(4)
O6	C13	1.202(3)	C4	C12	1.490(4)
O7	C14	1.327(3)	C5	C6	1.532(3)
O7	C18	1.443(3)	C5	C10	1.517(4)
O8	C14	1.202(3)	C6	C7	1.347(3)
C1	C2	1.483(4)	C6	C13	1.479(3)
C1	C5	1.580(3)	C7	C8	1.429(3)
C1	C8	1.523(3)	C8	C14	1.487(4)

Table 252. Angles (°) for Sb-Me_2 at **236 K**

C11	O1	C15	115.3(2)	C4	C5	C10	120.8(2)
C12	O3	C16	116.4(2)	C6	C5	C10	116.3(2)
C13	O5	C17	115.8(2)	C4	C6	C5	42.2(1)
C14	O7	C18	115.1(2)	C5	C6	C7	112.0(2)
C2	C1	C5	104.1(2)	C5	C6	C13	122.6(2)
C2	C1	C8	70.3(2)	C7	C6	C13	124.5(2)
C2	C1	C9	125.8(2)	C6	C7	C8	111.0(2)
C5	C1	C8	103.6(2)	C1	C8	C2	53.8(2)
C5	C1	C9	119.7(2)	C1	C8	C7	109.5(2)
C8	C1	C9	122.3(2)	C2	C8	C7	116.6(2)
C1	C2	C3	108.9(2)	C2	C8	C14	112.5(2)
C1	C2	C8	55.9(2)	C7	C8	C14	123.2(2)
C1	C2	C11	128.4(2)	O1	C11	O2	124.9(3)
C3	C2	C8	118.0(2)	O1	C11	C2	113.1(2)
C3	C2	C11	116.0(3)	O2	C11	C2	121.9(3)
C8	C2	C11	116.7(2)	O3	C12	O4	123.9(3)
C2	C3	C4	110.9(2)	C1	C8	C14	121.9(2)
C3	C4	C5	111.2(2)	O3	C12	C4	111.0(2)
C3	C4	C12	121.2(3)	O4	C12	C4	124.9(2)
C5	C4	C6	42.8(1)	O5	C13	O6	124.5(2)
C5	C4	C12	127.6(2)	O5	C13	C6	110.6(2)
C1	C5	C4	102.6(2)	O6	C13	C6	124.9(2)
C1	C5	C6	102.6(2)	O7	C14	O8	123.9(2)
C1	C5	C10	116.1(2)	O7	C14	C8	111.6(2)
C4	C5	C6	95.0(2)	O8	C14	C8	124.5(2)

Table 253. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for $Sb-Me_2$ at **236 K**

Atom	Min.	Int'med.	Max.
O1	0.167	0.212	0.277
O2	0.175	0.256	0.374
O3	0.151	0.202	0.266
O4	0.180	0.229	0.283
O5	0.156	0.199	0.247
O6	0.161	0.218	0.256
O7	0.157	0.198	0.219
O8	0.161	0.211	0.327
C1	0.163	0.165	0.181
C2	0.172	0.196	0.243
C3	0.171	0.183	0.192
C4	0.170	0.190	0.200
C5	0.158	0.163	0.189
C6	0.164	0.171	0.235
C7	0.160	0.166	0.194
C8	0.162	0.170	0.228
C9	0.163	0.218	0.227
C10	0.166	0.209	0.219
C11	0.176	0.220	0.226
C12	0.169	0.183	0.216
C13	0.158	0.187	0.208
C14	0.158	0.200	0.216
C15	0.168	0.285	0.343
C16	0.153	0.244	0.300
C17	0.147	0.248	0.272
C18	0.154	0.218	0.262



R = $COOCH_3$

1,5-Dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-Me_2)

Table 8–254. X-ray Crystal Data for Sb-Me_2 at **265 K**

Formula	$C_{18}H_{20}O_8$
Formula weight	364.36
Melting point (°C)	102-103
Crystal size (mm)	0.23 x 0.25 x 0.37
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.598(1)
b (Å)	10.823(1)
c (Å)	24.590(1)
Cell volume ($Å^3$)	1755.87(0.17)
Z	4
d_{calc} (g cm^{-3})	1.378
μ(Cu $K\alpha$) (cm^{-1})	8.82
Maximum θ (°)	75
Unique reflections	2104
Observed reflections [$I > 3.0\sigma(I)$]	1758
Number of variables	235
R	0.039
R_w	0.050
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.22
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.20

Table 255. Final Atomic Parameters for Sb-Me_2 at **265 K**

Atom	x	y	z	B(Å^2)
O1	0.2933(4)	0.9697(2)	0.39582(8)	4.48(4)
O2	0.1447(5)	0.8949(3)	0.3212(1)	7.20(6)
O3	0.2985(4)	0.4396(2)	0.48420(7)	4.05(4)
O4	0.0957(4)	0.4090(2)	0.41296(9)	5.05(5)
O5	0.7073(4)	0.3629(2)	0.31306(8)	3.77(4)
O6	0.5837(4)	0.3303(2)	0.39701(8)	4.16(4)
O7	0.7451(3)	0.8069(2)	0.25616(7)	3.41(4)
O8	0.6205(5)	0.9488(2)	0.31262(9)	5.27(5)
C1	0.5654(4)	0.7447(2)	0.39618(9)	2.54(4)
C2	0.3644(5)	0.7639(3)	0.3708(1)	3.78(6)
C3	0.2362(4)	0.6599(2)	0.3831(1)	2.94(5)
C4	0.3373(4)	0.5731(2)	0.4109(1)	3.12(5)
C5	0.5610(4)	0.6051(2)	0.41528(9)	2.56(4)
C6	0.6192(5)	0.5357(2)	0.3634(1)	3.29(5)
C7	0.6242(4)	0.6102(2)	0.31967(9)	2.71(4)
C8	0.5887(5)	0.7353(2)	0.3345(1)	3.19(5)
C9	0.6799(5)	0.8386(3)	0.4291(1)	3.68(6)
C10	0.6812(5)	0.5747(3)	0.4661(1)	3.65(6)
C11	0.2581(5)	0.8835(3)	0.3590(1)	3.99(6)
C12	0.2321(5)	0.4639(3)	0.4344(1)	3.31(5)
C13	0.6344(5)	0.3991(2)	0.3611(1)	3.06(5)
C14	0.6509(5)	0.8430(2)	0.3012(1)	3.30(5)
C15	0.1963(7)	1.0877(3)	0.3862(2)	6.7(1)
C16	0.1951(6)	0.3419(3)	0.5133(1)	5.09(7)
C17	0.7236(6)	0.2304(3)	0.3051(1)	4.83(7)
C18	0.8185(5)	0.9059(3)	0.2220(1)	4.19(6)
H3	0.090	0.653	0.372	3.2
H7	0.650	0.581	0.282	3.0
H9A	0.667	0.922	0.412	4.0
H9B	0.622	0.842	0.467	4.0
H9C	0.826	0.815	0.431	4.0
H10A	0.668	0.485	0.474	4.0
H10B	0.827	0.595	0.460	4.0
H10C	0.628	0.624	0.497	4.0
H15A	0.232	1.146	0.416	7.4
H15B	0.244	1.122	0.351	7.4
H15C	0.046	1.076	0.385	7.4
H16A	0.258	0.332	0.550	5.6
H16B	0.049	0.364	0.517	5.6
H16C	0.208	0.263	0.493	5.6
H17A	0.779	0.213	0.268	5.3
H17B	0.816	0.195	0.333	5.3
H17C	0.586	0.192	0.309	5.3
H18A	0.887	0.870	0.189	4.6
H18B	0.702	0.959	0.210	4.6
H18C	0.917	0.957	0.243	4.6

The parameters of the hydrogen atoms were not refined.

Table 256. Final Anisotropic Thermal Parameters (U's) for Sb-Me2 at **265 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.069(1)	0.050(1)	0.051(1)	0.025(1)	0.002(1)	-0.0043(9)
O2	0.106(2)	0.071(1)	0.097(2)	0.030(2)	-0.056(1)	-0.002(1)
O3	0.068(1)	0.048(1)	0.0379(8)	-0.016(1)	0.012(1)	0.0057(8)
O4	0.061(1)	0.069(1)	0.062(1)	-0.027(1)	-0.005(1)	0.008(1)
O5	0.067(1)	0.0284(8)	0.048(1)	0.002(1)	0.007(1)	-0.0030(8)
O6	0.072(1)	0.0346(9)	0.051(1)	0.003(1)	0.006(1)	0.0110(9)
O7	0.050(1)	0.0393(8)	0.0398(8)	0.0001(9)	0.0097(9)	0.0097(8)
O8	0.099(2)	0.0316(9)	0.069(1)	0.003(1)	0.033(1)	0.0078(9)
C1	0.035(1)	0.030(1)	0.031(1)	-0.000(1)	0.001(1)	-0.001(1)
C2	0.047(2)	0.034(1)	0.063(2)	0.003(1)	-0.012(1)	0.006(1)
C3	0.034(1)	0.041(1)	0.037(1)	-0.000(1)	0.003(1)	0.000(1)
C4	0.040(1)	0.039(1)	0.039(1)	-0.005(1)	0.002(1)	0.004(1)
C5	0.037(1)	0.031(1)	0.029(1)	0.000(1)	-0.001(1)	0.001(1)
C6	0.060(2)	0.031(1)	0.034(1)	0.002(1)	-0.005(1)	-0.001(1)
C7	0.041(1)	0.029(1)	0.033(1)	0.000(1)	0.004(1)	0.001(1)
C8	0.058(2)	0.030(1)	0.033(1)	-0.004(1)	0.007(1)	0.001(1)
C9	0.053(2)	0.038(1)	0.049(1)	-0.004(1)	-0.005(1)	-0.009(1)
C10	0.054(2)	0.049(1)	0.036(1)	0.001(1)	-0.006(1)	0.007(1)
C11	0.055(2)	0.042(1)	0.054(1)	0.009(1)	-0.006(2)	0.004(1)
C12	0.044(1)	0.040(1)	0.042(1)	-0.002(1)	0.009(1)	-0.001(1)
C13	0.045(1)	0.030(1)	0.042(1)	0.002(1)	-0.005(1)	0.002(1)
C14	0.050(2)	0.032(1)	0.044(1)	-0.001(1)	0.004(1)	0.006(1)
C15	0.102(3)	0.061(2)	0.093(3)	0.043(2)	-0.004(3)	-0.009(2)
C16	0.085(2)	0.052(2)	0.056(2)	-0.019(2)	0.022(2)	0.012(1)
C17	0.082(2)	0.031(1)	0.071(2)	0.015(2)	0.004(2)	-0.008(1)
C18	0.053(2)	0.057(2)	0.049(1)	0.000(2)	0.008(1)	0.023(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 257. Interatomic Distances (Å) for Sb-Me_2 at **265 K**

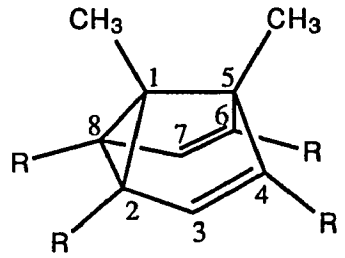
O1	C11	1.321(4)	C1	C9	1.503(4)
O1	C15	1.448(4)	C2	C3	1.440(4)
O2	C11	1.198(4)	C2	C8	1.756(4)
O3	C12	1.327(3)	C2	C11	1.501(4)
O3	C16	1.448(4)	C3	C4	1.340(4)
O4	C12	1.201(4)	C3	C7	3.046(4)
O5	C13	1.336(3)	C4	C5	1.519(4)
O5	C17	1.450(3)	C4	C6	2.234(4)
O6	C13	1.202(3)	C4	C12	1.487(4)
O7	C14	1.328(3)	C5	C6	1.530(3)
O7	C18	1.446(4)	C5	C10	1.516(4)
O8	C14	1.197(3)	C6	C7	1.344(3)
C1	C2	1.480(4)	C6	C13	1.482(4)
C1	C5	1.583(3)	C7	C8	1.421(4)
C1	C8	1.528(3)	C8	C14	1.483(4)

Table 258. Angles (°) for Sb-Me_2 at **265 K**

C11	O1	C15	115.6(3)	C4	C5	C10	121.1(2)
C12	O3	C16	116.5(2)	C6	C5	C10	116.7(2)
C13	O5	C17	115.8(2)	C4	C6	C5	42.7(1)
C14	O7	C18	115.0(2)	C5	C6	C7	112.2(2)
C2	C1	C5	104.0(2)	C5	C6	C13	122.5(2)
C2	C1	C8	71.4(2)	C7	C6	C13	124.6(2)
C2	C1	C9	125.7(2)	C6	C7	C8	111.3(2)
C5	C1	C8	103.5(2)	C1	C8	C2	53.0(2)
C5	C1	C9	119.7(2)	C1	C8	C7	109.5(2)
C8	C1	C9	122.0(2)	C1	C8	C14	121.6(2)
C1	C2	C3	109.2(2)	C2	C8	C7	115.9(2)
C1	C2	C8	55.6(2)	C2	C8	C14	112.1(2)
C1	C2	C11	128.4(3)	C7	C8	C14	124.2(2)
C3	C2	C8	117.7(2)	O1	C11	O2	124.6(3)
C3	C2	C11	116.1(3)	O1	C11	C2	113.2(3)
C8	C2	C11	116.5(2)	O2	C11	C2	122.1(3)
C2	C3	C4	111.3(3)	O3	C12	O4	123.7(3)
C3	C4	C5	111.1(2)	O3	C12	C4	111.2(2)
C3	C4	C12	121.5(3)	O4	C12	C4	124.9(3)
C5	C4	C6	43.1(1)	O5	C13	O6	124.6(2)
C5	C4	C12	127.4(2)	O5	C13	C6	110.5(2)
C1	C5	C4	102.4(2)	O6	C13	C6	124.9(2)
C1	C5	C6	102.5(2)	O7	C14	O8	123.8(3)
C1	C5	C10	116.2(2)	O7	C14	C8	111.0(2)
C4	C5	C6	94.2(2)	O8	C14	C8	125.2(3)

Table 259. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for $Sb-Me_2$ at **265 K**

Atom	Min.	Int'med.	Max.
O1	0.176	0.229	0.294
O2	0.186	0.275	0.404
O3	0.163	0.220	0.281
O4	0.194	0.245	0.307
O5	0.166	0.216	0.262
O6	0.171	0.233	0.273
O7	0.166	0.210	0.240
O8	0.173	0.222	0.348
C1	0.172	0.178	0.188
C2	0.174	0.208	0.265
C3	0.180	0.196	0.202
C4	0.180	0.203	0.211
C5	0.170	0.178	0.192
C6	0.176	0.183	0.246
C7	0.169	0.177	0.208
C8	0.168	0.182	0.245
C9	0.175	0.228	0.239
C10	0.177	0.227	0.236
C11	0.187	0.233	0.249
C12	0.184	0.199	0.228
C13	0.169	0.199	0.219
C14	0.171	0.209	0.229
C15	0.184	0.302	0.362
C16	0.167	0.257	0.316
C17	0.158	0.268	0.294
C18	0.168	0.231	0.279



R = $COOCH_3$

1,5-Dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-Me_2)

Table 8–260. X-ray Crystal Data for Sb-Me_2 at **294 K**

Formula	$C_{18}H_{20}O_8$
Formula weight	364.36
Melting point (°C)	102-103
Crystal size (mm)	0.23 x 0.25 x 0.37
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.624(1)
b (Å)	10.834(1)
c (Å)	24.641(1)
Cell volume (Å^3)	1768.24(0.17)
Z	4
d_{calc} (g cm^{-3})	1.369
μ(Cu $K\alpha$) (cm^{-1})	8.76
Maximum θ(°)	75
Unique reflections	2116
Observed reflections [$I > 3.0\sigma(I)$]	1693
Number of variables	235
R	0.042
R_w	0.054
$(\Delta\rho)_{max}$ (e Å^{-3})	0.21
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.18

Table 261. Final Atomic Parameters for Sb-Me_2 at **294 K**

Atom	x	y	z	B($Å^2$)
O1	0.2934(4)	0.9694(2)	0.39583(9)	5.06(5)
O2	0.1471(5)	0.8949(3)	0.3214(1)	8.26(8)
O3	0.2969(4)	0.4401(2)	0.48373(8)	4.72(5)
O4	0.0979(4)	0.4090(2)	0.4123(1)	5.82(6)
O5	0.7053(4)	0.3629(2)	0.31354(8)	4.23(5)
O6	0.5849(4)	0.3305(2)	0.39734(9)	4.79(5)
O7	0.7457(4)	0.8068(2)	0.25667(8)	3.87(4)
O8	0.6228(5)	0.9480(2)	0.3133(1)	6.11(6)
C1	0.5648(5)	0.7442(2)	0.3964(1)	2.91(5)
C2	0.3639(6)	0.7639(3)	0.3715(1)	4.26(7)
C3	0.2369(5)	0.6604(3)	0.3831(1)	3.36(6)
C4	0.3383(5)	0.5730(3)	0.4106(1)	3.47(6)
C5	0.5602(5)	0.6053(2)	0.4155(1)	2.90(5)
C6	0.6166(6)	0.5355(3)	0.3636(1)	3.74(6)
C7	0.6249(5)	0.6104(3)	0.3200(1)	3.04(5)
C8	0.5915(6)	0.7351(3)	0.3351(1)	3.69(6)
C9	0.6786(6)	0.8382(3)	0.4293(1)	4.27(7)
C10	0.6789(6)	0.5744(3)	0.4661(1)	4.08(7)
C11	0.2595(6)	0.8833(3)	0.3590(1)	4.54(7)
C12	0.2324(6)	0.4639(3)	0.4342(1)	3.78(6)
C13	0.6336(5)	0.3998(3)	0.3617(1)	3.39(6)
C14	0.6528(6)	0.8424(3)	0.3015(1)	3.79(6)
C15	0.1969(8)	1.0870(4)	0.3859(2)	7.7(1)
C16	0.1947(7)	0.3424(3)	0.5128(2)	5.98(9)
C17	0.7225(7)	0.2310(3)	0.3054(2)	5.51(9)
C18	0.8180(6)	0.9058(3)	0.2225(1)	4.79(7)
H3	0.092	0.654	0.372	3.7
H7	0.651	0.582	0.282	3.3
H9A	0.666	0.921	0.412	4.7
H9B	0.621	0.842	0.467	4.7
H9C	0.824	0.814	0.431	4.7
H10A	0.665	0.484	0.474	4.5
H10B	0.825	0.595	0.460	4.5
H10C	0.626	0.624	0.497	4.5
H15A	0.231	1.146	0.416	8.4
H15B	0.245	1.121	0.350	8.4
H15C	0.047	1.075	0.384	8.4
H16A	0.256	0.333	0.550	6.6
H16B	0.048	0.363	0.517	6.6
H16C	0.209	0.263	0.492	6.6
H17A	0.777	0.214	0.268	6.0
H17B	0.816	0.195	0.333	6.0
H17C	0.586	0.192	0.309	6.0
H18A	0.886	0.870	0.190	5.3
H18B	0.702	0.958	0.211	5.3
H18C	0.917	0.957	0.243	5.3

The parameters of the hydrogen atoms were not refined.

Table 262. Final Anisotropic Thermal Parameters (U's) for Sb-Me_2 at **294 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.077(2)	0.057(1)	0.058(1)	0.028(1)	0.000(1)	-0.005(1)
O2	0.121(2)	0.083(2)	0.110(2)	0.035(2)	-0.062(2)	-0.003(2)
O3	0.082(2)	0.055(1)	0.043(1)	-0.018(1)	0.015(1)	0.006(1)
O4	0.071(2)	0.079(2)	0.071(1)	-0.034(1)	-0.005(1)	0.010(1)
O5	0.075(2)	0.0321(9)	0.053(1)	0.003(1)	0.007(1)	-0.0027(9)
O6	0.084(2)	0.039(1)	0.059(1)	0.002(1)	0.009(1)	0.012(1)
O7	0.057(1)	0.044(1)	0.0454(9)	0.000(1)	0.010(1)	0.0108(9)
O8	0.117(2)	0.035(1)	0.081(1)	0.004(1)	0.039(2)	0.008(1)
C1	0.040(1)	0.034(1)	0.036(1)	0.001(1)	0.001(1)	-0.001(1)
C2	0.054(2)	0.039(1)	0.069(2)	0.004(2)	-0.015(2)	0.006(1)
C3	0.040(2)	0.046(1)	0.042(1)	-0.000(1)	0.005(1)	0.000(1)
C4	0.047(2)	0.042(1)	0.043(1)	-0.008(1)	0.003(1)	0.005(1)
C5	0.042(1)	0.034(1)	0.034(1)	0.001(1)	-0.002(1)	0.001(1)
C6	0.069(2)	0.034(1)	0.039(1)	0.003(2)	-0.006(2)	0.000(1)
C7	0.045(2)	0.032(1)	0.039(1)	-0.000(1)	0.003(1)	0.001(1)
C8	0.063(2)	0.037(1)	0.040(1)	-0.006(2)	0.009(2)	0.001(1)
C9	0.060(2)	0.044(1)	0.058(2)	-0.002(2)	-0.004(2)	-0.013(1)
C10	0.061(2)	0.055(2)	0.039(1)	0.002(2)	-0.007(2)	0.008(1)
C11	0.062(2)	0.050(2)	0.060(2)	0.011(2)	-0.008(2)	0.003(2)
C12	0.051(2)	0.045(1)	0.047(1)	-0.003(2)	0.010(2)	-0.001(1)
C13	0.048(2)	0.034(1)	0.047(1)	0.003(1)	-0.006(1)	0.002(1)
C14	0.059(2)	0.037(1)	0.048(1)	-0.004(2)	0.005(2)	0.006(1)
C15	0.113(3)	0.068(2)	0.110(3)	0.051(2)	-0.001(3)	-0.009(2)
C16	0.102(3)	0.057(2)	0.068(2)	-0.020(2)	0.029(2)	0.011(2)
C17	0.096(3)	0.034(1)	0.079(2)	0.015(2)	0.002(3)	-0.006(2)
C18	0.063(2)	0.063(2)	0.056(2)	0.001(2)	0.012(2)	0.025(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 263. Interatomic Distances (Å) for Sb-Me_2 at **294 K**

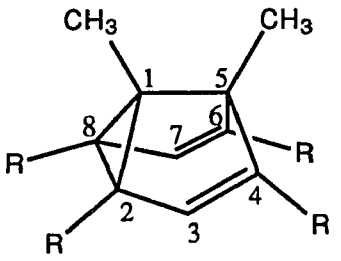
O1	C11	1.320(4)	C1	C9	1.504(4)
O1	C15	1.446(5)	C2	C3	1.430(5)
O2	C11	1.196(5)	C2	C8	1.781(5)
O3	C12	1.319(4)	C2	C11	1.499(5)
O3	C16	1.446(5)	C3	C4	1.345(4)
O4	C12	1.200(4)	C3	C7	3.051(4)
O5	C13	1.340(4)	C4	C5	1.516(4)
O5	C17	1.447(4)	C4	C6	2.215(5)
O6	C13	1.199(4)	C4	C12	1.492(4)
O7	C14	1.322(4)	C5	C6	1.531(4)
O7	C18	1.446(4)	C5	C10	1.513(4)
O8	C14	1.197(4)	C6	C7	1.347(4)
C1	C2	1.480(5)	C6	C13	1.475(4)
C1	C5	1.577(4)	C7	C8	1.418(4)
C1	C8	1.522(4)	C8	C14	1.484(4)

Table 264. Angles (°) for Sb-Me_2 at **294 K**

C11	O1	C15	115.5(3)	C4	C5	C10	121.2(2)
C12	O3	C16	116.7(3)	C6	C5	C10	116.9(3)
C13	O5	C17	116.4(2)	C4	C6	C5	43.1(2)
C14	O7	C18	115.2(2)	C5	C6	C7	112.2(2)
C2	C1	C5	104.1(2)	C5	C6	C13	122.5(2)
C2	C1	C8	72.8(2)	C7	C6	C13	124.9(3)
C2	C1	C9	125.2(3)	C6	C7	C8	111.0(2)
C5	C1	C8	103.6(2)	C1	C8	C2	52.5(2)
C5	C1	C9	119.6(2)	C1	C8	C7	109.9(2)
C8	C1	C9	121.4(3)	C1	C8	C14	122.3(2)
C1	C2	C3	109.5(3)	C2	C8	C7	115.5(3)
C1	C2	C8	54.7(2)	C2	C8	C14	112.0(3)
C1	C2	C11	128.6(3)	C7	C8	C14	123.8(3)
C3	C2	C8	117.4(2)	O1	C11	O2	124.4(3)
C3	C2	C11	116.5(3)	O1	C11	C2	112.9(3)
C8	C2	C11	116.0(3)	O2	C11	C2	122.4(3)
C2	C3	C4	111.0(3)	O3	C12	O4	124.1(3)
C3	C4	C5	111.2(3)	O3	C12	C4	111.2(3)
C3	C4	C12	121.3(3)	O4	C12	C4	124.6(3)
C5	C4	C6	43.6(2)	O5	C13	O6	123.8(3)
C5	C4	C12	127.5(3)	O5	C13	C6	110.6(2)
C1	C5	C4	102.5(2)	O6	C13	C6	125.5(3)
C1	C5	C6	102.6(2)	O7	C14	O8	123.9(3)
C1	C5	C10	116.6(2)	O7	C14	C8	111.4(2)
C4	C5	C6	93.3(2)	O8	C14	C8	124.7(3)

Table 265. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-Me_2 at **294 K**

Atom	Min.	Int'med.	Max.
O1	0.191	0.243	0.311
O2	0.201	0.296	0.431
O3	0.176	0.235	0.305
O4	0.203	0.261	0.334
O5	0.177	0.228	0.278
O6	0.183	0.246	0.296
O7	0.179	0.224	0.255
O8	0.183	0.239	0.377
C1	0.183	0.192	0.201
C2	0.185	0.221	0.281
C3	0.190	0.214	0.214
C4	0.182	0.214	0.230
C5	0.180	0.187	0.206
C6	0.184	0.194	0.266
C7	0.177	0.195	0.215
C8	0.183	0.198	0.259
C9	0.189	0.244	0.259
C10	0.185	0.241	0.251
C11	0.204	0.245	0.267
C12	0.197	0.211	0.245
C13	0.180	0.206	0.232
C14	0.183	0.223	0.247
C15	0.186	0.331	0.383
C16	0.184	0.269	0.347
C17	0.173	0.282	0.316
C18	0.177	0.249	0.297



R = $COOCH_3$

1,5-Dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-Me_2)

Table 8–266. X-ray Crystal Data for Sb-Me_2 at **295 K**

Formula	$C_{18}H_{20}O_8$
Formula weight	364.36
Melting point (°C)	102-103
Crystal size (mm)	0.23 x 0.25 x 0.37
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.623(1)
b (Å)	10.835(1)
c (Å)	24.6482)
Cell volume (Å^3)	1768.64(0.42)
Z	4
d_{calc} (g cm^{-3})	1.368
μ(Cu $K\alpha$) (cm^{-1})	8.76
Maximum θ(°)	75
Unique reflections	2116
Observed reflections [$I > 3.0\sigma(I)$]	1892
Number of variables	235
R	0.042
R_w	0.059
$(\Delta\rho)_{max}$ (e Å^{-3})	0.25
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.17

Table 267. Final Atomic Parameters for Sb-Me_2 at **295 K**

Atom	x	y	z	B(Å^2)
O1	0.2931(4)	0.9692(2)	0.39592(8)	5.30(5)
O2	0.1480(5)	0.8945(3)	0.3212(1)	8.50(7)
O3	0.2961(4)	0.4401(2)	0.48353(7)	4.91(4)
O4	0.0978(4)	0.4093(2)	0.41221(9)	6.03(5)
O5	0.7057(4)	0.3632(2)	0.31350(7)	4.43(4)
O6	0.5851(4)	0.3309(2)	0.39758(7)	5.04(5)
O7	0.7455(3)	0.8067(2)	0.25664(7)	4.05(4)
O8	0.6231(5)	0.9483(2)	0.31331(9)	6.36(5)
C1	0.5646(4)	0.7445(2)	0.39640(8)	3.07(4)
C2	0.3647(5)	0.7637(3)	0.3711(1)	4.53(6)
C3	0.2375(4)	0.6601(2)	0.38298(9)	3.62(5)
C4	0.3387(4)	0.5731(2)	0.4107(1)	3.71(5)
C5	0.5602(4)	0.6053(2)	0.41550(9)	3.16(4)
C6	0.6171(5)	0.5358(2)	0.36357(9)	3.96(5)
C7	0.6245(4)	0.6101(2)	0.31994(9)	3.21(4)
C8	0.5907(5)	0.7351(2)	0.33504(9)	3.82(5)
C9	0.6787(5)	0.8384(3)	0.4294(1)	4.47(6)
C10	0.6793(5)	0.5745(3)	0.4661(1)	4.23(5)
C11	0.2591(5)	0.8835(3)	0.3589(1)	4.71(6)
C12	0.2332(5)	0.4633(2)	0.4340(1)	3.94(5)
C13	0.6340(4)	0.3998(2)	0.3617(1)	3.67(5)
C14	0.6529(5)	0.8422(2)	0.3015(1)	3.91(5)
C15	0.1968(8)	1.0872(4)	0.3859(2)	7.9(1)
C16	0.1947(7)	0.3425(3)	0.5127(1)	6.20(8)
C17	0.7239(7)	0.2316(3)	0.3056(1)	5.77(8)
C18	0.8178(5)	0.9056(3)	0.2223(1)	5.06(6)
H3	0.092	0.653	0.372	4.3
H7	0.650	0.581	0.282	3.8
H9A	0.666	0.921	0.412	5.4
H9B	0.621	0.842	0.467	5.4
H9C	0.824	0.814	0.431	5.4
H10A	0.666	0.484	0.474	5.1
H10B	0.825	0.595	0.460	5.1
H10C	0.626	0.624	0.497	5.1
H15A	0.231	1.146	0.416	9.5
H15B	0.246	1.121	0.351	9.5
H15C	0.047	1.076	0.384	9.5
H16A	0.256	0.334	0.550	7.4
H16B	0.048	0.363	0.516	7.4
H16C	0.210	0.263	0.492	7.4
H17A	0.779	0.215	0.269	6.9
H17B	0.818	0.197	0.333	6.9
H17C	0.588	0.192	0.309	6.9
H18A	0.885	0.870	0.190	6.1
H18B	0.701	0.958	0.211	6.1
H18C	0.917	0.957	0.243	6.1

The parameters of the hydrogen atoms were not refined.

Table 268. Final Anisotropic Thermal Parameters (U's) for Sb-Me_2 at 295 K

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.083(1)	0.055(1)	0.064(1)	0.026(1)	0.002(1)	-0.0048(9)
O2	0.133(2)	0.078(1)	0.112(2)	0.039(2)	-0.064(1)	-0.006(1)
O3	0.087(1)	0.053(1)	0.0464(8)	-0.018(1)	0.014(1)	0.0061(8)
O4	0.076(1)	0.078(1)	0.074(1)	-0.033(1)	-0.004(1)	0.008(1)
O5	0.081(1)	0.0320(7)	0.0555(9)	0.004(1)	0.007(1)	-0.0031(7)
O6	0.089(1)	0.0400(8)	0.063(1)	0.006(1)	0.009(1)	0.0120(8)
O7	0.061(1)	0.0447(8)	0.0485(8)	-0.0012(9)	0.0095(9)	0.0108(7)
O8	0.125(2)	0.0344(8)	0.082(1)	0.004(1)	0.040(1)	0.0061(9)
C1	0.044(1)	0.0334(9)	0.039(1)	0.001(1)	0.003(1)	-0.0014(9)
C2	0.058(2)	0.039(1)	0.075(2)	0.004(1)	-0.016(1)	0.006(1)
C3	0.044(1)	0.046(1)	0.047(1)	-0.001(1)	0.003(1)	0.001(1)
C4	0.052(1)	0.043(1)	0.046(1)	-0.006(1)	0.002(1)	0.005(1)
C5	0.047(1)	0.035(1)	0.0374(9)	0.002(1)	-0.001(1)	0.0020(9)
C6	0.074(2)	0.035(1)	0.041(1)	0.005(1)	-0.005(1)	-0.001(1)
C7	0.049(1)	0.0320(9)	0.041(1)	0.001(1)	0.004(1)	0.0012(9)
C8	0.070(2)	0.034(1)	0.041(1)	-0.004(1)	0.010(1)	-0.0007(9)
C9	0.067(2)	0.045(1)	0.057(1)	-0.005(1)	-0.007(1)	-0.011(1)
C10	0.061(2)	0.056(1)	0.043(1)	-0.001(1)	-0.008(1)	0.008(1)
C11	0.067(2)	0.047(1)	0.066(1)	0.011(1)	-0.008(2)	0.004(1)
C12	0.055(1)	0.045(1)	0.050(1)	-0.004(1)	0.010(1)	-0.000(1)
C13	0.052(1)	0.034(1)	0.053(1)	0.003(1)	-0.005(1)	0.003(1)
C14	0.061(2)	0.036(1)	0.052(1)	-0.002(1)	0.005(1)	0.007(1)
C15	0.119(3)	0.067(2)	0.114(3)	0.050(2)	0.001(3)	-0.006(2)
C16	0.109(3)	0.055(1)	0.071(2)	-0.020(2)	0.029(2)	0.013(1)
C17	0.102(3)	0.034(1)	0.083(2)	0.016(2)	0.005(2)	-0.008(1)
C18	0.063(2)	0.066(2)	0.062(1)	0.000(2)	0.011(1)	0.027(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 269. Interatomic Distances (Å) for Sb-Me_2 at **295 K**

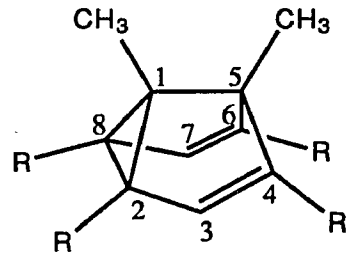
O1	C11	1.320(4)	C1	C9	1.506(4)
O1	C15	1.449(5)	C2	C3	1.433(4)
O2	C11	1.191(4)	C2	C8	1.768(4)
O3	C12	1.313(3)	C2	C11	1.505(4)
O3	C16	1.444(4)	C3	C4	1.344(4)
O4	C12	1.198(4)	C3	C7	3.046(4)
O5	C13	1.341(3)	C4	C5	1.512(4)
O5	C17	1.444(3)	C4	C6	2.216(4)
O6	C13	1.201(3)	C4	C12	1.495(4)
O7	C14	1.321(3)	C5	C10	1.512(3)
O7	C18	1.446(3)	C5	C6	1.532(3)
O8	C14	1.203(3)	C6	C7	1.344(3)
C1	C2	1.479(4)	C6	C13	1.478(3)
C1	C5	1.580(3)	C7	C8	1.422(3)
C1	C8	1.526(3)	C8	C14	1.483(3)

Table 270. Angles (°) for Sb-Me_2 at **295 K**

C11	O1	C15	115.3(3)	C4	C5	C10	121.3(2)
C12	O3	C16	117.1(2)	C6	C5	C10	116.9(2)
C13	O5	C17	116.2(2)	C4	C6	C5	42.9(1)
C14	O7	C18	115.3(2)	C5	C6	C7	112.6(2)
C2	C1	C5	104.1(2)	C5	C6	C13	122.2(2)
C2	C1	C8	72.1(2)	C7	C6	C13	124.7(2)
C2	C1	C9	125.6(2)	C6	C7	C8	110.8(2)
C5	C1	C8	103.5(2)	C1	C8	C2	52.7(2)
C5	C1	C9	119.5(2)	C1	C8	C7	109.9(2)
C8	C1	C9	121.6(2)	C1	C8	C14	122.2(2)
C1	C2	C3	109.3(2)	C2	C8	C7	115.6(2)
C1	C2	C8	55.2(2)	C2	C8	C14	112.2(2)
C1	C2	C11	128.4(2)	C7	C8	C14	123.7(2)
C3	C2	C8	117.6(2)	O1	C11	O2	125.0(3)
C3	C2	C11	116.3(3)	O1	C11	C2	113.0(3)
C8	C2	C11	116.4(2)	O2	C11	C2	121.8(3)
C2	C3	C4	111.1(3)	O3	C12	O4	124.1(3)
C3	C4	C5	111.2(2)	O3	C12	C4	111.2(2)
C3	C4	C12	121.4(3)	O4	C12	C4	124.4(2)
C5	C4	C12	127.4(2)	O5	C13	O6	124.3(2)
C5	C4	C6	43.6(1)	O5	C13	C6	110.4(2)
C1	C5	C4	102.4(2)	O6	C13	C6	125.2(2)
C1	C5	C6	102.4(2)	O7	C14	O8	123.8(2)
C1	C5	C10	116.5(2)	O7	C14	C8	111.6(2)
C4	C5	C6	93.4(2)	O8	C14	C8	124.5(2)

Table 271. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for $Sb-Me_2$ at **295 K**

Atom	Min.	Int'med.	Max.
O1	0.195	0.254	0.314
O2	0.206	0.289	0.444
O3	0.183	0.236	0.312
O4	0.210	0.270	0.336
O5	0.177	0.233	0.288
O6	0.187	0.252	0.306
O7	0.183	0.231	0.259
O8	0.183	0.243	0.386
C1	0.181	0.197	0.213
C2	0.189	0.228	0.291
C3	0.204	0.216	0.222
C4	0.193	0.221	0.234
C5	0.183	0.196	0.219
C6	0.185	0.201	0.275
C7	0.178	0.199	0.225
C8	0.182	0.196	0.271
C9	0.191	0.251	0.266
C10	0.193	0.240	0.256
C11	0.200	0.253	0.274
C12	0.202	0.213	0.253
C13	0.180	0.220	0.241
C14	0.181	0.230	0.250
C15	0.192	0.337	0.387
C16	0.184	0.273	0.356
C17	0.171	0.290	0.326
C18	0.187	0.252	0.306



R = $COOCH_3$

1,5-Dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-Me_2)

Table 8–272. X-ray Crystal Data for Sb-Me_2 at **322 K**

Formula	$C_{18}H_{20}O_8$
Formula weight	364.36
Melting point (°C)	102-103
Crystal size (mm)	0.14 x 0.24 x 0.50
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.639(3)
b (Å)	10.835(1)
c (Å)	24.664(2)
Cell volume (Å^3)	1774.22(0.88)
Z	4
d_{calc} (g cm^{-3})	1.364
μ(Cu $K\alpha$) (cm^{-1})	8.73
Maximum θ (°)	60
Unique reflections	1557
Observed reflections [$I > 3.0\sigma(I)$]	1088
Number of variables	235
R	0.039
R_w	0.045
$(\Delta\rho)_{max}$ (e Å^{-3})	0.14
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.16

Table 273. Final Atomic Parameters for Se-Me_2 at 322 K

Atom	x	y	z	B(Å^2)
O1	0.2938(5)	0.9690(3)	0.3959(1)	5.72(8)
O2	0.1499(6)	0.8951(4)	0.3215(2)	9.5(1)
O3	0.2943(5)	0.4409(3)	0.4833(1)	5.33(8)
O4	0.0999(5)	0.4090(3)	0.4113(1)	6.70(9)
O5	0.7039(5)	0.3634(2)	0.3141(1)	4.69(7)
O6	0.5860(5)	0.3305(3)	0.3977(1)	5.40(8)
O7	0.7464(5)	0.8069(2)	0.2573(1)	4.34(7)
O8	0.6258(6)	0.9471(3)	0.3139(1)	6.76(9)
C1	0.5651(6)	0.7441(4)	0.3966(1)	3.13(8)
C2	0.3621(7)	0.7639(4)	0.3726(2)	4.6(1)
C3	0.2389(7)	0.6609(4)	0.3829(2)	3.80(9)
C4	0.3409(7)	0.5730(4)	0.4102(2)	3.79(9)
C5	0.5597(6)	0.6055(4)	0.4154(2)	3.17(8)
C6	0.6130(7)	0.5347(4)	0.3641(2)	4.0(1)
C7	0.6245(6)	0.6101(4)	0.3205(2)	3.25(9)
C8	0.5932(7)	0.7349(4)	0.3355(2)	4.0(1)
C9	0.6781(8)	0.8377(4)	0.4296(2)	4.7(1)
C10	0.6774(8)	0.5741(4)	0.4663(2)	4.7(1)
C11	0.2599(8)	0.8828(4)	0.3596(2)	5.1(1)
C12	0.2335(8)	0.4641(4)	0.4335(2)	4.3(1)
C13	0.6335(7)	0.3999(4)	0.3619(2)	3.81(9)
C14	0.6545(7)	0.8419(4)	0.3023(2)	4.1(1)
C15	0.197(1)	1.0866(5)	0.3857(3)	9.1(2)
C16	0.1917(9)	0.3426(4)	0.5117(2)	6.8(1)
C17	0.723(1)	0.2315(4)	0.3063(2)	6.0(1)
C18	0.8171(8)	0.9051(5)	0.2226(2)	5.4(1)
H3	0.095	0.654	0.372	4.6
H7	0.652	0.581	0.283	3.9
H9A	0.666	0.921	0.412	5.7
H9B	0.620	0.841	0.467	5.7
H9C	0.823	0.814	0.432	5.7
H10A	0.663	0.484	0.474	5.6
H10B	0.823	0.594	0.461	5.6
H10C	0.624	0.623	0.497	5.6
H15A	0.231	1.146	0.415	10.9
H15B	0.244	1.120	0.350	10.9
H15C	0.047	1.074	0.384	10.9
H16A	0.250	0.333	0.549	8.1
H16B	0.045	0.363	0.515	8.1
H16C	0.209	0.264	0.491	8.1
H17A	0.777	0.215	0.269	7.2
H17B	0.817	0.197	0.334	7.2
H17C	0.588	0.192	0.310	7.2
H18A	0.884	0.869	0.190	6.5
H18B	0.700	0.957	0.211	6.5
H18C	0.916	0.957	0.243	6.5

The parameters of the hydrogen atoms were not refined.

Table 274. Final Anisotropic Thermal Parameters (U's) for Se-Me_2 at **322 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.085(2)	0.061(2)	0.071(2)	0.028(2)	0.004(2)	-0.005(2)
O2	0.134(3)	0.098(3)	0.128(3)	0.041(3)	-0.069(3)	-0.006(3)
O3	0.089(2)	0.066(2)	0.048(2)	-0.017(2)	0.016(2)	0.008(2)
O4	0.082(2)	0.093(2)	0.080(2)	-0.041(2)	-0.007(2)	0.013(2)
O5	0.080(2)	0.037(1)	0.061(2)	0.003(2)	0.009(2)	-0.003(1)
O6	0.092(2)	0.044(2)	0.069(2)	0.003(2)	0.014(2)	0.013(2)
O7	0.065(2)	0.051(2)	0.049(1)	0.000(2)	0.011(2)	0.013(1)
O8	0.128(3)	0.038(2)	0.090(2)	0.006(2)	0.044(2)	0.006(2)
C1	0.042(2)	0.039(2)	0.038(2)	-0.001(2)	0.003(2)	-0.002(2)
C2	0.057(3)	0.038(2)	0.080(3)	0.006(2)	-0.015(3)	0.007(2)
C3	0.046(3)	0.051(2)	0.047(2)	-0.004(2)	0.005(2)	-0.001(2)
C4	0.053(3)	0.045(2)	0.046(2)	-0.003(2)	0.003(2)	0.009(2)
C5	0.039(2)	0.042(2)	0.039(2)	0.000(2)	-0.000(2)	0.002(2)
C6	0.068(3)	0.042(2)	0.042(2)	0.005(3)	-0.004(3)	0.002(2)
C7	0.041(2)	0.037(2)	0.045(2)	0.003(2)	0.006(2)	-0.000(2)
C8	0.066(3)	0.039(2)	0.048(2)	-0.008(2)	0.008(3)	0.005(2)
C9	0.066(3)	0.049(2)	0.064(3)	-0.007(3)	-0.006(3)	-0.013(2)
C10	0.069(3)	0.065(3)	0.044(2)	-0.000(3)	-0.007(2)	0.006(2)
C11	0.065(3)	0.056(3)	0.072(3)	0.007(3)	-0.012(3)	0.002(2)
C12	0.060(3)	0.047(2)	0.055(2)	-0.001(3)	0.008(3)	0.002(2)
C13	0.052(3)	0.039(2)	0.053(2)	0.003(2)	-0.005(2)	0.005(2)
C14	0.057(3)	0.044(2)	0.053(2)	-0.000(3)	0.008(2)	0.008(2)
C15	0.139(6)	0.074(3)	0.131(5)	0.053(4)	0.010(5)	-0.000(4)
C16	0.114(5)	0.068(3)	0.076(3)	-0.017(4)	0.037(3)	0.017(3)
C17	0.102(4)	0.036(2)	0.089(3)	0.020(3)	0.004(4)	-0.008(2)
C18	0.065(3)	0.076(3)	0.064(3)	-0.005(3)	0.007(3)	0.028(3)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 275. Interatomic Distances (Å) for Sb-Me_2 at **322 K**

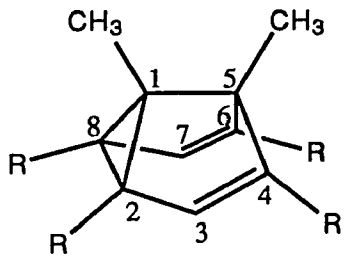
O1	C11	1.313(5)	C1	C9	1.501(6)
O1	C15	1.450(7)	C2	C3	1.407(6)
O2	C11	1.198(6)	C2	C8	1.815(7)
O3	C12	1.317(5)	C2	C11	1.491(6)
O3	C16	1.444(6)	C3	C4	1.348(6)
O4	C12	1.202(6)	C3	C7	3.038(6)
O5	C13	1.328(5)	C4	C5	1.500(6)
O5	C17	1.448(5)	C4	C6	2.174(6)
O6	C13	1.202(5)	C4	C12	1.494(6)
O7	C14	1.320(5)	C5	C6	1.522(5)
O7	C18	1.444(5)	C5	C10	1.518(6)
O8	C14	1.191(5)	C6	C7	1.353(5)
C1	C2	1.487(6)	C6	C13	1.467(6)
C1	C5	1.572(5)	C7	C8	1.417(6)
C1	C8	1.524(5)	C8	C14	1.477(6)

Table 276. Angles (°) for Sb-Me_2 at **322 K**

C11	O1	C15	115.5(4)	C4	C5	C10	121.1(3)
C12	O3	C16	116.6(4)	C6	C5	C10	117.1(3)
C13	O5	C17	116.3(3)	C4	C6	C5	43.6(2)
C14	O7	C18	115.9(3)	C5	C6	C7	111.7(3)
C2	C1	C5	103.5(3)	C5	C6	C13	123.7(3)
C2	C1	C8	74.1(3)	C7	C6	C13	124.5(4)
C2	C1	C9	124.8(4)	C6	C7	C8	111.2(3)
C5	C1	C8	103.4(3)	C1	C8	C2	52.0(2)
C5	C1	C9	119.8(3)	C1	C8	C7	109.8(3)
C8	C1	C9	121.3(3)	C1	C8	C14	122.1(3)
C1	C2	C3	109.9(4)	C2	C8	C7	114.9(3)
C1	C2	C8	53.9(2)	C2	C8	C14	112.1(3)
C1	C2	C11	128.5(4)	C7	C8	C14	124.4(4)
C3	C2	C8	116.4(3)	O1	C11	O2	124.1(4)
C3	C2	C11	117.3(4)	O1	C11	C2	113.0(4)
C8	C2	C11	115.2(3)	O2	C11	C2	122.8(4)
C2	C3	C4	111.0(4)	O3	C12	O4	123.8(4)
C3	C4	C5	111.3(4)	O3	C12	C4	111.4(4)
C3	C4	C12	120.7(4)	O4	C12	C4	124.7(4)
C5	C4	C6	44.4(2)	O5	C13	O6	123.9(4)
C5	C4	C12	127.9(4)	O5	C13	C6	111.2(3)
C1	C5	C4	102.8(3)	O6	C13	C6	124.8(4)
C1	C5	C6	103.4(3)	O7	C14	O8	123.4(4)
C1	C5	C10	116.5(3)	O7	C14	C8	111.5(3)
C4	C5	C6	92.0(3)	O8	C14	C8	125.1(4)

Table 277. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-Me_2 at **322 K**

Atom	Min.	Int'med.	Max.
O1	0.203	0.268	0.323
O2	0.219	0.319	0.459
O3	0.189	0.259	0.316
O4	0.213	0.277	0.364
O5	0.190	0.241	0.290
O6	0.197	0.259	0.315
O7	0.186	0.239	0.270
O8	0.193	0.248	0.397
C1	0.190	0.198	0.209
C2	0.181	0.233	0.296
C3	0.202	0.220	0.235
C4	0.189	0.233	0.233
C5	0.196	0.196	0.208
C6	0.195	0.211	0.264
C7	0.185	0.199	0.223
C8	0.183	0.222	0.264
C9	0.196	0.262	0.269
C10	0.201	0.256	0.266
C11	0.222	0.250	0.285
C12	0.214	0.225	0.257
C13	0.192	0.225	0.240
C14	0.195	0.227	0.256
C15	0.209	0.359	0.414
C16	0.190	0.291	0.371
C17	0.170	0.301	0.328
C18	0.196	0.261	0.314



R = $COOCH_3$

1,5-Dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-Me_2)

Table 8–278. X-ray Crystal Data for Sb-Me_2 at **335 K**

Formula	$C_{18}H_{20}O_8$
Formula weight	364.36
Melting point (°C)	102-103
Crystal size (mm)	0.14 x 0.24 x 0.50
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.652(4)
b (Å)	10.8421)
c (Å)	24.695(3)
Cell volume (Å^3)	1781.04(0.97)
Z	4
d_{calc} (g cm^{-3})	1.359
μ(Cu $K\alpha$) (cm^{-1})	8.70
Maximum θ(°)	60
Unique reflections	1564
Observed reflections [$I > 3.0\sigma(I)$]	1065
Number of variables	235
R	0.041
R_w	0.047
$(\Delta\rho)_{max}$ (e Å^{-3})	0.13
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.15

Table 279. Final Atomic Parameters for Sb-Me_2 at **335 K**

Atom	x	y	z	B(Å^2)
O1	0.2929(6)	0.9689(3)	0.3959(1)	5.98(9)
O2	0.1514(7)	0.8948(4)	0.3219(2)	10.1(1)
O3	0.2938(6)	0.4408(3)	0.4831(1)	5.57(8)
O4	0.1008(6)	0.4089(3)	0.4108(1)	7.2(1)
O5	0.7034(6)	0.3634(3)	0.3143(1)	4.94(8)
O6	0.5864(6)	0.3310(3)	0.3982(1)	5.73(8)
O7	0.7468(5)	0.8068(3)	0.2574(1)	4.59(7)
O8	0.6276(7)	0.9471(3)	0.3141(1)	7.1(1)
C1	0.5647(7)	0.7438(4)	0.3965(2)	3.37(9)
C2	0.3626(8)	0.7637(4)	0.3729(2)	5.0(1)
C3	0.2380(7)	0.6609(4)	0.3830(2)	3.8(1)
C4	0.3402(7)	0.5726(4)	0.4099(2)	3.9(1)
C5	0.5598(7)	0.6054(4)	0.4153(2)	3.43(9)
C6	0.6127(8)	0.5350(4)	0.3643(2)	4.2(1)
C7	0.6248(7)	0.6104(4)	0.3208(2)	3.4(1)
C8	0.5946(8)	0.7342(4)	0.3355(2)	4.1(1)
C9	0.6783(8)	0.8379(4)	0.4298(2)	5.1(1)
C10	0.6766(8)	0.5741(5)	0.4665(2)	5.0(1)
C11	0.2617(9)	0.8834(4)	0.3598(2)	5.4(1)
C12	0.2335(8)	0.4639(4)	0.4333(2)	4.5(1)
C13	0.6329(7)	0.3995(4)	0.3620(2)	4.1(1)
C14	0.6560(8)	0.8416(4)	0.3024(2)	4.2(1)
C15	0.196(1)	1.0867(5)	0.3847(3)	9.7(2)
C16	0.192(1)	0.3417(5)	0.5112(2)	7.1(2)
C17	0.722(1)	0.2318(4)	0.3062(2)	6.5(1)
C18	0.8183(8)	0.9053(5)	0.2231(2)	5.6(1)
H3	0.094	0.654	0.372	4.6
H7	0.652	0.582	0.283	4.1
H9A	0.667	0.921	0.412	6.2
H9B	0.620	0.841	0.467	6.2
H9C	0.823	0.814	0.432	6.2
H10A	0.663	0.484	0.474	6.0
H10B	0.822	0.595	0.461	6.0
H10C	0.622	0.623	0.497	6.0
H15A	0.228	1.146	0.414	11.7
H15B	0.247	1.119	0.349	11.7
H15C	0.047	1.074	0.382	11.7
H16A	0.250	0.333	0.548	8.5
H16B	0.045	0.361	0.514	8.5
H16C	0.210	0.263	0.491	8.5
H17A	0.776	0.215	0.269	7.8
H17B	0.816	0.197	0.334	7.8
H17C	0.587	0.192	0.310	7.8
H18A	0.884	0.869	0.190	6.7
H18B	0.702	0.958	0.212	6.7
H18C	0.918	0.957	0.244	6.7

The parameters of the hydrogen atoms were not refined.

Table 280. Final Anisotropic Thermal Parameters (U's) for Sb-Me_2 at **335 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.087(3)	0.068(2)	0.073(2)	0.034(2)	0.006(2)	-0.006(2)
O2	0.145(4)	0.096(3)	0.140(3)	0.049(3)	-0.078(3)	-0.008(3)
O3	0.093(3)	0.069(2)	0.050(2)	-0.018(2)	0.015(2)	0.008(2)
O4	0.084(3)	0.098(2)	0.090(2)	-0.042(2)	-0.005(2)	0.012(2)
O5	0.084(3)	0.041(2)	0.063(2)	0.005(2)	0.012(2)	-0.005(2)
O6	0.096(3)	0.047(2)	0.075(2)	0.004(2)	0.016(2)	0.018(2)
O7	0.062(2)	0.057(2)	0.056(2)	0.000(2)	0.011(2)	0.012(2)
O8	0.133(3)	0.040(2)	0.098(2)	0.003(2)	0.052(2)	0.009(2)
C1	0.047(3)	0.039(2)	0.042(2)	0.003(2)	0.001(2)	-0.005(2)
C2	0.057(3)	0.047(3)	0.085(3)	0.003(3)	-0.016(3)	0.009(3)
C3	0.041(3)	0.056(2)	0.048(2)	-0.002(3)	0.005(3)	-0.003(2)
C4	0.046(3)	0.049(3)	0.053(2)	-0.009(3)	0.001(3)	0.007(2)
C5	0.048(3)	0.045(2)	0.037(2)	0.005(3)	0.003(2)	0.002(2)
C6	0.073(3)	0.041(2)	0.045(2)	0.007(3)	-0.006(3)	-0.002(2)
C7	0.045(3)	0.037(2)	0.047(2)	0.003(2)	0.001(2)	-0.002(2)
C8	0.064(3)	0.041(2)	0.049(2)	-0.005(3)	0.008(3)	0.000(2)
C9	0.072(4)	0.058(3)	0.066(3)	-0.004(3)	-0.008(3)	-0.014(3)
C10	0.072(4)	0.070(3)	0.049(2)	0.002(3)	-0.008(3)	0.006(3)
C11	0.072(4)	0.060(3)	0.074(3)	0.017(3)	-0.011(3)	0.002(3)
C12	0.055(3)	0.055(3)	0.061(2)	-0.008(3)	0.010(3)	-0.001(2)
C13	0.055(3)	0.045(2)	0.057(2)	0.007(3)	-0.006(3)	0.003(2)
C14	0.059(3)	0.045(2)	0.055(3)	0.000(3)	0.007(3)	0.008(2)
C15	0.147(6)	0.076(4)	0.145(5)	0.058(4)	0.006(6)	-0.003(4)
C16	0.115(5)	0.071(3)	0.083(3)	-0.021(4)	0.038(4)	0.023(3)
C17	0.108(5)	0.034(2)	0.104(4)	0.015(3)	0.006(4)	-0.006(3)
C18	0.068(4)	0.079(3)	0.064(3)	0.003(3)	0.018(3)	0.031(3)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 281. Interatomic Distances (Å) for Sb-Me_2 at **335 K**

O1	C11	1.303(6)	C1	C9	1.513(6)
O1	C15	1.455(7)	C2	C3	1.411(6)
O2	C11	1.195(7)	C2	C8	1.827(7)
O3	C12	1.317(5)	C2	C11	1.496(7)
O3	C16	1.448(6)	C3	C4	1.349(6)
O4	C12	1.201(6)	C3	C7	3.046(6)
O5	C13	1.327(5)	C4	C5	1.509(7)
O5	C17	1.446(5)	C4	C6	2.173(7)
O6	C13	1.201(5)	C4	C12	1.492(6)
O7	C14	1.319(5)	C5	C6	1.515(6)
O7	C18	1.443(6)	C5	C10	1.521(6)
O8	C14	1.194(5)	C6	C7	1.351(6)
C1	C2	1.481(7)	C6	C13	1.477(6)
C1	C5	1.572(6)	C7	C8	1.405(6)
C1	C8	1.524(6)	C8	C14	1.480(6)

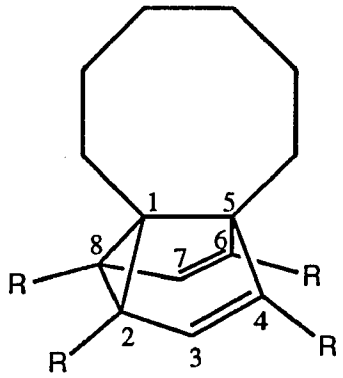
Table 282. Angles (°) for Sb-Me_2 at **335 K**

C11	O1	C15	115.1(4)	C4	C5	C10	121.1(4)
C12	O3	C16	116.5(4)	C6	C5	C10	117.4(4)
C13	O5	C17	116.3(3)	C4	C6	C5	44.0(2)
C14	O7	C18	115.7(3)	C5	C6	C7	111.8(4)
C2	C1	C5	103.7(3)	C5	C6	C13	123.6(3)
C2	C1	C8	74.9(3)	C7	C6	C13	124.5(4)
C2	C1	C9	124.6(4)	C6	C7	C8	111.4(4)
C5	C1	C8	103.3(3)	C1	C8	C2	51.5(3)
C5	C1	C9	119.6(3)	C1	C8	C7	109.8(3)
C8	C1	C9	121.2(4)	C1	C8	C14	121.9(4)
C1	C2	C3	110.4(4)	C2	C8	C7	114.7(4)
C1	C2	C8	53.6(3)	C2	C8	C14	112.0(3)
C1	C2	C11	128.3(4)	C7	C8	C14	124.7(4)
C3	C2	C8	116.5(4)	O1	C11	O2	124.0(5)
C3	C2	C11	117.3(4)	O1	C11	C2	113.4(4)
C8	C2	C11	114.9(4)	O2	C11	C2	122.3(4)
C2	C3	C4	110.6(4)	O3	C12	O4	124.1(4)
C3	C4	C5	111.4(4)	O3	C12	C4	111.5(4)
C3	C4	C12	120.8(4)	O4	C12	C4	124.2(4)
C5	C4	C6	44.2(2)	O5	C13	O6	124.6(4)
C5	C4	C12	127.7(4)	O5	C13	C6	111.0(3)
C1	C5	C4	102.6(3)	O6	C13	C6	124.3(4)
C1	C5	C6	103.2(3)	O7	C14	O8	123.3(4)
C1	C5	C10	116.6(4)	O7	C14	C8	111.5(4)
C4	C5	C6	91.9(3)	O8	C14	C8	125.2(4)

Table 283. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-Me_2 at **335 K**

Atom	Min.	Int'med.	Max.
O1	0.199	0.274	0.336
O2	0.213	0.321	0.483
O3	0.196	0.263	0.323
O4	0.221	0.296	0.369
O5	0.197	0.245	0.298
O6	0.195	0.270	0.327
O7	0.203	0.244	0.272
O8	0.197	0.249	0.413
C1	0.187	0.213	0.219
C2	0.202	0.233	0.305
C3	0.195	0.221	0.239
C4	0.193	0.226	0.245
C5	0.191	0.204	0.229
C6	0.199	0.208	0.276
C7	0.189	0.213	0.219
C8	0.198	0.216	0.261
C9	0.211	0.268	0.282
C10	0.212	0.267	0.273
C11	0.213	0.268	0.298
C12	0.212	0.236	0.265
C13	0.198	0.234	0.250
C14	0.200	0.232	0.257
C15	0.207	0.381	0.425
C16	0.182	0.310	0.374
C17	0.174	0.319	0.337
C18	0.187	0.262	0.329

8.7 SB-8



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–284. X-ray Crystal Data for Sb-8 at **20 K**

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.32 x 0.40 x 0.50
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.498(8)
b (Å)	14.388(13)
c (Å)	14.1293(11)
β (°)	109.21(2)
Cell volume ($Å^3$)	2015.21
Z	4
d_{calc} (g cm^{-3})	1.379
μ(Mo $K\alpha$) (cm^{-1})	0.98
Maximum θ (°)	25
Unique reflections	3361
Observed reflections [$I > 3.0\sigma(I)$]	2230
Number of variables	279
R	0.055
R_w	0.064
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.62
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	—

Table 285. Final Atomic Parameters for Sb-8 at **20 K**

Atom	x	y	z	B(Å^2)
O1	0.3971(2)	0.3274(1)	0.1827(1)	1.43(3)
O2	0.3101(2)	0.2684(2)	0.0261(2)	1.41(3)
O3	0.8988(2)	0.3809(2)	0.3217(2)	1.36(3)
O4	1.0110(2)	0.3346(2)	0.2188(2)	1.56(3)
O5	0.9771(2)	0.1274(2)	0.2697(2)	1.54(3)
O6	1.0346(3)	0.1383(2)	0.1293(2)	1.59(3)
O7	0.4235(2)	0.0759(2)	0.1266(2)	1.29(3)
O8	0.3925(2)	0.0775(2)	-0.0395(2)	1.35(3)
C1	0.6010(4)	0.2465(2)	0.0231(2)	1.21(4)
C2	0.5502(4)	0.2718(2)	0.1093(2)	1.28(4)
C3	0.6590(4)	0.3160(2)	0.1879(2)	1.19(4)
C4	0.7737(4)	0.3169(2)	0.1661(2)	1.21(4)
C5	0.7591(4)	0.2612(3)	0.0695(2)	1.20(4)
C6	0.8063(4)	0.1676(2)	0.1214(2)	1.22(4)
C7	0.7033(4)	0.1186(2)	0.1308(2)	1.24(4)
C8	0.5754(4)	0.1630(2)	0.0772(2)	1.16(4)
C9	0.5204(4)	0.2639(3)	-0.0870(2)	1.29(4)
C10	0.4835(4)	0.3639(3)	-0.1207(3)	1.66(5)
C11A	0.5960(4)	0.4260(3)	-0.1324(3)	1.73(5)
C12A	0.7004(4)	0.4543(3)	-0.0328(3)	1.60(5)
C13	0.8344(4)	0.4038(3)	-0.0109(3)	2.08(5)
C14	0.8331(4)	0.2976(3)	-0.0012(3)	1.44(4)
C15	0.4058(4)	0.2883(2)	0.0978(2)	1.20(4)
C16	0.9055(4)	0.3443(1)	0.2348(3)	1.30(4)
C17	0.9504(4)	0.1438(2)	0.1706(3)	1.37(4)
C18	0.4529(4)	0.1030(1)	0.0443(3)	1.19(4)
C19	0.2610(4)	0.3362(3)	0.1868(3)	1.67(5)
C20	1.0274(4)	0.3997(3)	0.3963(3)	1.53(5)
C21	1.1166(4)	0.1111(3)	0.3255(3)	1.80(6)
C22	0.3118(4)	0.0123(3)	0.1095(3)	1.56(5)
C11B	0.594(4)	0.439(3)	-0.076(3)	4.0(4)*
C12B	0.704(5)	0.415(2)	-0.108(3)	4.0(3)*
H3	0.6495	0.3424	0.2506	0.25
H7	0.7127	0.0592	0.1694	0.25
H9A	0.4341	0.2283	-0.1025	0.25
H9B	0.5745	0.2386	-0.1277	0.25
H10AA	0.4485	0.3939	-0.0704	0.25
H10AB	0.4102	0.3616	-0.1871	0.25
H11AA	0.5540	0.4837	-0.1689	0.25
H11AB	0.6431	0.3916	-0.1726	0.25
H12AA	0.6632	0.4404	0.0223	0.25
H12AB	0.7170	0.5227	-0.0346	0.25
H13AA	0.8970	0.4289	0.0536	0.25
H13AB	0.8704	0.4187	-0.0665	0.25
H14A	0.7878	0.2709	-0.0693	0.25
H14B	0.9286	0.2755	0.0248	0.25
H19A	0.2662	0.3583	0.2550	0.25
H19B	0.2103	0.3824	0.1354	0.25
H19C	0.2139	0.2748	0.1730	0.25
H20A	1.0138	0.4171	0.4609	0.25
H20B	1.0852	0.3429	0.4066	0.25
H20C	1.0723	0.4521	0.3732	0.25
H21A	1.1293	0.1003	0.3978	0.25
H21B	1.1512	0.0563	0.2978	0.25
H21C	1.1686	0.1676	0.3190	0.25
H22A	0.3035	-0.0054	0.1756	0.25
H22B	0.2274	0.0445	0.0680	0.25
H22C	0.3265	-0.0446	0.0738	0.25

Table 285 (cont'd). Final Atomic Parameters for Sb-8 at **20 K**

Atom	x	y	z	B(Å^2)
H10BA	0.4021	0.3809	-0.1025	0.25
H10BB	0.4605	0.3657	-0.1952	0.25
H11BA	0.6230	0.4384	-0.0014	0.25
H11BB	0.5590	0.5018	-0.1018	0.25
H12BA	0.7192	0.4643	-0.1525	0.25
H12BB	0.6833	0.3546	-0.1455	0.25
H13BA	0.8230	0.4359	0.0486	0.25
H13BB	0.9182	0.4268	-0.0220	0.25

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

Table 286. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **20 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0228(6)	0.0252(8)	0.0098(7)	0.0012(6)	0.0098(5)	-0.0010(6)
O2	0.0193(6)	0.0224(8)	0.0130(7)	-0.0008(6)	0.0069(5)	0.0006(7)
O3	0.0225(6)	0.0232(8)	0.0090(7)	0.0006(6)	0.0091(5)	-0.0026(6)
O4	0.0209(6)	0.0257(9)	0.0160(7)	-0.0016(6)	0.0107(5)	-0.0040(7)
O5	0.0235(7)	0.0249(9)	0.0111(7)	-0.0016(7)	0.0072(5)	0.0030(7)
O6	0.0228(7)	0.0259(9)	0.0150(8)	0.0025(7)	0.0107(5)	-0.0015(7)
O7	0.0230(6)	0.0202(7)	0.0096(7)	-0.0027(6)	0.0106(5)	-0.0001(6)
O8	0.0231(7)	0.0188(7)	0.0113(7)	-0.0016(6)	0.0081(6)	-0.0026(6)
C1	0.0236(9)	0.015(1)	0.0104(9)	0.0019(8)	0.0103(7)	0.0002(8)
C2	0.0250(9)	0.019(1)	0.0084(9)	0.0017(9)	0.0100(7)	0.0033(9)
C3	0.0263(9)	0.014(1)	0.0096(9)	0.0011(8)	0.0116(7)	0.0023(8)
C4	0.0252(9)	0.013(1)	0.0123(9)	0.0011(8)	0.0119(7)	-0.0004(9)
C5	0.0226(9)	0.018(1)	0.0085(9)	0.0000(8)	0.0102(7)	-0.0001(8)
C6	0.0257(9)	0.016(1)	0.008(1)	0.0008(9)	0.0109(8)	-0.0029(9)
C7	0.0266(9)	0.014(1)	0.0083(9)	-0.0020(8)	0.0084(7)	-0.0030(8)
C8	0.0247(9)	0.017(1)	0.005(1)	-0.0001(9)	0.0094(7)	-0.0039(9)
C9	0.0229(9)	0.018(1)	0.0100(9)	-0.0015(9)	0.0079(7)	-0.0005(9)
C10	0.028(1)	0.022(1)	0.013(1)	0.0023(9)	0.0075(8)	0.002(1)
C11A	0.032(1)	0.024(1)	0.010(1)	-0.005(1)	0.0081(9)	0.002(1)
C12A	0.032(1)	0.019(1)	0.013(1)	-0.001(1)	0.0116(9)	0.001(1)
C13	0.034(1)	0.029(1)	0.021(1)	-0.002(1)	0.0151(8)	0.010(1)
C14	0.0256(9)	0.024(1)	0.0096(9)	-0.0017(9)	0.0121(7)	0.0015(9)
C15	0.0277(9)	0.012(1)	0.0104(9)	0.0002(8)	0.0120(7)	0.0028(8)
C16	0.0279(9)	0.011(1)	0.0134(9)	0.0041(8)	0.0108(7)	0.0006(8)
C17	0.0283(9)	0.013(1)	0.011(1)	-0.0017(9)	0.0076(8)	-0.0014(9)
C18	0.0215(9)	0.014(1)	0.0129(9)	0.0030(8)	0.0105(7)	0.0031(9)
C19	0.0174(9)	0.034(1)	0.016(1)	0.0035(9)	0.0117(7)	0.002(1)
C20	0.024(1)	0.023(1)	0.012(1)	-0.001(1)	0.0073(8)	-0.002(1)
C21	0.023(1)	0.028(1)	0.015(1)	0.001(1)	0.004(1)	0.004(1)
C22	0.026(1)	0.020(1)	0.017(1)	-0.0052(9)	0.0124(8)	0.002(1)

The form of the anisotropic displacement parameter is:
exp[-2PI2{h2a2U(1,1) + k2b2U(2,2) + l2c2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)}] where a,b, and c are reciprocal lattice constants.

Table 287. Interatomic Distances (Å) for Sb-8 at **20 K**

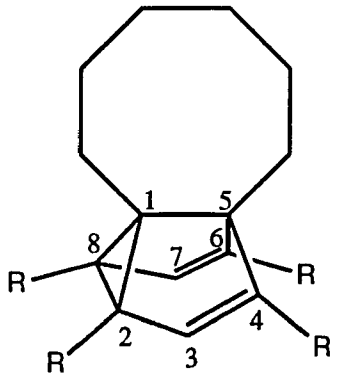
O1	C15	1.355(4)	C3	C4	1.337(5)
O1	C19	1.454(4)	C3	C7	3.031
O2	C15	1.203(4)	C4	C5	1.546(5)
O3	C16	1.359(4)	C4	C6	2.297(5)
O3	C20	1.439(4)	C4	C16	1.459(5)
O4	C16	1.209(4)	C5	C6	1.536(5)
O5	C17	1.355(4)	C5	C14	1.545(5)
O5	C21	1.436(4)	C6	C7	1.334(5)
O6	C17	1.211(4)	C6	C17	1.482(5)
O7	C18	1.355(4)	C7	C8	1.454(5)
O7	C22	1.444(4)	C8	C18	1.491(5)
O8	C18	1.202(5)	C9	C10	1.525(5)
C1	C2	1.526(4)	C10	C11A	1.533(6)
C1	C5	1.585(5)	C11A	C12A	1.527(5)
C1	C8	1.495(5)	C12A	C13	1.522(5)
C1	C9	1.527(5)	C13	C14	1.535(5)
C2	C3	1.452(5)	C10	C11B	1.56(4)
C2	C8	1.675(5)	C11B	C12B	1.41(6)
C2	C15	1.489(5)	C12B	C13	1.60(5)

Table 288. Angles (°) for Sb-8 at **20 K**

C15	O1	C19	115.1(3)	C6	C7	C8	110.8(3)
C16	O3	C20	114.8(3)	C1	C8	C2	57.2(2)
C17	O5	C21	115.0(3)	C1	C8	C7	109.2(3)
C18	O7	C22	116.1(3)	C1	C8	C18	126.0(3)
C2	C1	C5	103.4(3)	C2	C8	C7	118.1(3)
C2	C1	C8	67.3(2)	C2	C8	C18	115.4(3)
C2	C1	C9	123.5(3)	C7	C8	C18	117.5(3)
C5	C1	C8	103.6(3)	C1	C9	C10	118.1(3)
C5	C1	C9	123.6(3)	C9	C10	C11A	117.3(3)
C8	C1	C9	121.3(3)	C10	C11A	C12A	113.6(3)
C1	C2	C3	108.8(3)	C11A	C12A	C13	113.3(4)
C1	C2	C8	55.5(2)	C12A	C13	C14	117.3(3)
C1	C2	C15	124.2(3)	C5	C14	C13	114.6(3)
C3	C2	C8	117.5(3)	O1	C15	O2	124.3(3)
C3	C2	C15	122.0(3)	O1	C15	C2	109.4(3)
C8	C2	C15	111.4(3)	O2	C15	C2	126.3(3)
C2	C3	C4	111.7(3)	O3	C16	O4	122.5(3)
C3	C4	C5	111.3(3)	O3	C16	C4	112.7(3)
C3	C4	C16	125.3(3)	O4	C16	C4	124.8(3)
C5	C4	C6	41.7(2)	O5	C17	O6	123.4(4)
C5	C4	C16	121.6(3)	O5	C17	C6	110.9(3)
C1	C5	C4	102.7(3)	O6	C17	C6	125.7(3)
C1	C5	C6	102.1(3)	O7	C18	O8	124.2(3)
C1	C5	C14	117.3(3)	O7	C18	C8	108.4(3)
C4	C5	C6	96.3(3)	O8	C18	C8	127.3(3)
C4	C5	C14	118.0(3)				
C6	C5	C14	117.0(3)				
C4	C6	C5	42.0(3)	C9	C10	C11B	116(2)
C5	C6	C7	111.5(3)	C10	C11B	C12B	106(3)
C5	C6	C17	123.1(3)	C11B	C12B	C13	108(3)
C7	C6	C17	124.5(3)	C12B	C13	C14	98(2)

Table 289. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-8 at **20 K**

Atom	Min.	Int'med.	Max.
O1	0.078	0.151	0.160
O2	0.108	0.139	0.151
O3	0.074	0.150	0.154
O4	0.102	0.145	0.167
O5	0.095	0.150	0.163
O6	0.101	0.151	0.165
O7	0.071	0.138	0.158
O8	0.095	0.137	0.154
C1	0.080	0.123	0.156
C2	0.066	0.136	0.160
C3	0.067	0.118	0.164
C4	0.084	0.113	0.161
C5	0.065	0.135	0.152
C6	0.057	0.131	0.161
C7	0.075	0.121	0.164
C8	0.032	0.135	0.158
C9	0.090	0.132	0.153
C10	0.109	0.149	0.171
C11A	0.092	0.148	0.187
C12A	0.100	0.138	0.178
C13	0.097	0.184	0.189
C14	0.063	0.154	0.164
C15	0.068	0.114	0.168
C16	0.096	0.107	0.170
C17	0.100	0.116	0.169
C18	0.089	0.116	0.154
C19	0.088	0.144	0.187
C20	0.106	0.149	0.157
C21	0.119	0.157	0.172
C22	0.096	0.144	0.171



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–290. X-ray Crystal Data for Sb-8 at **115 K**

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.08 x 0.10 x 0.59
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.529(4)
b (Å)	14.481(3)
c (Å)	14.121(9)
β (°)	109.36(4)
Cell volume (Å^3)	2031.37(25.47)
Z	4
d_{calc} (g cm^{-3})	1.365
μ(Cu $K\alpha$) (cm^{-1})	8.28
Maximum θ(°)	60
Unique reflections	3009
Observed reflections [$I > 3.0\sigma(I)$]	2324
Number of variables	279
R	0.036
R_w	0.046
$(\Delta\rho)_{max}$ (e Å^{-3})	0.24
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.21

Table 291. Final Atomic Parameters for Sb-8 at **115 K**

Atom	x	y	z	B(Å^2)
O1	0.3958(1)	0.3284(1)	0.1821(1)	1.62(3)
O2	0.3099(1)	0.2683(1)	0.0273(1)	1.76(3)
O3	0.8973(1)	0.3787(1)	0.3212(1)	1.63(3)
O4	1.0091(1)	0.3336(1)	0.2191(1)	1.99(3)
O5	0.9750(1)	0.1285(1)	0.2705(1)	2.02(3)
O6	1.0300(2)	0.1371(1)	0.1300(1)	2.19(3)
O7	0.4223(1)	0.0762(1)	0.1252(1)	1.54(3)
O8	0.3908(1)	0.0787(1)	-0.0406(1)	1.72(3)
C1	0.5991(2)	0.2465(1)	0.0236(1)	1.14(4)
C2	0.5486(2)	0.2732(2)	0.1091(2)	1.46(4)
C3	0.6570(2)	0.3152(1)	0.1882(1)	1.13(4)
C4	0.7726(2)	0.3139(2)	0.1670(1)	1.27(4)
C5	0.7567(2)	0.2608(1)	0.0695(1)	1.14(4)
C6	0.8046(2)	0.1690(2)	0.1233(2)	1.62(4)
C7	0.7008(2)	0.1194(1)	0.1315(2)	1.28(4)
C8	0.5745(2)	0.1621(2)	0.0760(2)	1.42(4)
C9	0.5190(2)	0.2636(2)	-0.0864(1)	1.38(4)
C10	0.4805(2)	0.3635(2)	-0.1194(2)	1.86(5)
C11A	0.5934(3)	0.4250(2)	-0.1314(2)	1.90(5)
C12A	0.6993(2)	0.4527(2)	-0.0317(2)	1.73(5)
C13	0.8341(2)	0.4013(2)	-0.0106(2)	2.19(5)
C14	0.8308(2)	0.2957(2)	-0.0005(2)	1.62(4)
C15	0.4052(2)	0.2896(2)	0.0987(2)	1.32(4)
C16	0.9051(2)	0.3424(1)	0.2359(2)	1.23(4)
C17	0.9481(2)	0.1442(2)	0.1722(2)	1.56(4)
C18	0.4512(2)	0.1028(1)	0.0436(2)	1.31(4)
C19	0.2605(2)	0.3371(2)	0.1865(2)	1.98(5)
C20	1.0264(2)	0.3993(2)	0.3961(2)	1.94(5)
C21	1.1149(2)	0.1103(2)	0.3265(2)	2.66(6)
C22	0.3104(2)	0.0131(2)	0.1086(2)	2.02(5)
C11B	0.590(2)	0.438(1)	-0.065(1)	2.1(4)*
C12B	0.706(2)	0.420(1)	-0.109(1)	1.7(3)*
H3	0.648	0.342	0.251	1.2
H7	0.710	0.061	0.171	1.4
H9A	0.434	0.227	-0.102	1.5
H9B	0.574	0.240	-0.127	1.5
H10AA	0.447	0.393	-0.068	2.0
H10AB	0.406	0.362	-0.186	2.0
H11AA	0.552	0.483	-0.168	2.1
H11AB	0.639	0.391	-0.172	2.1
H12AA	0.663	0.439	0.024	1.9
H12AB	0.716	0.521	-0.033	1.9
H13AA	0.898	0.426	0.054	2.4
H13AB	0.869	0.415	-0.067	2.4
H14A	0.785	0.269	-0.069	1.8
H14B	0.926	0.273	0.026	1.8
H19A	0.264	0.367	0.251	2.2
H19B	0.205	0.376	0.129	2.2
H19C	0.219	0.274	0.182	2.2
H20A	1.012	0.426	0.457	2.1
H20B	1.080	0.341	0.415	2.1
H20C	1.076	0.445	0.368	2.1
H21A	1.125	0.099	0.399	2.9
H21B	1.145	0.054	0.298	2.9
H21C	1.171	0.164	0.321	2.9
H22A	0.298	-0.002	0.174	2.2
H22B	0.227	0.043	0.063	2.2
H22C	0.329	-0.045	0.077	2.2

Table 291 (cont.). Final Atomic Parameters for Sb-8 at **115 K**

Atom	x	y	z	B(Å^2)
H10BA	0.396	0.379	-0.106	2.0
H10BB	0.464	0.368	-0.193	2.0
H11BA	0.622	0.429	0.009	2.3
H11BB	0.553	0.502	-0.081	2.3
H12BA	0.722	0.476	-0.146	1.9
H12BB	0.686	0.365	-0.155	1.9
H13BA	0.824	0.433	0.050	2.4
H13BB	0.919	0.422	-0.020	2.4

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

Table 292. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **115 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0152(6)	0.0294(8)	0.0194(7)	0.0010(6)	0.0092(5)	0.0004(6)
O2	0.0153(6)	0.0274(8)	0.0214(7)	-0.0012(6)	0.0024(5)	-0.0014(7)
O3	0.0158(6)	0.0286(8)	0.0159(7)	-0.0016(6)	0.0029(5)	-0.0079(6)
O4	0.0150(6)	0.0352(9)	0.0266(7)	-0.0043(7)	0.0088(5)	-0.0102(7)
O5	0.0171(7)	0.0355(9)	0.0216(7)	0.0034(7)	0.0028(5)	0.0084(7)
O6	0.0238(7)	0.0307(9)	0.0307(8)	0.0044(7)	0.0120(5)	-0.0042(7)
O7	0.0189(6)	0.0206(8)	0.0191(7)	-0.0061(6)	0.0065(5)	0.0018(6)
O8	0.0260(7)	0.0187(8)	0.0178(7)	-0.0054(6)	0.0033(6)	-0.0025(6)
C1	0.0171(9)	0.013(1)	0.0135(9)	-0.0009(8)	0.0058(7)	-0.0018(8)
C2	0.0170(9)	0.026(1)	0.0137(9)	-0.0006(9)	0.0063(7)	-0.0026(9)
C3	0.0177(9)	0.011(1)	0.0140(9)	0.0000(8)	0.0048(7)	0.0008(8)
C4	0.0169(9)	0.019(1)	0.0132(9)	-0.0017(8)	0.0064(7)	-0.0030(9)
C5	0.0155(9)	0.015(1)	0.0128(9)	-0.0005(8)	0.0054(7)	-0.0016(8)
C6	0.0184(9)	0.023(1)	0.019(1)	0.0004(9)	0.0045(8)	0.0007(9)
C7	0.0208(9)	0.014(1)	0.0134(9)	0.0011(8)	0.0053(7)	-0.0017(8)
C8	0.0186(9)	0.018(1)	0.0168(9)	-0.0014(9)	0.0048(7)	0.0011(9)
C9	0.0195(9)	0.019(1)	0.0125(9)	-0.0026(9)	0.0033(7)	-0.0011(9)
C10	0.022(1)	0.023(1)	0.022(1)	-0.000(1)	0.0018(8)	0.006(1)
C11A	0.027(1)	0.023(1)	0.020(1)	-0.003(1)	0.0043(9)	0.005(1)
C12A	0.026(1)	0.017(1)	0.022(1)	-0.003(1)	0.0069(9)	0.003(1)
C13	0.026(1)	0.028(1)	0.030(1)	-0.005(1)	0.0105(8)	0.007(1)
C14	0.0209(9)	0.026(1)	0.0174(9)	-0.0027(9)	0.0093(7)	-0.0016(9)
C15	0.0182(9)	0.018(1)	0.0147(9)	-0.0012(8)	0.0059(7)	0.0037(8)
C16	0.0185(9)	0.014(1)	0.0157(9)	0.0003(8)	0.0075(7)	-0.0013(8)
C17	0.0205(9)	0.015(1)	0.022(1)	-0.0004(9)	0.0049(8)	0.0008(9)
C18	0.0172(9)	0.014(1)	0.0172(9)	0.0013(8)	0.0042(7)	0.0022(9)
C19	0.0165(9)	0.035(1)	0.028(1)	0.006(1)	0.0130(7)	0.006(1)
C20	0.019(1)	0.032(1)	0.017(1)	-0.002(1)	-0.0013(8)	-0.008(1)
C21	0.018(1)	0.040(1)	0.034(1)	0.004(1)	-0.004(1)	0.009(1)
C22	0.021(1)	0.027(1)	0.028(1)	-0.0117(9)	0.0066(8)	0.004(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 293. Interatomic Distances (Å) for Sb-8 at **115 K**

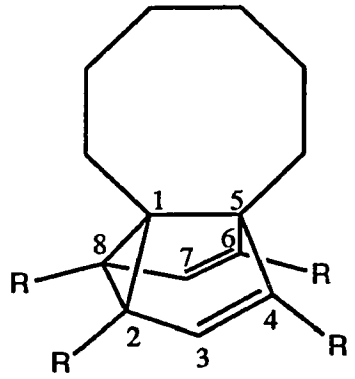
O1	C15	1.338(3)	C3	C4	1.345(3)
O1	C19	1.451(3)	C3	C7	3.023(3)
O2	C15	1.203(2)	C4	C5	1.537(3)
O3	C16	1.342(3)	C4	C6	2.244(3)
O3	C20	1.450(2)	C4	C16	1.471(2)
O4	C16	1.201(3)	C5	C6	1.532(3)
O5	C17	1.341(3)	C5	C14	1.535(3)
O5	C21	1.447(3)	C6	C7	1.344(3)
O6	C17	1.204(3)	C6	C17	1.482(3)
O7	C18	1.343(3)	C7	C8	1.440(3)
O7	C22	1.447(3)	C8	C18	1.497(3)
O8	C18	1.199(2)	C9	C10	1.533(3)
C1	C2	1.523(3)	C10	C11A	1.539(4)
C1	C5	1.582(3)	C11A	C12A	1.531(3)
C1	C8	1.495(3)	C12A	C13	1.541(3)
C1	C9	1.522(2)	C13	C14	1.538(3)
C2	C3	1.441(3)	C10	C11B	1.58(2)
C2	C8	1.722(3)	C11B	C12B	1.57(3)
C2	C15	1.487(3)	C12B	C13	1.60(2)

Table 294. Angles (°) for Sb-8 at **115 K**

C15	O1	C19	115.7(1)	C6	C7	C8	110.7(2)
C16	O3	C20	114.4(2)	C1	C8	C2	56.0(1)
C17	O5	C21	115.1(2)	C1	C8	C7	109.9(2)
C18	O7	C22	116.4(2)	C1	C8	C18	126.4(2)
C2	C1	C5	103.6(1)	C2	C8	C7	117.0(2)
C2	C1	C8	69.6(2)	C2	C8	C18	114.8(2)
C2	C1	C9	123.1(2)	C7	C8	C18	118.1(2)
C5	C1	C8	103.6(1)	C1	C9	C10	117.7(2)
C5	C1	C9	123.3(2)	C9	C10	C11A	116.4(2)
C8	C1	C9	120.6(2)	C10	C11A	C12A	113.8(2)
C1	C2	C3	109.1(2)	C11A	C12A	C13	113.3(2)
C1	C2	C8	54.4(1)	C12A	C13	C14	116.8(2)
C1	C2	C15	125.0(2)	C5	C14	C13	114.7(2)
C3	C2	C8	116.7(2)	O1	C15	O2	124.1(2)
C3	C2	C15	121.8(2)	O1	C15	C2	110.5(1)
C8	C2	C15	111.7(1)	O2	C15	C2	125.3(2)
C2	C3	C4	111.4(1)	O3	C16	O4	123.4(2)
C3	C4	C5	111.6(1)	O3	C16	C4	112.0(2)
C3	C4	C16	125.4(1)	O4	C16	C4	124.6(2)
C5	C4	C6	42.9(2)	O5	C17	O6	123.9(2)
C5	C4	C16	122.0(2)	O5	C17	C6	110.8(2)
C1	C5	C4	102.8(2)	O6	C17	C6	125.3(2)
C1	C5	C6	102.6(1)	O7	C18	O8	124.9(2)
C1	C5	C14	117.8(2)	O7	C18	C8	108.8(2)
C4	C5	C6	94.0(2)	O8	C18	C8	126.2(2)
C4	C5	C14	119.1(2)				
C6	C5	C14	116.8(2)				
C4	C6	C5	43.1(1)	C9	C10	C11B	114.9(7)
C5	C6	C7	111.3(2)	C10	C11B	C12B	104(1)
C5	C6	C17	124.0(2)	C11B	C12B	C13	103(1)
C7	C6	C17	124.3(2)	C12B	C13	C14	102.2(7)

Table 295. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-8 at **115 K**

Atom	Min.	Int'med.	Max.
O1	0.108	0.143	0.172
O2	0.120	0.158	0.166
O3	0.107	0.133	0.181
O4	0.116	0.141	0.205
O5	0.119	0.152	0.199
O6	0.132	0.173	0.189
O7	0.111	0.138	0.165
O8	0.118	0.143	0.176
C1	0.107	0.120	0.132
C2	0.111	0.130	0.162
C3	0.103	0.119	0.135
C4	0.106	0.127	0.144
C5	0.108	0.123	0.128
C6	0.132	0.146	0.152
C7	0.108	0.125	0.147
C8	0.126	0.130	0.145
C9	0.110	0.133	0.150
C10	0.125	0.148	0.182
C11A	0.127	0.150	0.183
C12A	0.120	0.150	0.170
C13	0.129	0.168	0.196
C14	0.120	0.142	0.164
C15	0.106	0.134	0.145
C16	0.111	0.124	0.138
C17	0.123	0.140	0.157
C18	0.113	0.132	0.140
C19	0.105	0.158	0.198
C20	0.101	0.163	0.191
C21	0.112	0.195	0.225
C22	0.100	0.161	0.201



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–296. X-ray Crystal Data for Sb-8 at **115 K**

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.08 x 0.10 x 0.59
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.531(1)
b (Å)	14.4971)
c (Å)	14.099(5)
β (°)	109.20(1)
Cell volume (Å^3)	2032.69(6.9)
Z	4
d_{calc} (g cm^{-3})	1.367
μ(Cu $K\alpha$) (cm^{-1})	8.29
Maximum θ(°)	60
Unique reflections	3015
Observed reflections [$I > 3.0\sigma(I)$]	2107
Number of variables	279
R	0.051
R_w	0.063
$(\Delta\rho)_{max}$ (e Å^{-3})	0.30
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.39

Table 297. Final Atomic Parameters for Sb-8 at **115 K**

Atom	x	y	z	B(Å^2)
O1	0.3950(2)	0.3291(2)	0.1819(2)	1.84(5)
O2	0.3094(2)	0.2690(2)	0.0274(2)	2.05(5)
O3	0.8966(2)	0.3785(2)	0.3213(2)	1.94(5)
O4	1.0086(2)	0.3334(2)	0.2187(2)	2.28(5)
O5	0.9740(2)	0.1289(2)	0.2702(2)	2.46(6)
O6	1.0292(2)	0.1373(2)	0.1295(2)	2.49(6)
O7	0.4217(2)	0.0763(2)	0.1249(2)	1.88(5)
O8	0.3902(2)	0.0785(2)	-0.0407(2)	2.17(5)
C1	0.5983(3)	0.2467(2)	0.0231(2)	1.50(7)
C2	0.5477(3)	0.2743(3)	0.1081(3)	1.87(7)
C3	0.6566(3)	0.3153(2)	0.1887(3)	1.43(7)
C4	0.7718(3)	0.3137(2)	0.1666(2)	1.53(7)
C5	0.7559(3)	0.2614(2)	0.0698(2)	1.51(7)
C6	0.8036(3)	0.1697(3)	0.1232(3)	1.96(8)
C7	0.7004(3)	0.1196(2)	0.1318(3)	1.62(7)
C8	0.5744(3)	0.1621(2)	0.0749(3)	1.91(8)
C9	0.5184(3)	0.2636(2)	-0.0865(3)	1.69(7)
C10	0.4807(3)	0.3635(3)	-0.1203(3)	2.21(8)
C11A	0.5927(4)	0.4251(3)	-0.1309(3)	2.13(9)
C12A	0.6994(4)	0.4526(3)	-0.0311(3)	1.96(8)
C13	0.8336(3)	0.4018(3)	-0.0095(3)	2.25(8)
C14	0.8301(3)	0.2963(2)	-0.0004(3)	1.89(7)
C15	0.4045(3)	0.2904(2)	0.0985(3)	1.82(7)
C16	0.9046(3)	0.3419(2)	0.2366(3)	1.68(7)
C17	0.9470(3)	0.1448(2)	0.1717(3)	1.93(7)
C18	0.4508(3)	0.1033(2)	0.0431(3)	1.74(7)
C19	0.2600(3)	0.3379(3)	0.1872(3)	2.36(8)
C20	1.0258(3)	0.3992(3)	0.3967(3)	2.23(8)
C21	1.1141(4)	0.1104(3)	0.3268(3)	3.1(1)
C22	0.3098(3)	0.0134(3)	0.1089(3)	2.40(8)
C11B	0.585(6)	0.440(5)	-0.055(5)	5(1)*
C12B	0.705(4)	0.418(3)	-0.109(3)	2.2(9)*
H3	0.648	0.341	0.252	1.6
H7	0.710	0.062	0.172	1.8
H9A	0.433	0.228	-0.102	1.9
H9B	0.573	0.239	-0.127	1.9
H10AA	0.445	0.393	-0.070	2.4
H10AB	0.408	0.361	-0.187	2.4
H11AA	0.551	0.483	-0.167	2.3
H11AB	0.639	0.391	-0.172	2.3
H12AA	0.663	0.439	0.025	2.2
H12AB	0.717	0.520	-0.033	2.2
H13AA	0.897	0.426	0.055	2.5
H13AB	0.869	0.416	-0.065	2.5
H14A	0.784	0.270	-0.069	2.1
H14B	0.925	0.273	0.026	2.1
H19A	0.264	0.367	0.252	2.6
H19B	0.204	0.377	0.130	2.6
H19C	0.218	0.275	0.183	2.6
H20A	1.011	0.426	0.457	2.5
H20B	1.080	0.341	0.416	2.5
H20C	1.076	0.444	0.369	2.5
H21A	1.124	0.100	0.399	3.4
H21B	1.145	0.054	0.299	3.4
H21C	1.170	0.165	0.322	3.4
H22A	0.298	-0.001	0.175	2.6
H22B	0.226	0.043	0.064	2.6
H22C	0.328	-0.045	0.077	2.6

Table 297 (cont.). Final Atomic Parameters for Sb-8 at **115 K**

Atom	x	y	z	B(Å^2)
H10BA	0.390	0.377	-0.115	2.4
H10BB	0.476	0.369	-0.192	2.4
H11BA	0.616	0.427	0.019	5.6
H11BB	0.549	0.505	-0.067	5.6
H12BA	0.718	0.472	-0.149	2.4
H12BB	0.683	0.362	-0.153	2.4
H13BA	0.823	0.433	0.050	2.5
H13BB	0.919	0.423	-0.019	2.5

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

Table 298. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **115 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0147(9)	0.032(1)	0.027(1)	0.0017(9)	0.0125(8)	0.000(1)
O2	0.016(1)	0.031(1)	0.030(1)	-0.002(1)	0.0057(8)	-0.001(1)
O3	0.016(1)	0.030(1)	0.026(1)	-0.002(1)	0.0057(8)	-0.011(1)
O4	0.016(1)	0.037(1)	0.035(1)	-0.004(1)	0.0108(9)	-0.009(1)
O5	0.019(1)	0.038(1)	0.035(1)	0.003(1)	0.0065(9)	0.011(1)
O6	0.026(1)	0.035(1)	0.038(1)	0.005(1)	0.0159(9)	-0.004(1)
O7	0.020(1)	0.023(1)	0.030(1)	-0.008(1)	0.0107(8)	0.001(1)
O8	0.028(1)	0.018(1)	0.034(1)	-0.008(1)	0.0065(9)	-0.005(1)
C1	0.017(1)	0.015(2)	0.027(2)	-0.001(1)	0.010(1)	-0.003(1)
C2	0.018(1)	0.031(2)	0.025(2)	-0.001(1)	0.011(1)	-0.001(2)
C3	0.019(1)	0.012(2)	0.025(2)	0.001(1)	0.010(1)	0.001(1)
C4	0.019(1)	0.022(2)	0.020(2)	-0.002(1)	0.009(1)	-0.003(1)
C5	0.016(1)	0.018(2)	0.025(2)	-0.002(1)	0.009(1)	-0.006(1)
C6	0.019(1)	0.025(2)	0.030(2)	0.001(1)	0.008(1)	0.004(2)
C7	0.021(1)	0.017(2)	0.024(2)	0.001(1)	0.009(1)	-0.002(1)
C8	0.019(1)	0.018(2)	0.037(2)	-0.001(1)	0.011(1)	0.005(2)
C9	0.018(1)	0.022(2)	0.021(2)	-0.001(1)	0.002(1)	0.001(2)
C10	0.022(2)	0.025(2)	0.034(2)	0.000(2)	0.005(1)	0.006(2)
C11A	0.026(2)	0.024(2)	0.028(2)	-0.004(2)	0.005(1)	0.006(2)
C12A	0.025(2)	0.017(2)	0.032(2)	-0.003(2)	0.009(1)	0.001(2)
C13	0.028(2)	0.026(2)	0.035(2)	-0.003(2)	0.015(1)	0.007(2)
C14	0.021(1)	0.025(2)	0.031(2)	-0.002(1)	0.015(1)	-0.002(2)
C15	0.019(1)	0.019(2)	0.035(2)	-0.001(1)	0.014(1)	0.005(2)
C16	0.015(1)	0.016(2)	0.034(2)	0.002(1)	0.010(1)	-0.002(1)
C17	0.024(2)	0.016(2)	0.034(2)	0.000(1)	0.011(1)	0.005(2)
C18	0.020(1)	0.013(2)	0.035(2)	-0.002(1)	0.012(1)	-0.003(2)
C19	0.015(1)	0.038(2)	0.042(2)	0.004(1)	0.017(1)	0.006(2)
C20	0.021(2)	0.036(2)	0.024(2)	-0.005(2)	0.003(1)	-0.010(2)
C21	0.019(2)	0.041(2)	0.048(2)	0.008(2)	-0.000(2)	0.013(2)
C22	0.022(2)	0.025(2)	0.044(2)	-0.010(1)	0.012(1)	0.004(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 299. Interatomic Distances (Å) for Sb-8 at **115 K**

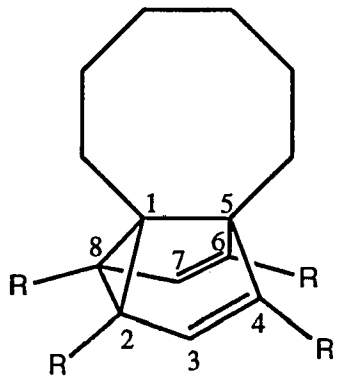
O1	C15	1.335(5)	C3	C4	1.348(5)
O1	C19	1.455(4)	C3	C7	3.023(5)
O2	C15	1.202(4)	C4	C5	1.522(5)
O3	C16	1.335(5)	C4	C6	2.231(5)
O3	C20	1.456(4)	C4	C16	1.480(4)
O4	C16	1.209(4)	C5	C6	1.528(5)
O5	C17	1.343(5)	C5	C14	1.535(5)
O5	C21	1.453(4)	C6	C7	1.346(5)
O6	C17	1.205(5)	C6	C17	1.483(4)
O7	C18	1.345(5)	C7	C8	1.443(4)
O7	C22	1.448(4)	C8	C18	1.495(4)
O8	C18	1.199(4)	C9	C10	1.536(5)
C1	C2	1.518(5)	C10	C11A	1.526(6)
C1	C5	1.586(4)	C11A	C12A	1.537(5)
C1	C8	1.490(5)	C12A	C13	1.533(5)
C1	C9	1.517(4)	C13	C14	1.536(5)
C2	C3	1.450(4)	C10	C11B	1.62(6)
C2	C8	1.741(5)	C11B	C12B	1.70(9)
C2	C15	1.487(5)	C12B	C13	1.62(4)

Table 300. Angles (°) for Sb-8 at **115 K**

C15	O1	C19	116.1(2)	C6	C7	C8	110.0(3)
C16	O3	C20	114.6(3)	C1	C8	C2	55.4(2)
C17	O5	C21	115.5(4)	C1	C8	C7	110.5(3)
C18	O7	C22	116.9(2)	C1	C8	C18	126.3(3)
C2	C1	C5	103.2(2)	C2	C8	C7	116.7(2)
C2	C1	C8	70.7(3)	C2	C8	C18	114.3(3)
C2	C1	C9	122.7(3)	C7	C8	C18	118.3(3)
C5	C1	C8	103.3(2)	C1	C9	C10	118.0(3)
C5	C1	C9	123.7(3)	C9	C10	C11A	116.9(3)
C8	C1	C9	120.4(3)	C10	C11A	C12A	114.7(3)
C1	C2	C3	109.5(3)	C11A	C12A	C13	113.9(3)
C1	C2	C8	53.9(2)	C12A	C13	C14	116.7(3)
C1	C2	C15	125.3(3)	C5	C14	C13	114.4(3)
C3	C2	C8	116.0(2)	O1	C15	O2	124.0(3)
C3	C2	C15	121.6(3)	O1	C15	C2	110.6(2)
C8	C2	C15	111.8(3)	O2	C15	C2	125.3(4)
C2	C3	C4	110.6(3)	O3	C16	O4	123.7(3)
C3	C4	C5	112.0(3)	O3	C16	C4	112.5(3)
C3	C4	C16	124.5(3)	O4	C16	C4	123.8(3)
C5	C4	C6	43.1(1)	O5	C17	O6	123.6(3)
C5	C4	C16	122.4(4)	O5	C17	C6	110.9(3)
C1	C5	C4	103.3(2)	O6	C17	C6	125.6(3)
C1	C5	C6	102.5(3)	O7	C18	O8	124.1(3)
C1	C5	C14	117.5(2)	O7	C18	C8	109.2(3)
C4	C5	C6	94.0(3)	O8	C18	C8	126.5(3)
C4	C5	C14	119.0(2)				
C6	C5	C14	116.8(2)				
C4	C6	C5	42.9(2)	C9	C10	C11B	114(2)
C5	C6	C7	111.6(3)	C10	C11B	C12B	95(4)
C5	C6	C17	124.0(3)	C11B	C12B	C13	100(3)
C7	C6	C17	123.9(3)	C12B	C13	C14	101(2)

Table 301. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-8 at **115 K**

Atom	Min.	Int'med.	Max.
O1	0.099	0.167	0.179
O2	0.124	0.175	0.179
O3	0.125	0.135	0.200
O4	0.119	0.164	0.213
O5	0.135	0.165	0.220
O6	0.133	0.191	0.201
O7	0.106	0.174	0.174
O8	0.115	0.179	0.193
C1	0.118	0.124	0.167
C2	0.118	0.160	0.178
C3	0.110	0.128	0.161
C4	0.123	0.137	0.156
C5	0.121	0.122	0.167
C6	0.137	0.152	0.181
C7	0.126	0.145	0.156
C8	0.122	0.140	0.195
C9	0.127	0.144	0.165
C10	0.145	0.151	0.201
C11A	0.138	0.156	0.193
C12A	0.125	0.160	0.183
C13	0.130	0.174	0.195
C14	0.119	0.156	0.183
C15	0.111	0.142	0.191
C16	0.110	0.133	0.185
C17	0.122	0.152	0.187
C18	0.112	0.133	0.189
C19	0.096	0.184	0.216
C20	0.124	0.165	0.205
C21	0.119	0.200	0.249
C22	0.104	0.183	0.216



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–302. X-ray Crystal Data for Sb-8 at **127 K**

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.08 x 0.10 x 0.59
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.538(1)
b (Å)	14.528(1)
c (Å)	14.106(6)
β (°)	109.21(1)
Cell volume (Å^3)	2039.23(7.76)
Z	4
d_{calc} (g cm^{-3})	1.363
μ(Cu $K\alpha$) (cm^{-1})	8.26
Maximum θ (°)	60
Unique reflections	3028
Observed reflections [$I > 3.0\sigma(I)$]	2191
Number of variables	279
R	0.042
R_w	0.053
$(\Delta\rho)_{max}$ (e Å^{-3})	0.21
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.24

Table 303. Final Atomic Parameters for Sb-8 at **127 K**

Atom	x	y	z	B(Å^2)
O1	0.3948(2)	0.3300(1)	0.1820(1)	1.95(4)
O2	0.3094(2)	0.2692(1)	0.0279(1)	2.06(4)
O3	0.8964(2)	0.3772(1)	0.3216(1)	1.93(4)
O4	1.0080(2)	0.3332(2)	0.2190(1)	2.30(4)
O5	0.9737(2)	0.1291(2)	0.2710(1)	2.47(5)
O6	1.0272(2)	0.1371(2)	0.1298(2)	2.59(5)
O7	0.4215(2)	0.0762(1)	0.1246(1)	1.87(4)
O8	0.3891(2)	0.0790(1)	-0.0414(1)	2.12(4)
C1	0.5968(3)	0.2465(2)	0.0235(2)	1.38(6)
C2	0.5479(3)	0.2753(2)	0.1091(2)	1.97(6)
C3	0.6554(3)	0.3151(2)	0.1881(2)	1.27(5)
C4	0.7718(3)	0.3121(2)	0.1673(2)	1.57(6)
C5	0.7547(2)	0.2608(2)	0.0695(2)	1.41(5)
C6	0.8029(3)	0.1705(2)	0.1245(2)	2.02(6)
C7	0.6991(3)	0.1197(2)	0.1318(2)	1.39(5)
C8	0.5738(3)	0.1611(2)	0.0751(2)	1.89(6)
C9	0.5176(3)	0.2637(2)	-0.0858(2)	1.69(6)
C10	0.4800(3)	0.3633(2)	-0.1196(2)	2.14(6)
C11A	0.5928(3)	0.4250(2)	-0.1309(2)	2.24(7)
C12A	0.6984(3)	0.4520(2)	-0.0317(2)	2.09(7)
C13	0.8333(3)	0.4012(2)	-0.0096(2)	2.29(6)
C14	0.8294(3)	0.2958(2)	-0.0001(2)	1.78(6)
C15	0.4047(3)	0.2908(2)	0.0996(2)	1.61(6)
C16	0.9040(3)	0.3413(2)	0.2361(2)	1.48(5)
C17	0.9455(3)	0.1451(2)	0.1727(2)	1.86(6)
C18	0.4502(3)	0.1028(2)	0.0429(2)	1.65(6)
C19	0.2596(3)	0.3382(2)	0.1876(2)	2.32(6)
C20	1.0251(3)	0.3990(2)	0.3957(2)	2.31(7)
C21	1.1135(3)	0.1100(3)	0.3266(3)	3.16(8)
C22	0.3092(3)	0.0139(2)	0.1083(2)	2.39(7)
C11B	0.584(4)	0.437(3)	-0.068(3)	2.3(7)*
C12B	0.709(4)	0.421(3)	-0.106(3)	2.5(8)*
H3	0.646	0.342	0.251	1.4
H7	0.708	0.061	0.171	1.5
H9A	0.432	0.228	-0.102	1.9
H9B	0.572	0.239	-0.126	1.9
H10AA	0.445	0.393	-0.069	2.4
H10AB	0.407	0.361	-0.186	2.4
H11AA	0.551	0.483	-0.167	2.5
H11AB	0.639	0.391	-0.172	2.5
H12AA	0.662	0.438	0.024	2.3
H12AB	0.716	0.520	-0.033	2.3
H13AA	0.896	0.426	0.055	2.5
H13AB	0.869	0.415	-0.065	2.5
H14A	0.784	0.270	-0.068	2.0
H14B	0.924	0.273	0.026	2.0
H19A	0.264	0.368	0.252	2.6
H19B	0.203	0.376	0.130	2.6
H19C	0.219	0.276	0.184	2.6
H20A	1.011	0.425	0.457	2.5
H20B	1.080	0.342	0.414	2.5
H20C	1.073	0.445	0.367	2.5
H21A	1.124	0.099	0.399	3.5
H21B	1.143	0.054	0.298	3.5
H21C	1.170	0.164	0.321	3.5
H22A	0.297	-0.001	0.174	2.6
H22B	0.226	0.044	0.063	2.6
H22C	0.327	-0.044	0.076	2.6

Table 303 (cont.). Final Atomic Parameters for Sb-8 at **127 K**

Atom	x	y	z	B(Å^2)
H10BA	0.395	0.378	-0.106	2.4
H10BB	0.465	0.367	-0.193	2.4
H11BA	0.612	0.430	0.006	2.5
H11BB	0.546	0.500	-0.087	2.5
H12BA	0.726	0.477	-0.141	2.8
H12BB	0.692	0.367	-0.152	2.8
H13BA	0.823	0.432	0.051	2.5
H13BB	0.919	0.422	-0.019	2.5

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

Table 304. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **127 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0153(8)	0.036(1)	0.0257(9)	0.0014(8)	0.0115(6)	-0.0001(9)
O2	0.0176(8)	0.033(1)	0.026(1)	-0.0007(8)	0.0057(7)	-0.0004(9)
O3	0.0171(8)	0.036(1)	0.0201(9)	-0.0032(8)	0.0052(6)	-0.0099(9)
O4	0.0158(8)	0.041(1)	0.033(1)	-0.0047(9)	0.0105(7)	-0.011(1)
O5	0.0189(9)	0.042(1)	0.031(1)	0.0037(9)	0.0054(7)	0.010(1)
O6	0.0273(9)	0.037(1)	0.037(1)	0.0064(9)	0.0152(7)	-0.004(1)
O7	0.0204(8)	0.027(1)	0.0234(9)	-0.0080(8)	0.0071(7)	0.0015(9)
O8	0.032(1)	0.021(1)	0.025(1)	-0.0076(8)	0.0058(8)	-0.0038(9)
C1	0.018(1)	0.015(1)	0.019(1)	-0.001(1)	0.0055(9)	-0.003(1)
C2	0.020(1)	0.037(2)	0.021(1)	-0.002(1)	0.0102(9)	-0.003(1)
C3	0.018(1)	0.014(1)	0.016(1)	0.001(1)	0.0056(9)	0.002(1)
C4	0.018(1)	0.027(1)	0.016(1)	-0.002(1)	0.0070(9)	-0.003(1)
C5	0.016(1)	0.019(1)	0.020(1)	-0.001(1)	0.0082(9)	-0.002(1)
C6	0.020(1)	0.032(2)	0.024(1)	-0.001(1)	0.006(1)	0.005(1)
C7	0.020(1)	0.019(1)	0.013(1)	0.001(1)	0.0055(9)	-0.003(1)
C8	0.021(1)	0.022(1)	0.029(1)	-0.002(1)	0.008(1)	0.003(1)
C9	0.020(1)	0.023(1)	0.020(1)	-0.000(1)	0.005(1)	0.002(1)
C10	0.026(1)	0.026(2)	0.025(1)	-0.001(1)	0.003(1)	0.007(1)
C11A	0.028(1)	0.028(2)	0.028(2)	-0.003(1)	0.006(1)	0.007(1)
C12A	0.030(1)	0.020(2)	0.029(2)	-0.002(1)	0.010(1)	0.006(1)
C13	0.028(1)	0.030(2)	0.032(1)	-0.004(1)	0.015(1)	0.006(1)
C14	0.022(1)	0.027(1)	0.023(1)	-0.001(1)	0.0133(9)	-0.003(1)
C15	0.016(1)	0.025(1)	0.021(1)	-0.002(1)	0.0073(9)	0.003(1)
C16	0.018(1)	0.020(1)	0.019(1)	0.001(1)	0.0071(9)	0.001(1)
C17	0.025(1)	0.020(1)	0.026(1)	-0.001(1)	0.009(1)	0.001(1)
C18	0.020(1)	0.017(1)	0.026(1)	-0.000(1)	0.009(1)	0.001(1)
C19	0.017(1)	0.041(2)	0.036(1)	0.004(1)	0.017(1)	0.006(1)
C20	0.020(1)	0.041(2)	0.022(1)	-0.003(1)	0.001(1)	-0.008(1)
C21	0.019(1)	0.048(2)	0.044(2)	0.007(1)	-0.002(1)	0.012(2)
C22	0.024(1)	0.029(2)	0.037(2)	-0.013(1)	0.010(1)	0.004(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 305. Interatomic Distances (Å) for Sb-8 at **127 K**

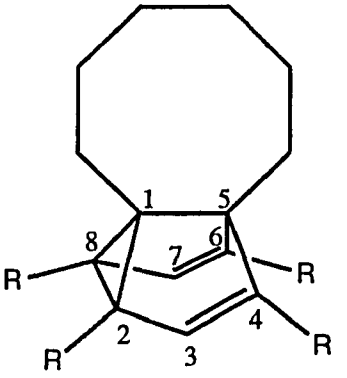
O1	C15	1.329(4)	C3	C4	1.353(4)
O1	C19	1.457(4)	C3	C7	3.024(4)
O2	C15	1.209(3)	C4	C5	1.526(4)
O3	C16	1.341(4)	C4	C6	2.199(4)
O3	C20	1.449(3)	C4	C16	1.474(3)
O4	C16	1.202(4)	C5	C6	1.523(4)
O5	C17	1.340(4)	C5	C14	1.532(4)
O5	C21	1.450(3)	C6	C7	1.353(4)
O6	C17	1.211(4)	C6	C17	1.478(4)
O7	C18	1.342(4)	C7	C8	1.432(3)
O7	C22	1.447(4)	C8	C18	1.494(4)
O8	C18	1.201(3)	C9	C10	1.534(4)
C1	C2	1.519(4)	C10	C11A	1.538(5)
C1	C5	1.588(3)	C11A	C12A	1.526(4)
C1	C8	1.497(4)	C12A	C13	1.540(4)
C1	C9	1.513(3)	C13	C14	1.538(4)
C2	C3	1.424(3)	C10	C11B	1.53(4)
C2	C8	1.772(4)	C11B	C12B	1.60(6)
C2	C15	1.488(4)	C12B	C13	1.57(3)

Table 306. Angles (°) for Sb-8 at **127 K**

C15	O1	C19	116.2(2)	C6	C7	C8	110.3(2)
C16	O3	C20	114.5(2)	C1	C8	C2	54.6(2)
C17	O5	C21	115.7(3)	C1	C8	C7	110.7(2)
C18	O7	C22	116.6(2)	C1	C8	C18	125.9(2)
C2	C1	C5	102.9(1)	C2	C8	C7	116.0(2)
C2	C1	C8	72.0(2)	C2	C8	C18	114.6(2)
C2	C1	C9	123.2(2)	C7	C8	C18	118.8(2)
C5	C1	C8	103.0(2)	C1	C9	C10	118.1(2)
C5	C1	C9	123.1(2)	C9	C10	C11A	116.9(2)
C8	C1	C9	120.6(2)	C10	C11A	C12A	114.2(3)
C1	C2	C3	110.1(2)	C11A	C12A	C13	114.1(3)
C1	C2	C8	53.5(2)	C12A	C13	C14	116.4(2)
C1	C2	C15	124.7(2)	C5	C14	C13	114.9(3)
C3	C2	C8	116.0(2)	O1	C15	O2	124.0(3)
C3	C2	C15	122.0(3)	O1	C15	C2	110.8(2)
C8	C2	C15	111.1(2)	O2	C15	C2	125.1(3)
C2	C3	C4	111.2(3)	O3	C16	O4	123.1(2)
C3	C4	C5	111.5(2)	O3	C16	C4	112.4(2)
C3	C4	C16	125.2(2)	O4	C16	C4	124.5(3)
C5	C4	C6	43.8(1)	O5	C17	O6	123.3(2)
C5	C4	C16	122.7(3)	O5	C17	C6	111.5(3)
C1	C5	C4	103.2(2)	O6	C17	C6	125.2(3)
C1	C5	C6	103.0(2)	O7	C18	O8	124.6(3)
C1	C5	C14	118.2(2)	O7	C18	C8	108.8(2)
C4	C5	C6	92.3(2)	O8	C18	C8	126.4(3)
C4	C5	C14	118.9(2)				
C6	C5	C14	117.1(2)				
C4	C6	C5	43.9(1)	C9	C10	C11B	116(1)
C5	C6	C7	111.5(2)	C10	C11B	C12B	106(3)
C5	C6	C17	124.6(3)	C11B	C12B	C13	106(3)
C7	C6	C17	123.6(3)	C12B	C13	C14	102(1)

Table 307. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-8 at **127 K**

Atom	Min.	Int'med.	Max.
O1	0.105	0.163	0.191
O2	0.133	0.165	0.183
O3	0.121	0.135	0.201
O4	0.118	0.160	0.219
O5	0.134	0.169	0.218
O6	0.137	0.193	0.206
O7	0.119	0.152	0.183
O8	0.127	0.164	0.194
C1	0.116	0.135	0.145
C2	0.122	0.150	0.194
C3	0.114	0.131	0.134
C4	0.119	0.131	0.168
C5	0.120	0.131	0.149
C6	0.140	0.149	0.186
C7	0.109	0.139	0.147
C8	0.135	0.151	0.176
C9	0.137	0.146	0.155
C10	0.134	0.159	0.196
C11A	0.143	0.161	0.197
C12A	0.129	0.174	0.180
C13	0.132	0.181	0.192
C14	0.116	0.156	0.172
C15	0.119	0.141	0.165
C16	0.129	0.135	0.146
C17	0.139	0.158	0.163
C18	0.132	0.139	0.161
C19	0.102	0.181	0.213
C20	0.121	0.170	0.210
C21	0.121	0.210	0.248
C22	0.109	0.185	0.212



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–308. X-ray Crystal Data for Sb-8 at **140 K**

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.08 x 0.10 x 0.59
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.548(1)
b (Å)	14.563(1)
c (Å)	14.101(3)
β (°)	109.30(1)
Cell volume (Å^3)	2044.33(7.94)
Z	4
d_{calc} (g cm^{-3})	1.359
μ(Cu $K\alpha$) (cm^{-1})	8.24
Maximum θ (°)	60
Unique reflections	3035
Observed reflections [$I > 3.0\sigma(I)$]	2173
Number of variables	279
R	0.040
R_w	0.047
$(\Delta\rho)_{max}$ (e Å^{-3})	0.21
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.23

Table 309. Final Atomic Parameters for Sb-8 at **140 K**

Atom	x	y	z	B(Å^2)
O1	0.3942(2)	0.3307(1)	0.1820(1)	2.13(4)
O2	0.3091(2)	0.2693(1)	0.0282(1)	2.25(4)
O3	0.8959(2)	0.3764(1)	0.3216(1)	2.17(4)
O4	1.0073(2)	0.3328(1)	0.2191(1)	2.53(4)
O5	0.9732(2)	0.1297(1)	0.2718(1)	2.75(4)
O6	1.0253(2)	0.1366(1)	0.1302(1)	2.93(4)
O7	0.4214(2)	0.0756(1)	0.1244(1)	2.09(4)
O8	0.3878(2)	0.0793(1)	-0.0412(1)	2.37(4)
C1	0.5964(2)	0.2463(2)	0.0242(2)	1.46(5)
C2	0.5472(2)	0.2761(2)	0.1092(2)	2.13(6)
C3	0.6549(2)	0.3150(2)	0.1884(2)	1.39(5)
C4	0.7716(2)	0.3107(2)	0.1683(2)	1.84(5)
C5	0.7540(2)	0.2606(2)	0.0695(2)	1.52(5)
C6	0.8020(2)	0.1711(2)	0.1258(2)	2.30(6)
C7	0.6977(2)	0.1197(2)	0.1316(2)	1.60(5)
C8	0.5736(2)	0.1606(2)	0.0745(2)	2.05(5)
C9	0.5168(2)	0.2637(2)	-0.0856(2)	1.81(5)
C10	0.4794(3)	0.3630(2)	-0.1190(2)	2.32(6)
C11A	0.5919(3)	0.4242(2)	-0.1309(2)	2.52(7)
C12A	0.6984(3)	0.4516(2)	-0.0311(2)	2.20(6)
C13	0.8324(3)	0.4000(2)	-0.0101(2)	2.58(6)
C14	0.8282(2)	0.2950(2)	-0.0003(2)	1.96(5)
C15	0.4041(2)	0.2915(2)	0.0994(2)	1.89(5)
C16	0.9035(2)	0.3407(2)	0.2361(2)	1.59(5)
C17	0.9449(2)	0.1451(2)	0.1730(2)	2.06(5)
C18	0.4496(2)	0.1026(2)	0.0426(2)	1.78(5)
C19	0.2596(2)	0.3389(2)	0.1869(2)	2.58(6)
C20	1.0249(3)	0.3989(2)	0.3958(2)	2.63(6)
C21	1.1129(3)	0.1097(2)	0.3266(2)	3.44(7)
C22	0.3082(3)	0.0140(2)	0.1078(2)	2.67(6)
C11B	0.587(3)	0.437(2)	-0.068(2)	2.4(5)*
C12B	0.706(2)	0.420(2)	-0.108(2)	1.9(5)*
H3	0.646	0.342	0.251	1.5
H7	0.707	0.061	0.171	1.8
H9A	0.431	0.228	-0.102	2.0
H9B	0.571	0.239	-0.126	2.0
H10AA	0.445	0.392	-0.068	2.6
H10AB	0.406	0.361	-0.186	2.6
H11AA	0.550	0.482	-0.167	2.8
H11AB	0.638	0.390	-0.172	2.8
H12AA	0.662	0.438	0.025	2.4
H12AB	0.716	0.519	-0.033	2.4
H13AA	0.896	0.424	0.054	2.8
H13AB	0.867	0.414	-0.066	2.8
H14A	0.783	0.269	-0.069	2.2
H14B	0.923	0.272	0.026	2.2
H19A	0.264	0.369	0.251	2.8
H19B	0.203	0.377	0.129	2.8
H19C	0.219	0.276	0.183	2.8
H20A	1.010	0.425	0.457	2.9
H20B	1.081	0.342	0.414	2.9
H20C	1.072	0.445	0.367	2.9
H21A	1.124	0.099	0.399	3.8
H21B	1.141	0.053	0.298	3.8
H21C	1.170	0.163	0.320	3.8
H22A	0.297	-0.001	0.174	2.9
H22B	0.225	0.044	0.063	2.9
H22C	0.325	-0.044	0.075	2.9

Table 309 (cont.). Final Atomic Parameters for Sb-8 at **140 K**

Atom	x	y	z	B(Å^2)
H10BA	0.395	0.379	-0.104	2.6
H10BB	0.461	0.366	-0.193	2.6
H11BA	0.617	0.430	0.007	2.7
H11BB	0.549	0.500	-0.087	2.7
H12BA	0.722	0.475	-0.144	2.1
H12BB	0.686	0.366	-0.154	2.1
H13BA	0.823	0.431	0.050	2.8
H13BB	0.918	0.420	-0.020	2.8

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

Table 310. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **140 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0169(7)	0.042(1)	0.0254(8)	0.0009(8)	0.0111(6)	0.0003(8)
O2	0.0168(8)	0.037(1)	0.0293(9)	-0.0018(8)	0.0041(6)	-0.0012(8)
O3	0.0181(7)	0.041(1)	0.0226(8)	-0.0030(8)	0.0053(6)	-0.0108(8)
O4	0.0178(7)	0.047(1)	0.0338(9)	-0.0057(8)	0.0112(6)	-0.0123(9)
O5	0.0208(8)	0.051(1)	0.0305(9)	0.0040(8)	0.0049(7)	0.0106(9)
O6	0.0315(8)	0.044(1)	0.0392(9)	0.0077(9)	0.0157(7)	-0.0030(9)
O7	0.0245(8)	0.0303(9)	0.0249(8)	-0.0093(8)	0.0084(6)	0.0002(8)
O8	0.0363(9)	0.0257(9)	0.0250(8)	-0.0092(8)	0.0063(7)	-0.0038(8)
C1	0.019(1)	0.019(1)	0.016(1)	-0.001(1)	0.0044(8)	-0.002(1)
C2	0.017(1)	0.043(2)	0.022(1)	-0.002(1)	0.0094(8)	-0.003(1)
C3	0.020(1)	0.016(1)	0.017(1)	0.001(1)	0.0058(8)	0.001(1)
C4	0.017(1)	0.035(1)	0.019(1)	-0.004(1)	0.0072(8)	-0.006(1)
C5	0.019(1)	0.021(1)	0.021(1)	-0.001(1)	0.0101(8)	-0.003(1)
C6	0.022(1)	0.035(1)	0.029(1)	-0.000(1)	0.0064(9)	0.007(1)
C7	0.024(1)	0.020(1)	0.017(1)	0.001(1)	0.0069(8)	-0.004(1)
C8	0.023(1)	0.026(1)	0.030(1)	-0.004(1)	0.0091(9)	0.004(1)
C9	0.024(1)	0.026(1)	0.018(1)	-0.002(1)	0.0047(9)	0.000(1)
C10	0.028(1)	0.030(1)	0.027(1)	0.000(1)	0.004(1)	0.008(1)
C11A	0.033(1)	0.032(2)	0.027(1)	-0.005(1)	0.005(1)	0.006(1)
C12A	0.029(1)	0.025(1)	0.029(1)	-0.003(1)	0.009(1)	0.005(1)
C13	0.030(1)	0.034(2)	0.036(1)	-0.005(1)	0.0151(9)	0.008(1)
C14	0.025(1)	0.032(1)	0.023(1)	-0.002(1)	0.0139(8)	-0.003(1)
C15	0.018(1)	0.029(1)	0.025(1)	-0.002(1)	0.0081(8)	0.005(1)
C16	0.019(1)	0.022(1)	0.020(1)	0.001(1)	0.0070(8)	0.000(1)
C17	0.024(1)	0.025(1)	0.029(1)	-0.002(1)	0.0081(9)	0.002(1)
C18	0.021(1)	0.021(1)	0.025(1)	0.001(1)	0.0070(9)	0.002(1)
C19	0.019(1)	0.046(2)	0.039(1)	0.006(1)	0.0178(9)	0.009(1)
C20	0.025(1)	0.046(2)	0.023(1)	-0.005(1)	-0.000(1)	-0.013(1)
C21	0.024(1)	0.053(2)	0.043(2)	0.007(1)	-0.003(1)	0.011(2)
C22	0.027(1)	0.035(2)	0.038(1)	-0.014(1)	0.008(1)	0.005(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 311. Interatomic Distances (Å) for Sb-8 at **140 K**

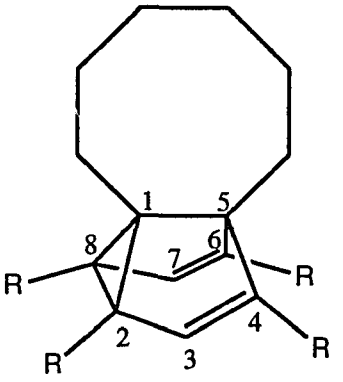
O1	C15	1.332(3)	C3	C4	1.353(4)
O1	C19	1.450(3)	C3	C7	3.028(3)
O2	C15	1.205(3)	C4	C5	1.528(3)
O3	C16	1.339(3)	C4	C6	2.173(4)
O3	C20	1.453(3)	C4	C16	1.470(3)
O4	C16	1.201(3)	C5	C6	1.523(4)
O5	C17	1.343(3)	C5	C14	1.531(4)
O5	C21	1.450(3)	C6	C7	1.355(4)
O6	C17	1.199(4)	C6	C17	1.481(3)
O7	C18	1.341(3)	C7	C8	1.421(3)
O7	C22	1.450(3)	C8	C18	1.496(3)
O8	C18	1.195(3)	C9	C10	1.531(4)
C1	C2	1.517(4)	C10	C11A	1.538(4)
C1	C5	1.585(3)	C11A	C12A	1.534(4)
C1	C8	1.493(4)	C12A	C13	1.541(4)
C1	C9	1.518(3)	C13	C14	1.537(4)
C2	C3	1.421(3)	C10	C11B	1.56(3)
C2	C8	1.798(4)	C11B	C12B	1.55(4)
C2	C15	1.487(4)	C12B	C13	1.60(2)

Table 312. Angles (°) for Sb-8 at **140 K**

C15	O1	C19	116.0(2)	C6	C7	C8	110.4(2)
C16	O3	C20	114.5(2)	C1	C8	C2	54.0(2)
C17	O5	C21	115.2(2)	C1	C8	C7	110.9(2)
C18	O7	C22	116.6(2)	C1	C8	C18	126.2(2)
C2	C1	C5	103.3(2)	C2	C8	C7	115.7(2)
C2	C1	C8	73.3(2)	C2	C8	C18	114.3(2)
C2	C1	C9	122.7(2)	C7	C8	C18	118.9(2)
C5	C1	C8	103.3(2)	C1	C9	C10	118.1(2)
C5	C1	C9	122.8(2)	C9	C10	C11A	116.8(2)
C8	C1	C9	120.2(2)	C10	C11A	C12A	114.1(3)
C1	C2	C3	110.0(2)	C11A	C12A	C13	113.4(3)
C1	C2	C8	52.7(2)	C12A	C13	C14	116.8(2)
C1	C2	C15	124.8(2)	C5	C14	C13	114.8(2)
C3	C2	C8	115.5(2)	O1	C15	O2	124.0(2)
C3	C2	C15	122.4(2)	O1	C15	C2	110.7(2)
C8	C2	C15	111.1(2)	O2	C15	C2	125.2(2)
C2	C3	C4	111.3(2)	O3	C16	O4	123.2(2)
C3	C4	C5	111.6(2)	O3	C16	C4	112.1(2)
C3	C4	C16	125.5(3)	O4	C16	C4	124.8(2)
C5	C4	C6	44.5(2)	O5	C17	O6	123.6(2)
C5	C4	C16	122.6(2)	O5	C17	C6	110.7(2)
C1	C5	C4	103.0(2)	O6	C17	C6	125.7(2)
C1	C5	C6	102.8(2)	O7	C18	O8	124.3(2)
C1	C5	C14	118.4(1)	O7	C18	C8	109.1(2)
C4	C5	C6	90.8(1)	O8	C18	C8	126.4(3)
C4	C5	C14	119.7(2)				
C6	C5	C14	117.6(2)				
C4	C6	C5	44.7(1)	C9	C10	C11B	116.0(9)
C5	C6	C7	111.5(2)	C10	C11B	C12B	106(2)
C5	C6	C17	124.5(2)	C11B	C12B	C13	105(2)
C7	C6	C17	124.0(2)	C12B	C13	C14	102.4(9)

Table 313. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-8 at **140 K**

Atom	Min.	Int'med.	Max.
O1	0.115	0.161	0.204
O2	0.128	0.179	0.192
O3	0.128	0.142	0.215
O4	0.125	0.163	0.233
O5	0.139	0.173	0.235
O6	0.152	0.200	0.220
O7	0.130	0.158	0.194
O8	0.137	0.167	0.208
C1	0.122	0.142	0.142
C2	0.122	0.150	0.209
C3	0.124	0.130	0.144
C4	0.125	0.131	0.193
C5	0.118	0.137	0.157
C6	0.148	0.159	0.201
C7	0.117	0.149	0.158
C8	0.134	0.162	0.184
C9	0.133	0.152	0.168
C10	0.141	0.169	0.199
C11A	0.151	0.166	0.213
C12A	0.142	0.168	0.187
C13	0.137	0.187	0.210
C14	0.120	0.162	0.184
C15	0.127	0.149	0.183
C16	0.133	0.143	0.150
C17	0.148	0.161	0.174
C18	0.139	0.147	0.164
C19	0.109	0.183	0.229
C20	0.115	0.185	0.229
C21	0.131	0.224	0.252
C22	0.123	0.186	0.228



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–314. X-ray Crystal Data for Sb-8 at **153 K**

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.08 x 0.10 x 0.59
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.554(1)
b (Å)	14.598(1)
c (Å)	14.108(4)
β (°)	109.33(1)
Cell volume (Å^3)	2051.15(8.75)
Z	4
d_{calc} (g cm^{-3})	1.355
μ(Cu $K\alpha$) (cm^{-1})	8.22
Maximum θ (°)	60
Unique reflections	3041
Observed reflections [$I > 3.0\sigma(I)$]	2142
Number of variables	279
R	0.040
R_w	0.046
$(\Delta\rho)_{max}$ (e Å^{-3})	0.18
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.20

Table 315. Final Atomic Parameters for Sb-8 at **153 K**

Atom	x	y	z	B(Å^2)
O1	0.3938(2)	0.3314(1)	0.1820(1)	2.36(4)
O2	0.3087(2)	0.2695(1)	0.0287(1)	2.61(4)
O3	0.8955(2)	0.3755(1)	0.3215(1)	2.36(4)
O4	1.0067(2)	0.3325(1)	0.2191(1)	2.78(4)
O5	0.9726(2)	0.1300(1)	0.2723(1)	2.93(4)
O6	1.0233(2)	0.1363(1)	0.1301(1)	3.24(4)
O7	0.4211(2)	0.0754(1)	0.1240(1)	2.28(4)
O8	0.3868(2)	0.0795(1)	-0.0417(1)	2.52(4)
C1	0.5957(2)	0.2461(2)	0.0248(2)	1.64(5)
C2	0.5464(2)	0.2769(2)	0.1089(2)	2.33(6)
C3	0.6543(2)	0.3148(2)	0.1885(2)	1.57(5)
C4	0.7717(2)	0.3092(2)	0.1687(2)	2.01(5)
C5	0.7529(2)	0.2605(2)	0.0695(2)	1.58(5)
C6	0.8016(2)	0.1717(2)	0.1271(2)	2.53(6)
C7	0.6964(2)	0.1198(2)	0.1316(2)	1.77(5)
C8	0.5732(2)	0.1599(2)	0.0742(2)	2.17(5)
C9	0.5162(2)	0.2636(2)	-0.0855(2)	1.95(5)
C10	0.4791(3)	0.3628(2)	-0.1183(2)	2.52(6)
C11A	0.5915(3)	0.4238(2)	-0.1304(2)	2.67(7)
C12A	0.6981(3)	0.4505(2)	-0.0312(2)	2.39(7)
C13	0.8318(3)	0.3991(2)	-0.0104(2)	2.76(6)
C14	0.8276(2)	0.2945(2)	-0.0006(2)	2.19(5)
C15	0.4036(2)	0.2919(2)	0.0992(2)	2.02(5)
C16	0.9029(2)	0.3398(2)	0.2361(2)	1.80(5)
C17	0.9432(2)	0.1453(2)	0.1739(2)	2.25(6)
C18	0.4493(2)	0.1024(2)	0.0425(2)	1.87(5)
C19	0.2591(2)	0.3395(2)	0.1869(2)	2.82(6)
C20	1.0237(3)	0.3984(2)	0.3958(2)	2.80(6)
C21	1.1125(3)	0.1095(2)	0.3264(2)	3.71(7)
C22	0.3078(3)	0.0145(2)	0.1078(2)	2.89(6)
C11B	0.583(2)	0.435(2)	-0.068(2)	2.5(4)*
C12B	0.706(2)	0.420(2)	-0.107(2)	2.9(5)*
H3	0.645	0.342	0.251	1.7
H7	0.705	0.061	0.170	1.9
H9A	0.430	0.228	-0.102	2.1
H9B	0.571	0.239	-0.126	2.1
H10AA	0.446	0.392	-0.067	2.8
H10AB	0.405	0.361	-0.184	2.8
H11AA	0.550	0.481	-0.166	2.9
H11AB	0.637	0.390	-0.172	2.9
H12AA	0.662	0.437	0.025	2.6
H12AB	0.716	0.518	-0.033	2.6
H13AA	0.896	0.423	0.054	3.0
H13AB	0.866	0.413	-0.067	3.0
H14A	0.782	0.268	-0.069	2.4
H14B	0.922	0.271	0.026	2.4
H19A	0.263	0.370	0.251	3.1
H19B	0.203	0.377	0.129	3.1
H19C	0.219	0.277	0.184	3.1
H20A	1.009	0.425	0.457	3.1
H20B	1.080	0.342	0.415	3.1
H20C	1.071	0.445	0.367	3.1
H21A	1.125	0.099	0.399	4.1
H21B	1.140	0.053	0.298	4.1
H21C	1.170	0.162	0.320	4.1
H22A	0.297	-0.001	0.174	3.2
H22B	0.224	0.045	0.064	3.2
H22C	0.324	-0.043	0.075	3.2

Table 315 (cont.). Final Atomic Parameters for Sb-8 at **153 K**

Atom	x	y	z	BÅ^2)
H10BA	0.395	0.378	-0.104	2.8
H10BB	0.462	0.367	-0.192	2.8
H11BA	0.613	0.427	0.007	2.8
H11BB	0.545	0.498	-0.086	2.8
H12BA	0.722	0.477	-0.141	3.2
H12BB	0.689	0.367	-0.155	3.2
H13BA	0.823	0.430	0.050	3.0
H13BB	0.917	0.419	-0.020	3.0

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

Table 316. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **153 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0193(7)	0.048(1)	0.0262(8)	0.0008(8)	0.0124(6)	0.0011(8)
O2	0.0192(8)	0.045(1)	0.0321(9)	-0.0018(8)	0.0045(6)	-0.0019(9)
O3	0.0212(7)	0.045(1)	0.0229(8)	-0.0037(8)	0.0069(6)	-0.0116(8)
O4	0.0195(7)	0.053(1)	0.0352(9)	-0.0070(8)	0.0124(6)	-0.0131(9)
O5	0.0237(8)	0.053(1)	0.0329(9)	0.0045(9)	0.0068(7)	0.0115(9)
O6	0.0361(9)	0.048(1)	0.043(1)	0.0106(9)	0.0175(7)	-0.0032(9)
O7	0.0255(8)	0.034(1)	0.0266(8)	-0.0099(8)	0.0078(6)	0.0019(8)
O8	0.0387(9)	0.0280(9)	0.0261(8)	-0.0088(8)	0.0065(7)	-0.0031(8)
C1	0.023(1)	0.022(1)	0.018(1)	-0.002(1)	0.0074(8)	-0.004(1)
C2	0.020(1)	0.050(2)	0.021(1)	-0.002(1)	0.0089(8)	-0.005(1)
C3	0.022(1)	0.018(1)	0.020(1)	0.000(1)	0.0078(8)	0.000(1)
C4	0.021(1)	0.037(1)	0.022(1)	-0.003(1)	0.0107(8)	-0.005(1)
C5	0.021(1)	0.023(1)	0.018(1)	-0.001(1)	0.0099(8)	-0.003(1)
C6	0.024(1)	0.040(2)	0.031(1)	0.000(1)	0.007(1)	0.006(1)
C7	0.027(1)	0.021(1)	0.019(1)	0.001(1)	0.0077(8)	-0.004(1)
C8	0.023(1)	0.029(1)	0.029(1)	-0.003(1)	0.0063(9)	0.005(1)
C9	0.026(1)	0.028(1)	0.018(1)	-0.001(1)	0.0056(9)	-0.000(1)
C10	0.030(1)	0.033(1)	0.029(1)	-0.001(1)	0.004(1)	0.010(1)
C11A	0.036(1)	0.035(2)	0.028(1)	-0.006(1)	0.008(1)	0.007(1)
C12A	0.034(1)	0.025(2)	0.030(1)	-0.004(1)	0.009(1)	0.005(1)
C13	0.033(1)	0.038(2)	0.038(1)	-0.004(1)	0.015(1)	0.009(1)
C14	0.028(1)	0.037(1)	0.024(1)	-0.004(1)	0.0162(8)	-0.002(1)
C15	0.021(1)	0.032(1)	0.024(1)	-0.003(1)	0.0088(8)	0.004(1)
C16	0.021(1)	0.026(1)	0.023(1)	0.000(1)	0.0093(8)	-0.001(1)
C17	0.026(1)	0.029(1)	0.030(1)	-0.002(1)	0.0082(9)	0.001(1)
C18	0.024(1)	0.022(1)	0.024(1)	-0.000(1)	0.0070(9)	0.002(1)
C19	0.020(1)	0.053(2)	0.042(1)	0.009(1)	0.0204(8)	0.009(1)
C20	0.027(1)	0.047(2)	0.027(1)	-0.008(1)	0.002(1)	-0.013(1)
C21	0.024(1)	0.062(2)	0.044(2)	0.008(1)	-0.003(1)	0.013(2)
C22	0.031(1)	0.039(2)	0.039(1)	-0.017(1)	0.011(1)	0.006(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 317. Interatomic Distances (Å) for Sb-8 at **153 K**

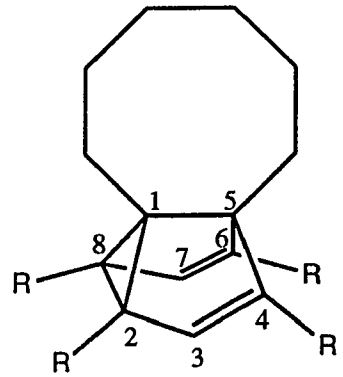
O1	C15	1.337(3)	C3	C4	1.360(4)
O1	C19	1.451(3)	C3	C7	3.029(3)
O2	C15	1.201(3)	C4	C5	1.524(3)
O3	C16	1.339(3)	C4	C6	2.145(4)
O3	C20	1.450(3)	C4	C16	1.466(3)
O4	C16	1.202(3)	C5	C6	1.525(4)
O5	C17	1.337(3)	C5	C14	1.537(4)
O5	C21	1.452(3)	C6	C7	1.363(4)
O6	C17	1.207(4)	C6	C17	1.472(3)
O7	C18	1.339(3)	C7	C8	1.410(3)
O7	C22	1.445(3)	C8	C18	1.492(3)
O8	C18	1.200(3)	C9	C10	1.532(4)
C1	C2	1.514(4)	C10	C11A	1.538(4)
C1	C5	1.581(3)	C11A	C12A	1.528(4)
C1	C8	1.496(4)	C12A	C13	1.538(4)
C1	C9	1.525(3)	C13	C14	1.536(4)
C2	C3	1.419(3)	C10	C11B	1.52(2)
C2	C8	1.825(4)	C11B	C12B	1.59(4)
C2	C15	1.484(4)	C12B	C13	1.58(2)

Table 318. Angles (°) for Sb-8 at **153 K**

C15	O1	C19	115.9(2)	C6	C7	C8	110.7(2)
C16	O3	C20	115.0(2)	C1	C8	C2	53.1(2)
C17	O5	C21	115.2(2)	C1	C8	C7	111.0(2)
C18	O7	C22	116.9(2)	C1	C8	C18	126.3(2)
C2	C1	C5	103.6(2)	C2	C8	C7	115.4(2)
C2	C1	C8	74.7(2)	C2	C8	C18	114.1(2)
C2	C1	C9	122.3(2)	C7	C8	C18	119.3(2)
C5	C1	C8	103.5(2)	C1	C9	C10	117.8(2)
C5	C1	C9	122.4(2)	C9	C10	C11A	116.8(2)
C8	C1	C9	119.9(2)	C10	C11A	C12A	114.0(3)
C1	C2	C3	110.0(2)	C11A	C12A	C13	113.6(3)
C1	C2	C8	52.2(2)	C12A	C13	C14	116.7(2)
C1	C2	C15	125.0(2)	C5	C14	C13	114.5(2)
C3	C2	C8	115.0(2)	O1	C15	O2	123.8(2)
C3	C2	C15	122.7(2)	O1	C15	C2	110.7(2)
C8	C2	C15	110.8(2)	O3	C16	O4	122.8(2)
C2	C3	C4	111.2(2)	O3	C16	C4	112.3(2)
C3	C4	C5	111.5(2)	O4	C16	C4	124.9(2)
C3	C4	C16	125.3(3)	O5	C17	O6	123.5(2)
C5	C4	C6	45.3(1)	O5	C17	C6	111.2(2)
C5	C4	C16	123.1(2)	O6	C17	C6	125.3(2)
C1	C5	C4	103.2(1)	O7	C18	O8	124.2(2)
C1	C5	C6	102.9(2)	O7	C18	C8	109.3(2)
C1	C5	C14	118.7(2)	O8	C18	C8	126.4(3)
C4	C5	C6	89.4(2)	O2	C15	C2	125.4(2)
C4	C5	C14	120.1(2)				
C6	C5	C14	117.6(2)				
C4	C6	C5	45.3(1)	C9	C10	C11B	116.0(8)
C5	C6	C7	111.1(2)	C10	C11B	C12B	107(2)
C5	C6	C17	125.1(2)	C11B	C12B	C13	106(2)
C7	C6	C17	123.8(2)	C12B	C13	C14	103.2(9)

Table 319. Root-Mean-Square Amplitudes of Thermal Vibration (Å) of Sb-8 at **153 K**

Atom	Min.	Int'med.	Max.
O1	0.120	0.166	0.218
O2	0.137	0.187	0.212
O3	0.134	0.147	0.224
O4	0.130	0.168	0.246
O5	0.149	0.176	0.241
O6	0.157	0.209	0.235
O7	0.135	0.162	0.205
O8	0.146	0.170	0.214
C1	0.125	0.146	0.159
C2	0.130	0.146	0.224
C3	0.134	0.138	0.150
C4	0.124	0.149	0.196
C5	0.116	0.146	0.159
C6	0.154	0.169	0.209
C7	0.122	0.156	0.167
C8	0.146	0.155	0.192
C9	0.135	0.164	0.170
C10	0.142	0.172	0.215
C11A	0.151	0.176	0.218
C12A	0.144	0.175	0.199
C13	0.145	0.191	0.217
C14	0.119	0.173	0.197
C15	0.132	0.154	0.188
C16	0.137	0.154	0.161
C17	0.159	0.168	0.179
C18	0.144	0.154	0.163
C19	0.103	0.193	0.243
C20	0.129	0.191	0.231
C21	0.132	0.231	0.265
C22	0.122	0.194	0.239



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–320. X-ray Crystal Data for Sb-8 at **181 K**

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.08 x 0.10 x 0.59
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.567(1)
b (Å)	14.663(1)
c (Å)	14.118(3)
β (°)	109.40(1)
Cell volume (Å^3)	2063.38(7.25)
Z	4
d_{calc} (g cm^{-3})	1.347
μ(Cu $K\alpha$) (cm^{-1})	8.17
Maximum θ (°)	60
Unique reflections	3055
Observed reflections [$I > 3.0\sigma(I)$]	2069
Number of variables	279
R	0.040
R_w	0.047
$(\Delta\rho)_{max}$ (e Å^{-3})	0.18
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.22

Table 321. Final Atomic Parameters for Sb-8 at **181 K**

Atom	x	y	z	B(Å^2)
O1	0.3930(2)	0.3326(1)	0.1820(1)	2.81(4)
O2	0.3082(2)	0.2696(1)	0.0297(1)	3.01(5)
O3	0.8949(2)	0.3737(1)	0.3214(1)	2.72(4)
O4	1.0054(2)	0.3316(2)	0.2188(1)	3.32(5)
O5	0.9713(2)	0.1302(2)	0.2729(1)	3.51(5)
O6	1.0198(2)	0.1352(2)	0.1303(2)	3.89(5)
O7	0.4204(2)	0.0748(1)	0.1238(1)	2.75(4)
O8	0.3847(2)	0.0801(1)	-0.0417(1)	3.07(4)
C1	0.5939(2)	0.2454(2)	0.0253(2)	1.85(5)
C2	0.5456(3)	0.2782(2)	0.1091(2)	2.70(6)
C3	0.6529(2)	0.3138(2)	0.1887(2)	1.74(5)
C4	0.7708(2)	0.3070(2)	0.1691(2)	2.37(6)
C5	0.7514(2)	0.2596(2)	0.0696(2)	1.79(5)
C6	0.7994(3)	0.1727(2)	0.1288(2)	2.87(6)
C7	0.6947(2)	0.1201(2)	0.1320(2)	2.04(6)
C8	0.5721(3)	0.1584(2)	0.0731(2)	2.44(6)
C9	0.5150(3)	0.2636(2)	-0.0845(2)	2.25(6)
C10	0.4780(3)	0.3621(2)	-0.1168(2)	2.93(7)
C11A	0.5907(3)	0.4229(2)	-0.1295(2)	3.12(8)
C12A	0.6973(3)	0.4493(2)	-0.0309(2)	2.84(8)
C13	0.8303(3)	0.3973(2)	-0.0106(2)	3.25(7)
C14	0.8259(2)	0.2932(2)	-0.0002(2)	2.49(6)
C15	0.4028(2)	0.2925(2)	0.1000(2)	2.26(6)
C16	0.9019(2)	0.3383(2)	0.2364(2)	2.12(6)
C17	0.9413(3)	0.1453(2)	0.1748(2)	2.58(6)
C18	0.4480(2)	0.1020(2)	0.0424(2)	2.25(6)
C19	0.2585(3)	0.3406(2)	0.1869(2)	3.40(7)
C20	1.0230(3)	0.3976(2)	0.3953(2)	3.26(7)
C21	1.1107(3)	0.1080(3)	0.3269(3)	4.41(9)
C22	0.3065(3)	0.0146(2)	0.1077(2)	3.44(7)
C11B	0.585(2)	0.435(1)	-0.068(1)	2.5(4)*
C12B	0.710(2)	0.419(1)	-0.107(1)	2.6(4)*
H3	0.644	0.341	0.251	1.9
H7	0.704	0.062	0.171	2.2
H9A	0.429	0.228	-0.101	2.5
H9B	0.570	0.240	-0.125	2.5
H10AA	0.445	0.391	-0.065	3.2
H10AB	0.403	0.361	-0.183	3.2
H11AA	0.549	0.480	-0.165	3.4
H11AB	0.635	0.389	-0.171	3.4
H12AA	0.662	0.436	0.025	3.1
H12AB	0.716	0.516	-0.033	3.1
H13AA	0.895	0.422	0.053	3.6
H13AB	0.864	0.411	-0.067	3.6
H14A	0.780	0.267	-0.069	2.7
H14B	0.920	0.270	0.026	2.7
H19A	0.262	0.371	0.251	3.7
H19B	0.202	0.377	0.129	3.7
H19C	0.219	0.278	0.184	3.7
H20A	1.008	0.423	0.456	3.6
H20B	1.080	0.342	0.414	3.6
H20C	1.069	0.444	0.366	3.6
H21A	1.123	0.098	0.400	4.8
H21B	1.136	0.051	0.298	4.8
H21C	1.169	0.160	0.320	4.8
H22A	0.296	-0.001	0.174	3.8
H22B	0.223	0.046	0.064	3.8
H22C	0.321	-0.043	0.074	3.8

Table 321 (cont.). Final Atomic Parameters for Sb-8 at **181 K**

Atom	x	y	z	B(Å^2)
H10BA	0.395	0.378	-0.100	3.2
H10BB	0.458	0.365	-0.191	3.2
H11BA	0.616	0.429	0.007	2.7
H11BB	0.547	0.498	-0.088	2.7
H12BA	0.728	0.475	-0.141	2.8
H12BB	0.691	0.366	-0.155	2.8
H13BA	0.819	0.428	0.049	3.6
H13BB	0.917	0.417	-0.019	3.6

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

Table 322. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **181 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0240(8)	0.058(1)	0.0289(8)	0.0006(9)	0.0145(6)	-0.0013(9)
O2	0.0217(9)	0.053(1)	0.036(1)	-0.0032(9)	0.0036(7)	-0.004(1)
O3	0.0240(8)	0.054(1)	0.0244(8)	-0.0048(8)	0.0065(6)	-0.0144(9)
O4	0.0226(8)	0.066(1)	0.040(1)	-0.0080(9)	0.0137(7)	-0.016(1)
O5	0.0278(9)	0.068(1)	0.035(1)	0.008(1)	0.0062(7)	0.015(1)
O6	0.044(1)	0.059(1)	0.049(1)	0.015(1)	0.0218(8)	-0.002(1)
O7	0.0312(8)	0.042(1)	0.0304(9)	-0.0123(9)	0.0089(7)	0.0028(9)
O8	0.048(1)	0.034(1)	0.0288(9)	-0.0116(9)	0.0050(8)	-0.0043(9)
C1	0.026(1)	0.025(1)	0.019(1)	-0.001(1)	0.0071(9)	-0.003(1)
C2	0.020(1)	0.061(2)	0.022(1)	-0.004(1)	0.0081(9)	-0.006(1)
C3	0.025(1)	0.022(1)	0.020(1)	0.000(1)	0.0090(9)	0.001(1)
C4	0.023(1)	0.047(2)	0.022(1)	-0.005(1)	0.0099(9)	-0.009(1)
C5	0.024(1)	0.028(1)	0.019(1)	-0.001(1)	0.0111(8)	-0.003(1)
C6	0.026(1)	0.045(2)	0.035(1)	0.000(1)	0.006(1)	0.010(1)
C7	0.033(1)	0.024(1)	0.020(1)	0.003(1)	0.0086(9)	-0.003(1)
C8	0.026(1)	0.032(2)	0.032(1)	-0.004(1)	0.006(1)	0.006(1)
C9	0.029(1)	0.034(2)	0.020(1)	-0.002(1)	0.0053(9)	-0.001(1)
C10	0.036(1)	0.039(2)	0.031(1)	-0.001(1)	0.005(1)	0.011(1)
C11A	0.048(2)	0.037(2)	0.030(2)	-0.005(2)	0.008(1)	0.010(2)
C12A	0.042(2)	0.032(2)	0.032(2)	-0.002(1)	0.009(1)	0.005(1)
C13	0.039(1)	0.045(2)	0.044(1)	-0.008(1)	0.020(1)	0.010(1)
C14	0.029(1)	0.044(2)	0.027(1)	-0.003(1)	0.0152(9)	-0.003(1)
C15	0.021(1)	0.038(2)	0.027(1)	-0.004(1)	0.0093(9)	0.004(1)
C16	0.024(1)	0.031(1)	0.026(1)	-0.001(1)	0.0084(9)	-0.001(1)
C17	0.030(1)	0.031(2)	0.036(1)	-0.000(1)	0.011(1)	0.003(1)
C18	0.027(1)	0.026(1)	0.030(1)	-0.000(1)	0.006(1)	0.002(1)
C19	0.026(1)	0.065(2)	0.047(1)	0.010(1)	0.0233(9)	0.012(2)
C20	0.030(1)	0.058(2)	0.029(1)	-0.010(1)	0.000(1)	-0.015(1)
C21	0.029(2)	0.074(2)	0.051(2)	0.012(2)	-0.005(1)	0.016(2)
C22	0.039(1)	0.046(2)	0.045(2)	-0.018(1)	0.013(1)	0.006(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 323. Interatomic Distances (Å) for Sb-8 at **181 K**

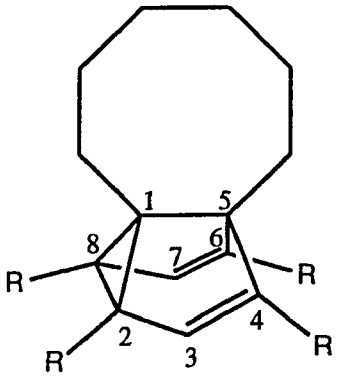
O1	C15	1.333(3)	C3	C4	1.366(4)
O1	C19	1.451(3)	C3	C7	3.024(4)
O2	C15	1.199(3)	C4	C5	1.519(4)
O3	C16	1.332(3)	C4	C6	2.098(4)
O3	C20	1.451(3)	C4	C16	1.469(3)
O4	C16	1.204(3)	C5	C6	1.515(4)
O5	C17	1.333(3)	C5	C14	1.533(4)
O5	C21	1.453(3)	C6	C7	1.363(4)
O6	C17	1.204(4)	C6	C17	1.478(4)
O7	C18	1.336(4)	C7	C8	1.403(3)
O7	C22	1.449(4)	C8	C18	1.488(4)
O8	C18	1.197(3)	C9	C10	1.525(4)
C1	C2	1.514(4)	C10	C11A	1.545(5)
C1	C5	1.585(3)	C11A	C12A	1.521(4)
C1	C8	1.497(4)	C12A	C13	1.539(4)
C1	C9	1.520(3)	C13	C14	1.536(4)
C2	C3	1.405(3)	C10	C11B	1.55(2)
C2	C8	1.875(4)	C11B	C12B	1.60(3)
C2	C15	1.487(4)	C12B	C13	1.56(2)

Table 324. Angles (°) for Sb-8 at **181 K**

C15	O1	C19	115.9(2)	C6	C7	C8	110.7(2)
C16	O3	C20	115.1(2)	C1	C8	C2	51.9(2)
C17	O5	C21	115.7(2)	C1	C8	C7	111.1(2)
C18	O7	C22	117.0(2)	C1	C8	C18	126.5(2)
C2	C1	C5	103.4(2)	C2	C8	C7	114.0(2)
C2	C1	C8	77.0(2)	C2	C8	C18	113.8(2)
C2	C1	C9	121.9(2)	C7	C8	C18	120.0(2)
C5	C1	C8	103.4(2)	C1	C9	C10	118.1(2)
C5	C1	C9	121.8(2)	C9	C10	C11A	116.8(2)
C8	C1	C9	119.7(2)	C10	C11A	C12A	114.0(3)
C1	C2	C3	110.6(2)	C11A	C12A	C13	113.4(3)
C1	C2	C8	51.1(2)	C12A	C13	C14	117.0(2)
C1	C2	C15	124.9(2)	C5	C14	C13	114.8(2)
C3	C2	C8	114.3(2)	O1	C15	O2	124.0(3)
C3	C2	C15	122.9(3)	O1	C15	C2	110.9(2)
C8	C2	C15	110.4(2)	O2	C15	C2	125.1(3)
C2	C3	C4	111.0(2)	O3	C16	O4	123.0(2)
C3	C4	C5	111.7(2)	O3	C16	C4	112.5(2)
C3	C4	C16	125.0(2)	O4	C16	C4	124.6(2)
C5	C4	C6	46.2(1)	O5	C17	O6	123.6(2)
C5	C4	C16	123.3(2)	O5	C17	C6	111.0(3)
C1	C5	C4	103.1(2)	O6	C17	C6	125.4(2)
C1	C5	C6	102.9(2)	O7	C18	O8	124.3(2)
C1	C5	C14	119.0(2)	O7	C18	C8	109.7(2)
C4	C5	C6	87.5(1)	O8	C18	C8	125.9(3)
C4	C5	C14	120.5(2)				
C6	C5	C14	118.4(2)				
C4	C6	C5	46.3(1)	C9	C10	C11B	116.6(7)
C5	C6	C7	111.6(2)	C10	C11B	C12B	108(1)
C5	C6	C17	125.2(3)	C11B	C12B	C13	105(1)
C7	C6	C17	123.2(3)	C12B	C13	C14	104.0(8)

Table 325. Root-Mean-Square Amplitudes of Thermal Vibration in (Å) for Sb-8 at **181 K**

Atom	Min.	Int'med.	Max.
O1	0.131	0.177	0.241
O2	0.143	0.201	0.231
O3	0.135	0.160	0.244
O4	0.141	0.179	0.272
O5	0.154	0.191	0.271
O6	0.170	0.225	0.261
O7	0.149	0.173	0.229
O8	0.152	0.187	0.242
C1	0.133	0.160	0.164
C2	0.139	0.147	0.248
C3	0.137	0.148	0.159
C4	0.134	0.149	0.223
C5	0.120	0.157	0.170
C6	0.159	0.176	0.229
C7	0.132	0.159	0.186
C8	0.154	0.162	0.206
C9	0.140	0.176	0.187
C10	0.152	0.190	0.228
C11A	0.152	0.196	0.239
C12A	0.162	0.189	0.214
C13	0.149	0.214	0.237
C14	0.137	0.177	0.211
C15	0.136	0.163	0.203
C16	0.153	0.160	0.178
C17	0.171	0.176	0.194
C18	0.157	0.163	0.186
C19	0.123	0.205	0.269
C20	0.128	0.208	0.254
C21	0.136	0.256	0.289
C22	0.145	0.209	0.257



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–326. X-ray Crystal Data for Sb-8 at **208 K**

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.08 x 0.10 x 0.59
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.578(1)
b (Å)	14.726(1)
c (Å)	14.145(2)
β (°)	109.47(1)
Cell volume (Å^3)	2077.44(5.74)
Z	4
d_{calc} (g cm^{-3})	1.338
μ(Cu $K\alpha$) (cm^{-1})	8.11
Maximum θ(°)	60
Unique reflections	3067
Observed reflections [$I > 3.0\sigma(I)$]	2007
Number of variables	279
R	0.041
R_w	0.048
$(\Delta\rho)_{max}$ (e Å^{-3})	0.18
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.20

Table 327. Final Atomic Parameters for Sb-8 at **208 K**

Atom	x	y	z	B(Å^2)
O1	0.3921(2)	0.3333(2)	0.1819(1)	3.21(5)
O2	0.3075(2)	0.2696(2)	0.0302(1)	3.60(5)
O3	0.8941(2)	0.3719(1)	0.3213(1)	3.16(5)
O4	1.0041(2)	0.3305(2)	0.2187(1)	3.94(5)
O5	0.9701(2)	0.1301(2)	0.2734(2)	4.01(5)
O6	1.0162(2)	0.1341(2)	0.1307(2)	4.58(6)
O7	0.4197(2)	0.0741(1)	0.1235(1)	3.20(5)
O8	0.3823(2)	0.0804(1)	-0.0420(1)	3.63(5)
C1	0.5922(2)	0.2450(2)	0.0259(2)	2.09(6)
C2	0.5445(3)	0.2796(2)	0.1092(2)	3.02(7)
C3	0.6520(2)	0.3132(2)	0.1891(2)	1.96(6)
C4	0.7704(3)	0.3049(2)	0.1699(2)	2.63(6)
C5	0.7500(2)	0.2587(2)	0.0698(2)	2.08(6)
C6	0.7971(3)	0.1732(2)	0.1305(2)	3.20(7)
C7	0.6929(3)	0.1197(2)	0.1326(2)	2.33(6)
C8	0.5707(3)	0.1574(2)	0.0728(2)	2.76(6)
C9	0.5131(3)	0.2629(2)	-0.0840(2)	2.60(6)
C10	0.4768(3)	0.3616(2)	-0.1156(2)	3.40(7)
C11A	0.5901(4)	0.4214(3)	-0.1284(3)	3.76(9)
C12A	0.6966(4)	0.4481(3)	-0.0304(3)	3.46(9)
C13	0.8300(3)	0.3950(2)	-0.0109(2)	3.89(8)
C14	0.8243(3)	0.2916(2)	0.0003(2)	2.90(6)
C15	0.4017(3)	0.2932(2)	0.1002(2)	2.67(6)
C16	0.9014(2)	0.3366(2)	0.2366(2)	2.37(6)
C17	0.9390(3)	0.1449(2)	0.1753(2)	2.98(7)
C18	0.4466(3)	0.1018(2)	0.0420(2)	2.54(6)
C19	0.2578(3)	0.3415(3)	0.1869(2)	3.96(8)
C20	1.0219(3)	0.3964(2)	0.3955(2)	3.91(8)
C21	1.1093(3)	0.1070(3)	0.3266(3)	5.2(1)
C22	0.3055(3)	0.0145(2)	0.1074(2)	3.97(8)
C11B	0.585(2)	0.433(1)	-0.066(1)	2.8(3)*
C12B	0.707(2)	0.418(1)	-0.106(1)	2.7(3)*
H3	0.644	0.340	0.252	2.2
H7	0.702	0.062	0.171	2.6
H9A	0.427	0.228	-0.101	2.9
H9B	0.567	0.239	-0.125	2.9
H10AA	0.445	0.391	-0.064	3.7
H10AB	0.402	0.361	-0.181	3.7
H11AA	0.549	0.478	-0.165	4.1
H11AB	0.635	0.387	-0.170	4.1
H12AA	0.662	0.436	0.026	3.8
H12AB	0.715	0.515	-0.032	3.8
H13AA	0.896	0.419	0.052	4.2
H13AB	0.863	0.407	-0.068	4.2
H14A	0.778	0.265	-0.068	3.2
H14B	0.918	0.268	0.027	3.2
H19A	0.262	0.372	0.251	4.4
H19B	0.201	0.378	0.129	4.4
H19C	0.218	0.280	0.185	4.4
H20A	1.006	0.422	0.456	4.3
H20B	1.080	0.341	0.415	4.3
H20C	1.068	0.443	0.366	4.3
H21A	1.122	0.097	0.399	5.7
H21B	1.133	0.050	0.298	5.7
H21C	1.168	0.158	0.320	5.7
H22A	0.296	-0.001	0.174	4.4
H22B	0.222	0.046	0.064	4.4
H22C	0.319	-0.042	0.073	4.4

Table 327 (cont.). Final Atomic Parameters for Sb-8 at **208 K**

Atom	x	y	z	B(Å^2)
H10BA	0.394	0.377	-0.099	3.7
H10BB	0.457	0.365	-0.190	3.7
H11BA	0.616	0.426	0.009	3.1
H11BB	0.547	0.496	-0.084	3.1
H12BA	0.725	0.475	-0.139	2.9
H12BB	0.687	0.367	-0.155	2.9
H13BA	0.822	0.426	0.050	4.2
H13BB	0.916	0.413	-0.021	4.2

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

Table 328. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **208 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0264(8)	0.066(1)	0.0348(9)	0.0016(9)	0.0171(6)	0.000(1)
O2	0.0246(9)	0.065(1)	0.042(1)	-0.003(1)	0.0040(8)	-0.005(1)
O3	0.0289(9)	0.062(1)	0.0284(9)	-0.0068(9)	0.0082(7)	-0.017(1)
O4	0.0251(8)	0.081(2)	0.047(1)	-0.011(1)	0.0163(7)	-0.021(1)
O5	0.032(1)	0.077(2)	0.040(1)	0.010(1)	0.0057(8)	0.014(1)
O6	0.052(1)	0.073(2)	0.054(1)	0.020(1)	0.0240(9)	-0.000(1)
O7	0.0370(9)	0.050(1)	0.034(1)	-0.0145(9)	0.0103(7)	0.004(1)
O8	0.056(1)	0.042(1)	0.033(1)	-0.015(1)	0.0062(9)	-0.003(1)
C1	0.030(1)	0.030(1)	0.018(1)	-0.003(1)	0.0069(9)	-0.004(1)
C2	0.025(1)	0.068(2)	0.024(1)	-0.006(1)	0.0116(9)	-0.005(1)
C3	0.027(1)	0.026(1)	0.023(1)	-0.000(1)	0.0095(9)	-0.001(1)
C4	0.025(1)	0.051(2)	0.026(1)	-0.004(1)	0.0115(9)	-0.011(1)
C5	0.028(1)	0.031(1)	0.022(1)	-0.001(1)	0.0116(9)	-0.005(1)
C6	0.032(1)	0.051(2)	0.036(1)	-0.001(1)	0.008(1)	0.011(1)
C7	0.034(1)	0.029(1)	0.025(1)	0.001(1)	0.009(1)	-0.005(1)
C8	0.030(1)	0.040(2)	0.033(1)	-0.004(1)	0.009(1)	0.007(1)
C9	0.038(1)	0.038(2)	0.020(1)	-0.003(1)	0.005(1)	0.000(1)
C10	0.043(2)	0.043(2)	0.037(2)	-0.000(1)	0.004(1)	0.010(1)
C11A	0.055(2)	0.045(2)	0.038(2)	-0.007(2)	0.009(2)	0.008(2)
C12A	0.049(2)	0.039(2)	0.040(2)	-0.004(2)	0.011(1)	0.005(2)
C13	0.046(1)	0.055(2)	0.053(2)	-0.009(1)	0.024(1)	0.011(2)
C14	0.037(1)	0.049(2)	0.030(1)	-0.003(1)	0.0199(9)	-0.002(1)
C15	0.027(1)	0.045(2)	0.032(1)	-0.003(1)	0.0124(9)	0.007(1)
C16	0.027(1)	0.036(2)	0.027(1)	-0.004(1)	0.0091(9)	-0.001(1)
C17	0.031(1)	0.042(2)	0.040(2)	0.001(1)	0.011(1)	0.001(1)
C18	0.031(1)	0.030(2)	0.032(1)	-0.000(1)	0.006(1)	0.004(1)
C19	0.030(1)	0.075(2)	0.054(2)	0.008(2)	0.026(1)	0.011(2)
C20	0.037(2)	0.069(2)	0.033(2)	-0.010(2)	-0.000(1)	-0.017(2)
C21	0.034(2)	0.088(3)	0.061(2)	0.014(2)	-0.004(2)	0.020(2)
C22	0.045(2)	0.055(2)	0.050(2)	-0.022(1)	0.014(1)	0.006(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 329. Interatomic Distances (Å) for Sb-8 at **208 K**

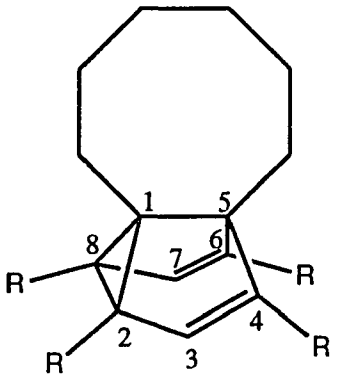
O1	C15	1.331(4)	C3	C4	1.372(4)
O1	C19	1.451(4)	C3	C7	3.030(4)
O2	C15	1.198(3)	C4	C5	1.520(4)
O3	C16	1.332(3)	C4	C6	2.064(4)
O3	C20	1.454(3)	C4	C16	1.468(3)
O4	C16	1.199(4)	C5	C6	1.512(4)
O5	C17	1.332(4)	C5	C14	1.528(4)
O5	C21	1.453(4)	C6	C7	1.363(4)
O6	C17	1.198(4)	C6	C17	1.481(4)
O7	C18	1.339(4)	C7	C8	1.402(3)
O7	C22	1.448(4)	C8	C18	1.484(4)
O8	C18	1.197(3)	C9	C10	1.531(4)
C1	C2	1.517(4)	C10	C11A	1.547(5)
C1	C5	1.587(3)	C11A	C12A	1.517(4)
C1	C8	1.503(4)	C12A	C13	1.556(5)
C1	C9	1.523(3)	C13	C14	1.534(5)
C2	C3	1.400(3)	C10	C11B	1.54(2)
C2	C8	1.918(5)	C11B	C12B	1.59(3)
C2	C15	1.486(4)	C12B	C13	1.57(1)

Table 330. Angles (°) for Sb-8 at **208 K**

C15	O1	C19	116.0(2)	C6	C7	C8	110.4(3)
C16	O3	C20	115.3(2)	C1	C8	C2	50.9(2)
C17	O5	C21	115.7(3)	C1	C8	C7	111.2(2)
C18	O7	C22	117.0(2)	C1	C8	C18	126.4(2)
C2	C1	C5	103.4(2)	C2	C8	C7	113.4(2)
C2	C1	C8	78.8(2)	C2	C8	C18	113.8(2)
C2	C1	C9	121.5(2)	C7	C8	C18	120.4(3)
C5	C1	C8	103.3(2)	C1	C9	C10	117.5(2)
C5	C1	C9	121.8(2)	C9	C10	C11A	116.5(3)
C8	C1	C9	119.1(2)	C10	C11A	C12A	114.2(3)
C1	C2	C3	110.8(2)	C11A	C12A	C13	112.6(3)
C1	C2	C8	50.2(2)	C12A	C13	C14	116.9(3)
C1	C2	C15	124.8(2)	C5	C14	C13	115.3(3)
C3	C2	C8	113.4(2)	O1	C15	O2	124.3(3)
C3	C2	C15	123.4(3)	O1	C15	C2	110.7(2)
C8	C2	C15	109.7(2)	O2	C15	C2	125.0(3)
C2	C3	C4	111.0(2)	O3	C16	O4	123.2(2)
C3	C4	C5	111.6(2)	O3	C16	C4	112.1(2)
C3	C4	C16	125.0(2)	O4	C16	C4	124.7(3)
C5	C4	C6	46.9(1)	O5	C17	O6	123.5(2)
C5	C4	C16	123.4(2)	O5	C17	C6	110.8(3)
C1	C5	C4	103.1(2)	O6	C17	C6	125.7(3)
C1	C5	C6	102.8(2)	O7	C18	O8	124.1(3)
C1	C5	C14	119.1(2)	O7	C18	C8	109.6(2)
C4	C5	C6	85.8(2)	O8	C18	C8	126.2(3)
C4	C5	C14	120.9(2)				
C6	C5	C14	119.1(2)				
C4	C6	C5	47.3(2)	C9	C10	C11B	116.2(6)
C5	C6	C7	112.2(2)	C10	C11B	C12B	108(1)
C5	C6	C17	125.0(3)	C11B	C12B	C13	105(1)
C7	C6	C17	122.6(3)	C12B	C13	C14	104.9(7)

Table 331. Root-Mean-Square Amplitudes of Thermal Vibration (Å) of Sb-8 at **208 K**

Atom	Min.	Int'med.	Max.
O1	0.138	0.192	0.256
O2	0.153	0.216	0.258
O3	0.145	0.174	0.263
O4	0.147	0.193	0.302
O5	0.162	0.211	0.286
O6	0.182	0.236	0.292
O7	0.161	0.183	0.250
O8	0.170	0.197	0.265
C1	0.131	0.170	0.182
C2	0.138	0.161	0.264
C3	0.148	0.160	0.164
C4	0.142	0.158	0.234
C5	0.132	0.166	0.184
C6	0.172	0.183	0.242
C7	0.146	0.178	0.189
C8	0.165	0.173	0.219
C9	0.140	0.188	0.209
C10	0.168	0.207	0.241
C11A	0.179	0.208	0.260
C12A	0.183	0.205	0.236
C13	0.165	0.232	0.258
C14	0.142	0.200	0.224
C15	0.148	0.176	0.221
C16	0.160	0.165	0.193
C17	0.175	0.200	0.207
C18	0.163	0.175	0.198
C19	0.140	0.225	0.284
C20	0.141	0.230	0.276
C21	0.152	0.274	0.316
C22	0.158	0.220	0.279



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–332. X-ray Crystal Data for Sb-8 at **236 K**

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.08 x 0.10 x 0.59
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.587(1)
b (Å)	14.784(1)
c (Å)	14.170(2)
β (°)	109.53(1)
Cell volume (Å^3)	2090.40(4.57)
Z	4
d_{calc} (g cm^{-3})	1.330
μ(Cu $K\alpha$) (cm^{-1})	8.06
Maximum θ (°)	60
Unique reflections	3086
Observed reflections	1924
[$I > 3.0\sigma(I)$]	
Number of variables	279
R	0.042
R_w	0.048
$(\Delta\rho)_{max}$ (e Å^{-3})	0.16
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.20

Table 333. Final Atomic Parameters for Sb-8 at **236 K**

Atom	x	y	z	B(Å^2)
O1	0.3916(2)	0.3344(2)	0.1818(1)	3.77(5)
O2	0.3066(2)	0.2696(2)	0.0309(2)	4.20(6)
O3	0.8933(2)	0.3703(2)	0.3212(1)	3.60(5)
O4	1.0029(2)	0.3294(2)	0.2187(2)	4.61(6)
O5	0.9688(2)	0.1295(2)	0.2737(2)	4.60(6)
O6	1.0131(2)	0.1328(2)	0.1307(2)	5.37(6)
O7	0.4187(2)	0.0733(2)	0.1228(1)	3.71(5)
O8	0.3802(2)	0.0810(2)	-0.0420(2)	4.20(5)
C1	0.5903(3)	0.2443(2)	0.0265(2)	2.40(6)
C2	0.5433(3)	0.2804(2)	0.1093(2)	3.28(7)
C3	0.6507(3)	0.3125(2)	0.1891(2)	2.31(6)
C4	0.7695(3)	0.3027(2)	0.1707(2)	2.95(7)
C5	0.7480(2)	0.2580(2)	0.0699(2)	2.32(6)
C6	0.7958(3)	0.1736(2)	0.1312(2)	3.50(7)
C7	0.6902(3)	0.1198(2)	0.1325(2)	2.66(7)
C8	0.5694(3)	0.1566(2)	0.0723(2)	3.07(7)
C9	0.5115(3)	0.2628(2)	-0.0835(2)	3.03(7)
C10	0.4758(3)	0.3606(2)	-0.1148(2)	3.89(8)
C11A	0.5886(4)	0.4202(3)	-0.1280(3)	4.4(1)
C12A	0.6951(4)	0.4463(3)	-0.0303(3)	4.0(1)
C13	0.8286(3)	0.3932(3)	-0.0111(3)	4.50(8)
C14	0.8225(3)	0.2905(2)	0.0005(2)	3.24(7)
C15	0.4004(3)	0.2934(2)	0.1005(2)	3.10(7)
C16	0.9007(3)	0.3353(2)	0.2368(2)	2.78(6)
C17	0.9369(3)	0.1442(2)	0.1756(2)	3.46(8)
C18	0.4454(3)	0.1016(2)	0.0421(2)	2.97(7)
C19	0.2575(3)	0.3426(3)	0.1870(2)	4.65(9)
C20	1.0212(3)	0.3957(3)	0.3951(2)	4.48(9)
C21	1.1071(3)	0.1053(3)	0.3263(3)	6.0(1)
C22	0.3044(3)	0.0142(3)	0.1069(3)	4.77(9)
C11B	0.584(2)	0.431(1)	-0.068(1)	3.7(3)*
C12B	0.704(1)	0.416(1)	-0.106(1)	3.3(3)*
H3	0.643	0.339	0.252	2.5
H7	0.699	0.062	0.171	2.9
H9A	0.426	0.228	-0.101	3.3
H9B	0.566	0.239	-0.124	3.3
H10AA	0.445	0.390	-0.063	4.3
H10AB	0.401	0.360	-0.180	4.3
H11AA	0.547	0.477	-0.164	4.8
H11AB	0.633	0.386	-0.169	4.8
H12AA	0.660	0.434	0.026	4.4
H12AB	0.714	0.512	-0.032	4.4
H13AA	0.895	0.417	0.052	4.9
H13AB	0.861	0.405	-0.069	4.9
H14A	0.777	0.264	-0.067	3.6
H14B	0.917	0.267	0.027	3.6
H19A	0.262	0.374	0.250	5.1
H19B	0.200	0.378	0.128	5.1
H19C	0.218	0.281	0.186	5.1
H20A	1.006	0.421	0.456	4.9
H20B	1.080	0.341	0.414	4.9
H20C	1.066	0.442	0.366	4.9
H21A	1.120	0.096	0.399	6.6
H21B	1.129	0.048	0.297	6.6
H21C	1.167	0.155	0.319	6.6
H22A	0.295	-0.002	0.173	5.2
H22B	0.221	0.046	0.065	5.2
H22C	0.317	-0.042	0.072	5.2

Table 333 (cont.). Final Atomic Parameters for Sb-8 at **236 K**

Atom	x	y	z	B(Å^2)
H10BA	0.395	0.377	-0.097	4.3
H10BB	0.453	0.364	-0.189	4.3
H11BA	0.616	0.424	0.007	4.0
H11BB	0.547	0.493	-0.087	4.0
H12BA	0.721	0.473	-0.139	3.6
H12BB	0.685	0.365	-0.155	3.6
H13BA	0.822	0.425	0.050	4.9
H13BB	0.914	0.411	-0.022	4.9

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

Table 334. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **236 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0332(9)	0.077(2)	0.038(1)	0.002(1)	0.0190(7)	-0.001(1)
O2	0.029(1)	0.078(2)	0.047(1)	-0.001(1)	0.0041(9)	-0.006(1)
O3	0.0333(9)	0.070(1)	0.032(1)	-0.007(1)	0.0090(7)	-0.020(1)
O4	0.0296(9)	0.096(2)	0.055(1)	-0.013(1)	0.0200(8)	-0.024(1)
O5	0.036(1)	0.088(2)	0.045(1)	0.011(1)	0.0062(9)	0.015(1)
O6	0.061(1)	0.086(2)	0.064(1)	0.026(1)	0.0297(9)	-0.000(1)
O7	0.042(1)	0.059(1)	0.039(1)	-0.017(1)	0.0114(8)	0.004(1)
O8	0.065(1)	0.051(1)	0.036(1)	-0.018(1)	0.007(1)	-0.006(1)
C1	0.034(1)	0.033(2)	0.023(1)	-0.001(1)	0.009(1)	-0.003(1)
C2	0.028(1)	0.072(2)	0.027(1)	-0.001(1)	0.011(1)	-0.005(2)
C3	0.030(1)	0.031(2)	0.027(1)	-0.002(1)	0.011(1)	-0.001(1)
C4	0.030(1)	0.056(2)	0.029(1)	-0.006(1)	0.013(1)	-0.010(1)
C5	0.033(1)	0.035(2)	0.025(1)	-0.002(1)	0.0155(9)	-0.007(1)
C6	0.034(1)	0.056(2)	0.040(2)	-0.000(2)	0.009(1)	0.009(2)
C7	0.041(1)	0.032(2)	0.027(1)	0.001(1)	0.010(1)	-0.005(1)
C8	0.034(1)	0.044(2)	0.037(1)	-0.003(1)	0.010(1)	0.007(2)
C9	0.042(1)	0.044(2)	0.024(1)	-0.002(1)	0.005(1)	-0.001(1)
C10	0.048(2)	0.055(2)	0.040(2)	0.002(2)	0.007(1)	0.013(2)
C11A	0.065(2)	0.052(3)	0.042(2)	-0.011(2)	0.009(2)	0.014(2)
C12A	0.060(2)	0.041(2)	0.046(2)	-0.004(2)	0.012(2)	0.004(2)
C13	0.053(2)	0.063(2)	0.062(2)	-0.009(2)	0.029(1)	0.016(2)
C14	0.040(1)	0.057(2)	0.033(1)	-0.003(1)	0.022(1)	-0.003(2)
C15	0.031(1)	0.052(2)	0.035(1)	-0.003(1)	0.011(1)	0.007(2)
C16	0.029(1)	0.044(2)	0.034(1)	-0.003(1)	0.012(1)	-0.001(1)
C17	0.037(1)	0.050(2)	0.043(2)	0.003(1)	0.011(1)	0.002(2)
C18	0.038(1)	0.037(2)	0.035(1)	-0.001(1)	0.009(1)	0.003(1)
C19	0.034(1)	0.089(3)	0.064(2)	0.010(2)	0.030(1)	0.011(2)
C20	0.046(2)	0.076(2)	0.039(2)	-0.015(2)	0.002(1)	-0.018(2)
C21	0.040(2)	0.104(3)	0.067(2)	0.019(2)	-0.006(2)	0.021(2)
C22	0.055(2)	0.063(2)	0.062(2)	-0.025(2)	0.019(1)	0.007(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 335. Interatomic Distances (Å) for Sb-8 at **236 K**

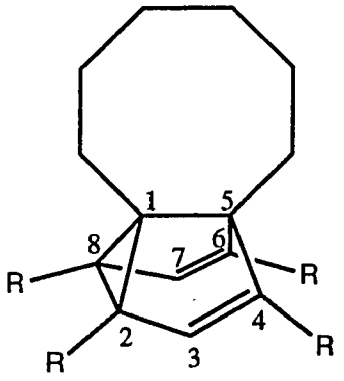
O1	C15	1.333(4)	C3	C4	1.374(4)
O1	C19	1.451(4)	C3	C7	3.026(4)
O2	C15	1.194(3)	C4	C5	1.520(4)
O3	C16	1.330(4)	C4	C6	2.034(5)
O3	C20	1.457(3)	C4	C16	1.472(3)
O4	C16	1.195(4)	C5	C6	1.508(4)
O5	C17	1.334(4)	C5	C14	1.530(4)
O5	C21	1.449(4)	C6	C7	1.376(4)
O6	C17	1.195(4)	C6	C17	1.479(4)
O7	C18	1.335(4)	C7	C8	1.389(4)
O7	C22	1.447(4)	C8	C18	1.481(4)
O8	C18	1.199(3)	C9	C10	1.523(5)
C1	C2	1.516(4)	C10	C11A	1.545(6)
C1	C5	1.587(3)	C11A	C12A	1.515(5)
C1	C8	1.499(4)	C12A	C13	1.560(5)
C1	C9	1.527(3)	C13	C14	1.531(5)
C2	C3	1.392(3)	C10	C11B	1.52(2)
C2	C8	1.949(5)	C11B	C12B	1.55(3)
C2	C15	1.488(4)	C12B	C13	1.58(1)

Table 336. Angles (°) for Sb-8 at **236 K**

C15	O1	C19	115.7(2)	C6	C7	C8	110.5(3)
C16	O3	C20	115.2(3)	C1	C8	C2	50.1(2)
C17	O5	C21	115.9(3)	C1	C8	C7	111.4(2)
C18	O7	C22	117.5(2)	C1	C8	C18	126.5(2)
C2	C1	C5	103.3(2)	C2	C8	C7	112.8(2)
C2	C1	C8	80.5(2)	C2	C8	C18	113.7(2)
C2	C1	C9	121.2(2)	C7	C8	C18	120.5(3)
C5	C1	C8	103.4(2)	C1	C9	C10	117.7(2)
C5	C1	C9	121.2(2)	C9	C10	C11A	116.8(3)
C8	C1	C9	119.1(2)	C10	C11A	C12A	113.8(3)
C1	C2	C3	111.0(2)	C11A	C12A	C13	112.6(3)
C1	C2	C8	49.4(2)	C12A	C13	C14	116.8(3)
C1	C2	C15	124.6(2)	C5	C14	C13	115.4(3)
C3	C2	C8	112.8(2)	O1	C15	O2	124.6(3)
C3	C2	C15	123.8(3)	O1	C15	C2	110.4(2)
C8	C2	C15	109.3(2)	O2	C15	C2	124.9(3)
C2	C3	C4	111.2(3)	O3	C16	O4	123.4(2)
C3	C4	C5	111.4(2)	O3	C16	C4	111.9(3)
C3	C4	C16	125.0(3)	O4	C16	C4	124.7(3)
C5	C4	C6	47.5(2)	O5	C17	O6	123.5(3)
C5	C4	C16	123.6(3)	O5	C17	C6	111.0(3)
C1	C5	C4	103.2(2)	O6	C17	C6	125.5(3)
C1	C5	C6	103.0(2)	O7	C18	O8	123.7(3)
C1	C5	C14	119.5(2)	O7	C18	C8	110.2(2)
C4	C5	C6	84.4(3)	O8	C18	C8	126.0(3)
C4	C5	C14	121.3(2)				
C6	C5	C14	118.9(3)				
C4	C6	C5	48.0(2)	C9	C10	C11B	116.2(6)
C5	C6	C7	111.6(2)	C10	C11B	C12B	110(1)
C5	C6	C17	125.8(3)	C11B	C12B	C13	106(1)
C7	C6	C17	122.3(3)	C12B	C13	C14	104.7(6)

Table 337. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-8 at **236 K**

Atom	Min.	Int'med.	Max.
O1	0.156	0.204	0.278
O2	0.165	0.230	0.282
O3	0.153	0.187	0.280
O4	0.157	0.209	0.327
O5	0.173	0.228	0.305
O6	0.188	0.256	0.321
O7	0.173	0.196	0.270
O8	0.175	0.217	0.286
C1	0.149	0.184	0.187
C2	0.154	0.170	0.269
C3	0.159	0.171	0.182
C4	0.153	0.171	0.244
C5	0.130	0.177	0.201
C6	0.182	0.197	0.247
C7	0.154	0.185	0.207
C8	0.180	0.184	0.224
C9	0.153	0.209	0.218
C10	0.179	0.227	0.254
C11A	0.178	0.223	0.290
C12A	0.196	0.215	0.257
C13	0.170	0.249	0.283
C14	0.147	0.209	0.240
C15	0.169	0.182	0.236
C16	0.166	0.184	0.211
C17	0.189	0.212	0.225
C18	0.181	0.190	0.210
C19	0.144	0.248	0.307
C20	0.157	0.248	0.290
C21	0.158	0.300	0.337
C22	0.172	0.247	0.301



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–338. X-ray Crystal Data for Sb-8 at **265 K**

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.08 x 0.10 x 0.59
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.597(1)
b (Å)	14.841(1)
c (Å)	14.200(1)
β (°)	109.60(1)
Cell volume (Å^3)	2103.84(3.53)
Z	4
d_{calc} (g cm^{-3})	1.321
μ(Cu $K\alpha$) (cm^{-1})	8.01
Maximum θ (°)	60
Unique reflections	3113
Observed reflections	1831
[$I > 3.0\sigma(I)$]	
Number of variables	279
R	0.043
R_w	0.048
$(\Delta\rho)_{max}$ (e Å^{-3})	0.16
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.18

Table 339. Final Atomic Parameters for Sb-8 at **265 K**

Atom	x	y	z	B(Å^2)
O1	0.3906(2)	0.3349(2)	0.1817(1)	4.27(6)
O2	0.3059(2)	0.2697(2)	0.0316(2)	4.83(6)
O3	0.8926(2)	0.3685(2)	0.3213(2)	4.08(5)
O4	1.0014(2)	0.3283(2)	0.2186(2)	5.28(6)
O5	0.9670(2)	0.1291(2)	0.2739(2)	5.20(6)
O6	1.0098(2)	0.1315(2)	0.1309(2)	6.26(7)
O7	0.4178(2)	0.0726(2)	0.1227(2)	4.24(5)
O8	0.3780(2)	0.0816(2)	-0.0419(2)	4.83(6)
C1	0.5884(3)	0.2435(2)	0.0275(2)	2.74(7)
C2	0.5428(3)	0.2805(3)	0.1097(2)	3.64(8)
C3	0.6496(3)	0.3121(2)	0.1894(2)	2.54(6)
C4	0.7683(3)	0.3010(2)	0.1711(2)	3.28(7)
C5	0.7466(3)	0.2569(2)	0.0704(2)	2.69(6)
C6	0.7934(3)	0.1734(2)	0.1325(2)	3.82(8)
C7	0.6880(3)	0.1193(2)	0.1326(2)	2.99(7)
C8	0.5679(3)	0.1559(2)	0.0724(2)	3.39(8)
C9	0.5104(3)	0.2623(2)	-0.0828(2)	3.47(8)
C10	0.4747(3)	0.3603(3)	-0.1137(3)	4.42(9)
C11A	0.5875(5)	0.4188(3)	-0.1267(3)	5.0(1)
C12A	0.6946(4)	0.4451(3)	-0.0301(3)	4.6(1)
C13	0.8271(3)	0.3909(3)	-0.0114(3)	4.98(9)
C14	0.8210(3)	0.2887(2)	0.0011(2)	3.77(8)
C15	0.3999(3)	0.2938(2)	0.1010(2)	3.39(7)
C16	0.8995(3)	0.3336(2)	0.2367(2)	3.14(7)
C17	0.9347(3)	0.1437(2)	0.1764(2)	3.89(8)
C18	0.4437(3)	0.1015(2)	0.0420(2)	3.40(8)
C19	0.2566(3)	0.3434(3)	0.1863(3)	5.3(1)
C20	1.0200(3)	0.3942(3)	0.3951(3)	5.0(1)
C21	1.1049(4)	0.1041(3)	0.3268(3)	7.0(1)
C22	0.3031(3)	0.0140(3)	0.1065(3)	5.4(1)
C11B	0.583(2)	0.431(1)	-0.066(1)	4.6(4)*
C12B	0.704(1)	0.414(1)	-0.106(1)	3.4(3)*
H3	0.642	0.339	0.252	2.8
H7	0.697	0.062	0.171	3.3
H9A	0.425	0.228	-0.101	3.8
H9B	0.565	0.239	-0.123	3.8
H10AA	0.444	0.389	-0.061	4.9
H10AB	0.399	0.360	-0.179	4.9
H11AA	0.547	0.475	-0.163	5.5
H11AB	0.631	0.384	-0.168	5.5
H12AA	0.660	0.434	0.026	5.1
H12AB	0.714	0.511	-0.033	5.1
H13AA	0.895	0.415	0.051	5.5
H13AB	0.858	0.402	-0.069	5.5
H14A	0.776	0.262	-0.066	4.1
H14B	0.915	0.266	0.028	4.1
H19A	0.261	0.375	0.249	5.8
H19B	0.200	0.379	0.128	5.8
H19C	0.217	0.282	0.185	5.8
H20A	1.004	0.419	0.455	5.5
H20B	1.079	0.340	0.415	5.5
H20C	1.064	0.441	0.366	5.5
H21A	1.118	0.095	0.399	7.7
H21B	1.126	0.047	0.298	7.7
H21C	1.166	0.153	0.320	7.7
H22A	0.295	-0.003	0.172	5.9
H22B	0.220	0.046	0.065	5.9
H22C	0.315	-0.042	0.071	5.9

Table 339 (cont.). Final Atomic Parameters for Sb-8 at **265 K**

Atom	x	y	z	B(Å^2)
H10BA	0.394	0.376	-0.096	4.9
H10BB	0.452	0.364	-0.188	4.9
H11BA	0.614	0.425	0.008	5.1
H11BB	0.545	0.493	-0.086	5.1
H12BA	0.722	0.470	-0.139	3.8
H12BB	0.684	0.363	-0.154	3.8
H13BA	0.821	0.423	0.049	5.5
H13BB	0.912	0.408	-0.022	5.5

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

Table 340. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **265 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0354(9)	0.089(2)	0.045(1)	0.003(1)	0.0230(7)	-0.001(1)
O2	0.034(1)	0.090(2)	0.052(1)	-0.002(1)	0.005(1)	-0.008(1)
O3	0.038(1)	0.079(2)	0.037(1)	-0.008(1)	0.0109(8)	-0.021(1)
O4	0.032(1)	0.113(2)	0.061(1)	-0.014(1)	0.0227(8)	-0.027(1)
O5	0.042(1)	0.101(2)	0.050(1)	0.012(1)	0.009(1)	0.017(1)
O6	0.074(1)	0.102(2)	0.070(1)	0.035(1)	0.035(1)	0.005(2)
O7	0.049(1)	0.067(1)	0.044(1)	-0.020(1)	0.0142(9)	0.004(1)
O8	0.076(1)	0.057(1)	0.042(1)	-0.020(1)	0.008(1)	-0.006(1)
C1	0.037(1)	0.042(2)	0.024(1)	-0.002(1)	0.008(1)	-0.004(1)
C2	0.030(1)	0.080(2)	0.030(1)	-0.005(2)	0.012(1)	-0.006(2)
C3	0.034(1)	0.032(2)	0.032(1)	-0.002(1)	0.014(1)	-0.003(1)
C4	0.033(1)	0.065(2)	0.029(1)	-0.005(1)	0.013(1)	-0.011(2)
C5	0.037(1)	0.041(2)	0.029(1)	-0.000(1)	0.018(1)	-0.005(1)
C6	0.039(2)	0.059(2)	0.042(2)	-0.000(2)	0.007(1)	0.010(2)
C7	0.045(2)	0.035(2)	0.033(2)	0.000(1)	0.012(1)	-0.004(1)
C8	0.040(2)	0.047(2)	0.040(2)	-0.005(1)	0.010(1)	0.007(2)
C9	0.048(2)	0.052(2)	0.029(2)	-0.004(2)	0.009(1)	-0.002(2)
C10	0.054(2)	0.060(2)	0.048(2)	-0.000(2)	0.008(2)	0.012(2)
C11A	0.069(3)	0.061(3)	0.051(3)	-0.009(3)	0.006(2)	0.018(3)
C12A	0.065(3)	0.048(3)	0.060(3)	-0.006(2)	0.017(2)	0.011(2)
C13	0.059(2)	0.074(3)	0.063(2)	-0.009(2)	0.030(1)	0.015(2)
C14	0.050(2)	0.064(2)	0.037(1)	-0.001(2)	0.025(1)	-0.002(2)
C15	0.031(1)	0.062(2)	0.036(2)	-0.003(1)	0.011(1)	0.008(2)
C16	0.035(1)	0.047(2)	0.038(2)	-0.002(1)	0.014(1)	-0.004(2)
C17	0.043(2)	0.056(2)	0.048(2)	0.000(2)	0.014(1)	-0.002(2)
C18	0.044(2)	0.041(2)	0.041(2)	-0.000(1)	0.010(1)	0.004(2)
C19	0.041(1)	0.101(3)	0.072(2)	0.013(2)	0.035(1)	0.012(2)
C20	0.049(2)	0.087(3)	0.044(2)	-0.015(2)	0.003(2)	-0.021(2)
C21	0.049(2)	0.118(4)	0.079(3)	0.026(2)	-0.005(2)	0.022(3)
C22	0.060(2)	0.075(3)	0.070(2)	-0.026(2)	0.022(2)	0.009(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 341. Interatomic Distances (Å) for Sb-8 at **265 K**

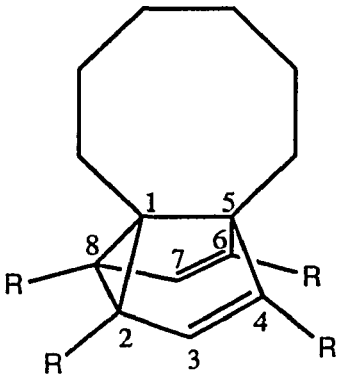
O1	C15	1.331(4)	C3	C4	1.378(4)
O1	C19	1.449(4)	C3	C7	3.037(4)
O2	C15	1.197(3)	C4	C5	1.518(4)
O3	C16	1.332(4)	C4	C6	2.013(5)
O3	C20	1.455(3)	C4	C16	1.472(4)
O4	C16	1.194(4)	C5	C6	1.505(4)
O5	C17	1.329(4)	C5	C14	1.527(5)
O5	C21	1.450(4)	C6	C7	1.376(5)
O6	C17	1.195(5)	C6	C17	1.483(4)
O7	C18	1.336(4)	C7	C8	1.384(4)
O7	C22	1.449(4)	C8	C18	1.479(4)
O8	C18	1.197(3)	C9	C10	1.530(5)
C1	C2	1.510(5)	C10	C11A	1.538(6)
C1	C5	1.592(4)	C11A	C12A	1.509(6)
C1	C8	1.497(5)	C12A	C13	1.562(6)
C1	C9	1.532(4)	C13	C14	1.531(5)
C2	C3	1.386(3)	C10	C11B	1.53(2)
C2	C8	1.967(5)	C11B	C12B	1.58(3)
C2	C15	1.490(4)	C12B	C13	1.56(1)

Table 342. Angles (°) for Sb-8 at **265 K**

C15	O1	C19	115.8(2)	C6	C7	C8	110.4(3)
C16	O3	C20	115.6(3)	C1	C8	C2	49.4(2)
C17	O5	C21	116.4(3)	C1	C8	C7	111.6(3)
C18	O7	C22	117.3(2)	C1	C8	C18	126.3(2)
C2	C1	C5	103.2(2)	C2	C8	C7	112.4(2)
C2	C1	C8	81.7(2)	C2	C8	C18	113.8(2)
C2	C1	C9	121.5(2)	C7	C8	C18	120.7(3)
C5	C1	C8	103.3(2)	C1	C9	C10	117.5(3)
C5	C1	C9	120.5(3)	C9	C10	C11A	116.4(3)
C8	C1	C9	119.2(2)	C10	C11A	C12A	114.5(4)
C1	C2	C3	111.6(3)	C11A	C12A	C13	112.3(4)
C1	C2	C8	48.9(2)	C12A	C13	C14	117.4(3)
C1	C2	C15	124.4(2)	C5	C14	C13	115.6(3)
C3	C2	C8	113.0(2)	O1	C15	O2	124.4(3)
C3	C2	C15	123.5(3)	O1	C15	C2	110.8(2)
C8	C2	C15	109.1(2)	O2	C15	C2	124.8(3)
C2	C3	C4	110.7(3)	O3	C16	O4	123.2(2)
C3	C4	C5	111.7(2)	O3	C16	C4	111.9(3)
C3	C4	C16	124.7(3)	O4	C16	C4	124.9(3)
C5	C4	C6	48.0(2)	O5	C17	O6	123.6(3)
C5	C4	C16	123.4(3)	O5	C17	C6	111.0(3)
C1	C5	C4	102.8(2)	O6	C17	C6	125.4(3)
C1	C5	C6	102.7(2)	O7	C18	O8	123.8(3)
C1	C5	C14	119.8(2)	O7	C18	C8	110.1(2)
C4	C5	C6	83.5(3)	O8	C18	C8	126.1(3)
C4	C5	C14	121.7(3)				
C6	C5	C14	119.5(3)				
C4	C6	C5	48.5(2)	C9	C10	C11B	116.6(6)
C5	C6	C7	111.9(2)	C10	C11B	C12B	108(1)
C5	C6	C17	125.4(3)	C11B	C12B	C13	106(1)
C7	C6	C17	122.1(3)	C12B	C13	C14	105.2(6)

Table 343. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-8 at **265 K**

Atom	Min.	Int'med.	Max.
O1	0.157	0.220	0.298
O2	0.179	0.244	0.304
O3	0.167	0.198	0.297
O4	0.163	0.221	0.354
O5	0.189	0.236	0.326
O6	0.205	0.265	0.354
O7	0.183	0.210	0.288
O8	0.189	0.229	0.308
C1	0.153	0.195	0.207
C2	0.163	0.175	0.284
C3	0.168	0.177	0.193
C4	0.158	0.178	0.260
C5	0.143	0.196	0.208
C6	0.184	0.213	0.257
C7	0.170	0.195	0.216
C8	0.189	0.194	0.236
C9	0.169	0.219	0.236
C10	0.197	0.236	0.271
C11A	0.195	0.240	0.310
C12A	0.199	0.245	0.275
C13	0.189	0.259	0.294
C14	0.159	0.230	0.254
C15	0.174	0.183	0.256
C16	0.185	0.191	0.220
C17	0.208	0.218	0.238
C18	0.191	0.205	0.224
C19	0.159	0.263	0.327
C20	0.168	0.254	0.310
C21	0.173	0.327	0.358
C22	0.187	0.261	0.319



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–344. X-ray Crystal Data for Sb-8 at **279 K**

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.08 x 0.10 x 0.59
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.602(1)
b (Å)	14.870(1)
c (Å)	14.215(2)
β (°)	109.64(1)
Cell volume (Å^3)	2110.61(3.69)
Z	4
d_{calc} (g cm^{-3})	1.317
μ(Cu $K\alpha$) (cm^{-1})	7.98
Maximum θ(°)	60
Unique reflections	3118
Observed reflections	1771
[$I > 3.0\sigma(I)$]	
Number of variables	279
R	0.044
R_w	0.050
$(\Delta\rho)_{max}$ (e Å^{-3})	0.16
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.19

Table 345. Final Atomic Parameters for Sb-8 at **279 K**

Atom	x	y	z	B(Å^2)
O1	0.3900(2)	0.3351(2)	0.1813(2)	4.51(6)
O2	0.3053(2)	0.2702(2)	0.0320(2)	5.30(7)
O3	0.8926(2)	0.3676(2)	0.3212(2)	4.29(6)
O4	1.0010(2)	0.3279(2)	0.2184(2)	5.62(7)
O5	0.9661(2)	0.1284(2)	0.2739(2)	5.56(7)
O6	1.0084(2)	0.1308(2)	0.1309(2)	6.62(8)
O7	0.4171(2)	0.0722(2)	0.1227(2)	4.55(6)
O8	0.3767(2)	0.0816(2)	-0.0418(2)	5.17(7)
C1	0.5881(3)	0.2435(2)	0.0274(2)	2.85(7)
C2	0.5416(3)	0.2807(3)	0.1095(2)	3.75(8)
C3	0.6492(3)	0.3115(2)	0.1893(2)	2.67(7)
C4	0.7683(3)	0.3004(2)	0.1713(2)	3.45(8)
C5	0.7452(3)	0.2564(2)	0.0705(2)	2.81(7)
C6	0.7922(3)	0.1736(3)	0.1330(2)	4.03(9)
C7	0.6870(3)	0.1192(2)	0.1331(2)	3.21(8)
C8	0.5669(3)	0.1556(2)	0.0721(2)	3.49(8)
C9	0.5094(3)	0.2620(2)	-0.0825(2)	3.67(8)
C10	0.4740(3)	0.3598(3)	-0.1130(3)	4.6(1)
C11A	0.5872(5)	0.4184(3)	-0.1265(3)	5.3(1)
C12A	0.6934(5)	0.4440(3)	-0.0300(4)	4.8(1)
C13	0.8263(3)	0.3902(3)	-0.0116(3)	5.4(1)
C14	0.8208(3)	0.2879(3)	0.0013(2)	4.05(8)
C15	0.3994(3)	0.2939(2)	0.1010(2)	3.57(8)
C16	0.8992(3)	0.3329(2)	0.2369(2)	3.36(8)
C17	0.9335(3)	0.1433(3)	0.1763(3)	4.21(9)
C18	0.4424(3)	0.1013(2)	0.0416(2)	3.57(8)
C19	0.2562(3)	0.3437(3)	0.1865(3)	5.7(1)
C20	1.0199(4)	0.3934(3)	0.3948(3)	5.4(1)
C21	1.1039(4)	0.1034(4)	0.3263(3)	7.5(1)
C22	0.3021(4)	0.0138(3)	0.1063(3)	5.8(1)
C11B	0.582(2)	0.431(1)	-0.067(1)	4.9(4)*
C12B	0.703(2)	0.414(1)	-0.107(1)	4.9(4)*
H3	0.641	0.338	0.252	2.9
H7	0.696	0.062	0.172	3.5
H9A	0.423	0.228	-0.100	4.0
H9B	0.564	0.239	-0.123	4.0
H10AA	0.444	0.389	-0.060	5.1
H10AB	0.398	0.360	-0.178	5.1
H11AA	0.546	0.475	-0.162	5.8
H11AB	0.631	0.384	-0.168	5.8
H12AA	0.659	0.432	0.026	5.3
H12AB	0.713	0.510	-0.032	5.3
H13AA	0.894	0.415	0.051	5.9
H13AB	0.857	0.401	-0.070	5.9
H14A	0.776	0.261	-0.066	4.4
H14B	0.915	0.265	0.029	4.4
H19A	0.261	0.376	0.250	6.3
H19B	0.199	0.379	0.128	6.3
H19C	0.217	0.282	0.186	6.3
H20A	1.004	0.419	0.455	5.9
H20B	1.079	0.339	0.414	5.9
H20C	1.064	0.440	0.366	5.9
H21A	1.117	0.094	0.399	8.2
H21B	1.125	0.047	0.297	8.2
H21C	1.165	0.153	0.319	8.2
H22A	0.294	-0.003	0.172	6.4
H22B	0.219	0.046	0.065	6.4
H22C	0.314	-0.042	0.070	6.4

Table 345 (cont.). Final Atomic Parameters for Sb-8 at **279 K**

Atom	x	y	z	B(Å^2)
H10BA	0.394	0.376	-0.094	5.1
H10BB	0.450	0.363	-0.187	5.1
H11BA	0.615	0.425	0.008	5.4
H11BB	0.545	0.492	-0.086	5.4
H12BA	0.722	0.470	-0.140	5.4
H12BB	0.683	0.363	-0.156	5.4
H13BA	0.819	0.422	0.048	5.9
H13BB	0.912	0.408	-0.022	5.9

The parameters of the hydrogen atoms were not refined.

Standard deviations are in parentheses.

Table 346. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **279 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.038(1)	0.092(2)	0.047(1)	0.002(1)	0.0227(8)	-0.001(1)
O2	0.037(1)	0.099(2)	0.058(1)	-0.003(1)	0.005(1)	-0.008(2)
O3	0.041(1)	0.083(2)	0.037(1)	-0.010(1)	0.0113(9)	-0.022(1)
O4	0.035(1)	0.122(2)	0.062(1)	-0.015(1)	0.0235(9)	-0.028(2)
O5	0.047(1)	0.106(2)	0.053(1)	0.014(1)	0.010(1)	0.021(2)
O6	0.073(1)	0.113(2)	0.073(2)	0.035(1)	0.035(1)	0.004(2)
O7	0.053(1)	0.072(2)	0.046(1)	-0.020(1)	0.014(1)	0.005(1)
O8	0.078(1)	0.063(2)	0.045(1)	-0.025(1)	0.008(1)	-0.006(1)
C1	0.040(1)	0.039(2)	0.030(2)	-0.001(1)	0.013(1)	-0.005(2)
C2	0.030(1)	0.081(3)	0.033(2)	-0.004(2)	0.014(1)	-0.004(2)
C3	0.037(1)	0.035(2)	0.032(1)	-0.000(1)	0.015(1)	-0.002(1)
C4	0.035(1)	0.066(2)	0.032(2)	-0.005(2)	0.014(1)	-0.012(2)
C5	0.037(1)	0.043(2)	0.031(1)	-0.001(1)	0.017(1)	-0.005(2)
C6	0.039(2)	0.066(2)	0.045(2)	0.002(2)	0.010(1)	0.011(2)
C7	0.051(2)	0.038(2)	0.034(2)	0.000(2)	0.015(1)	-0.004(2)
C8	0.041(2)	0.050(2)	0.041(2)	-0.005(2)	0.012(1)	0.005(2)
C9	0.054(2)	0.053(2)	0.028(2)	-0.001(2)	0.008(1)	-0.001(2)
C10	0.055(2)	0.065(2)	0.047(2)	0.000(2)	0.006(2)	0.016(2)
C11A	0.076(3)	0.062(3)	0.052(3)	-0.006(3)	0.007(2)	0.017(3)
C12A	0.071(3)	0.048(3)	0.058(3)	-0.003(2)	0.013(2)	0.010(2)
C13	0.062(2)	0.078(3)	0.073(2)	-0.012(2)	0.032(2)	0.014(2)
C14	0.052(2)	0.069(2)	0.042(2)	-0.004(2)	0.028(1)	-0.005(2)
C15	0.034(1)	0.062(2)	0.041(2)	-0.000(2)	0.014(1)	0.007(2)
C16	0.037(1)	0.053(2)	0.038(2)	-0.004(2)	0.014(1)	-0.005(2)
C17	0.045(2)	0.062(2)	0.054(2)	0.004(2)	0.017(1)	0.004(2)
C18	0.046(2)	0.044(2)	0.043(2)	-0.003(2)	0.012(1)	0.001(2)
C19	0.040(2)	0.112(3)	0.077(2)	0.014(2)	0.036(1)	0.013(2)
C20	0.053(2)	0.096(3)	0.046(2)	-0.018(2)	0.003(2)	-0.022(2)
C21	0.053(2)	0.130(4)	0.079(3)	0.025(3)	-0.006(2)	0.022(3)
C22	0.063(2)	0.083(3)	0.076(2)	-0.031(2)	0.022(2)	0.009(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 347. Interatomic Distances (Å) for Sb-8 at **279 K**

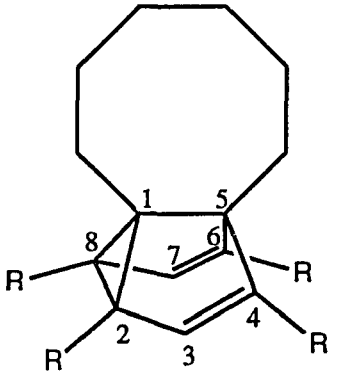
O1	C15	1.329(4)	C3	C4	1.379(5)
O1	C19	1.451(4)	C3	C7	3.032(4)
O2	C15	1.193(3)	C4	C5	1.519(4)
O3	C16	1.329(4)	C4	C6	2.002(5)
O3	C20	1.454(4)	C4	C16	1.469(4)
O4	C16	1.196(4)	C5	C6	1.502(5)
O5	C17	1.331(4)	C5	C14	1.536(5)
O5	C21	1.447(4)	C6	C7	1.379(5)
O6	C17	1.194(5)	C6	C17	1.485(4)
O7	C18	1.339(4)	C7	C8	1.388(4)
O7	C22	1.451(5)	C8	C18	1.482(4)
O8	C18	1.193(4)	C9	C10	1.528(5)
C1	C2	1.515(5)	C10	C11A	1.546(7)
C1	C5	1.581(4)	C11A	C12A	1.502(6)
C1	C8	1.503(5)	C12A	C13	1.564(6)
C1	C9	1.528(4)	C13	C14	1.536(6)
C2	C3	1.388(4)	C10	C11B	1.53(2)
C2	C8	1.978(5)	C11B	C12B	1.59(3)
C2	C15	1.485(4)	C12B	C13	1.57(1)

Table 348. Angles (°) for Sb-8 at **279 K**

C15	O1	C19	116.2(2)	C6	C7	C8	110.1(3)
C16	O3	C20	115.7(3)	C1	C8	C2	49.3(2)
C17	O5	C21	116.2(3)	C1	C8	C7	111.6(3)
C18	O7	C22	117.2(2)	C1	C8	C18	126.5(2)
C2	C1	C5	103.3(2)	C2	C8	C7	112.2(2)
C2	C1	C8	81.9(3)	C2	C8	C18	113.8(2)
C2	C1	C9	121.0(3)	C7	C8	C18	120.7(3)
C5	C1	C8	103.2(2)	C1	C9	C10	117.3(3)
C5	C1	C9	121.1(3)	C9	C10	C11A	116.4(3)
C8	C1	C9	118.7(2)	C10	C11A	C12A	113.9(4)
C1	C2	C3	111.0(3)	C11A	C12A	C13	112.4(4)
C1	C2	C8	48.8(2)	C12A	C13	C14	117.3(3)
C1	C2	C15	124.7(2)	C5	C14	C13	115.4(3)
C3	C2	C8	112.4(2)	O1	C15	O2	124.1(3)
C3	C2	C15	123.8(3)	O1	C15	C2	111.0(2)
C8	C2	C15	109.2(2)	O2	C15	C2	125.0(3)
C2	C3	C4	111.2(3)	O3	C16	O4	123.2(3)
C3	C4	C5	111.0(2)	O3	C16	C4	112.0(3)
C3	C4	C16	124.8(3)	O4	C16	C4	124.7(3)
C5	C4	C6	48.1(2)	O5	C17	O6	123.4(3)
C5	C4	C16	124.0(3)	O5	C17	C6	110.8(3)
C1	C5	C4	103.4(3)	O6	C17	C6	125.8(3)
C1	C5	C6	103.1(3)	O7	C18	O8	123.8(3)
C1	C5	C14	119.9(2)	O7	C18	C8	110.0(2)
C4	C5	C6	83.0(2)	O8	C18	C8	126.1(3)
C4	C5	C14	121.3(3)				
C6	C5	C14	119.2(3)				
C4	C6	C5	48.9(2)	C9	C10	C11B	117.1(6)
C5	C6	C7	111.9(3)	C10	C11B	C12B	108(1)
C5	C6	C17	125.6(3)	C11B	C12B	C13	105(1)
C7	C6	C17	121.7(3)	C12B	C13	C14	105.8(7)

Table 349. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-8 at **279 K**

Atom	Min.	Int'med.	Max.
O1	0.170	0.224	0.304
O2	0.186	0.257	0.317
O3	0.167	0.206	0.304
O4	0.170	0.226	0.365
O5	0.195	0.245	0.336
O6	0.209	0.273	0.365
O7	0.198	0.213	0.297
O8	0.193	0.235	0.322
C1	0.166	0.200	0.202
C2	0.164	0.184	0.286
C3	0.169	0.187	0.195
C4	0.163	0.186	0.264
C5	0.152	0.196	0.213
C6	0.191	0.214	0.266
C7	0.174	0.201	0.227
C8	0.192	0.200	0.236
C9	0.167	0.230	0.242
C10	0.192	0.243	0.282
C11A	0.199	0.251	0.314
C12A	0.203	0.244	0.288
C13	0.198	0.272	0.303
C14	0.165	0.234	0.268
C15	0.181	0.197	0.254
C16	0.191	0.191	0.234
C17	0.209	0.229	0.252
C18	0.204	0.204	0.229
C19	0.157	0.272	0.344
C20	0.173	0.267	0.324
C21	0.182	0.332	0.374
C22	0.187	0.272	0.336



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–350. X-ray Crystal Data for Sb-8 at **294 K**

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.08 x 0.10 x 0.59
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.607(1)
b (Å)	14.899(1)
c (Å)	14.230(1)
β (°)	109.68(1)
Cell volume (Å^3)	2117.40(3.19)
Z	4
d_{calc} (g cm^{-3})	1.313
μ(Cu $K\alpha$) (cm^{-1})	7.96
Maximum θ (°)	60
Unique reflections	3135
Observed reflections [$I > 3.0\sigma(I)$]	1704
Number of variables	279
R	0.044
R_w	0.049
$(\Delta\rho)_{max}$ (e Å^{-3})	0.17
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.17

Table 351. Final Atomic Parameters for Sb-8 at **294 K**

Atom	x	y	z	B(Å^2)
O1	0.3903(2)	0.3352(2)	0.1815(2)	4.81(6)
O2	0.3050(2)	0.2698(2)	0.0324(2)	5.58(7)
O3	0.8922(2)	0.3668(2)	0.3212(2)	4.64(6)
O4	1.0002(2)	0.3272(2)	0.2185(2)	6.03(7)
O5	0.9647(2)	0.1280(2)	0.2740(2)	5.84(7)
O6	1.0071(3)	0.1303(2)	0.1312(2)	7.15(8)
O7	0.4166(2)	0.0720(2)	0.1222(2)	4.85(6)
O8	0.3756(3)	0.0822(2)	-0.0416(2)	5.55(7)
C1	0.5871(3)	0.2434(2)	0.0277(2)	3.00(8)
C2	0.5414(3)	0.2808(3)	0.1096(2)	3.85(9)
C3	0.6484(3)	0.3111(2)	0.1894(2)	2.77(7)
C4	0.7674(3)	0.2995(2)	0.1714(2)	3.65(8)
C5	0.7448(3)	0.2564(2)	0.0709(2)	3.02(7)
C6	0.7914(3)	0.1739(3)	0.1335(3)	4.22(9)
C7	0.6864(3)	0.1191(2)	0.1334(2)	3.35(8)
C8	0.5666(3)	0.1551(2)	0.0723(2)	3.70(8)
C9	0.5091(3)	0.2618(3)	-0.0821(2)	4.06(9)
C10	0.4731(4)	0.3593(3)	-0.1127(3)	4.9(1)
C11A	0.5875(5)	0.4175(4)	-0.1254(4)	5.4(1)
C12A	0.6934(5)	0.4430(3)	-0.0303(4)	5.0(1)
C13	0.8261(4)	0.3892(3)	-0.0118(3)	5.6(1)
C14	0.8195(3)	0.2873(3)	0.0015(2)	4.24(9)
C15	0.3989(3)	0.2938(2)	0.1008(2)	3.70(8)
C16	0.8984(3)	0.3321(2)	0.2365(2)	3.68(8)
C17	0.9325(3)	0.1423(3)	0.1766(3)	4.38(9)
C18	0.4418(3)	0.1015(2)	0.0418(2)	3.91(9)
C19	0.2561(3)	0.3443(3)	0.1862(3)	6.0(1)
C20	1.0196(4)	0.3927(3)	0.3949(3)	5.7(1)
C21	1.1031(4)	0.1021(4)	0.3261(3)	7.8(1)
C22	0.3020(4)	0.0140(3)	0.1064(3)	6.1(1)
C11B	0.580(1)	0.432(1)	-0.065(1)	4.5(4)*
C12B	0.703(2)	0.414(1)	-0.108(1)	4.7(4)*
H3	0.641	0.338	0.252	3.0
H7	0.696	0.062	0.172	3.7
H9A	0.424	0.227	-0.100	4.5
H9B	0.564	0.239	-0.122	4.5
H10AA	0.443	0.388	-0.060	5.4
H10AB	0.398	0.359	-0.178	5.4
H11AA	0.547	0.474	-0.161	5.9
H11AB	0.631	0.383	-0.167	5.9
H12AA	0.660	0.431	0.026	5.5
H12AB	0.713	0.508	-0.033	5.5
H13AA	0.894	0.414	0.050	6.2
H13AB	0.857	0.400	-0.070	6.2
H14A	0.774	0.260	-0.066	4.7
H14B	0.913	0.264	0.029	4.7
H19A	0.261	0.376	0.249	6.6
H19B	0.199	0.380	0.127	6.6
H19C	0.216	0.283	0.185	6.6
H20A	1.004	0.418	0.455	6.3
H20B	1.079	0.339	0.414	6.3
H20C	1.063	0.439	0.366	6.3
H21A	1.117	0.093	0.398	8.6
H21B	1.123	0.045	0.297	8.6
H21C	1.164	0.151	0.319	8.6
H22A	0.295	-0.003	0.172	6.7
H22B	0.219	0.046	0.066	6.7
H22C	0.313	-0.041	0.070	6.7

Table 351 (cont.). Final Atomic Parameters for Sb-8 at **294 K**

Atom	x	y	z	B(Å^2)
H10BA	0.392	0.374	-0.095	5.4
H10BB	0.451	0.363	-0.187	5.4
H11BA	0.612	0.427	0.009	4.9
H11BB	0.541	0.493	-0.085	4.9
H12BA	0.722	0.469	-0.141	5.1
H12BB	0.681	0.363	-0.157	5.1
H13BA	0.819	0.421	0.048	6.2
H13BB	0.912	0.406	-0.022	6.2

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

Table 352. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **294 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.041(1)	0.098(2)	0.052(1)	0.003(1)	0.0253(8)	-0.002(1)
O2	0.039(1)	0.105(2)	0.060(2)	-0.004(1)	0.006(1)	-0.013(2)
O3	0.043(1)	0.091(2)	0.041(1)	-0.009(1)	0.0115(9)	-0.023(1)
O4	0.038(1)	0.133(2)	0.066(1)	-0.017(1)	0.0276(9)	-0.030(2)
O5	0.048(1)	0.111(2)	0.056(1)	0.017(1)	0.008(1)	0.019(2)
O6	0.081(2)	0.121(2)	0.080(2)	0.040(2)	0.039(1)	0.006(2)
O7	0.058(1)	0.075(2)	0.049(1)	-0.020(1)	0.016(1)	0.005(1)
O8	0.086(2)	0.067(2)	0.049(1)	-0.026(1)	0.011(1)	-0.006(1)
C1	0.043(2)	0.044(2)	0.027(2)	-0.000(2)	0.013(1)	-0.004(2)
C2	0.031(1)	0.083(3)	0.035(2)	-0.007(2)	0.013(1)	-0.006(2)
C3	0.039(1)	0.038(2)	0.033(2)	-0.000(1)	0.018(1)	-0.003(2)
C4	0.037(1)	0.070(2)	0.034(2)	-0.005(2)	0.016(1)	-0.015(2)
C5	0.042(1)	0.044(2)	0.034(2)	-0.001(2)	0.020(1)	-0.006(2)
C6	0.041(2)	0.069(3)	0.048(2)	0.003(2)	0.012(1)	0.010(2)
C7	0.050(2)	0.041(2)	0.034(2)	0.001(2)	0.012(1)	-0.005(2)
C8	0.043(2)	0.053(2)	0.044(2)	-0.003(2)	0.012(1)	0.009(2)
C9	0.058(2)	0.063(2)	0.028(2)	-0.005(2)	0.008(1)	-0.001(2)
C10	0.064(2)	0.069(3)	0.048(2)	0.004(2)	0.009(2)	0.018(2)
C11A	0.081(3)	0.065(3)	0.055(3)	-0.011(3)	0.016(2)	0.018(3)
C12A	0.073(3)	0.055(3)	0.057(3)	-0.004(3)	0.015(2)	0.011(3)
C13	0.068(2)	0.079(3)	0.074(2)	-0.012(2)	0.033(2)	0.019(2)
C14	0.053(2)	0.075(3)	0.043(2)	-0.004(2)	0.029(1)	-0.003(2)
C15	0.039(2)	0.065(2)	0.038(2)	-0.005(2)	0.015(1)	0.006(2)
C16	0.040(2)	0.059(2)	0.042(2)	-0.004(2)	0.016(1)	-0.007(2)
C17	0.047(2)	0.064(3)	0.056(2)	0.008(2)	0.017(1)	0.003(2)
C18	0.051(2)	0.050(2)	0.044(2)	-0.001(2)	0.013(1)	0.002(2)
C19	0.044(2)	0.116(3)	0.081(2)	0.014(2)	0.037(1)	0.010(3)
C20	0.057(2)	0.099(3)	0.050(2)	-0.019(2)	0.005(2)	-0.025(2)
C21	0.059(2)	0.137(4)	0.081(3)	0.030(3)	-0.003(2)	0.022(3)
C22	0.067(2)	0.085(3)	0.080(3)	-0.035(2)	0.025(2)	0.009(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 353. Interatomic Distances (Å) for Sb-8 at **294 K**

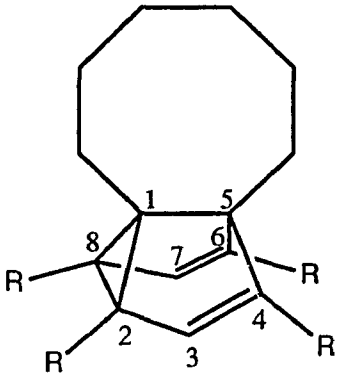
O1	C15	1.334(4)	C3	C4	1.381(5)
O1	C19	1.454(4)	C3	C7	3.033(5)
O2	C15	1.190(3)	C4	C5	1.512(5)
O3	C16	1.333(4)	C4	C6	1.987(5)
O3	C20	1.456(4)	C4	C16	1.469(4)
O4	C16	1.192(4)	C5	C6	1.500(5)
O5	C17	1.329(4)	C5	C14	1.530(5)
O5	C21	1.456(4)	C6	C7	1.381(5)
O6	C17	1.191(5)	C6	C17	1.490(4)
O7	C18	1.335(5)	C7	C8	1.383(4)
O7	C22	1.445(5)	C8	C18	1.480(5)
O8	C18	1.193(4)	C9	C10	1.528(5)
C1	C2	1.512(5)	C10	C11A	1.551(7)
C1	C5	1.587(4)	C11A	C12A	1.488(6)
C1	C8	1.508(5)	C12A	C13	1.563(6)
C1	C9	1.526(4)	C13	C14	1.534(6)
C2	C3	1.383(4)	C10	C11B	1.55(2)
C2	C8	1.990(5)	C11B	C12B	1.64(3)
C2	C15	1.486(5)	C12B	C13	1.58(1)

Table 354. Angles (°) for Sb-8 at **294 K**

C15	O1	C19	115.8(2)	C6	C7	C8	109.9(3)
C16	O3	C20	115.9(3)	C1	C8	C2	48.9(2)
C17	O5	C21	115.8(3)	C1	C8	C7	111.8(3)
C18	O7	C22	117.6(3)	C1	C8	C18	126.1(2)
C2	C1	C5	103.1(2)	C2	C8	C7	112.0(2)
C2	C1	C8	82.4(3)	C2	C8	C18	113.5(3)
C2	C1	C9	121.3(3)	C7	C8	C18	121.1(3)
C5	C1	C8	103.0(2)	C1	C9	C10	117.3(3)
C5	C1	C9	120.8(3)	C9	C10	C11A	115.7(3)
C8	C1	C9	118.8(3)	C10	C11A	C12A	114.7(4)
C1	C2	C3	111.5(3)	C11A	C12A	C13	112.6(4)
C1	C2	C8	48.7(2)	C12A	C13	C14	116.9(3)
C1	C2	C15	124.3(2)	C5	C14	C13	115.6(3)
C3	C2	C8	112.3(2)	O1	C15	O2	124.3(3)
C3	C2	C15	123.8(3)	O1	C15	C2	110.5(2)
C8	C2	C15	108.9(3)	O2	C15	C2	125.3(3)
C2	C3	C4	110.8(2)	O3	C16	O4	122.8(3)
C3	C4	C5	111.4(3)	O3	C16	C4	111.9(3)
C3	C4	C16	124.9(3)	O4	C16	C4	125.2(3)
C5	C4	C6	48.5(2)	O5	C17	O6	123.8(3)
C5	C4	C16	123.5(3)	O5	C17	C6	110.5(3)
C1	C5	C4	103.2(3)	O6	C17	C6	125.7(3)
C1	C5	C6	102.9(3)	O7	C18	O8	123.6(3)
C1	C5	C14	119.6(2)	O7	C18	C8	110.1(3)
C4	C5	C6	82.5(2)	O8	C18	C8	126.2(4)
C4	C5	C14	122.0(3)				
C6	C5	C14	119.4(3)				
C4	C6	C5	49.0(2)	C9	C10	C11B	117.7(6)
C5	C6	C7	112.3(3)	C10	C11B	C12B	106(1)
C5	C6	C17	126.0(3)	C11B	C12B	C13	104(1)
C7	C6	C17	120.8(3)	C12B	C13	C14	106.1(7)

Table 355. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-8 at **294 K**

Atom	Min.	Int'med.	Max.
O1	0.173	0.234	0.313
O2	0.190	0.259	0.330
O3	0.176	0.214	0.316
O4	0.172	0.233	0.381
O5	0.195	0.258	0.342
O6	0.216	0.283	0.381
O7	0.206	0.222	0.304
O8	0.207	0.242	0.332
C1	0.160	0.209	0.212
C2	0.169	0.185	0.290
C3	0.162	0.194	0.204
C4	0.162	0.191	0.275
C5	0.155	0.206	0.220
C6	0.199	0.218	0.271
C7	0.177	0.207	0.230
C8	0.193	0.205	0.247
C9	0.167	0.242	0.260
C10	0.193	0.262	0.286
C11A	0.199	0.258	0.315
C12A	0.210	0.251	0.287
C13	0.198	0.276	0.313
C14	0.166	0.241	0.275
C15	0.183	0.200	0.260
C16	0.193	0.202	0.249
C17	0.208	0.236	0.260
C18	0.208	0.222	0.237
C19	0.169	0.282	0.347
C20	0.178	0.273	0.332
C21	0.192	0.334	0.384
C22	0.185	0.280	0.346



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–356. X-ray Crystal Data for Sb-8 at **295 K**

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.12 x 0.20 x 0.67
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.607(1)
b (Å)	14.890(1)
c (Å)	14.228(1)
β (°)	109.72(1)
Cell volume (Å^3)	2115.34(16.8)
Z	4
d_{calc} (g cm^{-3})	1.314
μ(Cu $K\alpha$) (cm^{-1})	7.97
Maximum θ (°)	60
Unique reflections	3134
Observed reflections [$I > 3.0\sigma(I)$]	2449
Number of variables	279
R	0.046
R_w	0.059
$(\Delta\rho)_{max}$ (e Å^{-3})	0.16
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.24

Table 357. Final Atomic Parameters for Sb-8 at **295 K**

Atom	x	y	z	B(Å^2)
O1	0.6102(1)	0.3354(1)	0.3182(1)	5.01(4)
O2	0.6954(2)	0.2702(1)	0.4676(1)	5.85(5)
O3	0.1076(1)	0.3665(1)	0.1785(1)	4.77(4)
O4	0.0003(1)	0.3279(2)	0.2815(1)	6.34(5)
O5	0.0348(2)	0.1278(1)	0.2260(1)	6.03(5)
O6	-0.0070(2)	0.1304(1)	0.3684(1)	7.30(5)
O7	0.5838(2)	0.0720(1)	0.3775(1)	5.04(4)
O8	0.6244(2)	0.0820(1)	0.5417(1)	5.74(4)
C1	0.4129(2)	0.2432(1)	0.4719(1)	3.24(4)
C2	0.4596(2)	0.2813(2)	0.3903(1)	4.19(5)
C3	0.3513(2)	0.3112(1)	0.3104(1)	3.07(4)
C4	0.2327(2)	0.2997(2)	0.3286(1)	3.87(5)
C5	0.2562(2)	0.2561(1)	0.4298(1)	3.24(4)
C6	0.2086(2)	0.1735(2)	0.3667(2)	4.50(6)
C7	0.3138(2)	0.1189(1)	0.3665(1)	3.62(5)
C8	0.4340(2)	0.1555(2)	0.4277(2)	4.05(5)
C9	0.4920(2)	0.2622(2)	0.5818(1)	4.26(5)
C10	0.5262(3)	0.3598(2)	0.6129(2)	5.30(6)
C11A	0.4130(4)	0.4171(3)	0.6277(2)	5.96(9)
C12A	0.3050(4)	0.4428(2)	0.5293(3)	5.45(9)
C13	0.1755(3)	0.3892(2)	0.5118(2)	6.03(7)
C14	0.1813(2)	0.2875(2)	0.4983(1)	4.43(5)
C15	0.6009(2)	0.2944(2)	0.3989(1)	3.91(5)
C16	0.1015(2)	0.3327(2)	0.2629(1)	3.75(5)
C17	0.0672(2)	0.1435(2)	0.3231(2)	4.54(6)
C18	0.5588(2)	0.1014(2)	0.4580(2)	3.99(5)
C19	0.7445(2)	0.3445(2)	0.3139(2)	6.17(7)
C20	-0.0191(3)	0.3927(2)	0.1051(2)	5.97(7)
C21	-0.1028(3)	0.1015(3)	0.1738(2)	8.3(1)
C22	0.6983(3)	0.0138(2)	0.3941(2)	6.44(7)
C11B	0.419(1)	0.4285(7)	0.5689(7)	5.3(2)*
C12B	0.301(1)	0.4130(8)	0.6058(8)	5.7(2)*
H3	0.358	0.338	0.248	3.5
H7	0.305	0.062	0.328	4.4
H9A	0.579	0.229	0.599	5.1
H9B	0.439	0.238	0.622	5.1
H10AA	0.555	0.389	0.560	6.4
H10AB	0.603	0.360	0.677	6.4
H11AA	0.453	0.474	0.663	7.1
H11AB	0.371	0.382	0.669	7.1
H12AA	0.339	0.431	0.473	6.5
H12AB	0.285	0.508	0.531	6.5
H13AA	0.107	0.414	0.450	7.3
H13AB	0.146	0.400	0.570	7.3
H14A	0.226	0.260	0.565	5.3
H14B	0.087	0.265	0.470	5.3
H19A	0.740	0.376	0.251	7.4
H19B	0.801	0.380	0.373	7.4
H19C	0.785	0.284	0.315	7.4
H20A	-0.003	0.417	0.045	7.2
H20B	-0.079	0.339	0.086	7.2
H20C	-0.062	0.440	0.134	7.2
H21A	-0.116	0.091	0.102	10.0
H21B	-0.123	0.045	0.204	10.0
H21C	-0.164	0.150	0.180	10.0
H22A	0.706	-0.003	0.328	7.8
H22B	0.781	0.046	0.435	7.8
H22C	0.687	-0.041	0.430	7.8

Table 357 (cont.). Final Atomic Parameters for Sb-8 at **295 K**

Atom	x	y	z	B(Å^2)
H10BA	0.606	0.377	0.594	6.4
H10BB	0.551	0.363	0.687	6.4
H11BA	0.386	0.423	0.494	6.6
H11BB	0.456	0.490	0.588	6.6
H12BA	0.284	0.469	0.639	7.0
H12BB	0.323	0.362	0.655	7.0
H13BA	0.180	0.421	0.451	7.3
H13BB	0.091	0.406	0.524	7.3

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

Table 358. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0399(7)	0.104(1)	0.0538(7)	-0.0021(8)	0.0252(5)	0.0029(8)
O2	0.0376(8)	0.113(1)	0.0641(9)	0.0027(9)	0.0072(7)	0.013(1)
O3	0.0431(7)	0.093(1)	0.0435(7)	0.0119(8)	0.0133(5)	0.0214(8)
O4	0.0388(7)	0.139(2)	0.0710(9)	0.0180(9)	0.0283(6)	0.0316(9)
O5	0.0491(9)	0.115(1)	0.0588(9)	-0.0162(9)	0.0104(7)	-0.0174(9)
O6	0.080(1)	0.125(2)	0.081(1)	-0.040(1)	0.0387(7)	-0.006(1)
O7	0.0576(8)	0.080(1)	0.0526(8)	0.0212(8)	0.0167(6)	-0.0050(8)
O8	0.085(1)	0.073(1)	0.0503(8)	0.0267(9)	0.0098(8)	0.0078(8)
C1	0.044(1)	0.047(1)	0.0320(8)	0.0013(9)	0.0135(7)	0.0042(9)
C2	0.038(1)	0.089(2)	0.0348(9)	0.004(1)	0.0160(7)	0.007(1)
C3	0.0391(9)	0.046(1)	0.0345(8)	0.0011(9)	0.0162(6)	0.0032(8)
C4	0.0380(9)	0.075(1)	0.0372(9)	0.006(1)	0.0169(7)	0.013(1)
C5	0.0398(9)	0.052(1)	0.0362(8)	0.0009(9)	0.0194(6)	0.0062(9)
C6	0.043(1)	0.073(2)	0.051(1)	-0.001(1)	0.0115(9)	-0.010(1)
C7	0.051(1)	0.047(1)	0.0380(9)	-0.001(1)	0.0137(8)	0.0047(9)
C8	0.047(1)	0.057(1)	0.048(1)	0.005(1)	0.0133(8)	-0.005(1)
C9	0.058(1)	0.067(1)	0.0341(9)	0.005(1)	0.0107(8)	-0.001(1)
C10	0.066(1)	0.072(2)	0.057(1)	-0.003(1)	0.011(1)	-0.018(1)
C11A	0.083(2)	0.084(2)	0.053(2)	0.013(2)	0.015(2)	-0.015(2)
C12A	0.080(2)	0.064(2)	0.060(2)	0.011(2)	0.019(1)	-0.006(2)
C13	0.071(1)	0.088(2)	0.080(1)	0.010(1)	0.038(1)	-0.018(1)
C14	0.057(1)	0.077(2)	0.0461(9)	0.003(1)	0.0318(7)	0.005(1)
C15	0.039(1)	0.068(1)	0.0415(9)	0.003(1)	0.0146(7)	-0.005(1)
C16	0.0381(9)	0.065(1)	0.0414(9)	0.004(1)	0.0160(7)	0.004(1)
C17	0.048(1)	0.066(2)	0.058(1)	-0.007(1)	0.0180(9)	-0.003(1)
C18	0.050(1)	0.051(1)	0.047(1)	0.002(1)	0.0115(9)	-0.001(1)
C19	0.048(1)	0.121(2)	0.080(1)	-0.013(1)	0.0403(8)	-0.010(1)
C20	0.057(1)	0.105(2)	0.052(1)	0.020(1)	0.002(1)	0.022(1)
C21	0.056(2)	0.148(3)	0.090(2)	-0.030(2)	-0.003(2)	-0.024(2)
C22	0.070(1)	0.091(2)	0.083(2)	0.032(1)	0.026(1)	-0.012(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 359. Interatomic Distances (Å) for Sb-8 at **295 K**

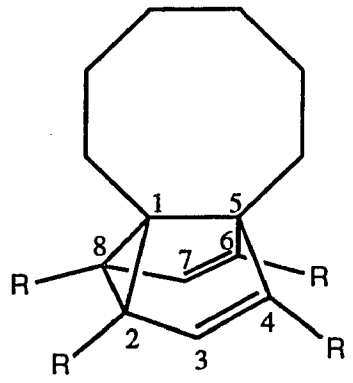
O1	C15	1.333(3)	C3	C4	1.378(3)
O1	C19	1.453(3)	C3	C7	3.035(3)
O2	C15	1.195(2)	C4	C5	1.522(3)
O3	C16	1.324(3)	C4	C6	1.996(4)
O3	C20	1.450(3)	C4	C16	1.474(3)
O4	C16	1.192(3)	C5	C6	1.505(3)
O5	C17	1.326(3)	C5	C14	1.523(3)
O5	C21	1.450(3)	C6	C7	1.381(3)
O6	C17	1.190(4)	C6	C17	1.486(3)
O7	C18	1.333(3)	C7	C8	1.389(3)
O7	C22	1.446(3)	C8	C18	1.484(3)
O8	C18	1.194(2)	C9	C10	1.526(4)
C1	C2	1.517(3)	C10	C11A	1.544(5)
C1	C5	1.577(3)	C11A	C12A	1.528(4)
C1	C8	1.499(3)	C12A	C13	1.535(5)
C1	C9	1.531(2)	C13	C14	1.530(4)
C2	C3	1.389(2)	C10	C11B	1.50(1)
C2	C8	1.990(4)	C11B	C12B	1.52(2)
C2	C15	1.476(3)	C12B	C13	1.58(1)

Table 360. Angles (°) for Sb-8 at **295 K**

C15	O1	C19	116.0(2)	C6	C7	C8	109.8(2)
C16	O3	C20	116.0(2)	C1	C8	C2	49.1(1)
C17	O5	C21	116.3(2)	C1	C8	C7	111.7(2)
C18	O7	C22	117.1(2)	C1	C8	C18	126.5(2)
C2	C1	C5	103.8(1)	C2	C8	C7	112.4(2)
C2	C1	C8	82.6(2)	C2	C8	C18	113.6(2)
C2	C1	C9	120.3(2)	C7	C8	C18	120.6(2)
C5	C1	C8	103.5(1)	C1	C9	C10	117.8(2)
C5	C1	C9	120.6(2)	C9	C10	C11A	116.5(2)
C8	C1	C9	118.8(2)	C10	C11A	C12A	113.0(3)
C1	C2	C3	110.7(2)	C11A	C12A	C13	111.8(3)
C1	C2	C8	48.3(1)	C12A	C13	C14	117.6(2)
C1	C2	C15	124.8(2)	C5	C14	C13	115.9(2)
C3	C2	C8	111.8(2)	O1	C15	C2	111.0(2)
C3	C2	C15	124.1(2)	O1	C15	O2	123.8(2)
C8	C2	C15	109.2(2)	O2	C15	C2	125.2(2)
C2	C3	C4	111.2(2)	O3	C16	O4	123.2(2)
C3	C4	C5	111.2(2)	O3	C16	C4	112.2(2)
C3	C4	C16	124.5(2)	O4	C16	C4	124.6(2)
C5	C4	C6	48.4(1)	O5	C17	O6	123.3(2)
C5	C4	C16	124.1(2)	O5	C17	C6	111.0(2)
C1	C5	C4	103.1(2)	O6	C17	C6	125.6(2)
C1	C5	C6	103.0(2)	O7	C18	O8	124.0(2)
C1	C5	C14	120.3(1)	O7	C18	C8	110.1(2)
C4	C5	C6	82.5(2)	O8	C18	C8	125.7(2)
C4	C5	C14	121.3(2)				
C6	C5	C14	119.4(2)				
C4	C6	C5	49.1(1)	C9	C10	C11B	117.1(4)
C5	C6	C7	111.9(2)	C10	C11B	C12B	110.3(8)
C5	C6	C17	125.6(2)	C11B	C12B	C13	107.3(8)
C7	C6	C17	121.6(2)	C12B	C13	C14	105.7(5)

Table 361. Root-Mean-Square Amplitudes of Thermal Vibration in Å for Sb-8 at **295 K**

Atom	Min.	Int'med.	Max.
O1	0.173	0.237	0.323
O2	0.191	0.263	0.341
O3	0.186	0.212	0.319
O4	0.175	0.242	0.389
O5	0.203	0.258	0.348
O6	0.219	0.286	0.385
O7	0.206	0.229	0.310
O8	0.205	0.253	0.335
C1	0.174	0.211	0.220
C2	0.174	0.197	0.300
C3	0.173	0.199	0.217
C4	0.172	0.195	0.281
C5	0.164	0.205	0.233
C6	0.205	0.227	0.278
C7	0.189	0.219	0.232
C8	0.213	0.213	0.252
C9	0.184	0.240	0.266
C10	0.209	0.265	0.296
C11A	0.215	0.267	0.330
C12A	0.232	0.251	0.301
C13	0.207	0.287	0.323
C14	0.168	0.248	0.280
C15	0.193	0.203	0.265
C16	0.187	0.203	0.257
C17	0.215	0.241	0.262
C18	0.212	0.223	0.239
C19	0.170	0.283	0.354
C20	0.181	0.283	0.338
C21	0.193	0.346	0.397
C22	0.201	0.285	0.350



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–362. X-ray Crystal Data for Sb-8 at **295 K**

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.18 x 0.33 x 0.40
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.602(2)
b (Å)	14.893(2)
c (Å)	14.223(3)
β (°)	109.66(2)
Cell volume (Å^3)	2114.91(11.94)
Z	4
d_{calc} (g cm^{-3})	1.314
μ(Cu $K\alpha$) (cm^{-1})	7.97
Maximum θ (°)	75
Unique reflections	4351
Observed reflections [$I > 3.0\sigma(I)$]	3007
Number of variables	279
R	0.052
R_w	0.064
$(\Delta\rho)_{max}$ (e Å^{-3})	0.17
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.28

Table 363. Final Atomic Parameters for Sb-8 at **295 K**

Atom	x	y	z	B(Å^2)
O1	0.6102(1)	0.3352(1)	0.3183(1)	4.84(4)
O2	0.6954(2)	0.2703(2)	0.4680(1)	5.68(4)
O3	0.1076(1)	0.3667(1)	0.1786(1)	4.57(4)
O4	0.0002(1)	0.3274(2)	0.2817(1)	6.08(5)
O5	0.0350(2)	0.1282(1)	0.2258(1)	5.77(5)
O6	-0.0068(2)	0.1301(2)	0.3690(1)	7.07(5)
O7	0.5838(2)	0.0721(1)	0.3777(1)	4.86(4)
O8	0.6242(2)	0.0819(1)	0.5417(1)	5.51(4)
C1	0.4129(2)	0.2431(1)	0.4722(1)	3.07(4)
C2	0.4591(2)	0.2811(2)	0.3904(1)	3.99(5)
C3	0.3516(2)	0.3112(1)	0.3103(1)	2.88(3)
C4	0.2327(2)	0.2997(2)	0.3289(1)	3.73(4)
C5	0.2562(2)	0.2561(1)	0.4298(1)	3.08(4)
C6	0.2092(2)	0.1736(2)	0.3667(2)	4.42(5)
C7	0.3140(2)	0.1190(1)	0.3666(1)	3.53(4)
C8	0.4339(2)	0.1553(2)	0.4279(2)	3.89(5)
C9	0.4917(2)	0.2618(2)	0.5818(1)	4.02(5)
C10	0.5269(3)	0.3593(2)	0.6127(2)	4.92(6)
C11A	0.4146(4)	0.4181(3)	0.6265(2)	5.44(8)
C12A	0.3057(4)	0.4430(2)	0.5294(2)	4.99(8)
C13	0.1743(2)	0.3889(2)	0.5113(2)	5.61(6)
C14	0.1805(2)	0.2872(2)	0.4983(1)	4.19(5)
C15	0.6013(2)	0.2942(2)	0.3988(2)	3.76(4)
C16	0.1014(2)	0.3323(2)	0.2626(1)	3.53(4)
C17	0.0671(2)	0.1433(2)	0.3230(2)	4.35(5)
C18	0.5593(2)	0.1011(2)	0.4583(2)	3.80(5)
C19	0.7443(2)	0.3443(2)	0.3140(2)	5.96(7)
C20	-0.0191(3)	0.3921(2)	0.1052(2)	5.71(7)
C21	-0.1025(3)	0.1021(3)	0.1736(3)	7.94(9)
C22	0.6983(3)	0.0140(2)	0.3938(2)	6.22(7)
C11B	0.417(1)	0.4292(7)	0.5649(7)	5.1(2)*
C12B	0.298(1)	0.4138(8)	0.6052(8)	5.6(2)*
H3	0.359	0.338	0.248	3.2
H7	0.305	0.062	0.328	3.9
H9A	0.578	0.228	0.599	4.4
H9B	0.438	0.238	0.622	4.4
H10AA	0.557	0.388	0.560	5.4
H10AB	0.603	0.359	0.678	5.4
H11AA	0.456	0.475	0.661	6.0
H11AB	0.372	0.385	0.669	6.0
H12AA	0.340	0.431	0.473	5.5
H12AB	0.285	0.508	0.531	5.5
H13AA	0.106	0.413	0.449	6.2
H13AB	0.144	0.400	0.570	6.2
H14A	0.225	0.260	0.566	4.6
H14B	0.087	0.264	0.470	4.6
H19A	0.740	0.376	0.251	6.6
H19B	0.801	0.380	0.373	6.6
H19C	0.785	0.283	0.315	6.6
H20A	-0.003	0.417	0.045	6.3
H20B	-0.078	0.338	0.086	6.3
H20C	-0.063	0.439	0.134	6.3
H21A	-0.116	0.092	0.101	8.7
H21B	-0.123	0.045	0.203	8.7
H21C	-0.164	0.151	0.180	8.7
H22A	0.706	-0.003	0.328	6.8
H22B	0.781	0.046	0.435	6.8
H22C	0.687	-0.041	0.430	6.8

Table 363 (cont.). Final Atomic Parameters for Sb-8 at **295 K**

Atom	x	y	z	B(Å^2)
H10BA	0.607	0.376	0.595	5.4
H10BB	0.549	0.363	0.687	5.4
H11BA	0.385	0.422	0.491	5.6
H11BB	0.454	0.491	0.583	5.6
H12BA	0.280	0.470	0.637	6.1
H12BB	0.319	0.364	0.655	6.1
H13BA	0.180	0.421	0.451	6.2
H13BB	0.089	0.406	0.522	6.2

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

Table 364. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0375(6)	0.099(1)	0.0558(7)	-0.0026(7)	0.0268(5)	0.0034(8)
O2	0.0348(7)	0.108(1)	0.0668(9)	0.0023(9)	0.0093(6)	0.012(1)
O3	0.0408(6)	0.088(1)	0.0448(6)	0.0108(7)	0.0147(5)	0.0210(7)
O4	0.0354(6)	0.131(2)	0.0720(8)	0.0174(8)	0.0278(5)	0.0321(9)
O5	0.0447(8)	0.109(1)	0.0604(9)	-0.0151(9)	0.0110(7)	-0.0169(9)
O6	0.0746(9)	0.120(2)	0.085(1)	-0.0401(9)	0.0412(7)	-0.004(1)
O7	0.0546(8)	0.075(1)	0.0543(7)	0.0200(7)	0.0169(6)	-0.0057(8)
O8	0.081(1)	0.068(1)	0.0517(8)	0.0260(9)	0.0114(7)	0.0077(8)
C1	0.0420(8)	0.042(1)	0.0339(7)	0.0011(8)	0.0144(6)	0.0040(7)
C2	0.0337(8)	0.085(2)	0.0366(8)	0.003(1)	0.0171(6)	0.0066(9)
C3	0.0358(7)	0.043(1)	0.0346(7)	0.0017(7)	0.0167(5)	0.0031(7)
C4	0.0334(8)	0.073(1)	0.0386(8)	0.0060(9)	0.0162(6)	0.0134(9)
C5	0.0384(7)	0.046(1)	0.0376(7)	0.0015(7)	0.0199(5)	0.0058(7)
C6	0.042(1)	0.068(1)	0.055(1)	-0.000(1)	0.0121(8)	-0.011(1)
C7	0.050(1)	0.043(1)	0.0410(8)	0.0000(9)	0.0152(7)	0.0026(8)
C8	0.0424(9)	0.054(1)	0.0493(9)	0.0048(9)	0.0127(7)	-0.0079(9)
C9	0.055(1)	0.061(1)	0.0336(8)	0.003(1)	0.0115(7)	0.0001(9)
C10	0.059(1)	0.067(1)	0.055(1)	-0.001(1)	0.012(1)	-0.017(1)
C11A	0.077(2)	0.070(2)	0.054(2)	0.011(2)	0.015(1)	-0.018(1)
C12A	0.074(2)	0.058(2)	0.059(1)	0.009(2)	0.023(1)	-0.007(1)
C13	0.063(1)	0.081(2)	0.078(1)	0.011(1)	0.0357(9)	-0.019(1)
C14	0.0511(9)	0.073(1)	0.0464(8)	0.004(1)	0.0307(6)	0.0065(9)
C15	0.0345(8)	0.064(1)	0.0460(9)	0.0027(9)	0.0154(6)	-0.0059(9)
C16	0.0350(8)	0.059(1)	0.0434(8)	0.0055(9)	0.0176(6)	0.0056(9)
C17	0.043(1)	0.060(1)	0.061(1)	-0.007(1)	0.0157(8)	-0.001(1)
C18	0.049(1)	0.046(1)	0.0470(9)	0.0024(9)	0.0132(8)	-0.0017(9)
C19	0.0431(9)	0.115(2)	0.082(1)	-0.014(1)	0.0391(7)	-0.010(1)
C20	0.053(1)	0.099(2)	0.055(1)	0.018(1)	0.006(1)	0.022(1)
C21	0.057(2)	0.135(3)	0.089(2)	-0.027(2)	-0.002(2)	-0.024(2)
C22	0.070(1)	0.084(2)	0.083(2)	0.033(1)	0.027(1)	-0.008(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 365. Interatomic Distances (Å) for Sb-8 at **295 K**

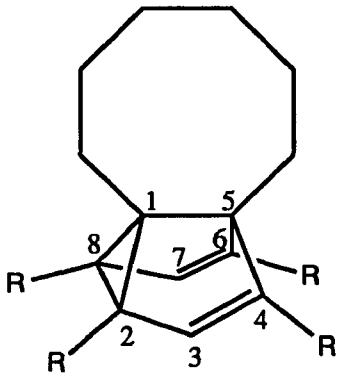
O1	C15	1.328(3)	C3	C4	1.382(3)
O1	C19	1.449(3)	C3	C7	3.035(3)
O2	C15	1.196(2)	C4	C5	1.517(3)
O3	C16	1.322(3)	C4	C6	1.991(4)
O3	C20	1.447(3)	C4	C16	1.476(2)
O4	C16	1.195(3)	C5	C6	1.503(3)
O5	C17	1.327(3)	C5	C14	1.529(3)
O5	C21	1.449(3)	C6	C7	1.377(3)
O6	C17	1.194(4)	C6	C17	1.494(3)
O7	C18	1.330(3)	C7	C8	1.387(3)
O7	C22	1.445(3)	C8	C18	1.490(3)
O8	C18	1.189(2)	C9	C10	1.527(4)
C1	C2	1.515(3)	C10	C11A	1.543(5)
C1	C5	1.578(3)	C11A	C12A	1.518(4)
C1	C8	1.499(3)	C12A	C13	1.554(5)
C1	C9	1.526(2)	C13	C14	1.529(4)
C2	C3	1.387(2)	C10	C11B	1.54(1)
C2	C8	1.990(4)	C11B	C12B	1.57(2)
C2	C15	1.485(3)	C12B	C13	1.57(1)

Table 366. Angles (°) for Sb-8 at **295 K**

C15	O1	C19	115.8(2)	C6	C7	C8	109.7(2)
C16	O3	C20	116.0(2)	C1	C8	C2	49.0(1)
C17	O5	C21	116.1(2)	C1	C8	C7	111.8(2)
C18	O7	C22	117.1(2)	C1	C8	C18	126.4(2)
C2	C1	C5	103.4(1)	C2	C8	C7	112.1(2)
C2	C1	C8	82.6(2)	C2	C8	C18	113.6(2)
C2	C1	C9	120.6(2)	C7	C8	C18	120.7(2)
C5	C1	C8	103.4(1)	C1	C9	C10	117.7(2)
C5	C1	C9	120.8(2)	C9	C10	C11A	116.9(2)
C8	C1	C9	118.7(2)	C10	C11A	C12A	113.9(3)
C1	C2	C3	111.3(2)	C11A	C12A	C13	112.9(3)
C1	C2	C8	48.3(1)	C12A	C13	C14	117.4(2)
C1	C2	C15	124.7(2)	C5	C14	C13	115.5(2)
C3	C2	C8	112.2(2)	O1	C15	O2	124.3(2)
C3	C2	C15	123.7(2)	O1	C15	C2	110.9(2)
C8	C2	C15	109.1(2)	O2	C15	C2	124.8(2)
C2	C3	C4	110.6(2)	O3	C16	O4	123.4(2)
C3	C4	C5	111.4(1)	O3	C16	C4	112.5(2)
C3	C4	C16	124.1(2)	O4	C16	C4	124.1(2)
C5	C4	C6	48.5(1)	O5	C17	O6	123.9(2)
C5	C4	C16	124.3(2)	O5	C17	C6	110.7(2)
C1	C5	C4	103.3(2)	O6	C17	C6	125.3(2)
C1	C5	C6	102.9(2)	O7	C18	O8	124.4(2)
C1	C5	C14	120.3(1)	O7	C18	C8	109.9(2)
C4	C5	C6	82.5(2)	O8	C18	C8	125.5(2)
C4	C5	C14	121.3(2)				
C6	C5	C14	119.3(2)				
C4	C6	C5	49.1(1)	C9	C10	C11B	116.2(4)
C5	C6	C7	112.2(2)	C10	C11B	C12B	108.7(8)
C5	C6	C17	125.5(2)	C11B	C12B	C13	105.6(8)
C7	C6	C17	121.5(2)	C12B	C13	C14	106.2(5)

Table 367. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-8 at **295 K**

Atom	Min.	Int'med.	Max.
O1	0.162	0.241	0.315
O2	0.186	0.263	0.334
O3	0.189	0.203	0.312
O4	0.166	0.241	0.382
O5	0.198	0.254	0.339
O6	0.199	0.293	0.379
O7	0.199	0.232	0.302
O8	0.205	0.248	0.326
C1	0.177	0.203	0.209
C2	0.164	0.196	0.294
C3	0.166	0.193	0.211
C4	0.170	0.188	0.278
C5	0.163	0.201	0.223
C6	0.203	0.225	0.276
C7	0.197	0.212	0.225
C8	0.200	0.210	0.253
C9	0.183	0.236	0.252
C10	0.207	0.248	0.288
C11A	0.203	0.256	0.316
C12A	0.215	0.252	0.282
C13	0.191	0.277	0.316
C14	0.164	0.239	0.274
C15	0.180	0.211	0.257
C16	0.175	0.205	0.248
C17	0.200	0.249	0.252
C18	0.211	0.214	0.233
C19	0.161	0.284	0.346
C20	0.189	0.268	0.331
C21	0.197	0.341	0.382
C22	0.194	0.287	0.342



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–368. X-ray Crystal Data for Sb-8 at **335 K**[a]

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.12 x 0.24 x 0.40
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.616(1)
b (Å)	14.963(1)
c (Å)	14.27(6)
β (°)	109.801)
Cell volume (Å^3)	2132.88(11.08)
Z	4
d_{calc} (g cm^{-3})	1.303
μ(Cu $K\alpha$) (cm^{-1})	7.90
Maximum θ(°)	60
Unique reflections	3112
Observed reflections [$I > 3.0\sigma(I)$]	1447
Number of variables	279
R	0.053
R_w	0.058
$(\Delta\rho)_{max}$ (e Å^{-3})	0.16
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.22

[a] The crystal of Sb-8 at 335 K was mounted with silicone rubber.

Table 369. Final Atomic Parameters for Sb-8 at **335 K**

Atom	x	y	z	B(Å^2)
O1	0.6108(3)	0.3355(3)	0.3182(2)	5.9(1)
O2	0.6966(3)	0.2704(3)	0.4668(3)	6.9(1)
O3	0.1090(3)	0.3635(2)	0.1785(2)	5.55(9)
O4	0.0014(3)	0.3257(3)	0.2816(2)	7.7(1)
O5	0.0375(3)	0.1264(3)	0.2260(2)	7.1(1)
O6	-0.0025(3)	0.1287(3)	0.3688(3)	8.5(1)
O7	0.5854(3)	0.0711(2)	0.3779(2)	5.89(9)
O8	0.6278(4)	0.0830(2)	0.5411(2)	6.7(1)
C1	0.4147(4)	0.2420(3)	0.4712(3)	3.9(1)
C2	0.4603(4)	0.2803(3)	0.3902(3)	4.5(1)
C3	0.3518(4)	0.3101(3)	0.3094(3)	3.5(1)
C4	0.2345(4)	0.2972(3)	0.3281(3)	4.3(1)
C5	0.2574(4)	0.2552(3)	0.4281(3)	3.9(1)
C6	0.2120(4)	0.1726(3)	0.3648(3)	5.0(1)
C7	0.3172(4)	0.1181(3)	0.3661(3)	4.4(1)
C8	0.4364(4)	0.1543(3)	0.4279(3)	4.4(1)
C9	0.4941(5)	0.2607(4)	0.5804(3)	4.9(1)
C10	0.5273(5)	0.3578(4)	0.6100(4)	6.3(2)
C11A	0.4143(8)	0.4148(5)	0.6254(5)	6.6(2)
C12A	0.3072(7)	0.4414(5)	0.5288(6)	6.5(2)
C13	0.1762(5)	0.3863(4)	0.5121(4)	7.1(2)
C14	0.1834(5)	0.2855(4)	0.4978(3)	5.3(1)
C15	0.6015(4)	0.2953(3)	0.3969(3)	4.5(1)
C16	0.1018(4)	0.3306(3)	0.2621(3)	4.6(1)
C17	0.0692(5)	0.1416(4)	0.3219(4)	5.6(1)
C18	0.5599(4)	0.1004(3)	0.4576(3)	4.7(1)
C19	0.7450(5)	0.3463(5)	0.3136(4)	7.6(2)
C20	-0.0193(5)	0.3901(4)	0.1049(4)	6.9(2)
C21	-0.1000(6)	0.0995(5)	0.1744(5)	9.7(2)
C22	0.6988(5)	0.0128(4)	0.3937(4)	7.6(2)
C11B	0.422(2)	0.429(1)	0.569(1)	7.1(5)*
C12B	0.300(2)	0.413(2)	0.605(1)	8.4(6)*
H3	0.359	0.337	0.247	3.9
H7	0.309	0.061	0.328	4.8
H9A	0.581	0.227	0.597	5.4
H9B	0.441	0.237	0.621	5.4
H10AA	0.554	0.387	0.556	6.9
H10AB	0.605	0.358	0.674	6.9
H11AA	0.455	0.470	0.662	7.2
H11AB	0.371	0.380	0.666	7.2
H12AA	0.341	0.430	0.472	7.2
H12AB	0.287	0.506	0.531	7.2
H13AA	0.106	0.411	0.451	7.8
H13AB	0.148	0.396	0.571	7.8
H14A	0.230	0.258	0.565	5.8
H14B	0.090	0.262	0.470	5.8
H19A	0.740	0.378	0.251	8.4
H19B	0.801	0.382	0.372	8.4
H19C	0.787	0.286	0.315	8.4
H20A	-0.004	0.414	0.044	7.6
H20B	-0.080	0.337	0.086	7.6
H20C	-0.062	0.437	0.134	7.6
H21A	-0.114	0.090	0.102	10.7
H21B	-0.119	0.043	0.204	10.7
H21C	-0.162	0.147	0.181	10.7
H22A	0.706	-0.004	0.328	8.3
H22B	0.782	0.044	0.435	8.3
H22C	0.687	-0.042	0.429	8.3

Table 369 (cont.). Final Atomic Parameters for Sb-8 at **335 K**

Atom	x	y	z	B(Å)
H10BA	0.605	0.374	0.589	6.9
H10BB	0.555	0.360	0.684	6.9
H11BA	0.390	0.427	0.495	7.8
H11BB	0.462	0.489	0.593	7.8
H12BA	0.279	0.469	0.636	9.2
H12BB	0.321	0.364	0.656	9.2
H13BA	0.180	0.419	0.452	7.8
H13BB	0.091	0.402	0.524	7.8

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

Table 370. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **335 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.044(2)	0.120(3)	0.061(2)	-0.002(2)	0.019(1)	0.008(2)
O2	0.046(2)	0.128(3)	0.075(2)	0.000(2)	0.003(2)	0.017(2)
O3	0.045(2)	0.108(3)	0.052(2)	0.014(2)	0.008(1)	0.026(2)
O4	0.043(2)	0.164(4)	0.086(2)	0.022(2)	0.024(2)	0.038(2)
O5	0.056(2)	0.131(3)	0.069(2)	-0.021(2)	0.005(2)	-0.020(2)
O6	0.087(2)	0.146(4)	0.096(2)	-0.049(2)	0.036(2)	-0.009(3)
O7	0.063(2)	0.089(3)	0.065(2)	0.026(2)	0.012(2)	-0.005(2)
O8	0.093(2)	0.081(3)	0.063(2)	0.033(2)	0.003(2)	0.008(2)
C1	0.042(2)	0.060(3)	0.040(2)	0.006(2)	0.005(2)	0.010(2)
C2	0.035(2)	0.093(4)	0.041(2)	0.006(3)	0.011(2)	0.012(3)
C3	0.037(2)	0.045(3)	0.049(2)	-0.001(2)	0.012(2)	0.005(2)
C4	0.041(2)	0.080(4)	0.042(2)	0.008(3)	0.011(2)	0.014(3)
C5	0.047(2)	0.053(3)	0.050(2)	-0.000(2)	0.017(2)	0.007(2)
C6	0.051(3)	0.069(4)	0.061(3)	-0.009(3)	0.007(2)	-0.008(3)
C7	0.058(3)	0.047(3)	0.051(3)	0.007(3)	0.006(2)	-0.000(2)
C8	0.042(2)	0.057(3)	0.059(3)	0.007(2)	0.008(2)	-0.009(3)
C9	0.058(3)	0.070(4)	0.046(3)	0.002(3)	0.004(2)	-0.001(3)
C10	0.072(3)	0.080(4)	0.068(3)	0.003(3)	0.001(3)	-0.022(3)
C11A	0.088(5)	0.082(6)	0.063(4)	0.006(5)	0.005(4)	-0.026(5)
C12A	0.080(5)	0.067(5)	0.084(5)	0.002(5)	0.007(4)	-0.012(5)
C13	0.084(3)	0.092(4)	0.095(4)	0.021(3)	0.033(3)	-0.020(3)
C14	0.063(3)	0.088(4)	0.054(3)	0.005(3)	0.025(2)	0.005(3)
C15	0.038(2)	0.074(4)	0.052(3)	0.005(3)	0.007(2)	-0.007(3)
C16	0.041(2)	0.079(4)	0.055(3)	0.003(3)	0.016(2)	0.013(3)
C17	0.056(3)	0.084(4)	0.071(3)	-0.008(3)	0.018(2)	-0.008(3)
C18	0.055(3)	0.053(3)	0.058(3)	0.007(3)	0.004(2)	-0.001(3)
C19	0.048(3)	0.147(6)	0.102(4)	-0.019(3)	0.035(2)	-0.013(4)
C20	0.055(3)	0.121(5)	0.064(3)	0.023(3)	-0.007(3)	0.027(3)
C21	0.064(4)	0.165(7)	0.107(4)	-0.044(4)	-0.014(3)	-0.027(5)
C22	0.078(3)	0.096(4)	0.107(4)	0.040(3)	0.024(3)	-0.008(4)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 371. Interatomic Distances (Å) for Sb-8 at **335 K**

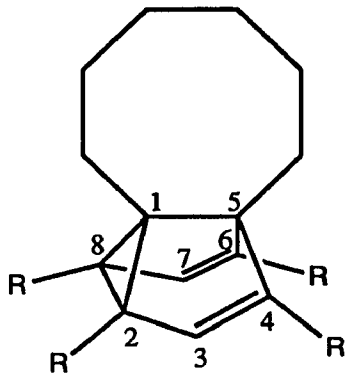
O1	C15	1.308(6)	C3	C4	1.373(7)
O1	C19	1.457(6)	C3	C7	3.040(6)
O2	C15	1.212(5)	C4	C5	1.501(6)
O3	C16	1.316(6)	C4	C6	1.973(7)
O3	C20	1.466(5)	C4	C16	1.491(5)
O4	C16	1.191(6)	C5	C6	1.510(7)
O5	C17	1.314(6)	C5	C14	1.530(7)
O5	C21	1.452(6)	C6	C7	1.378(7)
O6	C17	1.186(7)	C6	C17	1.504(6)
O7	C18	1.329(6)	C7	C8	1.384(6)
O7	C22	1.442(7)	C8	C18	1.474(6)
O8	C18	1.194(5)	C9	C10	1.519(8)
C1	C2	1.510(7)	C10	C11A	1.55(1)
C1	C5	1.585(6)	C11A	C12A	1.513(9)
C1	C8	1.502(7)	C12A	C13	1.56(1)
C1	C9	1.525(5)	C13	C14	1.527(8)
C2	C3	1.399(5)	C10	C11B	1.51(2)
C2	C8	2.001(7)	C11B	C12B	1.57(3)
C2	C15	1.486(6)	C12B	C13	1.57(2)

Table 372. Angles (°) for Sb-8 at **335 K**

C15	O1	C19	116.7(3)	C6	C7	C8	109.8(4)
C16	O3	C20	115.2(4)	C1	C8	C2	48.5(3)
C17	O5	C21	115.8(4)	C1	C8	C7	111.7(4)
C18	O7	C22	117.9(3)	C1	C8	C18	127.3(3)
C2	C1	C5	102.9(3)	C2	C8	C7	111.6(3)
C2	C1	C8	83.3(4)	C2	C8	C18	114.3(3)
C2	C1	C9	120.2(4)	C7	C8	C18	120.1(4)
C5	C1	C8	103.7(3)	C1	C9	C10	117.1(4)
C5	C1	C9	121.3(4)	C9	C10	C11A	116.7(5)
C8	C1	C9	118.2(4)	C10	C11A	C12A	113.2(6)
C1	C2	C3	111.3(4)	C11A	C12A	C13	110.9(6)
C1	C2	C8	48.2(3)	C12A	C13	C14	117.3(5)
C1	C2	C15	125.8(3)	C5	C14	C13	116.1(5)
C3	C2	C8	112.2(3)	O1	C15	O2	124.3(4)
C3	C2	C15	122.5(4)	O1	C15	C2	112.5(3)
C8	C2	C15	110.0(3)	O2	C15	C2	123.2(5)
C2	C3	C4	110.1(4)	O3	C16	O4	124.4(4)
C3	C4	C5	112.2(4)	O3	C16	C4	111.5(4)
C5	C4	C16	123.7(4)	O4	C16	C4	124.1(4)
C5	C4	C6	49.3(3)	O5	C17	O6	124.9(4)
C5	C4	C16	123.7(4)	O5	C17	C6	110.1(5)
C1	C5	C4	103.4(3)	O6	C17	C6	124.8(4)
C1	C5	C6	102.2(4)	O7	C18	O8	123.6(4)
C1	C5	C14	119.3(3)	O7	C18	C8	110.7(3)
C4	C5	C6	81.9(3)	O8	C18	C8	125.7(5)
C4	C5	C14	122.7(4)				
C6	C5	C14	120.1(4)				
C4	C6	C5	48.9(3)	C9	C10	C11B	119.6(8)
C5	C6	C7	112.5(4)	C10	C11B	C12B	111(1)
C5	C6	C17	124.8(4)	C11B	C12B	C13	108(1)
C7	C6	C17	121.6(4)	C12B	C13	C14	107.4(9)

Table 373. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-8 at **335 K**

Atom	Min.	Int'med.	Max.
O1	0.206	0.246	0.349
O2	0.204	0.292	0.368
O3	0.185	0.242	0.344
O4	0.197	0.270	0.424
O5	0.205	0.297	0.372
O6	0.237	0.307	0.416
O7	0.217	0.253	0.336
O8	0.209	0.278	0.367
C1	0.175	0.232	0.252
C2	0.184	0.201	0.309
C3	0.192	0.205	0.234
C4	0.187	0.214	0.291
C5	0.207	0.217	0.244
C6	0.206	0.269	0.274
C7	0.205	0.220	0.275
C8	0.199	0.222	0.278
C9	0.201	0.262	0.275
C10	0.216	0.271	0.343
C11A	0.211	0.283	0.354
C12A	0.244	0.266	0.342
C13	0.227	0.303	0.354
C14	0.219	0.250	0.298
C15	0.190	0.235	0.283
C16	0.201	0.224	0.291
C17	0.230	0.267	0.297
C18	0.208	0.230	0.285
C19	0.194	0.314	0.390
C20	0.170	0.316	0.363
C21	0.180	0.394	0.426
C22	0.209	0.318	0.377



R = $COOCH_3$

1,5-Cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene
(Sb-8)

Table 8–374. X-ray Crystal Data for Sb-8 at **360 K**[a]

Formula	$C_{22}H_{26}O_8$
Formula weight	418.45
Melting point (°C)	170-171
Crystal size (mm)	0.10 x 0.25 x 0.27
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.631(1)
b (Å)	15.018(3)
c (Å)	14.290(4)
β (°)	109.88(1)
Cell volume (Å^3)	2145.55(10.51)
Z	4
d_{calc} (g cm^{-3})	1.295
μ(Cu $K\alpha$) (cm^{-1})	7.85
Maximum θ(°)	60
Unique reflections	3169
Observed reflections [$I > 3.0\sigma(I)$]	1474
Number of variables	279
R	0.046
R_w	0.052
$(\Delta\rho)_{max}$ (e Å^{-3})	0.18
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.17

[a] The crystal of Sb-8 at 360 K was mounted with 3M Epoxy Adhesive 2216 B/A.

Table 375. Final Atomic Parameters for Sb-8 at **360 K**

Atom	x	y	z	B(Å^2)
O1	0.6116(2)	0.3358(2)	0.3186(2)	6.12(8)
O2	0.6964(3)	0.2708(3)	0.4664(2)	7.7(1)
O3	0.1087(2)	0.3627(2)	0.1786(2)	5.93(8)
O4	0.0027(3)	0.3251(3)	0.2814(2)	8.1(1)
O5	0.0382(3)	0.1256(3)	0.2257(2)	7.7(1)
O6	-0.0009(3)	0.1281(3)	0.3677(2)	9.4(1)
O7	0.5850(3)	0.0701(2)	0.3776(2)	6.38(8)
O8	0.6293(3)	0.0836(2)	0.5407(2)	7.37(9)
C1	0.4161(3)	0.2415(3)	0.4703(3)	4.0(1)
C2	0.4610(3)	0.2803(3)	0.3893(3)	4.8(1)
C3	0.3532(3)	0.3095(3)	0.3094(3)	3.64(9)
C4	0.2345(3)	0.2964(3)	0.3274(3)	4.5(1)
C5	0.2589(3)	0.2536(3)	0.4280(2)	3.90(9)
C6	0.2119(4)	0.1725(3)	0.3649(3)	5.1(1)
C7	0.3180(4)	0.1182(3)	0.3655(3)	4.5(1)
C8	0.4371(4)	0.1537(3)	0.4270(3)	4.6(1)
C9	0.4942(4)	0.2607(3)	0.5796(3)	5.1(1)
C10	0.5272(4)	0.3580(3)	0.6098(3)	6.6(1)
C11A	0.4135(7)	0.4139(5)	0.6261(5)	7.3(2)
C12A	0.3078(7)	0.4398(5)	0.5284(5)	7.1(2)
C13	0.1774(4)	0.3846(4)	0.5127(3)	7.7(1)
C14	0.1846(4)	0.2842(3)	0.4971(3)	5.6(1)
C15	0.6024(4)	0.2946(3)	0.3974(3)	4.9(1)
C16	0.1035(4)	0.3296(3)	0.2626(3)	4.7(1)
C17	0.0726(4)	0.1405(3)	0.3215(3)	5.7(1)
C18	0.5620(4)	0.1002(3)	0.4578(3)	4.9(1)
C19	0.7451(4)	0.3469(4)	0.3138(3)	7.8(1)
C20	-0.0182(4)	0.3895(4)	0.1050(3)	7.5(1)
C21	-0.0980(5)	0.0980(5)	0.1741(4)	10.7(2)
C22	0.6998(4)	0.0128(4)	0.3939(4)	8.1(2)
C11B	0.421(1)	0.426(1)	0.568(1)	6.7(4)*
C12B	0.299(2)	0.410(1)	0.602(1)	7.8(5)*
H3	0.360	0.336	0.247	4.0
H7	0.309	0.062	0.327	4.9
H9A	0.581	0.228	0.597	5.6
H9B	0.441	0.237	0.620	5.6
H10AA	0.553	0.388	0.556	7.2
H10AB	0.605	0.359	0.674	7.2
H11AA	0.452	0.469	0.664	8.0
H11AB	0.370	0.378	0.666	8.0
H12AA	0.342	0.428	0.473	7.8
H12AB	0.287	0.505	0.530	7.8
H13AA	0.106	0.409	0.453	8.4
H13AB	0.151	0.393	0.573	8.4
H14A	0.230	0.257	0.564	6.1
H14B	0.091	0.262	0.469	6.1
H19A	0.739	0.379	0.251	8.6
H19B	0.801	0.383	0.372	8.6
H19C	0.787	0.287	0.315	8.6
H20A	-0.002	0.413	0.045	8.2
H20B	-0.079	0.337	0.086	8.2
H20C	-0.060	0.437	0.134	8.2
H21A	-0.112	0.089	0.102	11.7
H21B	-0.116	0.041	0.203	11.7
H21C	-0.161	0.145	0.181	11.7
H22A	0.706	-0.005	0.328	8.9
H22B	0.783	0.046	0.433	8.9
H22C	0.690	-0.041	0.431	8.9

Table 375 (cont.). Final Atomic Parameters for Sb-8 at **360 K**

Atom	x	y	z	B(Å^2)
H10BA	0.605	0.375	0.589	7.2
H10BB	0.554	0.361	0.684	7.2
H11BA	0.391	0.424	0.494	7.3
H11BB	0.459	0.486	0.592	7.3
H12BA	0.278	0.465	0.633	8.7
H12BB	0.319	0.360	0.652	8.7
H13BA	0.180	0.417	0.452	8.4
H13BB	0.093	0.400	0.525	8.4

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

Table 376. Final Anisotropic Thermal Parameters (U's) for Sb-8 at **360 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.052(1)	0.118(3)	0.071(1)	-0.004(2)	0.031(1)	0.004(2)
O2	0.055(2)	0.145(3)	0.081(2)	0.001(2)	0.009(1)	0.020(2)
O3	0.059(1)	0.109(2)	0.055(1)	0.015(2)	0.016(1)	0.031(2)
O4	0.054(1)	0.173(3)	0.090(2)	0.026(2)	0.034(1)	0.041(2)
O5	0.071(2)	0.143(3)	0.070(2)	-0.025(2)	0.013(1)	-0.023(2)
O6	0.103(2)	0.155(3)	0.110(2)	-0.056(2)	0.053(1)	-0.013(2)
O7	0.080(2)	0.090(2)	0.069(2)	0.027(2)	0.020(1)	-0.008(2)
O8	0.108(2)	0.089(2)	0.065(2)	0.036(2)	0.006(2)	0.005(2)
C1	0.052(2)	0.054(3)	0.043(2)	0.002(2)	0.014(1)	0.006(2)
C2	0.044(2)	0.092(4)	0.048(2)	0.000(2)	0.020(1)	0.008(2)
C3	0.050(2)	0.046(3)	0.046(2)	-0.001(2)	0.021(1)	0.005(2)
C4	0.045(2)	0.082(3)	0.047(2)	0.010(2)	0.020(1)	0.019(2)
C5	0.060(2)	0.049(3)	0.046(2)	0.002(2)	0.026(1)	0.005(2)
C6	0.058(2)	0.073(3)	0.061(2)	-0.005(2)	0.018(2)	-0.007(2)
C7	0.068(2)	0.046(3)	0.054(2)	0.000(2)	0.017(2)	0.003(2)
C8	0.061(2)	0.059(3)	0.055(2)	0.004(2)	0.017(2)	-0.009(2)
C9	0.068(2)	0.073(3)	0.046(2)	0.004(2)	0.010(2)	-0.001(2)
C10	0.089(3)	0.084(4)	0.067(3)	-0.006(3)	0.010(2)	-0.025(3)
C11A	0.107(5)	0.088(5)	0.070(4)	0.018(5)	0.015(3)	-0.030(4)
C12A	0.111(5)	0.067(5)	0.085(4)	0.009(4)	0.022(4)	-0.014(4)
C13	0.098(3)	0.101(4)	0.106(3)	0.018(3)	0.054(2)	-0.019(3)
C14	0.073(2)	0.092(4)	0.058(2)	0.007(2)	0.037(2)	0.005(2)
C15	0.054(2)	0.082(3)	0.050(2)	0.001(2)	0.019(2)	-0.003(2)
C16	0.051(2)	0.072(3)	0.058(2)	0.007(2)	0.022(1)	0.008(2)
C17	0.059(2)	0.077(4)	0.080(3)	-0.008(2)	0.023(2)	-0.004(3)
C18	0.066(2)	0.054(3)	0.061(2)	0.006(2)	0.013(2)	-0.002(2)
C19	0.060(2)	0.144(5)	0.110(3)	-0.019(3)	0.051(2)	-0.008(3)
C20	0.074(3)	0.131(5)	0.064(3)	0.028(3)	0.003(2)	0.027(3)
C21	0.076(3)	0.186(6)	0.113(4)	-0.048(4)	-0.008(3)	-0.031(4)
C22	0.093(3)	0.104(4)	0.108(3)	0.044(3)	0.032(2)	-0.011(3)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 377. Interatomic Distances (Å) for Sb-8 at **360 K**

O1	C15	1.318(5)	C3	C4	1.385(5)
O1	C19	1.453(5)	C3	C7	3.040(6)
O2	C15	1.195(4)	C4	C5	1.514(5)
O3	C16	1.317(5)	C4	C6	1.974(6)
O3	C20	1.457(5)	C4	C16	1.473(5)
O4	C16	1.191(5)	C5	C6	1.496(6)
O5	C17	1.310(5)	C5	C14	1.530(6)
O5	C21	1.445(5)	C6	C7	1.391(6)
O6	C17	1.196(6)	C6	C17	1.477(5)
O7	C18	1.330(5)	C7	C8	1.379(5)
O7	C22	1.447(6)	C8	C18	1.485(5)
O8	C18	1.183(4)	C9	C10	1.531(7)
C1	C2	1.511(6)	C10	C11A	1.552(9)
C1	C5	1.583(5)	C11A	C12A	1.515(8)
C1	C8	1.505(6)	C12A	C13	1.565(9)
C1	C9	1.526(5)	C13	C14	1.530(7)
C2	C3	1.385(4)	C10	C11B	1.49(2)
C2	C8	2.017(6)	C11B	C12B	1.55(3)
C2	C15	1.483(5)	C12B	C13	1.53(1)

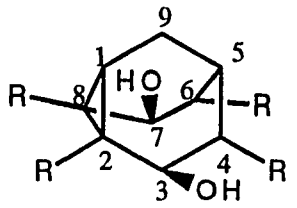
Table 378. Angles (°) for Sb-8 at **360 K**

C15	O1	C19	116.9(3)	C6	C7	C8	110.1(4)
C16	O3	C20	116.5(3)	C1	C8	C2	48.2(2)
C17	O5	C21	117.3(4)	C1	C8	C7	111.6(3)
C18	O7	C22	117.1(3)	C1	C8	C18	126.5(3)
C2	C1	C5	103.3(3)	C2	C8	C7	111.5(3)
C2	C1	C8	83.9(3)	C2	C8	C18	114.1(3)
C2	C1	C9	120.5(3)	C7	C8	C18	121.0(4)
C5	C1	C8	103.2(3)	C1	C9	C10	117.5(3)
C5	C1	C9	120.4(3)	C9	C10	C11A	116.3(4)
C8	C1	C9	118.8(3)	C10	C11A	C12A	111.8(5)
C1	C2	C3	111.4(3)	C11A	C12A	C13	109.8(6)
C1	C2	C8	47.9(2)	C12A	C13	C14	117.2(4)
C1	C2	C15	124.8(3)	C5	C14	C13	116.9(4)
C3	C2	C8	112.0(3)	O1	C15	O2	124.1(4)
C3	C2	C15	123.5(4)	O1	C15	C2	111.7(3)
C8	C2	C15	109.4(3)	O2	C15	C2	124.2(4)
C2	C3	C4	110.7(3)	O3	C16	O4	123.1(3)
C3	C4	C5	111.3(3)	O3	C16	C4	112.1(3)
C3	C4	C16	124.2(3)	O4	C16	C4	124.7(4)
C5	C4	C6	48.6(2)	O5	C17	O6	123.1(4)
C5	C4	C16	124.1(4)	O5	C17	C6	112.2(4)
C1	C5	C4	103.3(3)	O6	C17	C6	124.6(4)
C1	C5	C6	103.3(3)	O7	C18	O8	124.5(4)
C1	C5	C14	119.9(3)	O7	C18	C8	109.6(3)
C4	C5	C6	81.9(3)	O8	C18	C8	125.8(4)
C4	C5	C14	121.7(3)				
C6	C5	C14	119.5(3)				
C4	C6	C5	49.4(2)	C9	C10	C11B	118.1(6)
C5	C6	C7	111.7(3)	C10	C11B	C12B	111(1)
C5	C6	C17	126.9(4)	C11B	C12B	C13	109(1)
C7	C6	C17	120.4(4)	C12B	C13	C14	107.4(8)

Table 379. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for Sb-8 at **360 K**

Atom	Min.	Int'med.	Max.
O1	0.204	0.269	0.344
O2	0.227	0.297	0.390
O3	0.199	0.251	0.350
O4	0.212	0.271	0.437
O5	0.231	0.296	0.390
O6	0.242	0.326	0.437
O7	0.233	0.260	0.347
O8	0.229	0.279	0.387
C1	0.201	0.231	0.239
C2	0.197	0.222	0.306
C3	0.192	0.221	0.230
C4	0.193	0.207	0.301
C5	0.191	0.222	0.250
C6	0.235	0.250	0.275
C7	0.211	0.234	0.266
C8	0.218	0.241	0.267
C9	0.212	0.263	0.283
C10	0.218	0.303	0.336
C11A	0.214	0.294	0.380
C12A	0.240	0.296	0.355
C13	0.229	0.340	0.351
C14	0.205	0.273	0.308
C15	0.221	0.233	0.288
C16	0.217	0.233	0.276
C17	0.236	0.279	0.288
C18	0.226	0.240	0.281
C19	0.196	0.331	0.387
C20	0.200	0.317	0.379
C21	0.207	0.399	0.452
C22	0.219	0.325	0.392

8–8 X-RAY STRUCTURES RELATED TO BARBARALANE



R = $COOCH_3$

2,4,6,8-Tetracarbomethoxytetracyclo[3.3.$0^{2,8}0^{4,6}$]nonane-3,7-exoexodiol
(War War II)

Table 8–380. X-ray Crystal Data for War War II at **295 K**

Formula	$C_{17}H_{20}O_{10}$
Formula weight	384.34
Melting point (°C)	185-186
Crystal size (mm)	0.06 x 0.10 x 0.44
Crystal system	monoclinic
Space group	C2
a (Å)	20.154(2)
b (Å)	6.216(1)
c (Å)	14.942(2)
β (°)	90.64(1)
Cell volume (Å^3)	1871.59
Z	4[a]
d_{calc} (g cm^{-3})	1.364
μ(Cu $K\alpha$) (cm^{-1})	9.35
Maximum θ(°)	75
Unique reflections	2107
Observed reflections [$I > 3.0\sigma(I)$]	1989
Number of variables	257
R	0.058
R_w	0.079
$(\Delta\rho)_{max}$ (e Å^{-3})	0.29
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.40

[a] The asymetric unit contains two independent half molecules.

Table 8-381. Final Atomic Parameters for War War II at **295 K**

Atom	x	y	z	B(Å^2)
O1	0.3634(1)	1.100	0.5858(2)	3.96(5)
O2	0.3171(1)	0.7805(6)	0.5682(2)	5.97(7)
O3	0.3894(1)	1.1065(5)	0.3645(2)	3.93(4)
O4	0.3455(1)	0.7831(6)	0.3456(2)	5.81(6)
O13	0.52260(9)	0.8258(4)	0.3137(1)	2.54(3)
C1	0.4383(1)	0.6160(5)	0.4856(2)	2.70(5)
C2	0.4325(1)	0.8246(4)	0.5365(2)	1.99(4)
C3	0.5116(1)	0.9000(4)	0.4031(2)	1.84(4)
C4	0.4444(1)	0.8254(5)	0.4355(2)	2.04(4)
C5	0.500	0.4828(7)	0.500	3.33(8)
C6	0.3645(1)	0.8944(6)	0.5658(2)	2.66(5)
C7	0.3876(1)	0.8974(5)	0.3768(2)	2.55(5)
C8	0.3002(2)	1.1896(8)	0.6111(3)	4.84(8)
C9	0.3362(2)	1.2007(8)	0.3108(3)	5.14(8)
O1'	0.3662(1)	-0.2186(5)	0.0980(2)	3.77(5)
O2'	0.3145(1)	0.0765(6)	0.0486(2)	5.87(7)
O3'	0.6191(1)	-0.2250(4)	0.1257(1)	3.43(4)
O4'	0.6435(1)	0.1096(6)	0.1717(2)	4.94(5)
O13'	0.4743(1)	0.0814(4)	0.1828(1)	2.89(4)
C1'	0.5615(1)	0.2592(5)	0.0148(2)	2.67(5)
C2'	0.4323(1)	0.0491(5)	0.0353(2)	2.23(4)
C3'	0.4879(1)	-0.0171(5)	0.0985(2)	2.01(4)
C4'	0.5553(1)	0.0534(4)	0.0656(2)	2.07(4)
C5'	0.500	0.3946(7)	0.000	3.33(8)
C6'	0.3644(1)	-0.0240(6)	0.0616(2)	2.86(5)
C7'	0.6114(1)	-0.0128(5)	0.1265(2)	2.55(5)
C8'	0.3025(2)	-0.3145(9)	0.1192(3)	5.15(9)
C9'	0.6721(2)	-0.3093(8)	0.1802(3)	4.51(7)
O20A	0.5403(2)	0.4045(6)	0.2754(3)	6.02(8)
O20B	0.467(1)	0.487(5)	0.244(1)	6.5(5)*
H1	0.396	0.532	0.477	3.1
H3	0.512	1.059	0.403	1.9
H5A	0.507	0.389	0.446	3.6
H5B	0.494	0.389	0.554	3.6
H8A	0.305	1.345	0.625	5.6
H8B	0.267	1.168	0.561	5.6
H8C	0.283	1.111	0.666	5.6
H9A	0.343	1.357	0.307	6.0
H9B	0.336	1.134	0.250	6.0
H9C	0.293	1.169	0.341	6.0
H1'	0.604	0.339	0.024	3.1
H3'	0.488	-0.180	0.106	2.4
H5A'	0.506	0.483	-0.054	4.1
H5B'	0.494	0.483	0.054	4.1
H8A'	0.312	-0.466	0.146	6.3
H8B'	0.280	-0.228	0.164	6.3
H8C'	0.275	-0.334	0.065	6.3
H9A'	0.674	-0.474	0.175	5.7
H9B'	0.716	-0.252	0.160	5.7
H9C'	0.666	-0.273	0.245	5.7
HO13	0.505	0.918	0.273	3.0
HO20AA	0.525	0.540	0.280	7.5
HO20AB	0.511	0.326	0.242	7.5
HO20BA	0.503	0.563	0.267	11.0
HO20BB	0.489	0.350	0.229	11.0

The starred atoms were refine isotropically.
The parameters of the hydrogen atoms were not refined.

Table 8-382. Final Anisotropic Thermal Parameters (U's) for War War II at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0295(9)	0.044(1)	0.077(1)	0.007(1)	0.009(1)	-0.006(1)
O2	0.038(1)	0.067(2)	0.123(2)	-0.023(1)	0.024(1)	-0.023(2)
O3	0.049(1)	0.043(1)	0.057(1)	0.008(1)	-0.0242(9)	0.001(1)
O4	0.060(1)	0.067(2)	0.093(2)	-0.029(1)	-0.042(1)	0.015(2)
O13	0.0437(9)	0.0309(9)	0.0219(7)	0.0041(9)	0.0009(7)	-0.0024(8)
C1	0.047(1)	0.023(1)	0.033(1)	-0.009(1)	-0.001(1)	-0.001(1)
C2	0.028(1)	0.023(1)	0.025(1)	-0.003(1)	0.0001(9)	0.0006(9)
C3	0.029(1)	0.021(1)	0.0202(9)	0.0000(9)	-0.0001(8)	0.0006(9)
C4	0.029(1)	0.025(1)	0.024(1)	-0.004(1)	-0.0026(9)	-0.0011(9)
C5	0.063(2)	0.020(2)	0.044(2)	0	-0.002(2)	0
C6	0.028(1)	0.043(2)	0.031(1)	-0.005(1)	0.0013(9)	0.002(1)
C7	0.030(1)	0.039(1)	0.029(1)	-0.005(1)	-0.0025(9)	-0.002(1)
C8	0.038(1)	0.066(2)	0.080(2)	0.022(2)	0.008(2)	-0.001(2)
C9	0.062(2)	0.072(3)	0.061(2)	0.029(2)	-0.019(2)	0.009(2)
O1'	0.0337(9)	0.050(1)	0.060(1)	-0.004(1)	0.0016(9)	0.015(1)
O2'	0.035(1)	0.089(2)	0.100(2)	0.021(1)	0.002(1)	0.028(2)
O3'	0.046(1)	0.036(1)	0.048(1)	0.008(1)	-0.0173(8)	-0.003(1)
O4'	0.066(1)	0.054(1)	0.066(1)	-0.010(1)	-0.0390(9)	-0.007(1)
O13'	0.048(1)	0.039(1)	0.0237(7)	0.007(1)	0.0028(7)	-0.0052(8)
C1'	0.044(1)	0.023(1)	0.034(1)	-0.010(1)	-0.004(1)	-0.001(1)
C2'	0.032(1)	0.027(1)	0.026(1)	0.008(1)	-0.0007(9)	-0.001(1)
C3'	0.031(1)	0.022(1)	0.024(1)	0.003(1)	-0.0010(9)	-0.001(1)
C4'	0.032(1)	0.023(1)	0.023(1)	-0.003(1)	-0.0033(9)	-0.0015(9)
C5'	0.064(3)	0.017(2)	0.046(2)	0	-0.006(2)	0
C6'	0.032(1)	0.046(2)	0.031(1)	0.006(1)	-0.001(1)	0.000(1)
C7'	0.030(1)	0.039(1)	0.027(1)	-0.003(1)	-0.0042(9)	0.002(1)
C8'	0.043(2)	0.083(3)	0.069(2)	-0.021(2)	0.004(2)	0.014(2)
C9'	0.046(2)	0.061(2)	0.063(2)	0.016(2)	-0.018(1)	0.005(2)
O20A	0.084(2)	0.041(2)	0.104(2)	-0.002(2)	0.009(2)	-0.034(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-383. Bond Distances (Å) for War War II at **295 K**

		Unprimed	Primed
O1	C6	1.313(4)	1.327(5)
O1	C8	1.446(4)	1.453(5)
O2	C6	1.190(4)	1.199(4)
O3	C7	1.314(4)	1.328(4)
O3	C9	1.455(5)	1.436(4)
O4	C7	1.197(4)	1.201(4)
O13	C3	1.432(3)	1.430(3)
C1	C2	1.508(4)	1.511(4)
C1	C4	1.507(4)	1.494(4)
C1	C5	1.507(4)	1.513(4)
C2	C3	1.512(3)	1.514(3)
C2	C4	1.530(3)	1.531(3)
C2	C6	1.506(4)	1.498(4)
C3	C4	1.516(3)	1.514(3)
C4	C7	1.503(4)	1.502(4)

Table 8-384. Bond Angles (°) for War War II at **295 K**

			Unprimed	Primed
C6	O1	C8	116.8(2)	116.3(3)
C7	O3	C9	117.0(3)	116.3(3)
C2	C1	C4	61.0(2)	61.3(2)
C2	C1	C5	118.0(2)	118.7(2)
C4	C1	C5	118.3(2)	118.5(2)
C1	C2	C3	120.4(2)	118.6(2)
C1	C2	C4	59.5(2)	58.8(2)
C1	C2	C6	118.1(2)	118.2(2)
C3	C2	C4	117.6(2)	119.4(2)
C3	C2	C6	114.3(2)	115.2(2)
C4	C2	C6	116.1(2)	115.1(2)
O13	C3	C2	109.5(2)	106.6(2)
O13	C3	C4	110.4(2)	110.1(2)
C2	C3	C4	112.1(2)	112.3(2)
C1	C4	C2	59.5(2)	59.9(2)
C1	C4	C3	120.1(2)	119.6(2)
C1	C4	C7	118.8(2)	118.4(2)
C2	C4	C3	117.9(2)	118.1(2)
C2	C4	C7	116.7(2)	117.5(2)
C3	C4	C7	113.6(2)	113.4(2)
C1	C5	C1	113.4(3)	112.4(3)
O1	C6	O2	123.8(3)	124.1(3)
O1	C6	C2	111.3(2)	111.3(2)
O2	C6	C2	124.8(3)	124.5(3)
O3	C7	O4	123.6(3)	124.9(3)
O3	C7	C4	110.7(2)	110.7(2)
O4	C7	C4	125.7(3)	124.3(3)

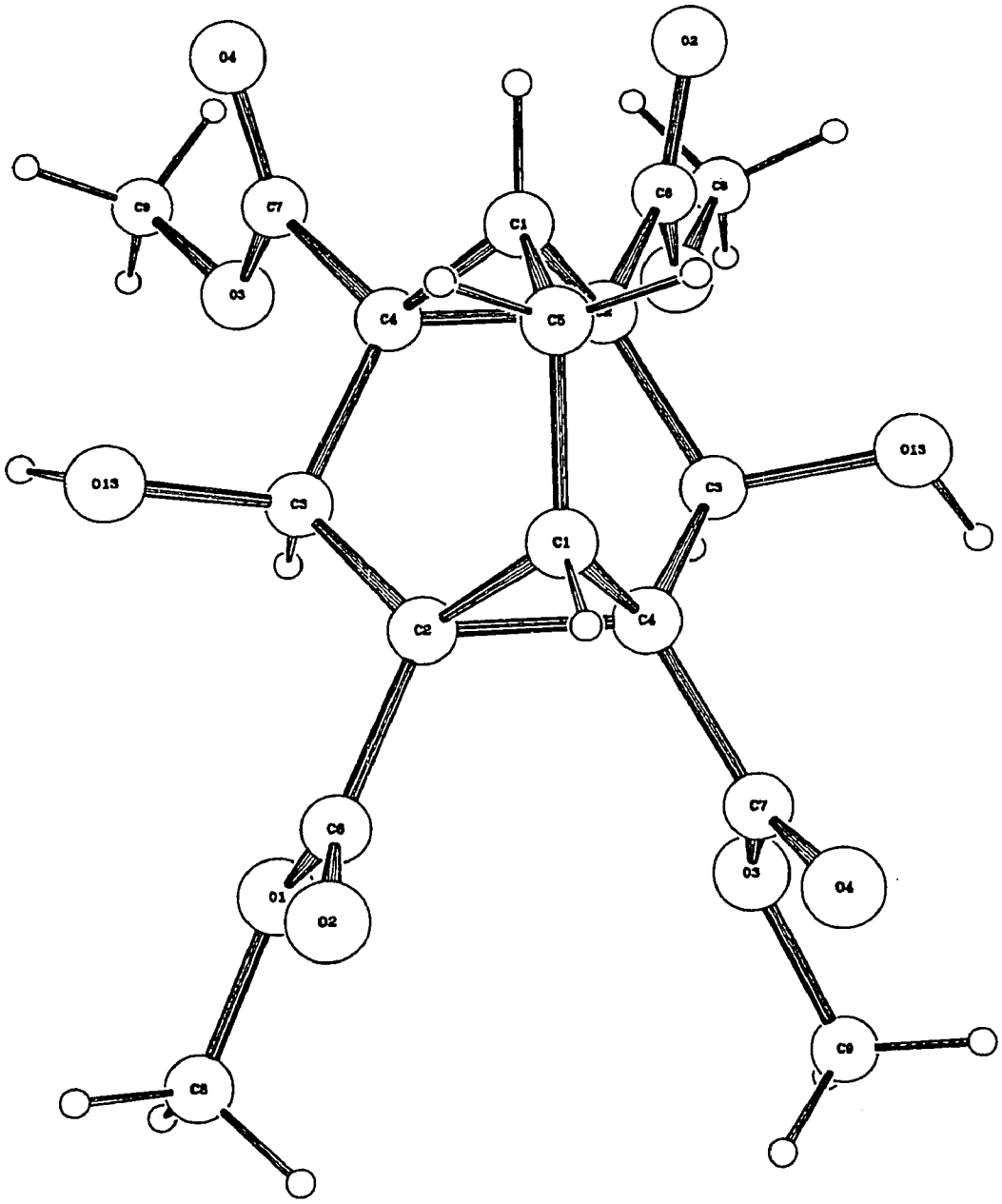


Figure 8–2. *ORTEP* drawing of War War II (unprimed) at **295 K.**

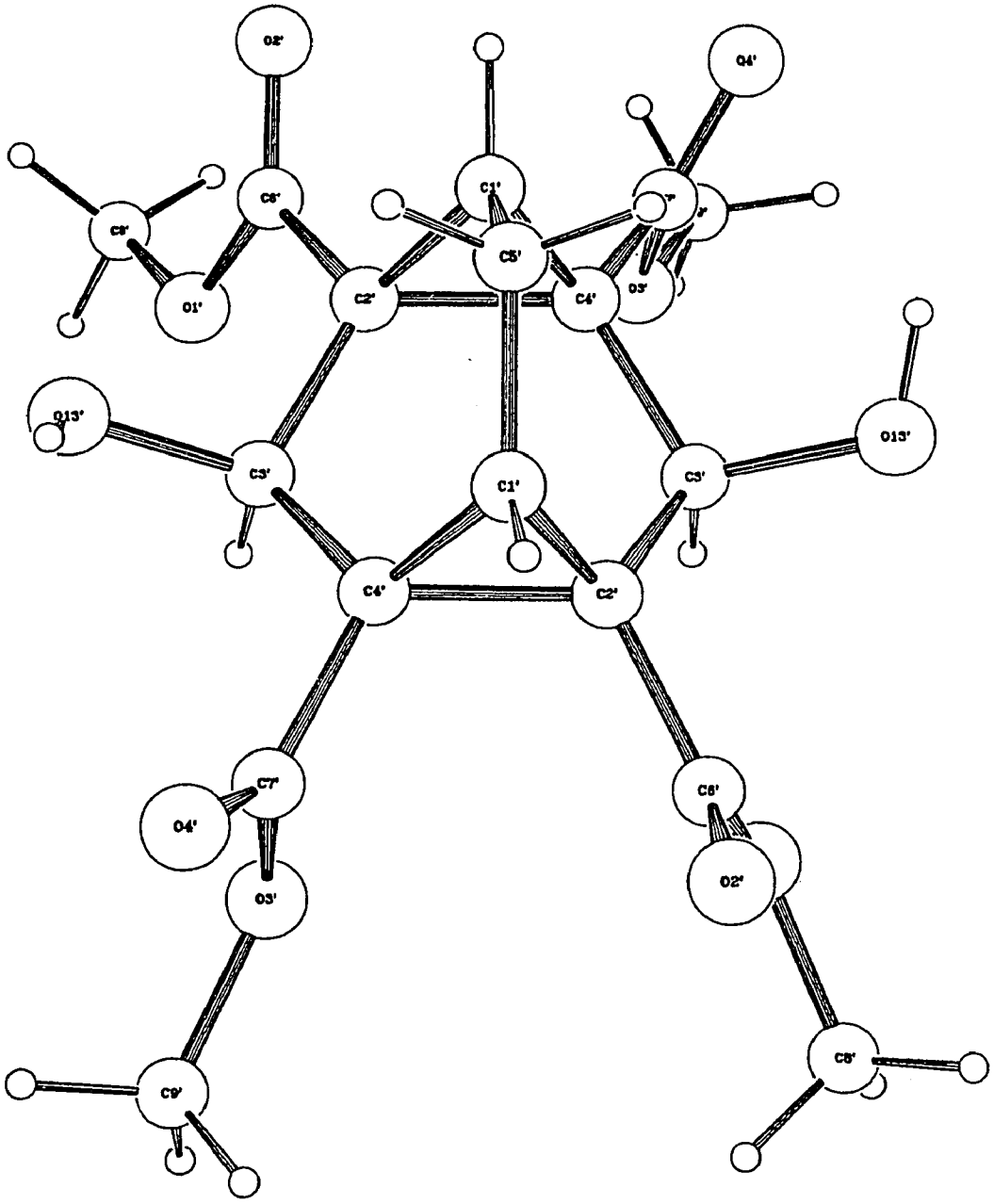
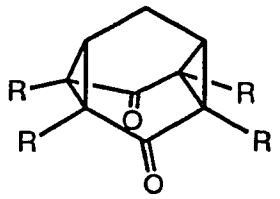


Figure 8–3. *ORTEP* drawing of War War II (primed) at **295 K.**



R = $COOCH_3$

2,4,6,8-Tetracarbomethoxytetracyclo[3.3.$0^{2,8}0^{4,6}$]-3,7-dione
[War War III]

Table 8–385. X-ray Crystal Data for War War III at **295 K**

Formula	$C_{17}H_{16}O_{10}$
Formula weight	380.31
Melting point (°C)	245–246
Crystal size (mm)	0.06 x 0.10 x 0.44
Crystal system	monoclinic
Space group	C2/c
a (Å)	20.832(2)
b (Å)	5.911(1)
c (Å)	13.877(2)
β (°)	99.76(1)
Cell volume (Å^3)	1684.14
Z	4
d_{calc} (g cm^{-3})	1.500
μ(Cu $K\alpha$) (cm^{-1})	10.4
Maximum θ (°)	75
Unique reflections	1736
Observed reflections [$I > 3.0\sigma(I)$]	1186
Number of variables	123
R	0.051
R_w	0.065
$(\Delta\rho)_{max}$ (e Å^{-3})	0.29
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.24

Table 8-386. Final Atomic Parameters for War War III at 295 K

Atom	x	y	z	B(Å^2)
O1	0.35259(8)	0.1988(3)	0.1822(2)	3.54(4)
O2	0.31803(9)	0.5485(4)	0.1395(2)	4.61(5)
O3	0.58670(9)	0.2004(4)	0.0885(2)	4.04(4)
O4	0.64606(9)	0.5154(4)	0.1185(2)	4.46(5)
O5	0.45787(9)	0.3404(4)	0.0639(2)	4.08(5)
C1	0.4422(1)	0.7056(5)	0.2650(2)	3.40(6)
C2	0.4299(1)	0.4893(4)	0.2087(2)	2.81(5)
C3	0.4768(1)	0.4234(4)	0.1435(2)	2.94(5)
C4	0.5463(1)	0.4848(4)	0.1790(2)	2.91(5)
C5	0.500	0.8478(7)	0.250	4.1(1)
C6	0.3600(1)	0.4205(5)	0.1725(2)	3.02(5)
C7	0.5982(1)	0.4074(5)	0.1236(2)	3.14(5)
C8	0.2860(1)	0.1149(6)	0.1538(3)	4.44(7)
C9	0.6368(2)	0.1010(7)	0.0410(3)	5.04(8)
H1	0.402	0.792	0.275	4.0
H5	0.487	0.945	0.191	4.9
H8A	0.285	-0.053	0.164	5.3
H8B	0.257	0.189	0.195	5.3
H8C	0.270	0.151	0.083	5.3
H9A	0.623	-0.054	0.017	6.0
H9B	0.643	0.197	-0.016	6.0
H9C	0.679	0.092	0.089	6.0

The parameters of the hydrogen atoms were not refined.

Table 8-387. Final Anisotropic Thermal Parameters (U's) for War War III at 295 K

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0328(8)	0.0297(9)	0.070(1)	-0.0036(8)	0.0023(8)	0.003(1)
O2	0.0388(9)	0.042(1)	0.087(2)	0.0051(9)	-0.011(1)	0.013(1)
O3	0.0518(9)	0.041(1)	0.065(1)	-0.0080(9)	0.0225(9)	-0.008(1)
O4	0.0421(9)	0.054(1)	0.076(1)	-0.0135(9)	0.0175(9)	-0.003(1)
O5	0.0451(9)	0.060(1)	0.047(1)	-0.011(1)	0.0018(8)	-0.001(1)
C1	0.035(1)	0.024(1)	0.068(2)	0.002(1)	0.003(1)	-0.002(1)
C2	0.030(1)	0.026(1)	0.049(1)	-0.001(1)	0.000(1)	0.005(1)
C3	0.034(1)	0.028(1)	0.047(1)	-0.007(1)	0.001(1)	0.009(1)
C4	0.033(1)	0.028(1)	0.047(1)	-0.003(1)	0.002(1)	0.004(1)
C5	0.041(2)	0.023(2)	0.089(3)	0	0.002(2)	0
C6	0.032(1)	0.033(1)	0.048(1)	0.000(1)	0.002(1)	0.004(1)
C7	0.036(1)	0.039(1)	0.043(1)	-0.005(1)	0.004(1)	0.005(1)
C8	0.039(1)	0.044(2)	0.084(2)	-0.013(1)	0.005(1)	-0.006(2)
C9	0.069(2)	0.059(2)	0.071(2)	-0.003(2)	0.034(1)	-0.009(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-388. Bond Distances (Å) for War War III at 295 K

O1	C6	1.329(3)	C1	C4	1.517(4)
O1	C8	1.462(3)	C1	C5	1.512(3)
O2	C6	1.188(3)	C2	C3	1.491(4)
O3	C7	1.323(4)	C2	C4	1.553(4)
O3	C9	1.450(4)	C2	C6	1.514(3)
O4	C7	1.197(3)	C3	C4	1.493(3)
O5	C3	1.211(3)	C4	C7	1.500(4)
C1	C2	1.498(4)			

Table 8-389. Bond Angles (°) for War War III at 295 K

C6	O1	C8	115.4(2)	C1	C4	C2	58.4(2)
C7	O3	C9	116.3(2)	C1	C4	C3	116.0(2)
C2	C1	C4	62.0(2)	C1	C4	C7	117.4(2)
C2	C1	C5	118.2(2)	C2	C4	C3	117.5(2)
C4	C1	C5	119.3(2)	C2	C4	C7	112.6(2)
C1	C2	C3	117.9(2)	C3	C4	C7	119.9(2)
C1	C2	C4	59.6(2)	C1	C5	C1	112.4(3)
C1	C2	C6	118.1(2)	O1	C6	O2	125.2(2)
C3	C2	C4	118.3(2)	O1	C6	C2	110.7(2)
C3	C2	C6	114.9(2)	O2	C6	C2	124.2(3)
C4	C2	C6	117.0(2)	O3	C7	O4	124.9(3)
O5	C3	C2	120.9(2)	O3	C7	C4	111.7(2)
O5	C3	C4	123.2(3)	O4	C7	C4	123.2(3)
C2	C3	C4	115.7(2)				

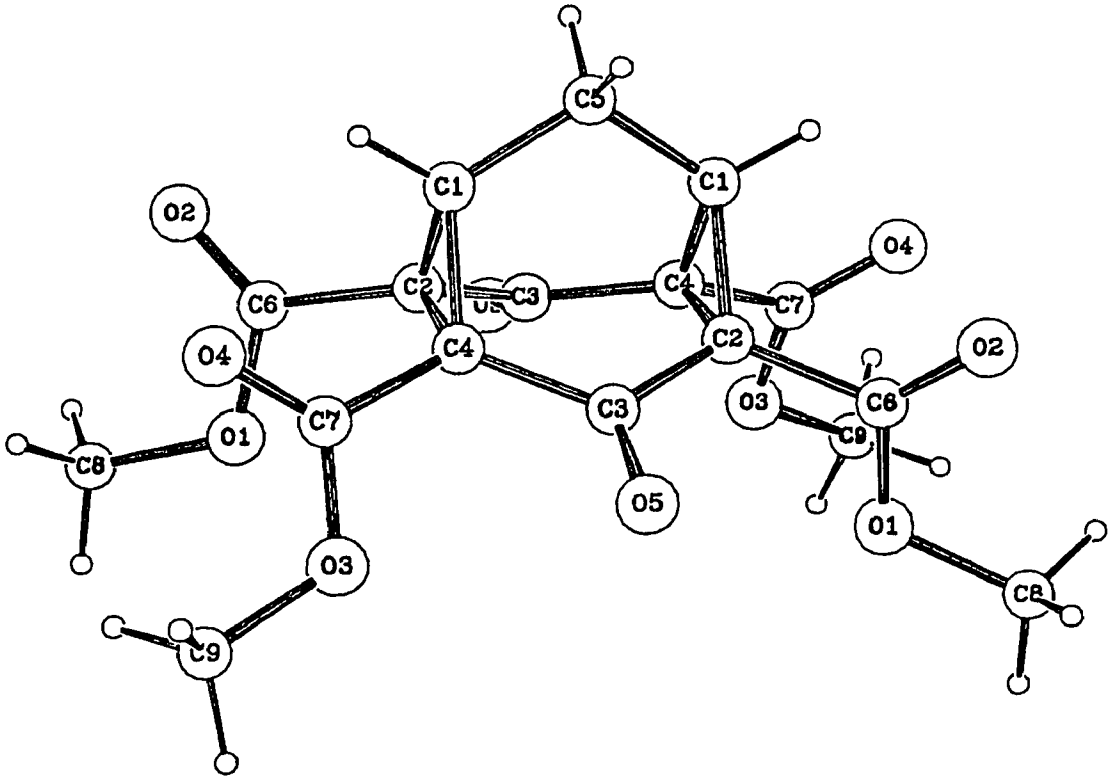


Figure 8–4. *ORTEP* drawing of War War III at **295 K.**

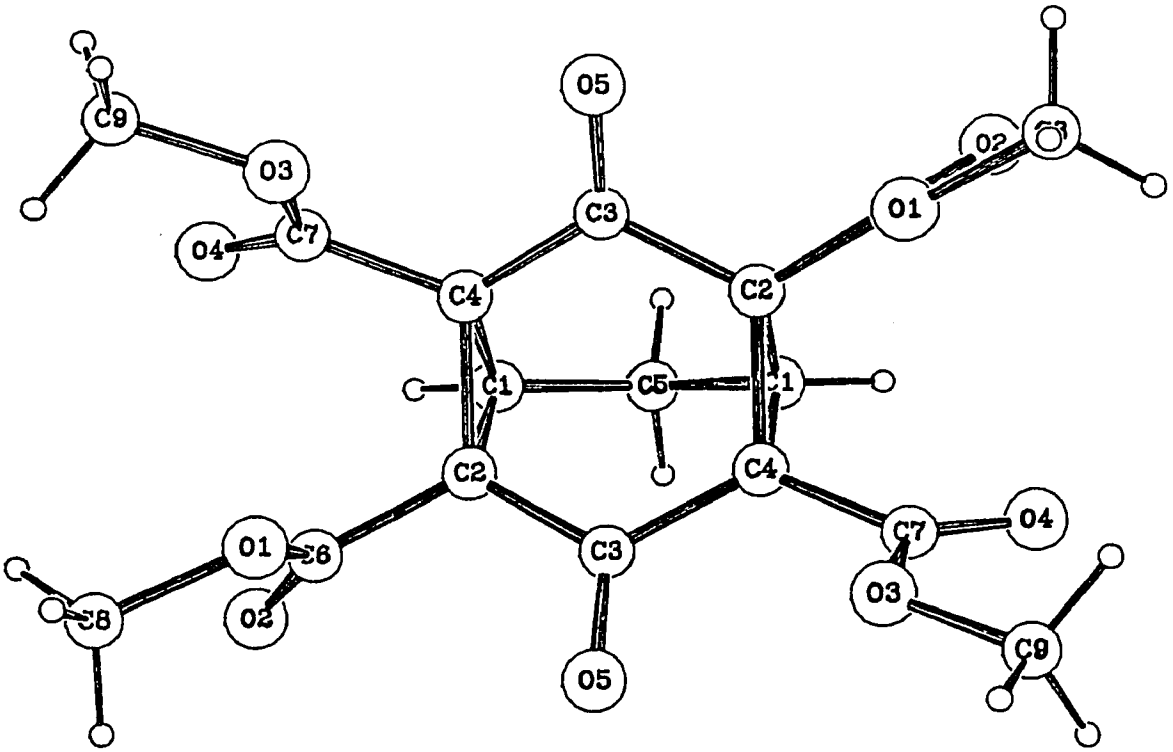
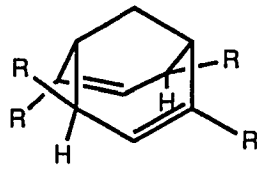


Figure 8–5. *ORTEP* drawing of War War III at **295 K.**



$R = COOCH_3$

2,4,6,8-Tetracarbomethoxytetracyclo[3.3.1]nona-2,6-diene
(Dihydro-2,4,6,8-tetracarbomethoxybarbaralane)
(War War IV)

Table 8–390. X-ray Crystal Data for War War IV at **295 K**

Formula	$C_{17}H_{20}O_8$
Formula weight	352.34
Melting point (°C)	158–159
Crystal size (mm)	0.04 x 0.30 x 0.45
Crystal system	orthorhombic
Space group	*Ac2a*
a (Å)	10.083(1)
b (Å)	9.925(1)
c (Å)	17.742(1)
Cell volume (Å^3)	1775.64
Z	4
d_{calc} (g cm^{-3})	1.318
μ(Cu $K\alpha$) (cm^{-1})	8.53
Maximum θ (°)	75
Unique reflections	973
Observed reflections [$I > 3.0\sigma(I)$]	765
Number of variables	113
R	0.046
R_w	0.055
$(\Delta\rho)_{max}$ (e Å^{-3})	0.18
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.18

Table 8-391. Final Atomic Parameters for War War IV at **295 K**

Atom	x	y	z	B(Å^2)
O1	0.2846(3)	0.200	0.1566(2)	5.89(6)
O2	0.4548(3)	0.3108(5)	0.2059(2)	7.34(8)
O3	0.8798(2)	0.3606(4)	0.0825(2)	5.94(7)
O4	0.7727(3)	0.5504(3)	0.1059(2)	6.07(6)
C1	0.5215(3)	0.4393(4)	0.0686(2)	3.63(6)
C2	0.4070(3)	0.3424(4)	0.0759(2)	3.53(6)
C3	0.6696(3)	0.3074(4)	-0.0191(2)	3.43(6)
C4	0.6509(3)	0.3579(4)	0.0603(2)	3.34(5)
C5	0.500	0.5289(5)	0.000	3.80(9)
C6	0.3862(3)	0.2853(4)	0.1530(2)	4.36(7)
C7	0.7730(3)	0.4369(4)	0.0850(2)	3.74(6)
C8	0.2557(6)	0.1420(7)	0.2309(2)	7.7(1)
C9	1.0028(4)	0.4219(7)	0.1103(3)	7.1(1)
H1	0.528	0.498	0.114	4.4
H3	0.744	0.244	-0.029	4.1
H4	0.642	0.279	0.095	4.0
H5	0.580	0.587	-0.008	4.6
H8A	0.178	0.080	0.227	9.2
H8B	0.335	0.091	0.249	9.2
H8C	0.234	0.216	0.267	9.2
H9A	1.077	0.356	0.106	8.5
H9B	1.024	0.504	0.080	8.5
H9C	0.991	0.448	0.164	8.5

The parameters of the hydrogen atoms were not refined.

Table 392. Final Anisotropic Thermal Parameters (U's) for War-War IV at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.066(2)	0.094(2)	0.063(1)	-0.012(2)	0.011(1)	0.024(2)
O2	0.091(2)	0.135(3)	0.053(1)	-0.021(2)	-0.010(2)	0.010(2)
O3	0.037(1)	0.071(2)	0.118(2)	0.005(1)	-0.012(1)	-0.026(2)
O4	0.064(2)	0.053(1)	0.114(2)	-0.004(1)	-0.016(2)	-0.025(2)
C1	0.041(2)	0.045(1)	0.052(2)	0.002(1)	0.001(1)	-0.007(2)
C2	0.038(1)	0.048(2)	0.048(2)	0.004(1)	0.007(1)	0.003(1)
C3	0.035(1)	0.044(1)	0.052(2)	0.001(1)	0.002(1)	-0.005(1)
C4	0.037(1)	0.040(1)	0.050(1)	0.001(1)	-0.001(1)	-0.005(1)
C5	0.045(2)	0.036(2)	0.063(3)	0	-0.000(2)	0
C6	0.050(2)	0.067(2)	0.049(2)	0.006(2)	0.008(2)	0.004(2)
C7	0.040(2)	0.053(2)	0.049(1)	-0.002(2)	-0.001(1)	-0.006(2)
C8	0.097(3)	0.123(4)	0.073(2)	-0.010(4)	0.029(2)	0.034(2)
C9	0.038(2)	0.125(4)	0.105(3)	-0.001(2)	-0.016(2)	-0.025(3)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-393. Bond Distances (Å) for War-War IV at **295 K**

O1	C6	1.333(4)	C1	C4	1.542(5)
O1	C8	1.466(5)	C1	C5	1.523(4)
O2	C6	1.194(5)	C1	C5	1.523(4)
O3	C7	1.318(4)	C2	C3	1.317(4)
O3	C9	1.466(6)	C2	C6	1.494(5)
O4	C7	1.186(5)	C3	C4	1.507(5)
C1	C2	1.509(5)	C4	C7	1.524(5)

Table 8-394. Bond Angles (°) for War-War IV at **295 K**

C6	O1	C8	116.4(3)	C1	C4	C7	112.7(3)
C7	O3	C9	116.2(4)	C3	C4	C7	109.9(3)
C2	C1	C4	108.8(3)	C1	C5	C1	108.6(4)
C2	C1	C5	109.4(2)	O1	C6	O2	122.9(4)
C4	C1	C5	110.5(2)	O1	C6	C2	113.2(3)
C1	C2	C3	123.4(3)	O2	C6	C2	123.9(4)
C1	C2	C6	115.4(3)	O3	C7	O4	123.9(3)
C3	C2	C6	121.2(3)	O3	C7	C4	110.8(3)
C2	C3	C4	123.7(3)	O4	C7	C4	125.3(3)
C1	C4	C3	111.7(3)				

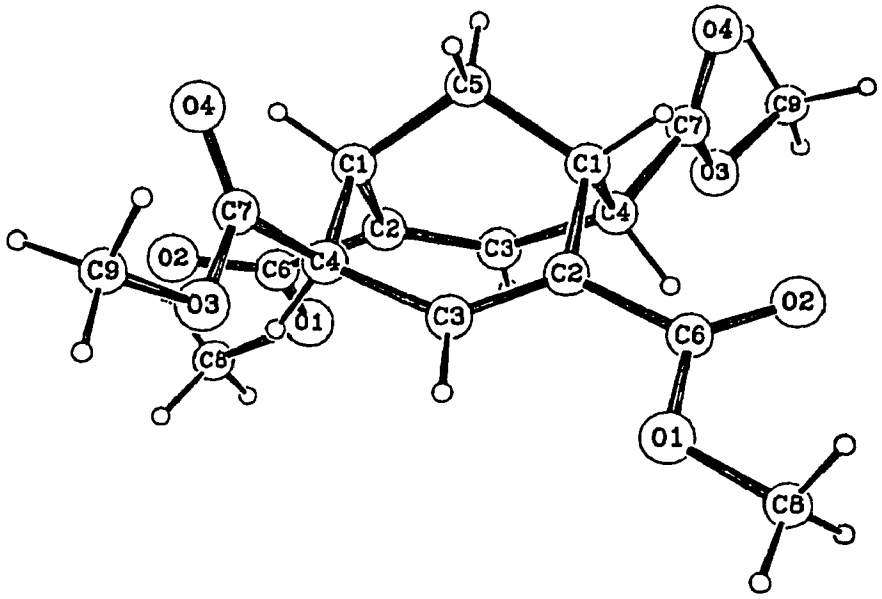


Figure 8–6. *ORTEP* drawing of War-War IV at **295 K.**

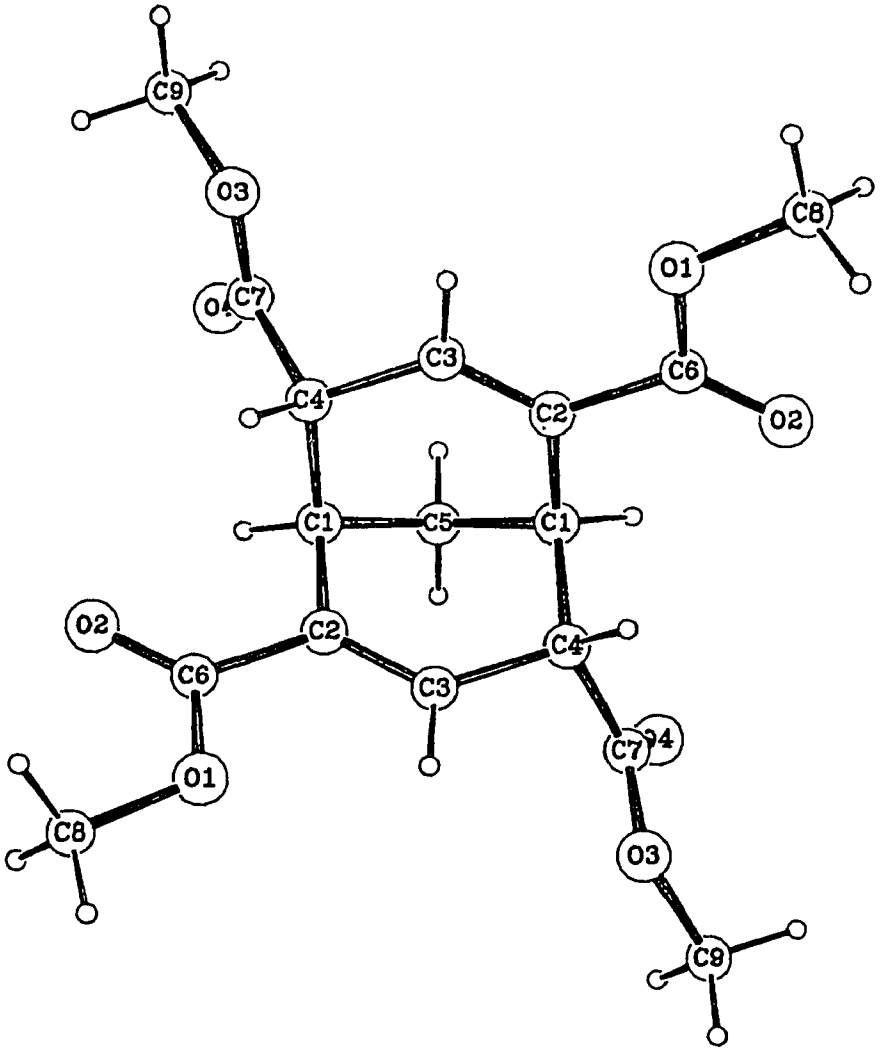
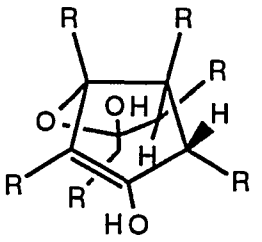


Figure 8–7. *ORTEP* drawing of War-War IV at **295 K.**



R = $COOCH_3$

2-Oxa-bicyclo[3.3.0]oct-7-ene-1,4,5,6,8-penatcarbomethoxy-3-carbomethoxymethylene-3,7-diol
(War-War V)

Table 8–395 X-ray Crystal Data for War-War V at **295 K**

Formula	$C_{20}H_{24}O_{15}$
Formula weight	504.41
Melting point (°C)	174–175
Crystal size (mm)	0.20 x 0.40 x 0.43
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	16.699(1)
b (Å)	8.073(1)
c (Å)	16.931(1)
β (°)	90.19(1)°
Cell volume (Å^3)	2282.57(0.12)
Z	4
d_{calc} (g cm^{-3})	1.468
μ(Cu $K\alpha$) (cm^{-1})	10.7
Maximum θ (°)	75
Unique reflections	4689
Observed reflections [$I > 3.0\sigma(I)$]	3521
Number of variables	316
R	0.043
R_w	0.055
$(\Delta\rho)_{max}$ (e Å^{-3})	0.31
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.24

Table 8-396. Final Atomic Parameters for War-War V at **295 K**

Atom	x	y	z	B(Å^2)
O3	0.29253(8)	0.8876(2)	0.56426(8)	3.10(3)
O7	0.22613(9)	0.3208(2)	0.30747(8)	3.42(3)
O8	0.17818(8)	0.4763(2)	0.41337(8)	2.65(2)
O11	0.0808(1)	0.6487(2)	0.3191(1)	4.38(3)
O12	0.14687(9)	0.8847(2)	0.34178(9)	3.45(3)
O21	0.14261(9)	0.7966(3)	0.60861(9)	4.24(4)
O22	0.06521(8)	0.6815(2)	0.51525(9)	3.80(3)
O41	0.42833(9)	0.6542(2)	0.5111(1)	3.80(3)
O42	0.46563(8)	0.8362(2)	0.4189(1)	3.80(3)
O51	0.2637(1)	0.6206(2)	0.23888(8)	3.68(3)
O52	0.32129(9)	0.8567(2)	0.27768(8)	3.25(3)
O61	0.4268(1)	0.5231(2)	0.3070(1)	4.99(4)
O62	0.40354(9)	0.2713(2)	0.35470(9)	3.72(3)
O81	0.2697(1)	0.3353(2)	0.5620(1)	4.76(4)
O82	0.15852(9)	0.1859(2)	0.54606(9)	3.92(3)
C1	0.1965(1)	0.6478(2)	0.4063(1)	2.14(3)
C2	0.1988(1)	0.7310(2)	0.4860(1)	2.34(3)
C3	0.2700(1)	0.8025(2)	0.5006(1)	2.28(3)
C4	0.3273(1)	0.7925(2)	0.4332(1)	2.16(3)
C5	0.2878(1)	0.6619(2)	0.3778(1)	2.05(3)
C6	0.3154(1)	0.4829(2)	0.3935(1)	2.14(3)
C7	0.2406(1)	0.3729(2)	0.3850(1)	2.35(3)
C8	0.2398(1)	0.2164(3)	0.4354(1)	2.84(4)
C11	0.1341(1)	0.7232(3)	0.3503(1)	2.54(3)
C12	0.1338(1)	0.7394(3)	0.5429(1)	2.79(4)
C13	0.0945(2)	0.9702(3)	0.2867(2)	4.66(5)
C14	0.4124(1)	0.7505(3)	0.4598(1)	2.55(3)
C15	0.2909(1)	0.7090(3)	0.2902(1)	2.49(3)
C16	0.3875(1)	0.4308(3)	0.3458(1)	2.73(4)
C18	0.2258(1)	0.2542(3)	0.5211(1)	2.78(4)
C23	-0.0027(1)	0.6863(4)	0.5687(2)	5.46(7)
C43	0.5487(1)	0.7962(4)	0.4350(2)	5.39(7)
C53	0.3154(2)	0.9242(3)	0.1982(1)	4.67(5)
C63	0.4713(2)	0.2057(3)	0.3119(2)	4.72(5)
C83	0.1365(2)	0.2181(5)	0.6275(2)	6.61(8)
HO3	0.250	0.882	0.597	3.7
HO7	0.236	0.408	0.276	4.1
H4	0.335	0.900	0.406	2.6
H6	0.337	0.471	0.448	2.6
H8A	0.293	0.159	0.430	3.4
H8B	0.196	0.142	0.416	3.4
H13A	0.109	1.090	0.285	5.6
H13B	0.100	0.921	0.233	5.6
H13C	0.037	0.959	0.305	5.6
H23A	-0.051	0.640	0.541	6.6
H23B	0.010	0.618	0.617	6.6
H23C	-0.013	0.803	0.585	6.6
H43A	0.584	0.867	0.402	6.5
H43B	0.561	0.817	0.492	6.5
H43C	0.558	0.677	0.423	6.5
H53A	0.340	1.037	0.197	5.6
H53B	0.343	0.850	0.160	5.6
H53C	0.257	0.934	0.183	5.6
H63A	0.478	0.084	0.324	5.7
H63B	0.463	0.221	0.254	5.7
H63C	0.522	0.265	0.329	5.7

Table 8-396 (cont'd). Final Atomic Parameters for War-War V at **295 K**

Atom	x	y	z	B(Å^2)
H83A	0.085	0.161	0.640	8.0
H83B	0.179	0.175	0.663	8.0
H83C	0.130	0.340	0.636	8.0

The parameters of the hydrogen atoms were not refined.

Table 8-397. Final Anisotropic Thermal Parameters (U's) for War-War V at **295K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O3	0.0409(7)	0.0426(8)	0.0342(7)	-0.0069(6)	0.0007(6)	-0.0106(6)
O7	0.0617(9)	0.0391(8)	0.0292(6)	-0.0149(7)	-0.0028(6)	-0.0057(6)
O8	0.0298(6)	0.0260(6)	0.0447(7)	-0.0051(5)	0.0040(5)	0.0011(6)
O11	0.0517(8)	0.052(1)	0.0625(9)	-0.0126(8)	-0.0259(7)	0.0068(8)
O12	0.0514(8)	0.0309(7)	0.0487(8)	0.0004(6)	-0.0169(6)	0.0051(7)
O21	0.0469(8)	0.080(1)	0.0347(7)	-0.0073(8)	0.0072(6)	-0.0169(8)
O22	0.0288(6)	0.071(1)	0.0447(8)	-0.0078(7)	0.0058(6)	-0.0102(8)
O41	0.0430(7)	0.0485(9)	0.0531(8)	0.0014(7)	-0.0106(7)	0.0128(7)
O42	0.0288(6)	0.0562(9)	0.0594(9)	-0.0080(7)	-0.0002(7)	0.0122(8)
O51	0.0656(9)	0.0465(8)	0.0275(6)	-0.0143(8)	-0.0038(7)	0.0017(6)
O52	0.0558(8)	0.0346(7)	0.0332(6)	-0.0110(7)	-0.0029(6)	0.0110(6)
O61	0.0576(8)	0.0447(9)	0.088(1)	0.0043(8)	0.0413(7)	0.0152(9)
O62	0.0492(7)	0.0321(7)	0.0601(9)	0.0097(6)	0.0209(7)	0.0011(7)
O81	0.074(1)	0.064(1)	0.0431(8)	-0.0223(9)	-0.0112(8)	-0.0054(8)
O82	0.0508(8)	0.060(1)	0.0376(7)	-0.0119(8)	0.0085(7)	0.0013(7)
C1	0.0273(7)	0.0230(8)	0.0309(8)	-0.0029(7)	0.0007(7)	-0.0005(7)
C2	0.0309(8)	0.0295(9)	0.0286(8)	0.0001(7)	-0.0001(7)	-0.0012(8)
C3	0.0325(8)	0.0256(8)	0.0284(8)	0.0003(7)	-0.0017(7)	-0.0010(7)
C4	0.0277(7)	0.0241(8)	0.0301(8)	-0.0027(7)	-0.0013(7)	-0.0007(7)
C5	0.0272(7)	0.0235(8)	0.0270(8)	-0.0018(7)	0.0001(6)	0.0009(7)
C6	0.0302(8)	0.0224(8)	0.0287(8)	-0.0011(7)	0.0015(7)	-0.0005(7)
C7	0.0344(8)	0.0257(8)	0.0291(8)	-0.0031(7)	0.0014(7)	-0.0034(7)
C8	0.048(1)	0.0250(9)	0.0352(9)	-0.0044(8)	0.0053(8)	-0.0010(8)
C11	0.0294(8)	0.034(1)	0.0328(8)	-0.0018(8)	-0.0015(7)	0.0006(8)
C12	0.0311(8)	0.040(1)	0.0350(9)	-0.0014(8)	0.0015(7)	0.0001(9)
C13	0.069(1)	0.049(1)	0.058(1)	0.010(1)	-0.023(1)	0.014(1)
C14	0.0306(8)	0.0292(9)	0.0372(9)	-0.0031(7)	-0.0014(7)	-0.0044(8)
C15	0.0316(8)	0.0328(9)	0.0303(8)	-0.0023(8)	0.0026(7)	0.0038(8)
C16	0.0357(9)	0.0309(9)	0.0372(9)	-0.0003(8)	0.0057(8)	-0.0019(8)
C18	0.0416(9)	0.0298(9)	0.0344(9)	0.0004(8)	-0.0016(8)	0.0037(8)
C23	0.036(1)	0.107(2)	0.065(1)	-0.010(1)	0.018(1)	-0.011(2)
C43	0.029(1)	0.091(2)	0.085(2)	-0.007(1)	-0.002(1)	0.009(2)
C53	0.087(2)	0.053(1)	0.038(1)	-0.015(1)	-0.004(1)	0.022(1)
C63	0.055(1)	0.050(1)	0.075(2)	0.017(1)	0.027(1)	-0.003(1)
C83	0.102(2)	0.102(2)	0.048(1)	-0.017(2)	0.031(1)	-0.011(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-398. Bond Distances (Å) for War-War V **295 K**

O3	C3	1.332(2)	O62	C63	1.446(3)
O7	C7	1.398(2)	O81	C18	1.201(3)
O8	C1	1.423(2)	O82	C18	1.323(3)
O8	C7	1.420(2)	O82	C83	1.451(3)
O11	C11	1.194(3)	C1	C2	1.508(3)
O12	C11	1.329(3)	C1	C5	1.604(2)
O12	C13	1.451(3)	C1	C11	1.534(3)
O21	C12	1.213(3)	C2	C3	1.343(3)
O22	C12	1.322(2)	C2	C12	1.455(3)
O22	C23	1.455(3)	C3	C4	1.493(3)
O41	C14	1.195(3)	C4	C5	1.556(3)
O42	C14	1.324(2)	C4	C14	1.527(3)
O42	C43	1.450(3)	C5	C6	1.540(3)
O51	C15	1.212(2)	C5	C15	1.533(3)
O52	C15	1.314(2)	C6	C7	1.540(3)
O52	C53	1.454(3)	C6	C16	1.511(3)
O61	C16	1.192(3)	C7	C8	1.525(3)
O62	C16	1.324(3)	C8	C18	1.502(3)

Table 8-399. Bond Angles (°) for War-War V at **295 K**

C1	O8	C7	112.7(1)	C5	C6	C7	106.4(1)
C11	O12	C13	116.0(2)	C5	C6	C16	114.1(2)
C12	O22	C23	116.6(2)	C7	C6	C16	115.9(2)
C14	O42	C43	115.4(2)	O7	C7	O8	111.7(1)
C15	O52	C53	117.7(2)	O7	C7	C6	113.5(2)
C16	O62	C63	117.2(2)	O7	C7	C8	105.9(2)
C18	O82	C83	116.6(2)	O8	C7	C6	103.0(1)
O8	C1	C2	111.3(1)	O8	C7	C8	106.9(1)
O8	C1	C5	107.4(1)	C6	C7	C8	115.7(2)
O8	C1	C11	106.9(1)	C7	C8	C18	112.0(2)
C2	C1	C5	102.5(1)	O11	C11	O12	124.5(2)
C2	C1	C11	113.1(1)	O11	C11	C1	125.2(2)
C5	C1	C11	115.5(1)	O12	C11	C1	110.3(2)
C1	C2	C3	112.0(2)	O21	C12	O22	124.1(2)
C1	C2	C12	126.6(2)	O21	C12	C2	122.4(2)
C3	C2	C12	121.4(2)	O22	C12	C2	113.4(2)
O3	C3	C2	128.1(2)	O41	C14	O42	124.8(2)
O3	C3	C4	117.8(2)	O41	C14	C4	124.3(2)
C2	C3	C4	113.9(2)	O42	C14	C4	110.9(2)
C3	C4	C5	103.0(1)	O51	C15	O52	124.3(2)
C3	C4	C14	112.6(2)	O51	C15	C5	122.3(2)
C5	C4	C14	114.8(1)	O52	C15	C5	113.3(2)
C1	C5	C4	105.5(1)	O61	C16	O62	124.0(2)
C1	C5	C6	99.6(1)	O61	C16	C6	124.2(2)
C1	C5	C15	110.1(1)	O62	C16	C6	111.8(2)
C4	C5	C6	113.9(1)	O81	C18	O82	124.1(2)
C4	C5	C15	113.5(1)	O81	C18	C8	124.8(2)
C6	C5	C15	112.9(1)	O82	C18	C8	111.0(2)

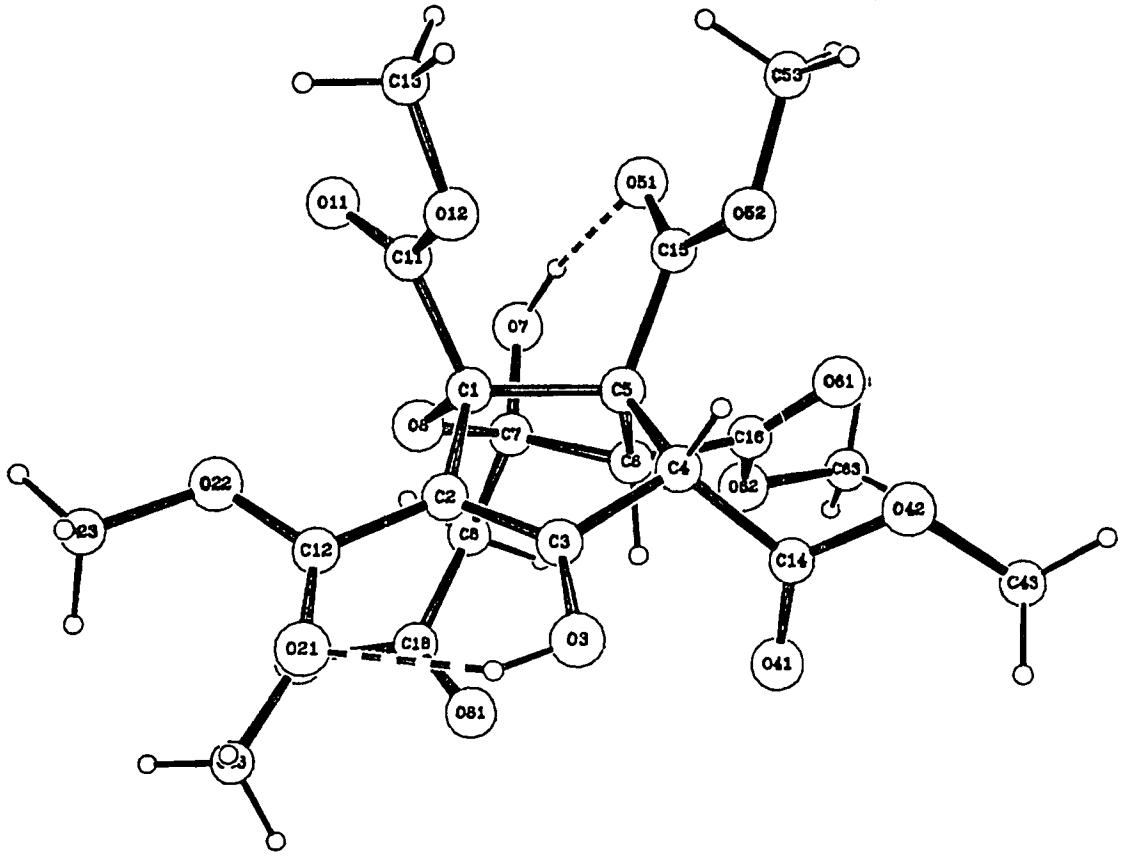
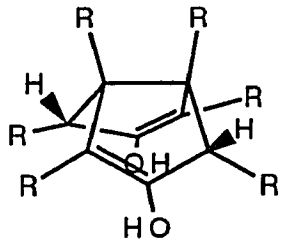


Figure 8–8. *ORTEP* drawing of War-War V at **295 K.**



R = $COOCH_3$

1,2,4,5,6,8-Hexacarbomethoxy-bicyclo[3.3.0]octane-3,7-dione
(War-War VI)

Table 8–400. X-ray Crystal Data for War-War VI at **295 K**

Formula	$C_{20}H_{22}O_{14}$
Formula weight	486.39
Melting point (°C)	210–213
Crystal size (mm)	0.10 x 0.19 x 0.32
Crystal system	monoclinic
Space group	*C2/c*
a (Å)	19.375(2)
b (Å)	8.189(1)
c (Å)	14.841(2)
β (°)	110.82(1)°
Cell volume (Å^3)	2200.94(7.8)
Z	4†
d_{calc} (g cm^{-3})	1.468
μ(Cu $K\alpha$) (cm^{-1})	10.5
Maximum θ (°)	75
Unique reflections	2263
Observed reflections [$I > 3.0\sigma(I)$]	1761
Number of variables	154
R	0.041
R_w	0.054
$(\Delta\rho)_{max}$ (e Å^{-3})	0.21
$(\Delta\rho)_{min}$ (e Å^{-3})	–0.21

† The asymmetric unit contains one half independent molecule. Half of the molecule is related to the other half by a two-fold rotation axis.

Table 8-401. Final Atomic Parameters for War-War VI at **295 K**

Atom	x	y	z	B(Å^2)
O3	0.54638(7)	0.6592(2)	0.07902(8)	3.15(3)
O11	0.37784(7)	0.1816(2)	0.1858(1)	4.28(3)
O12	0.47190(7)	0.1847(2)	0.1326(1)	3.77(3)
O21	0.39974(8)	0.6693(2)	-0.01121(9)	3.58(3)
O22	0.33655(7)	0.4819(2)	0.03967(9)	3.50(3)
O41	0.65084(8)	0.7236(2)	0.2983(1)	4.29(3)
O42	0.71382(6)	0.5062(2)	0.2770(1)	3.77(3)
C1	0.45718(8)	0.4190(2)	0.2158(1)	2.01(3)
C2	0.45807(8)	0.5312(2)	0.1354(1)	2.30(3)
C3	0.52705(8)	0.5690(2)	0.1412(1)	2.27(3)
C4	0.58561(8)	0.4824(2)	0.2204(1)	2.22(3)
C11	0.42931(9)	0.2489(2)	0.1774(1)	2.54(3)
C12	0.39590(9)	0.5701(2)	0.0485(1)	2.71(3)
C13	0.4555(2)	0.0178(3)	0.0999(2)	6.11(6)
C14	0.65293(9)	0.5868(2)	0.2705(1)	2.79(3)
C23	0.2730(1)	0.4996(4)	-0.0482(2)	5.74(7)
C43	0.7831(1)	0.5905(4)	0.3228(2)	5.53(6)
HO3	0.503	0.687	0.033	3.8
H4	0.602	0.386	0.192	2.7
H13A	0.490	-0.018	0.068	7.4
H13B	0.461	-0.055	0.156	7.4
H13C	0.404	0.011	0.053	7.4
H23A	0.232	0.427	-0.045	6.9
H23B	0.256	0.616	-0.055	6.9
H23C	0.287	0.469	-0.105	6.9
H43A	0.825	0.518	0.324	6.7
H43B	0.784	0.693	0.286	6.7
H43C	0.789	0.619	0.391	6.7

The parameters of the hydrogen atoms were not refined.

Table 8-402. Final Anisotropic Thermal Parameters (U's) for War-War VI at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O3	0.0447(6)	0.0428(7)	0.0367(5)	-0.0019(5)	0.0198(4)	0.0097(5)
O11	0.0499(6)	0.0488(7)	0.0740(8)	-0.0216(6)	0.0342(5)	-0.0180(7)
O12	0.0530(6)	0.0393(6)	0.0615(6)	-0.0081(6)	0.0329(4)	-0.0197(6)
O21	0.0502(7)	0.0503(7)	0.0323(5)	0.0088(6)	0.0109(5)	0.0127(6)
O22	0.0308(5)	0.0651(8)	0.0302(5)	-0.0037(6)	0.0025(4)	0.0037(6)
O41	0.0519(7)	0.0445(7)	0.0654(8)	-0.0161(6)	0.0192(6)	-0.0133(7)
O42	0.0262(5)	0.0685(9)	0.0497(6)	-0.0092(6)	0.0147(4)	-0.0096(7)
C1	0.0241(6)	0.0284(7)	0.0241(5)	0.0006(6)	0.0088(4)	-0.0004(6)
C2	0.0306(6)	0.0305(7)	0.0256(6)	0.0005(6)	0.0090(5)	0.0012(6)
C3	0.0337(6)	0.0285(7)	0.0258(6)	-0.0008(6)	0.0125(5)	0.0005(6)
C4	0.0260(6)	0.0307(7)	0.0290(6)	-0.0019(6)	0.0112(4)	-0.0002(6)
C11	0.0298(6)	0.0341(8)	0.0312(6)	-0.0015(6)	0.0093(5)	-0.0033(6)
C12	0.0362(7)	0.0391(8)	0.0270(6)	0.0067(7)	0.0105(5)	0.0008(6)
C13	0.103(1)	0.045(1)	0.102(1)	-0.015(1)	0.059(1)	-0.036(1)
C14	0.0327(7)	0.0436(9)	0.0311(6)	-0.0092(7)	0.0132(5)	-0.0005(7)
C23	0.037(1)	0.126(2)	0.039(1)	-0.005(1)	-0.0059(9)	0.008(1)
C43	0.0305(8)	0.106(2)	0.071(1)	-0.026(1)	0.0148(8)	-0.013(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-403. Bond Distances (Å) for War-War VI at **295 K**

O3	C3	1.336(2)	O42	C43	1.446(3)
O11	C11	1.184(2)	C1	C1	1.608(2)
O12	C11	1.337(3)	C1	C2	1.511(2)
O12	C13	1.448(3)	C1	C4	1.553(2)
O21	C12	1.223(2)	C1	C11	1.529(2)
O22	C12	1.324(2)	C2	C3	1.344(2)
O22	C23	1.447(2)	C2	C12	1.453(2)
O41	C14	1.200(2)	C3	C4	1.491(2)
O42	C14	1.325(2)	C4	C14	1.515(2)

Table 8-404. Bond Angles (°) for War-War VI

C11	O12	C13	115.9(2)	C2	C3	C4	113.7(1)
C12	O22	C23	117.7(2)	C1	C4	C3	102.6(1)
C14	O42	C43	116.8(2)	C1	C4	C14	116.3(1)
C1	C1	C2	101.5(1)	C3	C4	C14	113.5(1)
C1	C1	C4	105.7(1)	O11	C11	O12	124.2(2)
C1	C1	C11	112.6(1)	O11	C11	C1	125.6(2)
C2	C1	C4	115.9(1)	O12	C11	C1	110.2(1)
C2	C1	C11	111.2(1)	O21	C12	O22	124.4(1)
C4	C1	C11	109.7(1)	O21	C12	C2	122.9(2)
C1	C2	C3	112.3(1)	O22	C12	C2	112.6(2)
C1	C2	C12	126.6(1)	O41	C14	O42	125.3(2)
C3	C2	C12	119.9(2)	O41	C14	C4	124.5(2)
O3	C3	C2	126.8(1)	O42	C14	C4	110.1(2)
O3	C3	C4	119.1(1)				

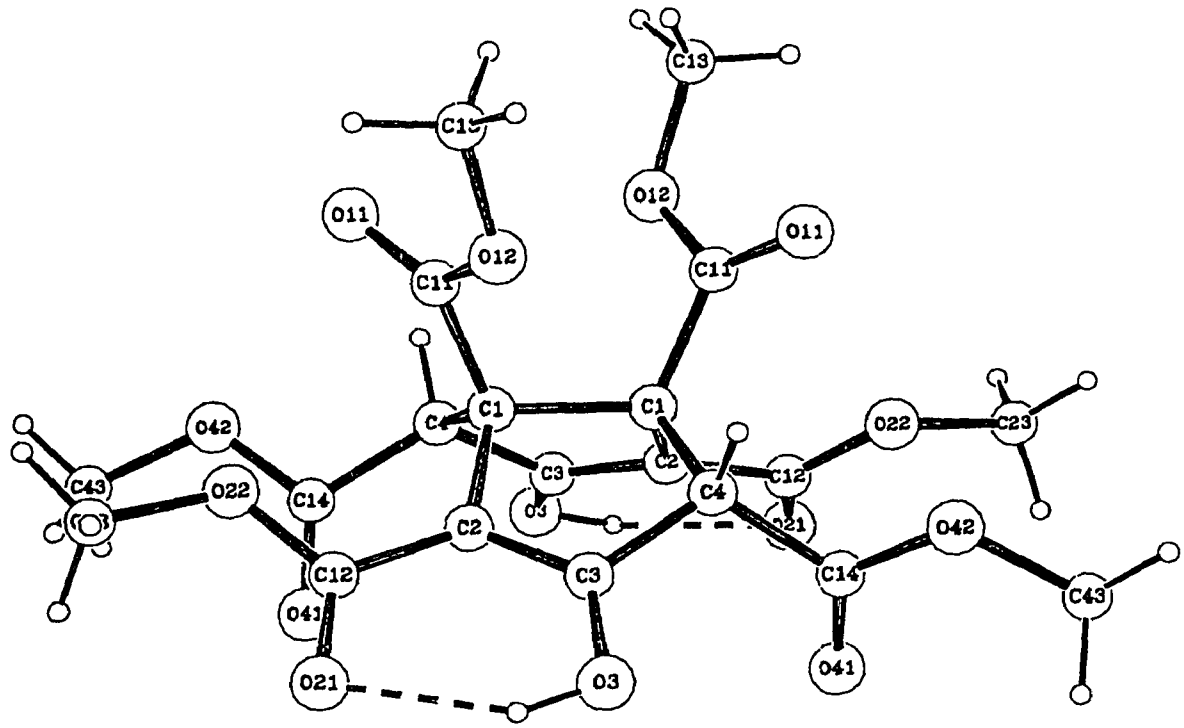
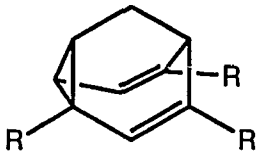


Figure 8–9. *ORTEP* drawing of War-War VI at **295 K.**



R = $COOCH_3$

2,4,6-Tricarbomethoxybarbaralane
(War-War VII)

Table 8–405. X-ray Crystal Data for War-War VII at **295 K**

Formula	$C_{15}H_{16}O_6$
Formula weight	292.29
Melting point (°C)	106–107
Crystal size (mm)	0.06 x 0.31 x 0.38
Crystal system	orthorhombic
Space group	$Pc2_1b$
a (Å)	6.765(1)
b (Å)	9.512(1)
c (Å)	21.735(1)
Cell volume (Å^3)	1398.71(9)
Z	4
d_{calc} (g cm^{-3})	1.388
μ(Cu $K\alpha$) (cm^{-1})	8.7
Maximum θ (°)	75
Unique reflections	1530
Observed reflections [$I > 3.0\sigma(I)$]	1191
Number of variables	189
R	0.036
R_w	0.043
$(\Delta\rho)_{max}$ (e Å^{-3})	0.14
$(\Delta\rho)_{min}$ (e Å^{-3})	–0.13

Table 8-406. Final Atomic Parameters for War-War VII at **295 K**

Atom	x	y	z	B(Å^2)
O1	0.1913(3)	1.016	0.3524(1)	3.77(4)
O2	0.0457(3)	0.9024(3)	0.2747(1)	4.50(5)
O3	0.7826(3)	0.8854(3)	0.4482(1)	4.16(4)
O4	0.9548(3)	0.6974(3)	0.4188(1)	4.96(5)
O5	0.4621(4)	0.3194(3)	0.4159(1)	5.24(5)
O6	0.7749(4)	0.3686(3)	0.3928(2)	5.86(6)
C1	0.3925(4)	0.7211(4)	0.2630(1)	3.20(5)
C2	0.3369(4)	0.8065(3)	0.3200(1)	2.85(5)
C3	0.4925(4)	0.8302(3)	0.3659(1)	2.93(5)
C4	0.6521(4)	0.7469(3)	0.3688(1)	2.82(5)
C5	0.6652(4)	0.6213(3)	0.3267(1)	3.11(5)
C6	0.5213(4)	0.5146(3)	0.3528(1)	3.03(5)
C7	0.3283(4)	0.5347(3)	0.3445(1)	3.09(5)
C8	0.2566(4)	0.6518(3)	0.3072(1)	3.06(5)
C9	0.6011(4)	0.6654(4)	0.2617(1)	3.61(6)
C21	0.1761(4)	0.9115(3)	0.3119(1)	3.25(5)
C22	0.0337(5)	1.1197(4)	0.3521(2)	4.61(7)
C41	0.8126(4)	0.7703(3)	0.4139(1)	3.14(5)
C42	0.9342(6)	0.9156(5)	0.4936(2)	5.28(8)
C61	0.6027(4)	0.3960(4)	0.3888(2)	3.51(6)
C62	0.5261(7)	0.2016(4)	0.4530(2)	6.08(9)
H1	0.335	0.753	0.223	3.8
H3	0.479	0.910	0.396	3.5
H5	0.802	0.582	0.324	3.7
H7	0.232	0.469	0.364	3.7
H8	0.109	0.668	0.304	3.6
H9A	0.692	0.740	0.246	4.3
H9B	0.607	0.582	0.234	4.3
H22A	0.060	1.193	0.384	5.5
H22B	0.027	1.165	0.310	5.5
H22C	-0.095	1.072	0.361	5.5
H42A	0.899	1.003	0.517	6.4
H42B	0.945	0.835	0.523	6.4
H42C	1.064	0.930	0.472	6.4
H62A	0.407	0.153	0.471	7.2
H62B	0.602	0.134	0.427	7.2
H62C	0.612	0.236	0.487	7.2

The parameters of the hydrogen atoms were not refined.

Table 8-407. Final Anisotropic Thermal Parameters (U's) for War-War VII at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.046(1)	0.042(1)	0.056(1)	0.016(1)	-0.004(1)	-0.002(1)
O2	0.052(1)	0.053(1)	0.065(1)	0.008(1)	-0.022(1)	0.004(1)
O3	0.058(1)	0.047(1)	0.053(1)	0.002(1)	-0.022(1)	-0.009(1)
O4	0.049(1)	0.067(2)	0.073(1)	0.019(1)	-0.023(1)	-0.008(1)
O5	0.062(1)	0.047(1)	0.090(2)	0.014(1)	0.008(1)	0.024(1)
O6	0.052(1)	0.059(2)	0.112(2)	0.014(1)	-0.015(1)	0.015(2)
C1	0.043(1)	0.045(1)	0.034(1)	-0.003(1)	-0.002(1)	-0.002(1)
C2	0.036(1)	0.034(1)	0.038(1)	0.003(1)	-0.003(1)	-0.001(1)
C3	0.037(1)	0.035(1)	0.039(1)	0.001(1)	-0.002(1)	0.000(1)
C4	0.033(1)	0.034(1)	0.040(1)	-0.003(1)	-0.001(1)	-0.000(1)
C5	0.029(1)	0.039(1)	0.051(1)	0.002(1)	0.003(1)	-0.007(1)
C6	0.041(1)	0.028(1)	0.046(1)	0.003(1)	0.003(1)	-0.007(1)
C7	0.040(1)	0.034(1)	0.044(1)	-0.000(1)	0.001(1)	-0.004(1)
C8	0.034(1)	0.038(1)	0.044(1)	-0.001(1)	-0.003(1)	-0.003(1)
C9	0.043(1)	0.053(2)	0.041(2)	-0.000(2)	0.006(1)	-0.009(1)
C21	0.038(1)	0.038(1)	0.048(1)	0.000(1)	-0.000(1)	0.006(1)
C22	0.049(2)	0.055(2)	0.071(2)	0.021(1)	0.005(2)	0.008(2)
C41	0.038(1)	0.035(1)	0.046(1)	-0.003(1)	-0.003(1)	0.004(1)
C42	0.069(2)	0.074(3)	0.057(2)	-0.014(2)	-0.026(2)	-0.004(2)
C61	0.046(1)	0.034(1)	0.054(2)	0.007(1)	-0.001(1)	-0.009(1)
C62	0.093(3)	0.045(2)	0.093(2)	0.017(2)	0.001(3)	0.025(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-408. Interatomic Distances (Å) for War-War VII at **295 K**

O1	C21	1.336(3)	C2	C3	1.468(4)
O1	C22	1.449(4)	C2	C8	1.593(4)
O2	C21	1.199(4)	C2	C21	1.488(4)
O3	C41	1.339(4)	C3	C4	1.341(4)
O3	C42	1.453(4)	C4	C5	1.508(4)
O4	C41	1.190(4)	C4	C6	2.405(4)
O5	C61	1.335(4)	C4	C41	1.480(4)
O5	C62	1.445(5)	C5	C6	1.517(4)
O6	C61	1.197(4)	C5	C9	1.535(4)
C1	C2	1.528(4)	C6	C7	1.332(4)
C1	C8	1.484(4)	C6	C61	1.480(4)
C1	C9	1.507(4)	C7	C8	1.461(4)

Table 8-409. Bond Angles (°) for War-War VII at **295 K**

C21	O1	C22	116.5(2)	C6	C5	C9	110.2(2)
C41	O3	C42	115.6(3)	C5	C6	C7	118.8(3)
C61	O5	C62	117.1(3)	C5	C6	C61	118.0(2)
C2	C1	C8	63.8(2)	C7	C6	C61	123.1(3)
C2	C1	C9	115.6(2)	C6	C7	C8	120.7(3)
C8	C1	C9	115.8(3)	C1	C8	C2	59.4(2)
C1	C2	C3	117.1(2)	C1	C8	C7	119.5(2)
C1	C2	C8	56.7(2)	C2	C8	C7	119.6(2)
C1	C2	C21	116.2(2)	C1	C9	C5	110.1(2)
C3	C2	C8	120.4(2)	O1	C21	O2	123.7(3)
C3	C2	C21	120.1(3)	O1	C21	C2	111.6(2)
C8	C2	C21	110.5(2)	O2	C21	C2	124.7(3)
C2	C3	C4	121.3(3)	O3	C41	O4	123.3(3)
C3	C4	C5	119.1(2)	O3	C41	C4	112.3(2)
C3	C4	C41	122.2(3)	O4	C41	C4	124.3(3)
C5	C4	C41	118.6(2)	O5	C61	O6	122.9(3)
C4	C5	C6	105.3(2)	O5	C61	C6	112.6(3)
C4	C5	C9	109.0(3)	O6	C61	C6	124.5(3)

Table 8-410. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for War-War VII at **295 K**

Atom	Min.	Int'med.	Max.
O1	0.167	0.230	0.250
O2	0.180	0.239	0.285
O3	0.176	0.218	0.282
O4	0.173	0.248	0.312
O5	0.181	0.248	0.324
O6	0.187	0.264	0.344
C1	0.181	0.204	0.217
C2	0.179	0.189	0.201
C3	0.185	0.190	0.201
C4	0.175	0.190	0.201
C5	0.166	0.191	0.233
C6	0.157	0.204	0.221
C7	0.179	0.198	0.214
C8	0.181	0.195	0.213
C9	0.183	0.213	0.241
C21	0.187	0.194	0.226
C22	0.175	0.250	0.286
C41	0.182	0.194	0.220
C42	0.182	0.272	0.306
C61	0.168	0.216	0.242
C62	0.174	0.304	0.329

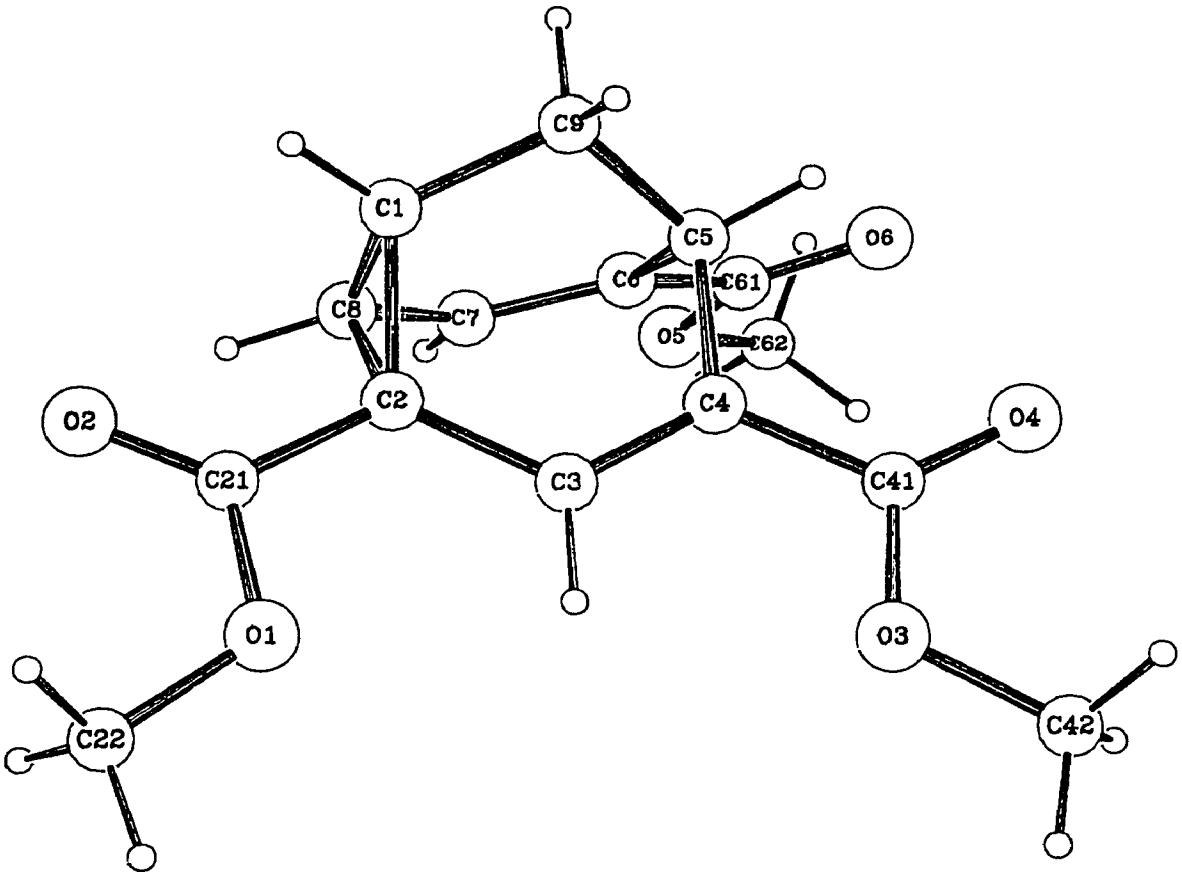
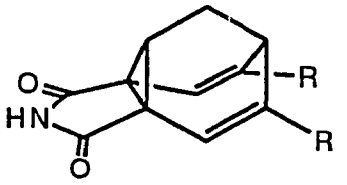


Figure 8–10. *ORTEP* drawing of War-War VII at **295 K.**



R = $COOCH_3$

4,6-DIcarbomethoxy-tricyclo[3.3.1.$0^{2,8}$]nona-3,6-diene-2,8-dicarbooximide
(4,6-DIcarbomethoxy-barbaralane-2,8-dicarbooximide)
(War-War VIII)

Table 8–411. X-ray Crystal Data for War-War VIII at **295 K**

Formula	$C_{15}H_{13}NO_6$
Formula weight	303.27
Melting point (°C)	267–269
Crystal size (mm)	0.05 x 0.13 x 0.30
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	6.863(1)
b (Å)	9.977(1)
c (Å)	10.404(1)
α (°)	92.36(1)
β (°)	106.09(1)
γ (°)	98.92(1)
Cell volume (Å^3)	673.55(0.89)
Z	2
d_{calc} (g cm^{-3})	1.495
μ(Cu $K\alpha$) (cm^{-1})	9.49
Maximum θ (°)	75
Unique reflections	2781
Observed reflections [$I > 3.0\sigma(I)$]	1854
Number of variables	199
R	0.041
R_w	0.051
$(\Delta\rho)_{max}$ (e Å^{-3})	0.23
$(\Delta\rho)_{min}$ (e Å^{-3})	–0.19

Table 8-412. Final Atomic Parameters for War-War VIII at **295 K**

Atom	x	y	z	B(Å^2)
O2	0.2514(3)	0.7902(2)	0.5391(2)	5.02(5)
O3	0.1931(3)	0.1342(2)	0.4735(2)	3.78(4)
O4	0.2093(3)	0.2976(2)	0.3342(2)	4.35(4)
O5	0.7497(3)	0.2586(2)	0.9297(2)	3.67(4)
O6	0.4960(3)	0.1096(2)	0.7881(2)	4.35(4)
O8	0.6591(3)	0.7698(2)	0.9598(2)	3.72(4)
N1	0.4299(3)	0.8108(2)	0.7635(2)	3.51(4)
C1	0.2051(3)	0.5483(2)	0.7712(2)	2.81(4)
C2	0.2987(3)	0.5917(2)	0.6600(2)	2.78(4)
C3	0.2754(3)	0.4925(2)	0.5475(2)	2.84(4)
C4	0.2498(3)	0.3595(2)	0.5643(2)	2.67(4)
C5	0.2494(3)	0.3148(2)	0.7018(2)	2.59(4)
C6	0.4680(3)	0.3438(2)	0.7938(2)	2.60(4)
C7	0.5574(3)	0.4728(2)	0.8397(2)	2.71(4)
C8	0.4388(3)	0.5831(2)	0.8045(2)	2.67(4)
C9	0.1190(3)	0.3990(2)	0.7614(2)	2.99(5)
C21	0.3180(4)	0.7401(2)	0.6420(3)	3.38(5)
C41	0.2172(4)	0.2634(2)	0.4451(2)	2.93(4)
C42	0.1454(6)	0.0329(3)	0.3614(3)	5.27(8)
C61	0.5704(4)	0.2251(2)	0.8338(2)	2.92(4)
C62	0.8506(4)	0.1462(3)	0.9797(3)	4.58(6)
C81	0.5272(4)	0.7289(2)	0.8562(2)	3.03(5)
HN1	0.439	0.906	0.782	4.2
H1	0.133	0.614	0.807	3.4
H3	0.279	0.524	0.458	3.4
H5	0.191	0.215	0.693	3.1
H7	0.704	0.493	0.897	3.3
H9A	-0.026	0.382	0.702	3.6
H9B	0.121	0.371	0.853	3.6
H42A	0.131	-0.060	0.394	6.3
H42B	0.014	0.044	0.295	6.3
H42C	0.259	0.045	0.318	6.3
H62A	0.982	0.182	1.051	5.5
H62B	0.758	0.083	1.019	5.5
H62C	0.880	0.096	0.904	5.5

The parameters of the hydrogen atoms were not refined.

Table 8-413. Final Anisotropic Thermal Parameters (U's) for War-War VIII at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O2	0.078(1)	0.0360(8)	0.066(1)	0.0141(8)	-0.001(1)	0.0188(7)
O3	0.072(1)	0.0276(7)	0.0426(8)	0.0061(7)	0.0154(7)	0.0008(6)
O4	0.087(1)	0.0394(8)	0.0438(8)	0.0122(8)	0.0250(8)	0.0074(7)
O5	0.0421(8)	0.0333(7)	0.0595(9)	0.0148(6)	0.0027(7)	0.0052(7)
O6	0.068(1)	0.0251(7)	0.061(1)	0.0135(7)	-0.0009(9)	-0.0042(7)
O8	0.0498(9)	0.0339(7)	0.0504(9)	0.0004(7)	0.0073(7)	-0.0030(7)
N1	0.049(1)	0.0223(7)	0.060(1)	0.0094(7)	0.0102(9)	0.0024(8)
C1	0.035(1)	0.0281(8)	0.043(1)	0.0085(8)	0.0098(9)	0.0020(8)
C2	0.036(1)	0.0250(8)	0.043(1)	0.0079(7)	0.0075(9)	0.0063(8)
C3	0.037(1)	0.0280(9)	0.041(1)	0.0060(8)	0.0070(9)	0.0050(8)
C4	0.034(1)	0.0269(8)	0.038(1)	0.0054(8)	0.0057(8)	0.0034(8)
C5	0.035(1)	0.0227(8)	0.038(1)	0.0024(7)	0.0064(8)	0.0023(7)
C6	0.037(1)	0.0255(8)	0.0373(9)	0.0082(7)	0.0103(8)	0.0058(7)
C7	0.037(1)	0.0256(8)	0.039(1)	0.0074(7)	0.0072(8)	0.0037(8)
C8	0.034(1)	0.0239(8)	0.040(1)	0.0055(7)	0.0054(8)	0.0015(8)
C9	0.036(1)	0.0331(9)	0.044(1)	0.0049(8)	0.0119(9)	0.0048(9)
C21	0.043(1)	0.0263(9)	0.057(1)	0.0097(8)	0.008(1)	0.0082(9)
C41	0.041(1)	0.0292(9)	0.040(1)	0.0059(8)	0.0093(9)	0.0038(8)
C42	0.118(2)	0.030(1)	0.051(1)	0.005(1)	0.028(1)	-0.005(1)
C61	0.044(1)	0.0280(8)	0.040(1)	0.0111(8)	0.0114(9)	0.0028(8)
C62	0.059(1)	0.050(1)	0.066(2)	0.033(1)	0.006(1)	0.010(1)
C81	0.042(1)	0.0266(9)	0.047(1)	0.0059(8)	0.0142(9)	0.0011(8)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-414. Interatomic Distances (Å) for War-War VIII at **295 K**

O2	C21	1.203(3)	C2	C3	1.458(3)
O3	C41	1.330(3)	C2	C8	1.558(3)
O3	C42	1.442(3)	C2	C21	1.491(3)
O4	C41	1.205(3)	C3	C4	1.336(3)
O5	C61	1.337(2)	C4	C5	1.516(3)
O5	C62	1.449(3)	C4	C6	2.468(3)
O6	C61	1.205(2)	C4	C41	1.480(3)
O8	C81	1.207(2)	C5	C6	1.516(3)
N1	C21	1.381(3)	C5	C9	1.546(4)
N1	C81	1.386(3)	C6	C7	1.343(3)
C1	C2	1.518(3)	C6	C61	1.485(3)
C1	C8	1.524(3)	C7	C8	1.468(3)
C1	C9	1.503(3)	C8	C81	1.502(3)

Table 8-415. Bond Angles (°) for War-War VIII at **295 K**

C41	O3	C42	116.1(2)	C7	C6	C61	122.9(2)
C61	O5	C62	115.8(2)	C6	C7	C8	119.4(2)
C21	N1	C81	113.3(2)	C1	C8	C2	59.0(1)
C2	C1	C8	61.6(1)	C1	C8	C7	118.0(2)
C2	C1	C9	114.9(2)	C1	C8	C81	114.4(2)
C8	C1	C9	115.2(2)	C2	C8	C7	122.7(2)
C1	C2	C3	118.7(2)	C2	C8	C81	104.2(2)
C1	C2	C8	59.4(1)	C7	C8	C81	122.1(2)
C1	C2	C21	114.4(2)	C1	C9	C5	110.1(2)
C3	C2	C8	123.3(2)	O2	C21	N1	125.7(2)
C3	C2	C21	120.8(2)	O2	C21	C2	126.2(2)
C8	C2	C21	104.9(2)	N1	C21	C2	108.1(2)
C2	C3	C4	119.9(2)	O3	C41	O4	123.7(2)
C3	C4	C5	119.0(2)	O3	C41	C4	112.2(2)
C3	C4	C41	117.4(2)	O4	C41	C4	124.1(2)
C5	C4	C41	123.6(2)	O5	C61	O6	123.3(2)
C4	C5	C6	108.9(2)	O5	C61	C6	113.1(2)
C4	C5	C9	109.2(2)	O6	C61	C6	123.5(2)
C6	C5	C9	107.9(2)	O8	C81	N1	125.1(2)
C5	C6	C7	119.6(2)	O8	C81	C8	127.0(2)
C5	C6	C61	117.4(2)	N1	C81	C8	107.9(2)

Table 8-416. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for War-War VIII at **295 K**

Atom	Min.	Int'med.	Max.
O2	0.161	0.244	0.324
O3	0.165	0.207	0.271
O4	0.191	0.205	0.295
O5	0.160	0.208	0.266
O6	0.150	0.223	0.305
O8	0.175	0.225	0.245
N1	0.145	0.219	0.254
C1	0.162	0.189	0.211
C2	0.152	0.189	0.217
C3	0.165	0.188	0.213
C4	0.163	0.179	0.207
C5	0.150	0.183	0.206
C6	0.154	0.193	0.195
C7	0.157	0.187	0.208
C8	0.154	0.180	0.213
C9	0.180	0.191	0.211
C21	0.154	0.206	0.250
C41	0.170	0.196	0.209
C42	0.166	0.228	0.348
C61	0.160	0.200	0.213
C62	0.154	0.256	0.292
C81	0.162	0.202	0.219

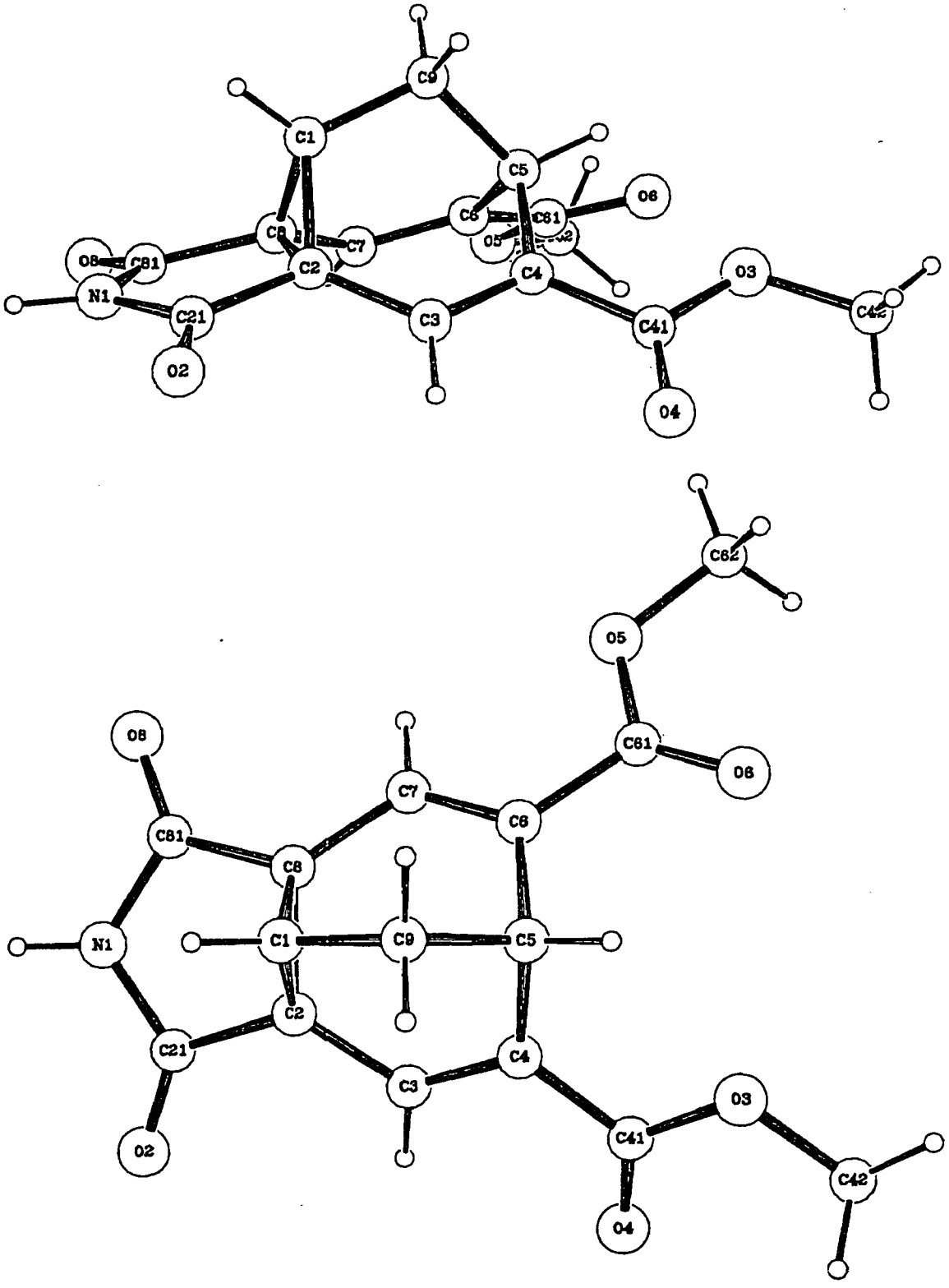


Figure 8–11. *ORTEP* drawings of War-War VIII at **295 K.**

Table 8-418. Final Atomic Parameters for War-War IX at **295 K**

Atom	x	y	z	B(Å^2)
O1	0.14211(7)	0.2203(2)	0.5353(2)	4.78(4)
O2	0.16750(8)	0.1102(2)	0.3701(2)	5.09(4)
O3	0.05051(7)	0.0284(2)	0.1763(2)	3.99(4)
C1	0.0408(1)	0.3840(3)	0.3608(2)	3.57(5)
C2	0.06814(9)	0.2373(3)	0.3262(2)	3.21(5)
C3	0.05135(9)	0.1895(3)	0.1838(2)	3.14(5)
C8	0.01483(9)	0.2406(3)	0.3919(2)	3.30(5)
C9	0.000	0.4785(4)	0.250	4.11(8)
C21	0.1310(1)	0.1826(3)	0.4096(2)	3.57(5)
C22	0.1994(1)	0.1601(4)	0.6249(3)	5.34(7)
C31	0.09717(9)	0.2496(3)	0.1122(2)	3.43(5)
C32	0.0951(1)	0.1889(4)	-0.0086(3)	5.03(7)
C33	0.1349(1)	0.2415(4)	-0.0789(3)	6.21(8)
C34	0.1777(1)	0.3531(4)	-0.0279(3)	5.50(7)
C35	0.1799(1)	0.4170(3)	0.0914(3)	5.00(7)
C36	0.1392(1)	0.3664(3)	0.1606(3)	4.12(6)
HO3	0.087	0.002	0.235	4.8
H1	0.069	0.440	0.437	4.3
H22A	0.203	0.195	0.716	6.4
H22B	0.198	0.048	0.622	6.4
H22C	0.237	0.195	0.599	6.4
H8	0.028	0.213	0.487	4.0
H9	0.028	0.543	0.215	4.9
H32	0.065	0.106	-0.046	6.0
H33	0.132	0.198	-0.167	7.5
H34	0.207	0.388	-0.077	6.6
H35	0.211	0.500	0.128	6.0
H36	0.140	0.414	0.246	4.9

The parameters of the hydrogen atoms were not refined.

Table 8-419. Final Anisotropic Thermal Parameters (U's) for War-War IX at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0342(7)	0.086(1)	0.0500(9)	0.0080(9)	-0.0055(7)	0.000(1)
O2	0.0435(8)	0.085(1)	0.061(1)	0.0223(9)	0.0094(7)	0.011(1)
O3	0.0406(8)	0.0402(9)	0.064(1)	0.0002(7)	0.0048(7)	0.0002(9)
C1	0.0298(9)	0.047(1)	0.051(1)	-0.004(1)	-0.0004(9)	-0.006(1)
C2	0.0235(8)	0.047(1)	0.046(1)	-0.002(1)	0.0008(8)	0.001(1)
C3	0.0286(9)	0.039(1)	0.047(1)	-0.0014(9)	0.0028(9)	0.001(1)
C8	0.0264(8)	0.051(1)	0.044(1)	-0.001(1)	0.0029(8)	-0.001(1)
C9	0.037(2)	0.044(2)	0.066(2)	0	0.001(2)	0
C21	0.0276(9)	0.051(1)	0.051(1)	-0.002(1)	0.0031(9)	0.008(1)
C22	0.034(1)	0.103(2)	0.053(2)	0.007(1)	-0.007(1)	0.019(2)
C31	0.0280(8)	0.047(1)	0.052(1)	0.004(1)	0.0067(9)	0.007(1)
C32	0.056(1)	0.068(2)	0.075(2)	-0.005(1)	0.032(1)	-0.012(1)
C33	0.074(1)	0.083(2)	0.095(2)	-0.003(2)	0.050(1)	-0.004(2)
C34	0.047(1)	0.078(2)	0.092(2)	0.012(1)	0.034(1)	0.025(2)
C35	0.037(1)	0.062(2)	0.082(2)	-0.003(1)	0.002(1)	0.029(1)
C36	0.034(1)	0.057(2)	0.056(1)	-0.005(1)	-0.002(1)	0.013(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-420. Bond Distances (Å) for War-War IX at **295 K**

O1	C21	1.334(3)	C2	C21	1.492(3)
O1	C22	1.446(3)	C3	C8	1.515(3)
O2	C21	1.199(3)	C3	C31	1.528(4)
O3	C3	1.442(3)	C31	C32	1.387(4)
C1	C2	1.532(3)	C31	C36	1.391(3)
C1	C8	1.480(4)	C32	C33	1.388(5)
C1	C9	1.517(3)	C33	C34	1.371(4)
C2	C3	1.516(3)	C34	C35	1.383(4)
C2	C8	1.531(3)	C35	C36	1.390(4)

Table 8-421. Bond Angles (°) for War-War IX at **295 K**

C21	O1	C22	116.0(2)	C1	C8	C2	61.1(2)
C2	C1	C8	61.1(2)	C1	C8	C3	121.0(2)
C2	C1	C9	118.3(2)	C2	C8	C3	119.7(2)
C8	C1	C9	118.5(2)	C1	C9	C1	112.2(3)
C1	C2	C3	119.0(2)	O1	C21	O2	123.0(2)
C1	C2	C8	57.8(2)	O1	C21	C2	112.5(2)
C1	C2	C21	119.8(2)	O2	C21	C2	124.5(2)
C3	C2	C8	117.9(2)	C3	C31	C32	118.6(2)
C3	C2	C21	114.7(2)	C3	C31	C36	122.9(2)
C8	C2	C21	115.7(2)	C32	C31	C36	118.5(2)
O3	C3	C2	109.4(2)	C31	C32	C33	120.9(3)
O3	C3	C8	106.1(2)	C32	C33	C34	120.0(3)
O3	C3	C31	108.9(2)	C33	C34	C35	120.1(3)
C2	C3	C8	111.4(2)	C34	C35	C36	119.9(3)
C2	C3	C31	113.4(2)	C31	C36	C35	120.6(3)
C8	C3	C31	107.4(2)				

Table 8-422. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for War-War IX at **295 K**

Atom	Min.	Int'med.	Max.
O1	0.161	0.260	0.297
O2	0.182	0.256	0.308
O3	0.197	0.201	0.269
C1	0.160	0.217	0.251
C2	0.148	0.214	0.232
C3	0.165	0.197	0.231
C8	0.159	0.221	0.226
C9	0.185	0.210	0.279
C21	0.163	0.211	0.254
C22	0.155	0.263	0.331
C31	0.164	0.212	0.242
C32	0.209	0.247	0.294
C33	0.215	0.287	0.328
C34	0.194	0.242	0.336
C35	0.187	0.207	0.335
C36	0.173	0.215	0.283

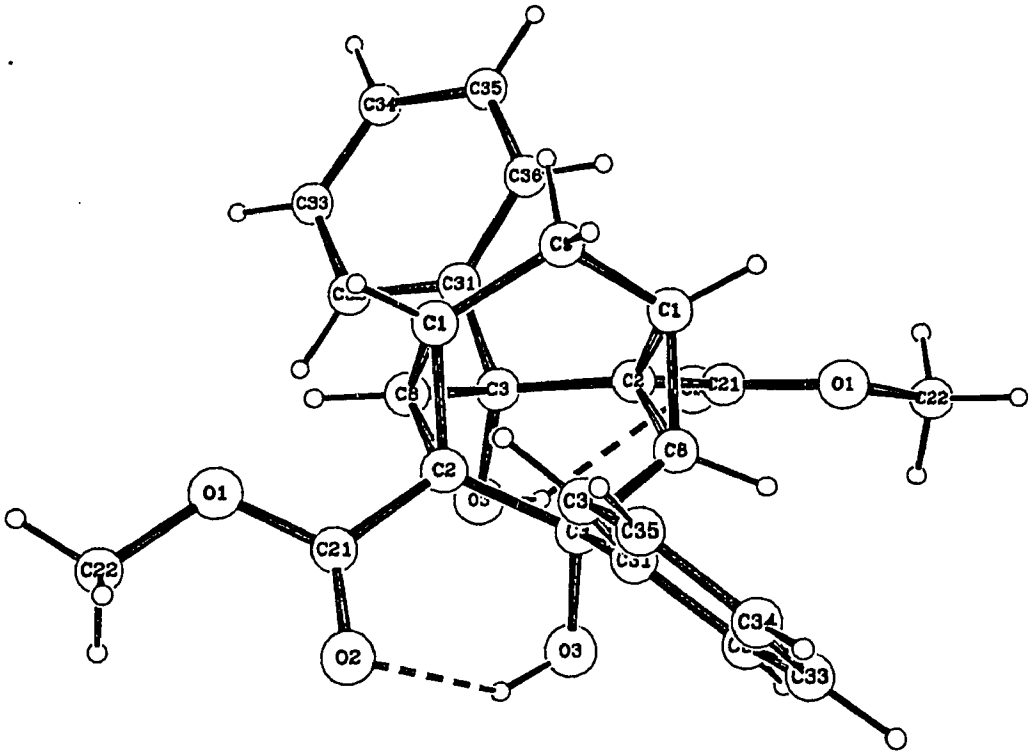


Figure 8–12. *ORTEP* drawing of War-War IX at **295 K.**

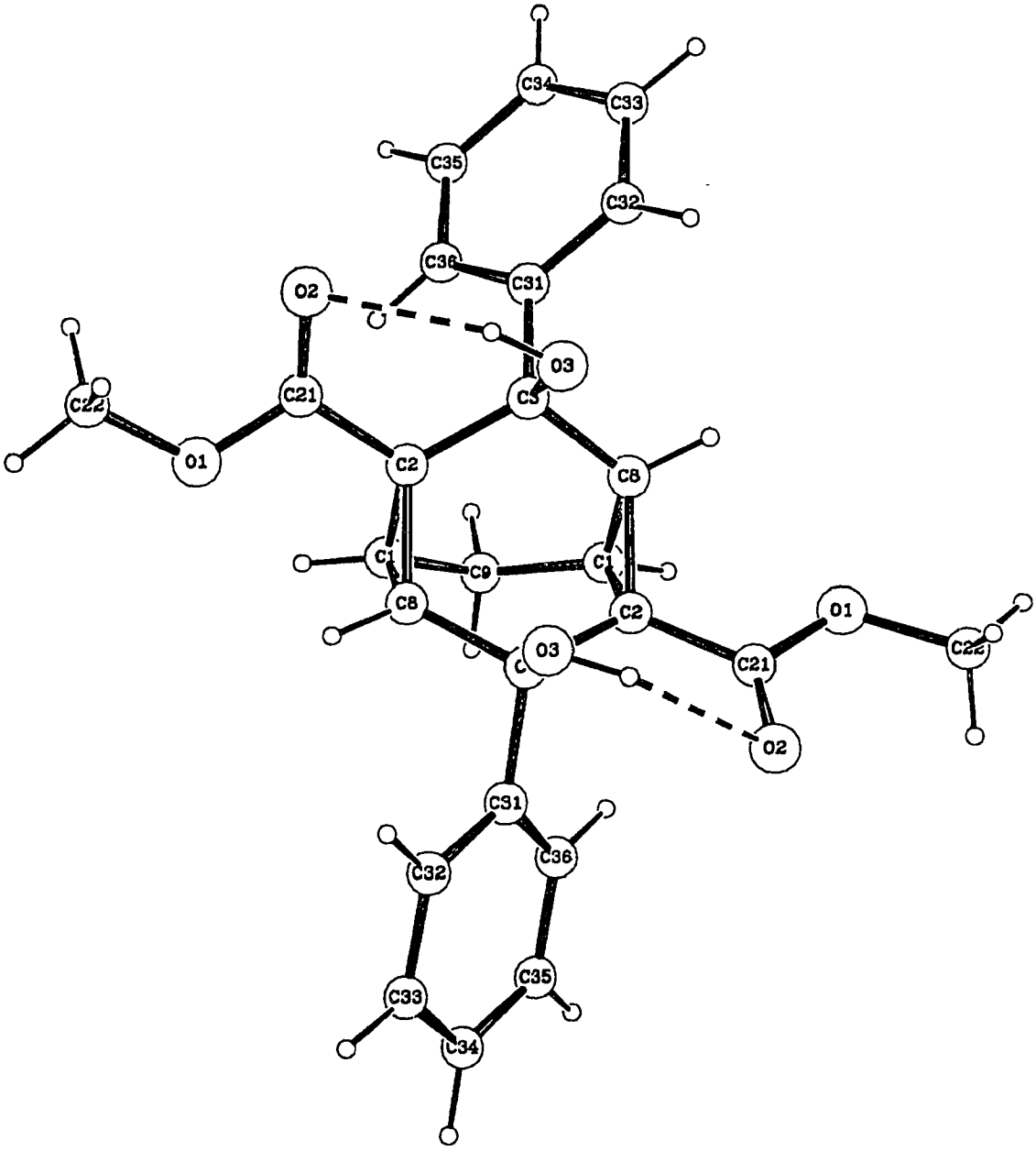
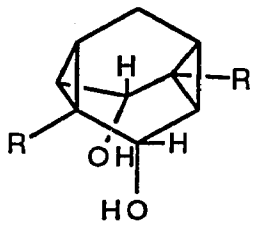


Figure 8–13. *ORTEP* drawing of War-War IX at **295 K.**



R = $COOCH_3$

2,6-Dicarbomethoxy-tetracyclo[3.3.1.$0^{2,8}0^{4,6}$]nonane-3,7-endoendodiol
(War War X)

Table 8–423. X-ray Crystal Data for War War X at **295 K**

Formula	$C_{13}H_{16}O_6$
Formula weight	268.27
Melting point (°C)	143–145
Crystal size (mm)	
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	8.690(2)
b (Å)	10.855(5)
c (Å)	13.274(2)
β (°)	95.31(3)
Cell volume (Å^3)	1246.74(2.83)
Z	4
d_{calc} (g cm^{-3})	1.429
μ(Cu $K\alpha$) (cm^{-1})	9.19
Maximum θ (°)	75
Unique reflections	2571
Observed reflections [$I > 3.0\sigma(I)$]	2083
Number of variables	176
R	0.057
R_w	0.078
$(\Delta\rho)_{max}$ (e Å^{-3})	0.30
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.34

Table 8-424. Final Atomic Parameters for War War X at **295 K**

Atom	x	y	z	B(Å^2)
O1	0.8173(2)	0.5228(2)	0.3101(2)	5.08(4)
O2	0.8871(2)	0.7044(2)	0.2523(1)	4.99(4)
O3	0.6265(2)	0.6092(2)	0.4783(1)	3.78(3)
O5	0.1231(2)	0.7539(2)	0.4573(1)	4.25(3)
O6	0.2269(2)	0.9407(2)	0.4736(1)	4.29(3)
O7	0.5699(2)	0.8661(2)	0.4832(1)	3.61(3)
C1	0.5490(3)	0.7491(2)	0.2182(2)	3.78(4)
C2	0.6346(2)	0.6806(2)	0.3067(1)	3.06(4)
C3	0.5466(2)	0.6060(2)	0.3779(2)	3.24(4)
C4	0.3818(2)	0.6482(2)	0.3808(2)	3.34(4)
C5	0.2994(2)	0.7100(2)	0.2906(2)	3.60(4)
C6	0.3548(2)	0.7868(2)	0.3836(2)	3.03(4)
C7	0.4955(2)	0.8678(2)	0.3817(1)	3.11(4)
C8	0.6073(2)	0.8199(2)	0.3089(2)	3.52(4)
C9	0.3787(3)	0.7263(3)	0.1957(2)	4.18(5)
C21	0.7925(2)	0.6399(2)	0.2878(2)	3.53(4)
C22	0.9682(3)	0.4752(3)	0.2934(3)	6.38(8)
C61	0.2325(2)	0.8365(2)	0.4428(2)	3.29(4)
C62	-0.0080(3)	0.7974(3)	0.5067(2)	5.34(6)
O3B	0.596(2)	0.542(2)	0.440(2)	6.3(5)*
HO3	0.624	0.690	0.498	4.5
HO7	0.635	0.932	0.493	3.9
H1	0.608	0.761	0.158	4.1
H3	0.543	0.519	0.352	3.5
H4	0.316	0.597	0.422	3.6
H5	0.186	0.696	0.280	3.9
H7	0.465	0.952	0.358	3.4
H8	0.690	0.885	0.312	3.8
H9A	0.362	0.650	0.154	4.5
H9B	0.330	0.798	0.157	4.5
H22A	0.975	0.386	0.312	6.9
H22B	0.984	0.484	0.220	6.9
H22C	1.050	0.522	0.335	6.9
H62A	-0.083	0.728	0.513	5.7
H62B	0.027	0.830	0.575	5.7
H62C	-0.062	0.865	0.465	5.7

The parameters of the hydrogen atoms were not refined.
The starred atom O3b was refined isotropically with occupancy of 0.10
Atom O3 was refined with an occupancy of 0.90

Table 8-425. Final Anisotropic Thermal Parameters (U's) for War War X at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0447(8)	0.0456(9)	0.106(1)	0.0038(7)	0.0242(8)	0.000(1)
O2	0.0451(7)	0.068(1)	0.080(1)	-0.0018(8)	0.0250(7)	0.0091(9)
O3	0.0419(8)	0.059(1)	0.0418(8)	0.0038(7)	-0.0002(6)	0.0127(8)
O5	0.0370(6)	0.064(1)	0.0626(9)	-0.0046(7)	0.0150(6)	-0.0063(8)
O6	0.0419(7)	0.055(1)	0.0666(9)	0.0010(7)	0.0090(7)	-0.0132(8)
O7	0.0450(7)	0.0555(9)	0.0359(6)	-0.0054(7)	-0.0009(6)	-0.0064(7)
C1	0.051(1)	0.060(1)	0.0331(9)	0.007(1)	0.0078(8)	0.0034(9)
C2	0.0353(8)	0.044(1)	0.0374(8)	-0.0022(8)	0.0049(7)	-0.0013(8)
C3	0.0352(8)	0.045(1)	0.0421(9)	-0.0000(8)	0.0027(8)	0.0026(9)
C4	0.0329(8)	0.047(1)	0.047(1)	-0.0019(8)	0.0039(8)	-0.000(1)
C5	0.0363(9)	0.054(1)	0.045(1)	0.0017(9)	-0.0028(8)	-0.008(1)
C6	0.0318(8)	0.048(1)	0.0353(8)	0.0008(8)	0.0012(7)	-0.0024(8)
C7	0.0357(8)	0.048(1)	0.0337(8)	-0.0007(8)	0.0024(7)	-0.0002(8)
C8	0.0402(9)	0.055(1)	0.0393(9)	-0.0024(9)	0.0076(8)	-0.0013(9)
C9	0.051(1)	0.070(2)	0.036(1)	0.008(1)	-0.0039(9)	-0.006(1)
C21	0.0370(9)	0.053(1)	0.045(1)	-0.0034(9)	0.0082(8)	-0.006(1)
C22	0.047(1)	0.062(2)	0.135(3)	0.011(1)	0.023(1)	-0.009(2)
C61	0.0333(8)	0.053(1)	0.0384(9)	-0.0002(8)	-0.0016(7)	-0.0006(9)
C62	0.042(1)	0.092(2)	0.072(1)	-0.000(1)	0.0224(9)	-0.008(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-426. Bond Distances (A) for War War X AT **295 K**

O1	C21	1.318(3)	C2	C3	1.506(3)
O1	C22	1.446(3)	C2	C8	1.531(3)
O2	C21	1.209(3)	C2	C21	1.485(3)
O3	C3	1.445(2)	C3	C4	1.507(3)
O5	C61	1.334(3)	C4	C5	1.496(3)
O5	C62	1.445(3)	C4	C6	1.524(3)
O6	C61	1.205(3)	C5	C6	1.530(3)
O7	C7	1.439(2)	C5	C9	1.501(3)
C1	C2	1.524(3)	C6	C7	1.508(3)
C1	C8	1.478(3)	C6	C61	1.481(3)
C1	C9	1.503(3)	C7	C8	1.524(3)

Table 8-427. Bond Angles (') for War War X AT **295 K**

C21	O1	C22	116.3(2)	C4	C6	C5	58.7(1)
C61	O5	C62	116.6(2)	C4	C6	C7	116.6(2)
C2	C1	C8	61.3(1)	C4	C6	C61	119.5(2)
C2	C1	C9	118.3(2)	C5	C6	C7	120.0(2)
C8	C1	C9	120.3(2)	C5	C6	C61	116.0(2)
C1	C2	C3	120.4(2)	C7	C6	C61	114.8(2)
C1	C2	C8	57.8(1)	O7	C7	C6	105.8(2)
C1	C2	C21	114.1(2)	O7	C7	C8	109.4(2)
C3	C2	C8	115.5(2)	C6	C7	C8	112.1(2)
C3	C2	C21	118.4(2)	C1	C8	C2	60.9(1)
C8	C2	C21	116.4(2)	C1	C8	C7	120.2(2)
O3	C3	C2	109.7(2)	C2	C8	C7	117.3(2)
O3	C3	C4	110.2(2)	C1	C9	C5	111.9(2)
C2	C3	C4	113.0(2)	O1	C21	O2	122.9(2)
C3	C4	C5	120.1(2)	O1	C21	C2	112.6(2)
C3	C4	C6	116.7(2)	O2	C21	C2	124.5(2)
C5	C4	C6	60.8(1)	O5	C61	O6	122.1(2)
C4	C5	C6	60.5(1)	O5	C61	C6	112.8(2)
C4	C5	C9	120.1(2)	O6	C61	C6	125.1(2)
C6	C5	C9	118.6(2)				

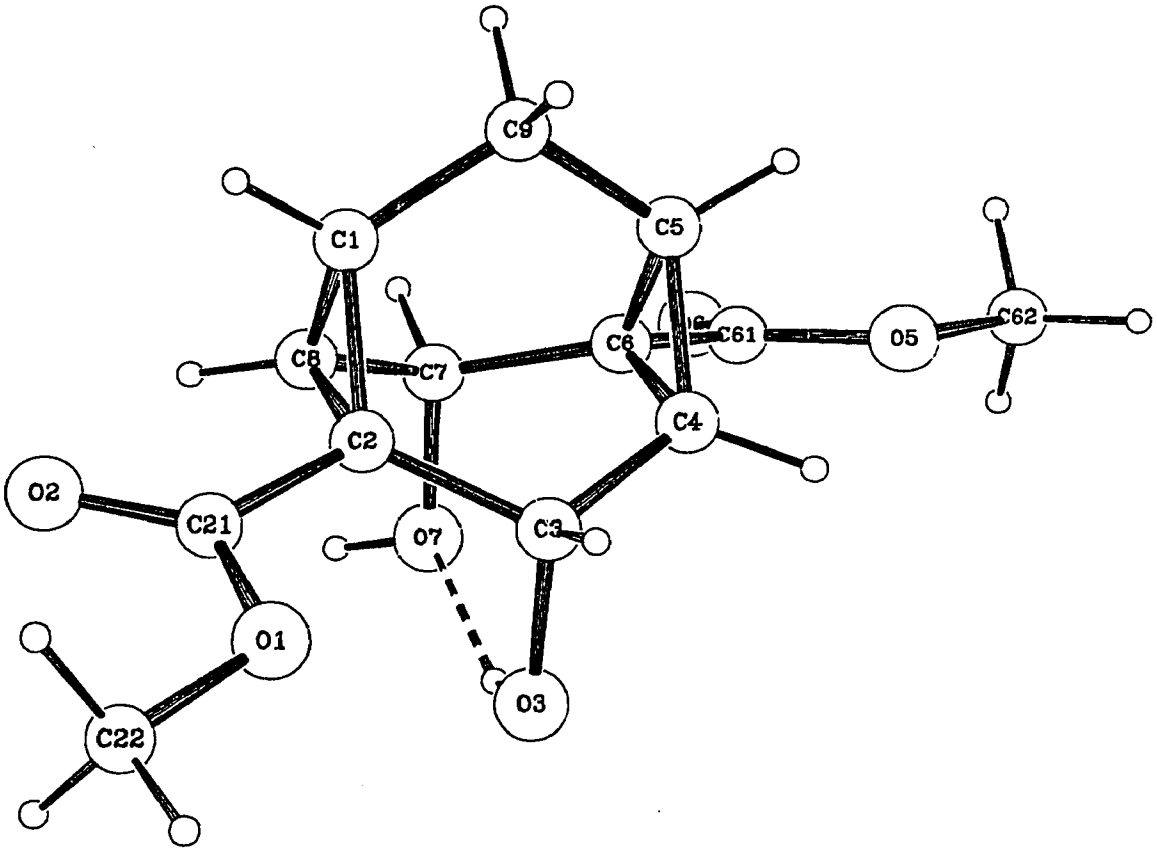
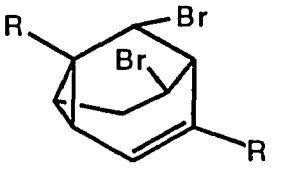


Figure 8–14. *ORTEP* drawing of War War X at **295 K.**



R = $COOCH_3$

6,9 Dibromo-1,4-dicarbomethoxy-tricyclo[3.3.1.$0^{2,8}$]nonane-3-ene
(War War XI)

Table 8–428. X-ray Crystal Data for War War XI at **295 K**

Formula	$C_{13}H_{14}Br_2O_4$
Formula weight	394.07
Melting point (°C)	121–123
Crystal size (mm)	0.11 x 0.26 x 0.50
Crystal system	monoclinic
Space group	*Cc*
a (Å)	30.750(2)
b (Å)	6.853(1)
c (Å)	14.499(1)
β (°)	113.82(1)
Cell volume (Å^3)	2795.11(5.51)
Z	8
d_{calc} (g cm^{-3})	1.873
μ(Cu $K\alpha$) (cm^{-1})	75.09
Maximum θ (°)	75
Unique reflections	2878
Observed reflections [$I > 3.0\sigma(I)$]	2503
Number of variables	341
R	0.037
R_w	0.049
$(\Delta\rho)_{max}$ (e Å^{-3})	0.55
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.77

Table 8-429. Final Atomic Parameters for War War XI at **295 K**

Atom	x	y	z	B(Å^2)
Br1	0.323	0.1613(1)	0.441	3.92(1)
Br2	0.47971(3)	0.3167(1)	0.70878(5)	4.21(2)
O11	0.4995(2)	0.3531(7)	0.4297(4)	4.2(1)
O12	0.4815(2)	0.0988(8)	0.4980(4)	5.0(1)
O41	0.4087(2)	0.9133(7)	0.7079(3)	4.1(1)
O42	0.3500(2)	0.7026(8)	0.6793(3)	4.5(1)
C1	0.4451(2)	0.3866(7)	0.5005(4)	3.0(1)
C2	0.4462(2)	0.6067(8)	0.4933(4)	2.53(9)
C3	0.4320(2)	0.7283(9)	0.5602(4)	3.1(1)
C4	0.4033(2)	0.6530(8)	0.6000(5)	3.1(1)
C5	0.3870(2)	0.4375(8)	0.5760(4)	2.8(1)
C6	0.3451(2)	0.4343(9)	0.4769(4)	2.6(1)
C7	0.3565(2)	0.526(1)	0.3940(5)	4.1(2)
C8	0.4085(2)	0.4999(8)	0.4074(4)	2.9(1)
C9	0.4272(2)	0.3196(7)	0.5732(4)	2.8(1)
C11	0.4768(2)	0.2652(8)	0.4783(4)	2.9(1)
C12	0.5267(2)	0.239(1)	0.3900(5)	3.8(1)
C41	0.3818(2)	0.7619(9)	0.6585(4)	3.4(1)
C42	0.3904(3)	1.0340(9)	0.7704(4)	4.0(1)
Br1'	0.76896(2)	0.1586(1)	1.12083(5)	3.94(1)
Br2'	0.61131(3)	0.3129(1)	0.85341(5)	3.97(2)
O11'	0.5957(2)	0.3479(7)	1.1427(3)	3.94(9)
O12'	0.6099(2)	0.0865(7)	1.0645(3)	4.2(1)
O41'	0.6863(2)	0.9249(6)	0.8609(3)	3.35(8)
O42'	0.7463(2)	0.7164(8)	0.8915(4)	4.8(1)
C1'	0.6501(2)	0.3971(9)	1.0658(4)	2.4(1)
C2'	0.6439(2)	0.6225(8)	1.0677(5)	3.7(1)
C3'	0.6597(2)	0.7210(9)	0.9936(5)	2.9(1)
C4'	0.6903(2)	0.6458(8)	0.9603(4)	2.8(1)
C5'	0.7066(2)	0.4424(8)	0.9824(4)	2.6(1)
C6'	0.7484(2)	0.434(1)	1.0879(5)	4.1(1)
C7'	0.7355(2)	0.5262(9)	1.1702(4)	3.2(1)
C8'	0.6842(2)	0.515(1)	1.1496(4)	3.2(1)
C9'	0.6665(2)	0.3099(8)	0.9866(4)	2.6(1)
C11'	0.6158(2)	0.257(1)	1.0894(5)	3.2(1)
C12'	0.5661(3)	0.215(1)	1.1756(6)	6.0(2)
C41'	0.7095(2)	0.756(1)	0.8943(4)	3.0(1)
C42'	0.7034(2)	1.030(1)	0.8001(5)	4.7(1)

Table 8-429 (cont.). Final Atomic Parameters for War War XI at **295 K**

Atom	x	y	z	B(Å^2)
H2	0.473	0.703	0.502	3.2
H3	0.444	0.865	0.577	3.5
H5	0.375	0.383	0.627	3.2
H6	0.322	0.524	0.485	2.9
H7A	0.347	0.660	0.386	4.4
H7B	0.336	0.449	0.330	4.4
H8	0.399	0.494	0.332	3.4
H9	0.413	0.185	0.552	3.0
H12A	0.543	0.321	0.357	4.4
H12B	0.551	0.157	0.444	4.4
H12C	0.504	0.146	0.337	4.4
H42A	0.415	1.140	0.800	4.5
H42B	0.360	1.090	0.725	4.5
H42C	0.388	0.951	0.823	4.5
H2'	0.620	0.715	1.069	4.1
H3'	0.646	0.853	0.968	3.8
H5'	0.714	0.391	0.926	3.2
H6'	0.778	0.503	1.089	4.9
H7A'	0.743	0.674	1.171	4.2
H7B'	0.754	0.471	1.236	4.2
H8'	0.696	0.510	1.224	4.0
H9'	0.677	0.173	1.005	3.5
H12A'	0.553	0.294	1.217	7.6
H12B'	0.538	0.169	1.113	7.6
H12C'	0.584	0.105	1.214	7.6
H42A'	0.687	1.156	0.774	5.7
H42B'	0.739	1.063	0.839	5.7
H42C'	0.702	0.950	0.739	5.7

The parameters of the hydrogen atoms were not refined.

Table 8-430. Final Anisotropic Thermal Parameters (U's) for War War XI at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Br1	0.0443(3)	0.0477(4)	0.0570(3)	-0.0140(3)	0.0203(2)	-0.0211(3)
Br2	0.0545(3)	0.0553(4)	0.0399(3)	-0.0087(3)	0.0085(3)	0.0086(3)
O11	0.061(2)	0.035(2)	0.079(2)	-0.000(2)	0.043(1)	0.005(2)
O12	0.066(2)	0.040(2)	0.102(3)	0.016(2)	0.053(2)	0.013(2)
O41	0.055(2)	0.039(2)	0.068(2)	-0.011(2)	0.032(2)	-0.012(2)
O42	0.074(2)	0.045(2)	0.075(2)	-0.017(2)	0.052(1)	-0.018(2)
C1	0.032(2)	0.021(2)	0.044(2)	-0.006(2)	-0.001(2)	-0.002(2)
C2	0.041(2)	0.026(3)	0.043(2)	-0.012(2)	0.030(1)	0.004(2)
C3	0.039(2)	0.028(2)	0.049(2)	0.001(2)	0.018(2)	0.011(2)
C4	0.039(2)	0.018(2)	0.058(3)	0.009(2)	0.018(2)	0.002(2)
C5	0.045(2)	0.022(2)	0.033(2)	0.005(2)	0.011(2)	0.011(2)
C6	0.027(2)	0.037(3)	0.031(2)	0.014(2)	0.008(1)	0.006(2)
C7	0.033(2)	0.070(5)	0.049(3)	-0.004(3)	0.012(2)	-0.003(3)
C8	0.050(3)	0.022(2)	0.032(2)	0.002(2)	0.010(2)	-0.004(2)
C9	0.039(2)	0.015(2)	0.047(2)	-0.012(2)	0.011(2)	-0.009(2)
C11	0.049(2)	0.027(2)	0.038(2)	-0.003(2)	0.021(2)	-0.006(2)
C12	0.050(2)	0.052(4)	0.045(2)	0.009(3)	0.022(2)	0.006(3)
C41	0.084(3)	0.011(2)	0.040(2)	-0.000(2)	0.032(2)	0.003(2)
C42	0.079(3)	0.030(3)	0.042(2)	0.019(3)	0.023(2)	-0.001(2)
Br1'	0.0467(3)	0.0446(4)	0.0582(3)	0.0145(3)	0.0211(2)	0.0148(3)
Br2'	0.0405(3)	0.0505(4)	0.0464(3)	0.0043(3)	0.0036(3)	-0.0140(3)
O11'	0.063(2)	0.048(3)	0.058(2)	-0.014(2)	0.045(1)	-0.010(2)
O12'	0.068(2)	0.024(2)	0.085(2)	-0.006(2)	0.048(2)	-0.010(2)
O41'	0.060(2)	0.021(2)	0.053(2)	0.008(2)	0.029(1)	0.013(2)
O42'	0.058(2)	0.050(3)	0.082(3)	0.020(2)	0.038(2)	0.017(2)
C1'	0.043(2)	0.023(3)	0.040(2)	-0.006(2)	0.032(1)	-0.007(2)
C2'	0.056(3)	0.019(2)	0.055(3)	-0.002(2)	0.011(2)	-0.005(2)
C3'	0.054(3)	0.020(2)	0.042(2)	0.008(2)	0.025(2)	0.003(2)
C4'	0.051(2)	0.033(2)	0.025(2)	0.021(2)	0.019(1)	0.004(2)
C5'	0.040(2)	0.026(2)	0.040(2)	0.014(2)	0.023(2)	0.009(2)
C6'	0.055(3)	0.039(3)	0.067(3)	0.023(2)	0.032(2)	0.018(3)
C7'	0.054(3)	0.032(3)	0.032(2)	-0.013(2)	0.012(2)	-0.014(2)
C8'	0.047(2)	0.043(4)	0.039(2)	-0.005(2)	0.024(1)	-0.015(2)
C9'	0.030(2)	0.038(3)	0.030(2)	-0.006(2)	0.010(1)	-0.016(2)
C11'	0.030(2)	0.036(3)	0.058(3)	-0.003(2)	0.021(2)	-0.012(3)
C12'	0.071(3)	0.073(5)	0.119(4)	-0.008(3)	0.076(2)	0.012(4)
C41'	0.021(2)	0.042(3)	0.045(3)	0.006(2)	0.009(2)	0.005(2)
C42'	0.073(3)	0.050(4)	0.077(3)	0.027(3)	0.054(2)	0.030(3)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-431. Bond Distances (Å) for War War XI at **295 K**

		Unprimed	Primed
Br1	C6	1.987(6)	1.985(7)
Br2	C9	1.976(5)	1.990(4)
O11	C11	1.319(9)	1.323(9)
O11	C12	1.43(1)	1.50(1)
O12	C11	1.170(8)	1.214(9)
O41	C41	1.339(7)	1.342(7)
O41	C42	1.494(9)	1.39(1)
O42	C41	1.21(1)	1.180(8)
C1	C2	1.514(8)	1.558(8)
C1	C8	1.570(7)	1.483(7)
C1	C9	1.45(1)	1.549(9)
C1	C11	1.415(9)	1.564(9)
C2	C3	1.473(9)	1.51(1)
C2	C8	1.505(7)	1.515(8)
C3	C4	1.34(1)	1.32(1)
C4	C5	1.554(8)	1.472(8)
C4	C41	1.47(1)	1.515(9)
C5	C6	1.492(6)	1.552(7)
C5	C9	1.493(9)	1.552(8)
C6	C7	1.52(1)	1.54(1)
C7	C8	1.54(1)	1.484(9)

Table 8-432. Bond Angles in Degrees for War War-XI at **295 K**

			Unprimed	Primed
C11	O11	C12	119.2(5)	112.8(6)
C41	O41	C42	116.9(6)	113.0(6)
C2	C1	C8	58.4(3)	59.7(4)
C2	C1	C9	113.1(5)	118.3(5)
C2	C1	C11	122.2(6)	120.5(6)
C8	C1	C9	115.6(5)	118.9(5)
C8	C1	C11	114.6(5)	118.2(5)
C9	C1	C11	118.6(5)	112.1(5)
C1	C2	C3	119.8(5)	110.8(6)
C1	C2	C8	62.7(3)	57.7(4)
C3	C2	C8	119.0(5)	112.3(6)
C2	C3	C4	119.2(5)	124.6(5)
C3	C4	C5	118.7(6)	121.2(6)
C3	C4	C41	125.5(5)	123.6(5)
C5	C4	C41	115.5(6)	115.2(5)
C4	C5	C6	107.8(4)	108.9(4)
C4	C5	C9	108.9(5)	110.9(5)
C6	C5	C9	111.6(5)	107.1(5)
Br1	C6	C5	109.7(4)	109.3(4)
Br1	C6	C7	110.4(4)	111.2(5)
C5	C6	C7	111.9(5)	112.2(5)
C6	C7	C8	114.3(5)	114.1(5)
C1	C8	C2	58.9(3)	62.6(3)
C1	C8	C7	120.9(6)	122.4(6)
C2	C8	C7	117.5(6)	126.8(6)
Br2	C9	C1	109.3(4)	108.1(3)
Br2	C9	C5	109.4(4)	109.6(4)
C1	C9	C5	114.3(4)	107.8(4)
O11	C11	O12	122.4(7)	125.4(7)
O11	C11	C1	114.5(5)	110.6(6)
O12	C11	C1	123.1(7)	123.9(6)
O41	C41	O42	121.0(6)	124.4(6)
O41	C41	C4	112.2(6)	111.8(5)
O42	C41	C4	124.9(6)	122.0(6)

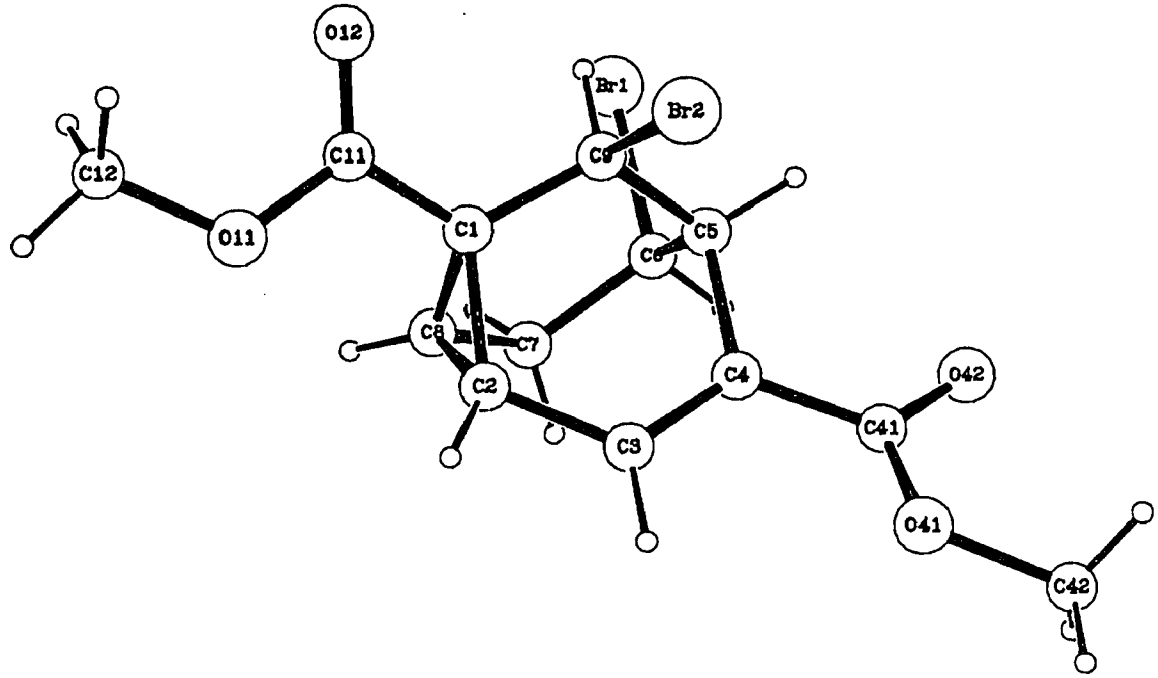


Figure 8–15. *ORTEP* drawing of War War XI (unprimed) at **295 K.**

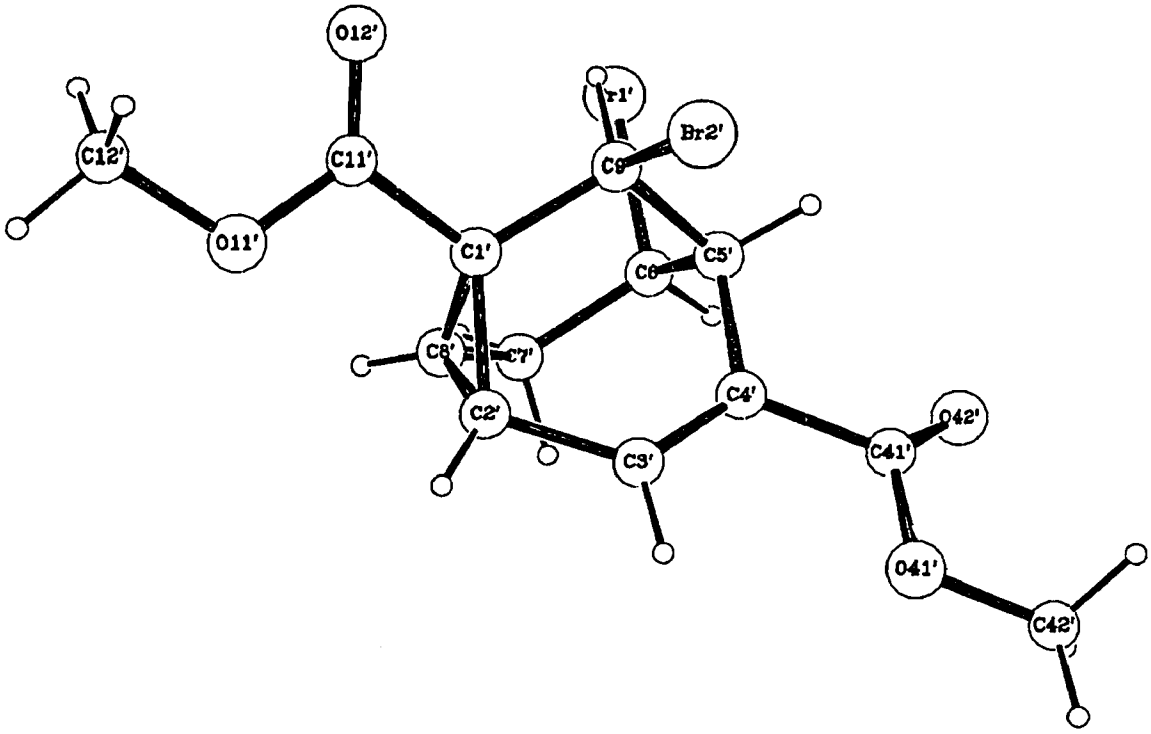
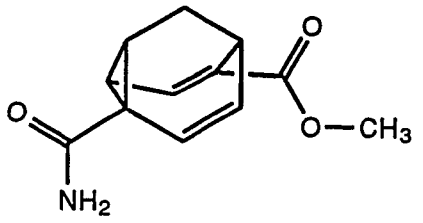


Figure 8–16. *ORTEP* drawing of War War XI (primed) at **295 K.**



2-Carboxamido-6-carbomethoxy-tricyclo[3.3.1.0^{2,8}]nona-3,6-dine
(2-Carboxamido-6-carbomethoxybarbaralane)
(War-War XII)

Table 8–433. X-ray Crystal Data for War-War XII at **295 K**

Formula	$C_{12}H_{13}NO_3$
Formula weight	219.24
Melting point (°C)	165–166
Crystal size (mm)	0.10 x 0.15 x 0.37
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	7.373(1)
b (Å)	17.066(2)
c (Å)	8.321(1)
β (°)	96.86(1)°
Cell volume (Å^3)	1039.58(1.15)
Z	4
d_{calc} (g cm^{-3})	1.401
μ(Cu $K\alpha$) (cm^{-1})	7.94
Maximum θ (°)	60
Unique reflections	1543
Observed reflections [$I > 3.0\sigma(I)$]	1187
Number of variables	145
R	0.060
R_w	0.074
$(\Delta\rho)_{max}$ (e Å^{-3})	0.301
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.28

Table 8-434. Final Atomic Parameters for War-War XII at **295 K**

Atom	x	y	z	B(Å^2)
O1	0.9984(3)	0.0384(2)	0.2059(3)	4.46(6)
O5	0.2397(3)	0.1672(2)	0.6480(3)	4.01(5)
O6	0.4131(4)	0.0851(2)	0.8060(3)	4.62(6)
N1	0.7782(4)	0.0523(2)	-0.0053(3)	3.64(6)
C1	0.8155(5)	0.1602(2)	0.3728(4)	3.31(7)
C2	0.7200(5)	0.0989(2)	0.2595(3)	2.81(7)
C3	0.5272(5)	0.1097(2)	0.2069(4)	3.23(7)
C4	0.4211(5)	0.1557(2)	0.2862(4)	3.35(8)
C5	0.5058(5)	0.1965(2)	0.4395(4)	3.15(7)
C6	0.5196(5)	0.1317(2)	0.5652(4)	2.84(7)
C7	0.6496(5)	0.0775(2)	0.5614(4)	2.97(7)
C8	0.7844(5)	0.0815(2)	0.4463(4)	3.02(7)
C9	0.6969(5)	0.2261(2)	0.4178(4)	3.65(8)
C21	0.8448(5)	0.0595(2)	0.1537(4)	3.07(7)
C61	0.3884(5)	0.1251(2)	0.6852(4)	2.97(7)
C62	0.1047(5)	0.1632(3)	0.7625(5)	4.81(9)
HN1A	0.657	0.069	-0.041	4.0
HN1B	0.851	0.030	-0.080	4.0
H1	0.953	0.168	0.375	3.6
H3	0.471	0.082	0.108	3.5
H4	0.289	0.163	0.246	3.7
H5	0.426	0.240	0.470	3.4
H7	0.654	0.033	0.640	3.2
H8	0.894	0.047	0.470	3.3
H9A	0.687	0.267	0.330	4.0
H9B	0.753	0.250	0.522	4.0
H62A	-0.002	0.197	0.723	5.2
H62B	0.063	0.108	0.771	5.2
H62C	0.161	0.182	0.871	5.2

The parameters of the hydrogen atoms were not refined.

Table 8-435. Final Anisotropic Thermal Parameters (U's) for War-War XII at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.051(1)	0.090(2)	0.029(1)	0.019(1)	0.008(1)	-0.017(1)
O5	0.057(1)	0.063(2)	0.035(1)	0.011(1)	0.018(1)	0.001(1)
O6	0.071(2)	0.083(2)	0.024(1)	0.006(2)	0.016(1)	0.015(1)
N1	0.062(2)	0.061(2)	0.018(1)	0.010(2)	0.012(1)	-0.003(1)
C1	0.055(2)	0.046(2)	0.026(2)	-0.002(2)	0.011(1)	-0.004(2)
C2	0.049(2)	0.045(2)	0.014(1)	0.003(2)	0.008(1)	-0.002(1)
C3	0.055(2)	0.051(2)	0.018(1)	0.005(2)	0.007(1)	0.002(1)
C4	0.056(2)	0.052(2)	0.020(2)	0.012(2)	0.008(1)	0.007(1)
C5	0.062(2)	0.038(2)	0.021(1)	0.008(2)	0.012(1)	0.000(1)
C6	0.052(2)	0.041(2)	0.016(1)	0.004(2)	0.008(1)	-0.001(1)
C7	0.055(2)	0.043(2)	0.015(1)	0.003(2)	0.003(1)	-0.001(1)
C8	0.049(2)	0.047(2)	0.018(1)	0.009(2)	0.004(1)	0.001(1)
C9	0.071(2)	0.041(2)	0.029(2)	-0.001(2)	0.016(2)	-0.003(2)
C21	0.048(2)	0.045(2)	0.025(2)	0.003(2)	0.011(1)	-0.002(1)
C61	0.050(2)	0.042(2)	0.022(1)	-0.001(2)	0.007(1)	-0.006(1)
C62	0.056(2)	0.079(3)	0.053(2)	-0.001(2)	0.030(2)	-0.013(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-436. Interatomic Distances (Å) for War-War XII at **295 K**

O1	C21	1.218(4)	C2	C8	1.597(4)
O5	C61	1.317(4)	C2	C21	1.506(5)
O5	C62	1.460(5)	C3	C4	1.336(5)
O6	C61	1.211(4)	C4	C5	1.520(4)
N1	C21	1.360(4)	C4	C6	2.384(5)
C1	C2	1.524(5)	C5	C6	1.517(5)
C1	C9	1.498(5)	C5	C9	1.528(5)
C1	C8	1.504(5)	C6	C61	1.475(5)
C2	C3	1.449(5)	C6	C7	1.335(5)
C7	C8	1.462(5)			

Table 8-437. Bond Angles (°) for War-War XII at **295 K**

C61	O5	C62	115.7(3)	C5	C6	C7	118.6(3)
C2	C1	C8	63.7(2)	C5	C6	C61	121.8(3)
C2	C1	C9	115.4(3)	C7	C6	C61	119.6(3)
C8	C1	C9	116.5(3)	C6	C7	C8	121.9(3)
C1	C2	C3	117.6(3)	C1	C8	C2	58.8(2)
C1	C2	C8	57.6(2)	C1	C8	C7	117.2(3)
C1	C2	C21	113.5(3)	C2	C8	C7	120.0(3)
C3	C2	C8	119.0(3)	C1	C9	C5	110.8(3)
C3	C2	C21	121.8(3)	O1	C21	N1	122.2(3)
C8	C2	C21	110.8(3)	O1	C21	C2	122.0(3)
C2	C3	C4	122.5(3)	N1	C21	C2	115.7(3)
C3	C4	C5	118.5(3)	O5	C61	O6	122.8(3)
C4	C5	C6	103.4(3)	O5	C61	C6	113.2(3)
C4	C5	C9	110.2(3)	O6	C61	C6	124.0(3)
C6	C5	C9	109.6(3)				

Table 8-438. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for War-War XII at **295 K**

Atom	Min.	Int'med.	Max.
O1	0.146	0.215	0.319
O5	0.167	0.229	0.269
O6	0.131	0.263	0.300
N1	0.121	0.229	0.267
C1	0.153	0.214	0.238
C2	0.112	0.209	0.225
C3	0.132	0.217	0.241
C4	0.136	0.205	0.258
C5	0.138	0.189	0.255
C6	0.124	0.199	0.230
C7	0.122	0.206	0.236
C8	0.134	0.199	0.239
C9	0.159	0.203	0.268
C21	0.147	0.210	0.226
C61	0.141	0.207	0.224
C62	0.163	0.263	0.295

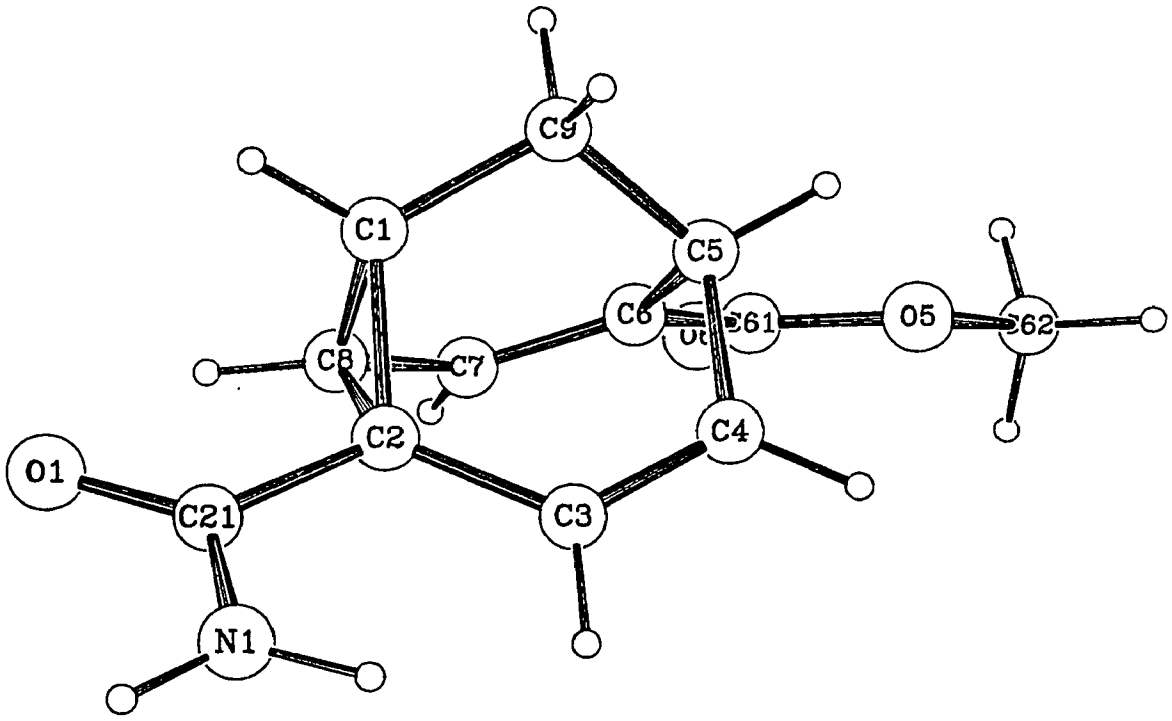
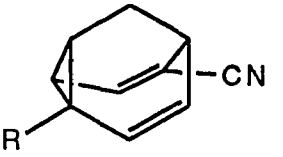


Figure 8–17. *ORTEP* drawing of War-War XII at **295 K.**



R = $COOCH_3$

2-Carbomethoxy-tricyclo[3.3.1.$0^{2,8}$]nona-3,6-dine-6-carbonitrile
(2-carbomethoxybarbaralane-6-carbonitrile)
(War-War XIII)

Table 8–439. X-ray Crystal Data for War-War XIII at **295 K**

Formula	$C_{12}H_{11}NO_2$
Formula weight	201.23
Melting point (°C)	107–108
Crystal size (mm)	0.21 x 0.28 x 0.44
Crystal system	monoclinic
Space group	*C2/c*
a (Å)	22.584(2) Å
b (Å)	6.044(1) Å
c (Å)	14.828(2) Å
β (°)	97.65(1)°
Cell volume (Å^3)	2005.84(2.29)
Z	8
d_{calc} (g cm^{-3})	1.333
μ(Cu $K\alpha$) (cm^{-1})	7.06
Maximum θ (°)	60
Unique reflections	1486
Observed reflections [$I > 3.0\sigma(I)$]	1272
Number of variables	136
R	0.041
R_w	0.058
$(\Delta\rho)_{max}$ (e Å^{-3})	0.15
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.17

Table 8-440. Final Atomic Parameters for War-War XIII at **295 K**

Atom	x	y	z	B(A2)
O1	0.06541(6)	0.9523(2)	0.31926(8)	3.74(3)
O2	0.05560(6)	0.6063(2)	0.36862(9)	4.75(3)
N1	0.30398(8)	0.4052(4)	0.0738(1)	6.70(6)
C1	0.08717(8)	0.4519(3)	0.1944(1)	3.36(4)
C2	0.10659(7)	0.6686(3)	0.2398(1)	2.96(3)
C3	0.13032(8)	0.8400(3)	0.1839(1)	3.41(4)
C4	0.15025(8)	0.7903(3)	0.1060(1)	3.68(4)
C5	0.15147(8)	0.5517(3)	0.0765(1)	3.66(4)
C6	0.20413(8)	0.4541(3)	0.1374(1)	3.43(4)
C7	0.19974(8)	0.4132(3)	0.2249(1)	3.48(4)
C8	0.14289(8)	0.4437(3)	0.2605(1)	3.25(4)
C9	0.09364(9)	0.4344(3)	0.0953(1)	3.95(4)
C21	0.07384(7)	0.7340(3)	0.3162(1)	3.23(4)
C22	0.0365(1)	1.0310(4)	0.3944(1)	4.64(5)
C61	0.26005(9)	0.4272(4)	0.1026(1)	4.43(5)
H1	0.051	0.381	0.214	4.0
H3	0.131	0.997	0.205	4.1
H4	0.164	0.910	0.067	4.3
H5	0.155	0.536	0.010	4.3
H7	0.236	0.361	0.266	4.1
H8	0.139	0.373	0.321	3.9
H9A	0.058	0.506	0.058	4.7
H9B	0.095	0.275	0.078	4.7
H22A	0.032	1.196	0.390	5.5
H22B	-0.004	0.962	0.392	5.5
H22C	0.061	0.990	0.453	5.5

The parameters of the hydrogen atoms were not refined.

Table 8-441. Final Anisotropic Thermal Parameters (U's) for War-War XIII at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0546(7)	0.0412(7)	0.0480(7)	0.0086(6)	0.0130(6)	0.0007(6)
O2	0.0791(8)	0.0484(7)	0.0585(7)	-0.0080(7)	0.0289(6)	0.0030(7)
N1	0.054(1)	0.131(2)	0.072(1)	0.013(1)	0.0193(9)	0.010(1)
C1	0.0425(9)	0.0383(9)	0.046(1)	-0.0069(8)	0.0050(8)	-0.0047(8)
C2	0.0406(8)	0.0323(9)	0.0393(8)	-0.0013(8)	0.0036(7)	0.0026(8)
C3	0.0476(9)	0.0342(9)	0.0482(9)	0.0010(8)	0.0073(8)	0.0066(8)
C4	0.050(1)	0.044(1)	0.0462(9)	0.0044(9)	0.0082(8)	0.0120(9)
C5	0.048(1)	0.053(1)	0.0382(9)	0.0023(9)	0.0057(8)	-0.0005(9)
C6	0.0426(9)	0.0389(9)	0.049(1)	0.0011(8)	0.0075(8)	-0.0030(8)
C7	0.0432(9)	0.0379(9)	0.049(1)	0.0043(8)	-0.0001(8)	0.0014(8)
C8	0.0492(9)	0.0307(9)	0.0436(9)	0.0024(8)	0.0064(8)	0.0040(8)
C9	0.047(1)	0.054(1)	0.048(1)	-0.0040(9)	0.0020(8)	-0.0097(9)
C21	0.0398(8)	0.0397(9)	0.0422(9)	-0.0025(8)	0.0024(7)	-0.0005(8)
C22	0.066(1)	0.058(1)	0.056(1)	0.014(1)	0.0191(9)	-0.008(1)
C61	0.049(1)	0.066(1)	0.053(1)	0.003(1)	0.0067(9)	0.002(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-442. Interatomic Distances (Å) for War-War XIII at **295 K**

O1	C21	1.335(2)	C2	C21	1.487(2)
O1	C22	1.444(3)	C3	C4	1.329(3)
O2	C21	1.206(2)	C4	C5	1.509(3)
N1	C61	1.139(3)	C4	C6	2.382(3)
C1	C2	1.510(2)	C5	C6	1.514(2)
C1	C8	1.489(2)	C5	C9	1.544(3)
C1	C9	1.500(3)	C6	C7	1.336(3)
C2	C3	1.471(3)	C6	C61	1.436(3)
C2	C8	1.596(2)	C7	C8	1.463(3)

Table 8-443. Bond Angles (°) for War-War XIII at **295 K**

C21	O1	C22	115.6(1)	C6	C5	C9	109.2(2)
C2	C1	C8	64.3(1)	C5	C6	C7	119.8(2)
C2	C1	C9	115.9(2)	C5	C6	C61	119.2(2)
C8	C1	C9	117.3(2)	C7	C6	C61	120.7(2)
C1	C2	C3	117.8(1)	C6	C7	C8	120.6(2)
C1	C2	C8	57.2(1)	C1	C8	C2	58.5(1)
C1	C2	C21	115.2(1)	C1	C8	C7	118.2(2)
C3	C2	C8	119.5(1)	C2	C8	C7	119.4(1)
C3	C2	C21	119.8(2)	C1	C9	C5	109.9(1)
C8	C2	C21	112.0(1)	O1	C21	O2	123.2(2)
C2	C3	C4	121.4(2)	O1	C21	C2	112.1(1)
C3	C4	C5	119.3(2)	O2	C21	C2	124.6(2)
C4	C5	C6	104.0(1)	N1	C61	C6	179.0(2)
C4	C5	C9	109.7(2)				

Table 8-444. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for War-War XIII at **295 K**

Atom	Min.	Int'med.	Max.
O1	0.190	0.213	0.246
O2	0.195	0.231	0.299
N1	0.216	0.271	0.367
C1	0.180	0.214	0.222
C2	0.177	0.196	0.207
C3	0.178	0.217	0.226
C4	0.182	0.220	0.242
C5	0.195	0.216	0.232
C6	0.194	0.207	0.224
C7	0.186	0.208	0.233
C8	0.172	0.211	0.223
C9	0.195	0.226	0.247
C21	0.191	0.203	0.212
C22	0.187	0.253	0.277
C61	0.221	0.230	0.258

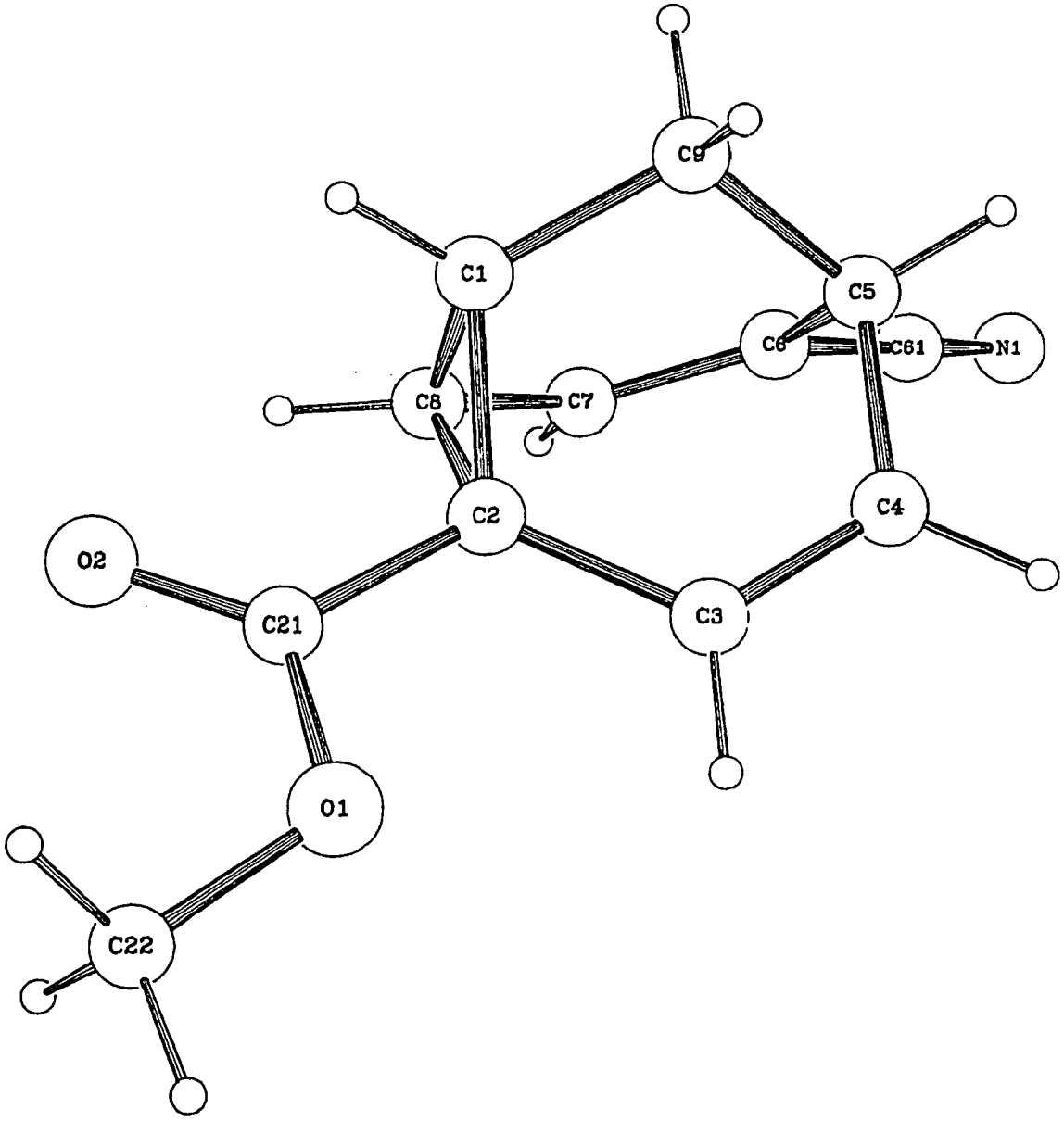
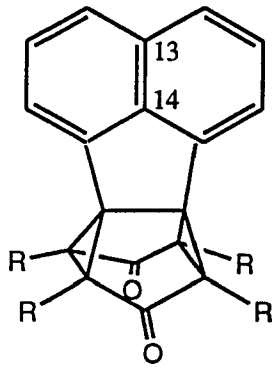


Figure 8–18. *ORTEP* drawing of War-War XIII at **295 K.**

8–9 X-RAY STRUCTURES RELATED TO SEMIBULLVALENE



R = $COOCH_3$

1,5-(1,2-Acenaphtho)-2,4,6,8-tetracarbomethoxy-tetracyclo[3.3.0^{2,8}0^{4,6}]-3,7-dione

(MC-1)

Table 8–445. X-ray Crystal Data for MC-1 at **295 K**

Formula	$C_{26}H_{18}O_{10}$
Formula weight	490.43
Melting point (°C)	207–208
Crystal size (mm)	0.06 x 0.10 x 0.44
Crystal system	monoclinic
Space group	*C2/c*
a (Å)	19.099(2)
b (Å)	10.319(1)
c (Å)	12.193(2)
β (°)	114.83(1)°
Cell volume (Å^3)	2180.82(10.42)
Z	4[a]
d_{calc} (g cm^{-3})	1.494
μ(Cu $K\alpha$) (cm^{-1})	9.41
Maximum θ (°)	75
Unique reflections	2162
Observed reflections [$I > 3.0\sigma(I)$]	1942
Number of variables	164
R	0.042
R_w	0.063
$(\Delta\rho)_{max}$ (e Å^{-3})	0.24
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.25

[a] Half of the molecule is related to the other half by a crystallographic 2-fold rotation axis, passing through C13 and C14.

Table 8-446. Final Atomic Parameters for MC-1 at **295 K**

Atom	x	y	z	B(Å^2)
O3	0.55651(6)	0.2371(1)	0.43893(9)	3.14(2)
O5	0.37918(6)	0.2557(1)	0.3706(1)	3.41(2)
O6	0.69772(6)	0.3799(1)	0.49096(9)	3.02(2)
O7	0.41229(6)	0.4426(1)	0.47417(9)	3.37(2)
O8	0.70709(6)	0.4504(1)	0.3234(1)	3.74(3)
C1	0.53840(6)	0.5119(1)	0.2432(1)	2.03(2)
C2	0.45823(7)	0.3931(1)	0.3239(1)	2.09(2)
C3	0.53745(7)	0.3280(1)	0.3719(1)	2.19(2)
C4	0.58424(7)	0.3959(1)	0.3156(1)	2.13(2)
C5	0.41313(7)	0.3711(1)	0.3980(1)	2.38(3)
C6	0.66974(7)	0.4098(1)	0.3748(1)	2.49(3)
C7	0.3367(1)	0.2168(2)	0.4395(2)	5.03(4)
C8	0.7773(1)	0.4160(2)	0.5632(2)	4.04(4)
C9	0.55817(7)	0.6500(1)	0.2362(1)	2.33(3)
C10	0.61532(8)	0.7114(2)	0.2161(1)	2.90(3)
C11	0.61473(9)	0.8494(2)	0.2125(1)	3.48(3)
C12	0.5600(1)	0.9215(2)	0.2288(2)	3.63(4)
C13	0.500	0.8602(2)	0.250	2.99(4)
C14	0.500	0.7243(2)	0.250	2.45(4)
H7A	0.3135	0.1292	0.4122	6
H7B	0.3725	0.2134	0.5273	6
H7C	0.2947	0.2810	0.4267	6
H8A	0.7924	0.3890	0.6489	4
H8B	0.8113	0.3717	0.5310	4
H8C	0.7830	0.5120	0.5595	4
H10	0.6562	0.6607	0.2041	3
H11	0.6561	0.8950	0.1974	4
H12	0.5620	1.0182	0.2260	4

The parameters of the hydrogen atoms were not refined.

Table 8-447. Final Anisotropic Thermal Parameters (U's) for MC-1 at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O3	0.0392(4)	0.0416(5)	0.0358(5)	0.0060(4)	0.0132(3)	0.0140(4)
O5	0.0502(5)	0.0438(5)	0.0411(5)	-0.0165(4)	0.0245(3)	-0.0038(4)
O6	0.0294(4)	0.0491(6)	0.0268(4)	-0.0004(4)	0.0024(3)	0.0016(4)
O7	0.0479(4)	0.0490(6)	0.0382(5)	-0.0051(4)	0.0249(3)	-0.0092(4)
O8	0.0313(4)	0.0671(7)	0.0431(5)	-0.0047(5)	0.0149(3)	0.0071(5)
C1	0.0245(5)	0.0293(6)	0.0222(5)	-0.0001(4)	0.0086(4)	0.0006(4)
C2	0.0267(4)	0.0303(6)	0.0220(5)	-0.0005(4)	0.0098(3)	-0.0006(4)
C3	0.0288(5)	0.0317(6)	0.0210(5)	-0.0008(5)	0.0089(4)	-0.0006(5)
C4	0.0253(5)	0.0313(6)	0.0227(5)	0.0018(4)	0.0083(3)	0.0009(5)
C5	0.0267(5)	0.0366(6)	0.0252(5)	-0.0004(5)	0.0090(4)	0.0015(5)
C6	0.0263(5)	0.0331(6)	0.0312(6)	0.0025(5)	0.0083(4)	-0.0002(5)
C7	0.0661(7)	0.081(1)	0.0524(8)	-0.0331(7)	0.0331(5)	0.0005(8)
C8	0.0341(7)	0.0533(9)	0.0440(9)	-0.0046(7)	-0.0052(7)	-0.0001(8)
C9	0.0306(5)	0.0304(6)	0.0231(5)	-0.0025(5)	0.0069(4)	-0.0000(5)
C10	0.0367(6)	0.0386(7)	0.0329(6)	-0.0074(5)	0.0128(4)	-0.0008(6)
C11	0.0491(7)	0.0398(7)	0.0396(7)	-0.0150(6)	0.0150(5)	-0.0005(6)
C12	0.0528(8)	0.0327(7)	0.0437(8)	-0.0093(6)	0.0117(6)	0.0004(6)
C13	0.0408(9)	0.0324(9)	0.0319(9)	0	0.0069(7)	0
C14	0.0321(7)	0.0323(9)	0.0233(8)	0	0.0064(6)	0

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-448. Interatomic Distances (Å) for MC-1 at **295 K**

O3	C3	1.196(2)	C2	C4	1.547(2)
O5	C5	1.330(2)	C2	C5	1.505(2)
O5	C7	1.449(3)	C3	C4	1.509(2)
O6	C6	1.324(2)	C4	C6	1.489(2)
O6	C8	1.450(2)	C9	C10	1.370(2)
O7	C5	1.191(2)	C9	C14	1.417(2)
O8	C6	1.205(2)	C10	C11	1.425(2)
C1	C4	1.526(2)	C11	C12	1.364(3)
C1	C9	1.485(2)	C12	C13	1.424(2)
C2	C3	1.529(2)	C13	C14	1.402(3)

Table 449. Bond Angles (°) for MC-1 at **295 K**

C5	O5	C7	115.7(1)	O7	C5	C2	125.0(1)
C6	O6	C8	116.1(1)	O6	C6	O8	125.2(1)
C4	C1	C9	133.42(9)	O6	C6	C4	111.4(1)
C3	C2	C5	115.3(1)	O8	C6	C4	123.3(1)
O3	C3	C2	125.1(1)	C1	C9	C10	134.0(1)
O3	C3	C4	127.3(1)	C1	C9	C14	106.3(1)
C2	C3	C4	107.6(1)	C10	C9	C14	119.6(1)
C1	C4	C3	108.8(1)	C9	C10	C11	118.1(2)
C1	C4	C6	116.8(1)	C10	C11	C12	122.5(2)
C3	C4	C6	124.2(1)	C11	C12	C13	120.6(2)
O5	C5	O7	125.9(2)	C12	C13	C14	116.4(1)
O5	C5	C2	109.0(1)	C9	C14	C13	122.76(9)

Table 8-450. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for MC-1 at **295 K**

Atom	Min.	Int'med.	Max.
O3	0.156	0.205	0.231
O5	0.165	0.197	0.253
O6	0.146	0.209	0.223
O7	0.166	0.208	0.239
O8	0.173	0.203	0.267
C1	0.148	0.161	0.171
C2	0.148	0.165	0.174
C3	0.145	0.174	0.179
C4	0.149	0.165	0.179
C5	0.156	0.170	0.193
C6	0.158	0.180	0.193
C7	0.164	0.236	0.330
C8	0.152	0.230	0.278
C9	0.149	0.171	0.192
C10	0.174	0.183	0.215
C11	0.169	0.199	0.253
C12	0.171	0.204	0.259
C13	0.171	0.160	0.228
C14	0.149	0.180	0.196

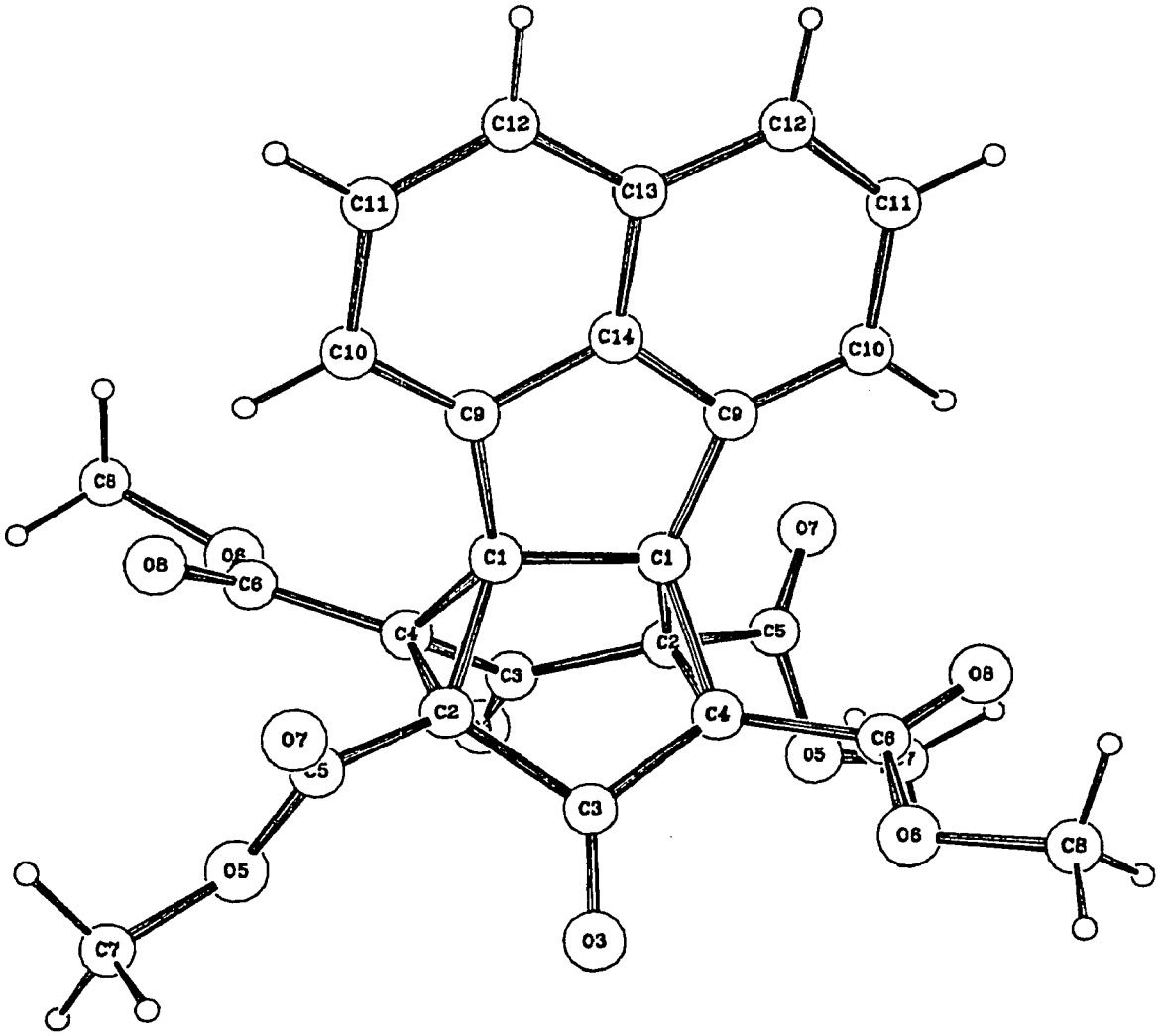
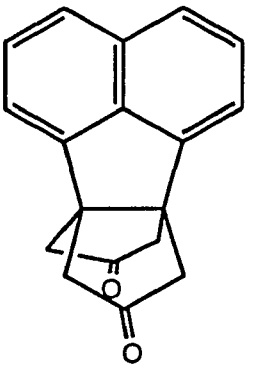


Figure 8–19. *ORTEP* drawing of MC-1 at **295 K.**



1,5-(1,2-Acenaphtho)bicyclo[3.3.0]-3,7-dione
(Acenaphtho diketone)
(MC-2)

Table 8–451. X-ray Crystal Data for MC-2 at **295 K**

Formula	$C_{18}H_{14}O_2$
Formula weight	262.31
Melting point (°C)	
Crystal size (mm)	0.09 x 0.12 x 0.38
Crystal system	monoclinic
Space group	*C*2/*c*
a (Å)	22.703(1)
b (Å)	8.165(3)
c (Å)	29.114(2)
β (°)	101.62(1)°
Cell volume (Å^3)	16
Z	1.318
d_{calc} (g cm^{-3})	6.4
μ(Cu $K\alpha$) (cm^{-1})	6.39
Maximum θ (°)	60
Unique reflections	3929
Observed reflections [$I > 3.0\sigma(I)$]	2582
Number of variables	361
R	0.046
R_w	0.052
$(\Delta\rho)_{max}$ (e Å^{-3})	0.19
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.22

Table 8-452. Final Atomic Parameters for MC-2 at **295 K**

Atom	x	y	z	B(Å^2)
O3	0.2435(1)	0.1465(4)	0.21057(8)	7.68(7)
O7	0.50770(9)	0.4052(4)	0.19167(8)	6.58(7)
C1	0.3529(1)	0.2966(3)	0.14698(8)	2.73(5)
C2	0.3113(1)	0.1566(4)	0.1570(1)	3.68(6)
C3	0.2871(1)	0.2067(4)	0.1992(1)	4.26(7)
C4	0.3237(1)	0.3469(4)	0.22392(9)	4.08(7)
C5	0.3475(1)	0.4354(3)	0.18487(8)	2.93(6)
C6	0.4111(1)	0.5067(4)	0.2000(1)	4.29(7)
C7	0.4534(1)	0.3902(4)	0.18315(9)	3.94(7)
C8	0.4199(1)	0.2541(4)	0.1548(1)	3.71(7)
C9	0.3265(1)	0.3778(3)	0.10068(8)	2.74(5)
C10	0.3238(1)	0.3285(4)	0.05530(9)	3.37(6)
C11	0.2889(1)	0.4225(4)	0.01895(9)	3.75(7)
C12	0.2566(1)	0.5563(4)	0.02723(9)	3.42(6)
C13	0.2593(1)	0.6116(3)	0.07381(9)	2.92(6)
C14	0.2287(1)	0.7459(4)	0.0888(1)	3.69(6)
C15	0.2353(1)	0.7806(4)	0.1355(1)	3.98(7)
C16	0.2731(1)	0.6868(4)	0.17088(9)	3.63(6)
C17	0.3033(1)	0.5560(3)	0.15731(8)	2.79(5)
C18	0.2958(1)	0.5192(3)	0.10929(8)	2.50(5)
O3'	0.6530(1)	0.6092(3)	0.08477(8)	6.33(6)
O7'	0.5882(1)	0.9783(4)	0.25679(7)	9.62(8)
C1'	0.5929(1)	0.9597(3)	0.13425(9)	3.03(6)
C2'	0.6432(1)	0.8841(4)	0.1125(1)	3.86(7)
C3'	0.6314(1)	0.7020(4)	0.10874(9)	3.72(6)
C4'	0.5887(1)	0.6560(4)	0.1401(1)	3.71(6)
C5'	0.5507(1)	0.8095(3)	0.14151(9)	2.92(6)
C6'	0.5331(1)	0.8400(4)	0.18926(9)	3.55(6)
C7'	0.5795(1)	0.9542(4)	0.2152(1)	4.54(7)
C8'	0.6148(1)	1.0347(4)	0.1831(1)	4.61(8)
C9'	0.5523(1)	1.0683(3)	0.09951(8)	2.92(6)
C10'	0.5599(1)	1.2238(4)	0.0837(1)	3.94(7)
C11'	0.5148(1)	1.2887(4)	0.0475(1)	4.58(7)
C12'	0.4647(1)	1.2020(4)	0.0275(1)	4.42(7)
C13'	0.4556(1)	1.0409(4)	0.04333(9)	3.66(6)
C14'	0.4070(1)	0.9346(5)	0.0266(1)	4.73(8)
C15'	0.4051(1)	0.7821(5)	0.0460(1)	5.13(8)
C16'	0.4505(1)	0.7245(4)	0.0834(1)	4.38(7)
C17'	0.4976(1)	0.8261(4)	0.10050(8)	3.04(6)
C18'	0.5002(1)	0.9809(4)	0.07996(8)	2.88(6)

Table 8-452 (cont.). Final Atomic Parameters for MC-2 at **295 K**

Atom	x	y	z	B(Å^2)
H2A	0.335	0.052	0.163	4.3
H2B	0.278	0.141	0.129	4.3
H4A	0.358	0.305	0.248	4.8
H4B	0.298	0.422	0.239	4.8
H6A	0.422	0.516	0.235	5.1
H6B	0.413	0.617	0.186	5.1
H8A	0.433	0.245	0.124	4.3
H8B	0.428	0.148	0.172	4.3
H10	0.346	0.229	0.048	3.9
H11	0.288	0.389	-0.014	4.5
H12	0.231	0.616	0.000	4.0
H14	0.202	0.816	0.065	4.4
H15	0.213	0.876	0.145	4.7
H16	0.277	0.716	0.205	4.3
H2A'	0.683	0.906	0.133	4.5
H2B'	0.642	0.932	0.081	4.5
H4A'	0.611	0.627	0.172	4.4
H4B'	0.563	0.561	0.127	4.4
H6A'	0.533	0.735	0.207	4.2
H6B'	0.492	0.891	0.184	4.2
H8A'	0.608	1.155	0.182	5.4
H8B'	0.659	1.013	0.194	5.4
H10'	0.596	1.290	0.098	4.6
H11'	0.520	1.402	0.036	5.5
H12'	0.434	1.252	0.001	5.2
H14'	0.374	0.970	0.001	5.6
H15'	0.370	0.708	0.034	6.1
H16'	0.448	0.612	0.097	5.1

The parameters of the hydrogen atoms were not refined.

Table 8-453. Final Anisotropic Thermal Parameters (U's) for MC-2 at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O3	0.114(1)	0.101(2)	0.094(1)	-0.038(1)	0.064(1)	-0.002(1)
O7	0.043(1)	0.121(2)	0.085(1)	-0.014(1)	0.010(1)	-0.018(2)
C1	0.038(1)	0.029(1)	0.036(1)	0.002(1)	0.006(1)	0.001(1)
C2	0.053(1)	0.037(2)	0.051(1)	-0.004(1)	0.015(1)	0.005(1)
C3	0.065(2)	0.052(2)	0.049(1)	-0.001(2)	0.021(1)	0.015(2)
C4	0.073(2)	0.049(2)	0.035(1)	0.005(2)	0.016(1)	0.006(1)
C5	0.042(1)	0.036(2)	0.033(1)	0.002(1)	0.006(1)	0.000(1)
C6	0.048(2)	0.057(2)	0.054(2)	-0.004(2)	0.001(1)	-0.005(2)
C7	0.042(1)	0.064(2)	0.041(1)	-0.003(2)	0.002(1)	0.008(2)
C8	0.040(1)	0.047(2)	0.053(2)	0.007(1)	0.006(1)	0.005(2)
C9	0.033(1)	0.035(2)	0.037(1)	-0.000(1)	0.010(1)	0.002(1)
C10	0.046(1)	0.044(2)	0.040(1)	-0.000(1)	0.012(1)	-0.003(1)
C11	0.052(1)	0.053(2)	0.036(1)	-0.013(2)	0.008(1)	-0.000(1)
C12	0.041(1)	0.047(2)	0.040(1)	-0.008(1)	0.003(1)	0.009(1)
C13	0.033(1)	0.034(2)	0.045(1)	-0.005(1)	0.012(1)	0.008(1)
C14	0.045(1)	0.037(2)	0.060(2)	0.001(1)	0.015(1)	0.012(1)
C15	0.052(1)	0.033(2)	0.071(2)	0.007(1)	0.023(1)	0.006(2)
C16	0.054(1)	0.035(2)	0.053(1)	-0.002(1)	0.021(1)	-0.005(1)
C17	0.039(1)	0.030(1)	0.039(1)	-0.003(1)	0.014(1)	-0.003(1)
C18	0.032(1)	0.028(1)	0.036(1)	-0.003(1)	0.009(1)	0.003(1)
O3'	0.096(1)	0.067(2)	0.092(1)	0.016(1)	0.052(1)	-0.013(1)
O7'	0.151(2)	0.171(3)	0.049(1)	-0.084(2)	0.034(1)	-0.044(2)
C1'	0.038(1)	0.035(2)	0.041(1)	-0.005(1)	0.007(1)	-0.004(1)
C2'	0.041(1)	0.046(2)	0.062(2)	0.001(1)	0.016(1)	0.008(2)
C3'	0.044(1)	0.049(2)	0.049(1)	0.010(1)	0.010(1)	0.002(2)
C4'	0.053(1)	0.035(2)	0.056(2)	0.002(1)	0.019(1)	0.002(1)
C5'	0.038(1)	0.033(2)	0.042(1)	-0.001(1)	0.013(1)	0.000(1)
C6'	0.046(1)	0.048(2)	0.043(1)	-0.004(1)	0.013(1)	-0.002(1)
C7'	0.063(2)	0.068(2)	0.042(1)	-0.006(2)	0.012(1)	-0.012(2)
C8'	0.068(2)	0.061(2)	0.044(2)	-0.019(2)	0.005(1)	-0.004(2)
C9'	0.040(1)	0.036(2)	0.038(1)	0.001(1)	0.014(1)	-0.004(1)
C10'	0.056(2)	0.036(2)	0.060(2)	0.003(1)	0.019(1)	0.000(2)
C11'	0.069(2)	0.043(2)	0.067(2)	0.013(2)	0.026(1)	0.010(2)
C12'	0.056(2)	0.067(2)	0.049(2)	0.020(2)	0.018(1)	0.012(2)
C13'	0.039(1)	0.060(2)	0.042(1)	0.008(1)	0.012(1)	-0.005(2)
C14'	0.046(1)	0.088(3)	0.046(2)	0.001(2)	0.009(1)	-0.003(2)
C15'	0.044(2)	0.091(3)	0.058(2)	-0.019(2)	0.004(1)	-0.007(2)
C16'	0.050(2)	0.062(2)	0.054(2)	-0.019(2)	0.009(1)	-0.007(2)
C17'	0.037(1)	0.041(2)	0.039(1)	-0.005(1)	0.014(1)	-0.005(1)
C18'	0.036(1)	0.039(2)	0.037(1)	0.003(1)	0.012(1)	-0.004(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-454. Bond Distances (Å) for MC-2 at **295 K**

		Unprimed	Primed
O3	C3	1.208(4)	1.201(4)
O7	C7	1.214(3)	1.202(4)
C1	C2	1.547(4)	1.543(4)
C1	C5	1.604(4)	1.596(4)
C1	C8	1.531(4)	1.537(4)
C1	C9	1.514(3)	1.510(3)
C2	C3	1.501(4)	1.511(4)
C3	C4	1.509(4)	1.507(4)
C4	C5	1.533(4)	1.527(4)
C5	C6	1.538(4)	1.542(4)
C5	C17	1.515(3)	1.522(3)
C6	C7	1.501(5)	1.494(4)
C7	C8	1.497(4)	1.499(5)
C9	C10	1.370(4)	1.374(4)
C9	C18	1.398(4)	1.400(3)
C10	C11	1.415(4)	1.416(4)
C11	C12	1.363(4)	1.367(4)
C12	C13	1.419(4)	1.422(5)
C13	C14	1.413(4)	1.412(4)
C13	C18	1.407(3)	1.404(3)
C14	C15	1.368(4)	1.372(5)
C15	C16	1.424(4)	1.419(4)
C16	C17	1.369(4)	1.366(4)
C17	C18	1.406(3)	1.404(4)

Table 8-455 Bond Angles (°)for MC-2 at **295 K**

			Unprimed	Primed
C2	C1	C5	104.9(2)	105.1(2)
C2	C1	C8	115.5(2)	114.3(2)
C2	C1	C9	110.2(2)	111.2(2)
C5	C1	C8	105.6(2)	105.9(2)
C5	C1	C9	103.4(2)	103.8(2)
C8	C1	C9	115.8(2)	115.2(2)
C1	C2	C3	106.9(2)	106.7(2)
O3	C3	C2	124.6(3)	125.1(3)
O3	C3	C4	125.6(3)	125.7(3)
C2	C3	C4	109.8(3)	109.2(2)
C3	C4	C5	104.3(2)	104.3(2)
C1	C5	C4	105.3(2)	105.7(2)
C1	C5	C6	105.4(2)	105.5(2)
C1	C5	C17	103.3(2)	103.2(2)
C4	C5	C6	114.6(2)	114.0(2)
C4	C5	C17	113.9(2)	114.5(2)
C6	C5	C17	112.9(2)	112.6(2)
C5	C6	C7	107.0(2)	105.8(2)
O7	C7	C6	124.0(3)	124.6(3)
O7	C7	C8	124.7(3)	123.8(3)
C6	C7	C8	111.3(2)	111.7(2)
C1	C8	C7	107.0(2)	106.8(2)
C1	C9	C10	131.5(3)	131.8(2)
C1	C9	C18	109.0(2)	108.9(2)
C10	C9	C18	119.2(2)	119.2(2)
C9	C10	C11	118.1(3)	118.3(3)
C10	C11	C12	122.9(2)	122.6(3)
C11	C12	C13	120.2(2)	120.2(3)
C12	C13	C14	127.8(2)	127.7(2)
C12	C13	C18	115.9(2)	116.1(2)
C14	C13	C18	116.3(2)	116.2(3)
C13	C14	C15	120.4(2)	120.2(3)
C14	C15	C16	122.5(3)	122.6(3)
C15	C16	C17	118.3(3)	118.2(3)
C16	C17	C5	132.1(2)	132.0(3)
C16	C17	C18	119.1(2)	119.3(2)
C5	C17	C18	108.8(2)	108.6(2)
C9	C18	C13	123.6(2)	123.5(3)
C9	C18	C17	112.9(2)	113.0(2)
C13	C18	C17	123.4(2)	123.5(2)

Table 8-456. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for MC-2 at **295 K**

	Unprimed			Primed		
Atom	Min.	Int'med.	Max.	Min.	Int'med.	Max.
O3	0.195	0.310	0.397	0.188	0.290	0.348
O7	0.201	0.284	0.359	0.187	0.286	0.499
C1	0.169	0.189	0.198	0.176	0.203	0.207
C2	0.184	0.223	0.237	0.194	0.209	0.256
C3	0.177	0.247	0.264	0.191	0.220	0.238
C4	0.179	0.222	0.272	0.188	0.210	0.249
C5	0.182	0.189	0.207	0.180	0.186	0.210
C6	0.202	0.240	0.254	0.197	0.211	0.227
C7	0.190	0.213	0.262	0.193	0.246	0.273
C8	0.186	0.225	0.236	0.198	0.226	0.292
C9	0.174	0.187	0.197	0.169	0.194	0.211
C10	0.191	0.210	0.218	0.190	0.222	0.254
C11	0.190	0.200	0.257	0.193	0.229	0.290
C12	0.182	0.191	0.246	0.200	0.206	0.292
C13	0.154	0.195	0.222	0.177	0.209	0.253
C14	0.175	0.210	0.256	0.212	0.215	0.297
C15	0.174	0.214	0.274	0.189	0.248	0.313
C16	0.184	0.204	0.250	0.189	0.233	0.276
C17	0.170	0.179	0.212	0.175	0.189	0.222
C18	0.156	0.183	0.193	0.165	0.199	0.206

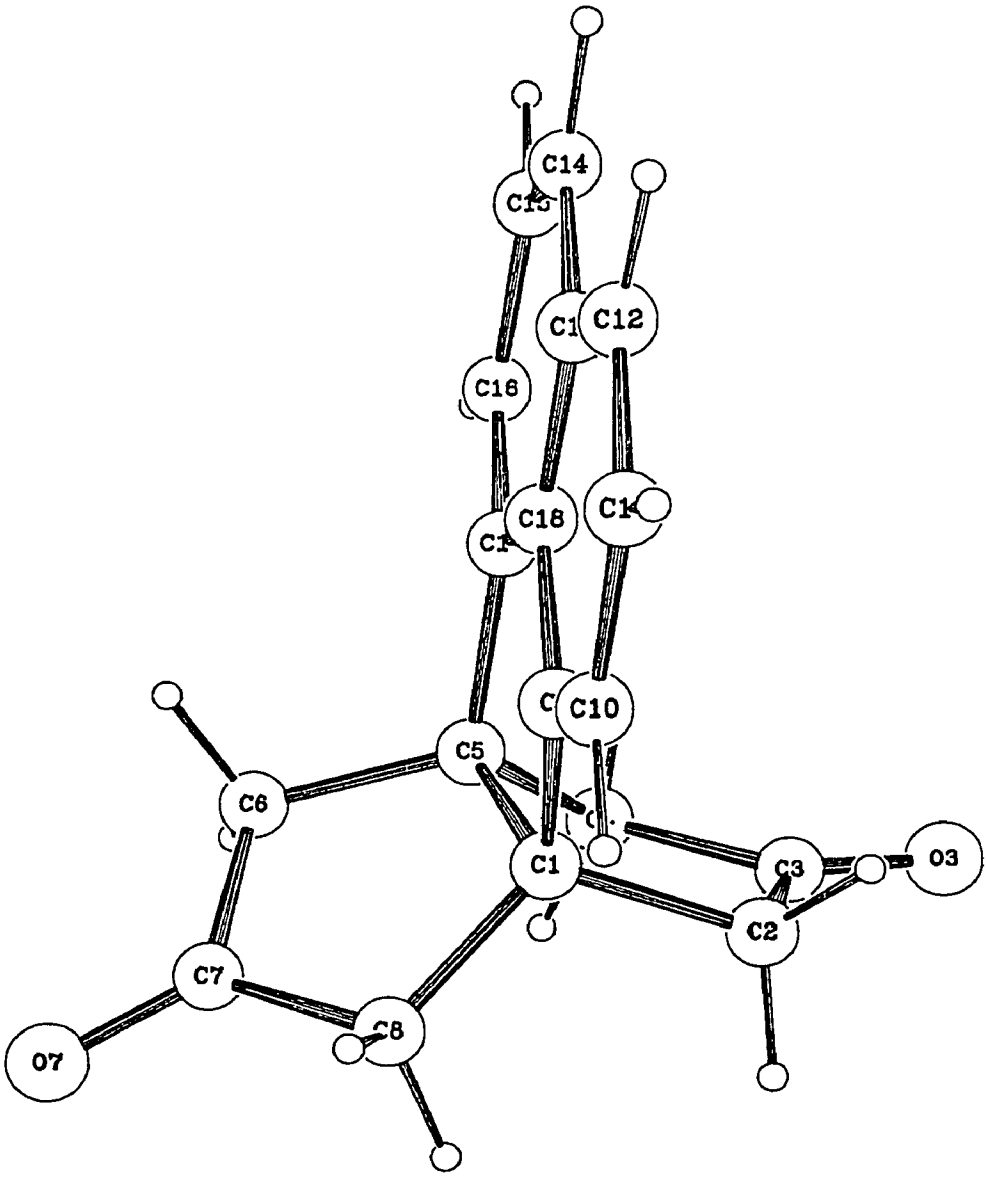


Figure 8–20. *ORTEP* drawing of MC-2 (unprimed) at **295 K.**

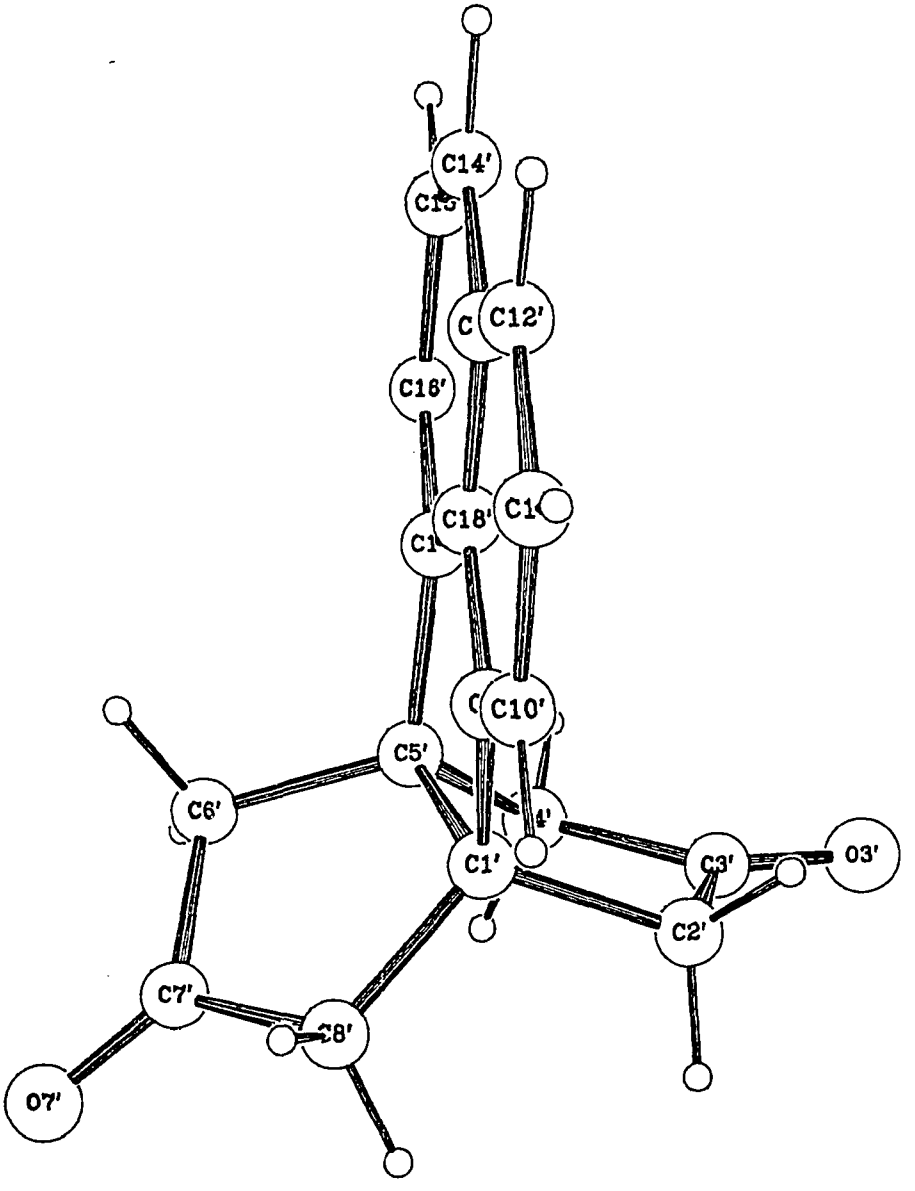
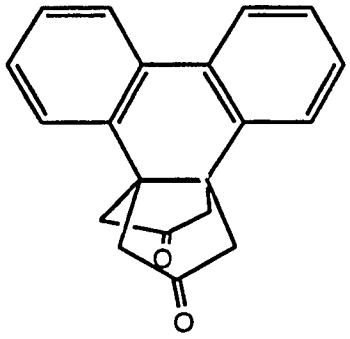


Figure 8–21. *ORTEP* drawing of MC-2 (primed) at **295 K.**



1,5-(9,10-Phenanthro)bicyclo[3.3.0]-3,7-dione
(Phenanthro diketone)
(MC-3)

Table 8–457. X-ray Crystal Data for MC-3 at **295 K**

Formula	$C_{20}H_{26}O_2$
Formula weight	298.429
Melting point (°C)	229–230
Crystal size (mm)	0.09 x 0.25 x 0.44
Crystal system	monoclinic
Space group	$P2_1/a$
a (Å)	14.250(2)
b (Å)	7.142(5)
c (Å)	15.303(3)
β (°)	110.75(1)
Cell volume (Å^3)	110.75(7.56)
Z	4
d_{calc} (g cm^{-3})	1.361
μ(Cu $K\alpha$) (cm^{-1})	6.28
Maximum θ (°)	60
Unique reflections	2153
Observed reflections [$I > 3.0\sigma(I)$]	1777
Number of variables	199
R	0.044
R_w	0.058
$(\Delta\rho)_{max}$ (e Å^{-3})	0.16
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.18

Table 8-458. Final Atomic Parameters for MC-3 at **295 K**

Atom	x	y	z	B(Å^2)
O2	0.5199(1)	0.5323(2)	0.3554(1)	5.58(4)
O7	0.3585(1)	-0.1552(2)	0.48114(9)	5.69(4)
C1	0.3063(1)	0.2548(3)	0.3400(1)	2.96(4)
C2	0.3939(1)	0.3780(3)	0.4013(1)	3.64(4)
C3	0.4586(1)	0.4083(3)	0.3435(1)	3.75(4)
C4	0.4347(1)	0.2631(3)	0.2679(1)	3.92(4)
C5	0.3597(1)	0.1294(3)	0.2875(1)	3.22(4)
C6	0.4113(1)	-0.0189(3)	0.3622(1)	4.26(5)
C7	0.3474(1)	-0.0368(3)	0.4220(1)	3.92(4)
C8	0.2699(1)	0.1154(3)	0.3974(1)	3.66(4)
C9	0.2215(1)	0.3714(3)	0.2749(1)	3.04(4)
C10	0.1897(1)	0.5331(3)	0.3073(1)	3.90(4)
C11	0.1123(1)	0.6417(3)	0.2494(1)	4.62(5)
C12	0.0660(1)	0.5898(3)	0.1574(1)	4.98(5)
C13	0.0948(1)	0.4287(3)	0.1247(1)	4.54(5)
C14	0.1713(1)	0.3147(3)	0.1824(1)	3.29(4)
C15	0.1976(1)	0.1360(3)	0.1481(1)	3.49(4)
C16	0.1336(2)	0.0557(3)	0.0648(1)	4.80(5)
C17	0.1591(2)	-0.1081(4)	0.0304(1)	5.86(6)
C18	0.2484(2)	-0.1959(4)	0.0791(2)	6.09(5)
C19	0.3116(1)	-0.1211(3)	0.1624(1)	5.05(5)
C20	0.2875(1)	0.0445(3)	0.1982(1)	3.57(4)
H2A	0.432	0.312	0.461	4.3
H2B	0.368	0.500	0.416	4.3
H4A	0.497	0.194	0.271	4.7
H4B	0.404	0.323	0.205	4.7
H6A	0.481	0.023	0.401	5.1
H6B	0.415	-0.142	0.332	5.1
H8A	0.202	0.065	0.359	4.3
H8B	0.267	0.176	0.455	4.3
H10	0.224	0.571	0.374	4.6
H11	0.090	0.757	0.274	5.5
H12	0.011	0.669	0.114	5.9
H13	0.060	0.392	0.058	5.4
H16	0.068	0.118	0.029	5.7
H17	0.113	-0.163	-0.030	7.0
H18	0.267	-0.314	0.054	7.3
H19	0.376	-0.187	0.198	6.0

The parameters of the hydrogen atoms were not refined.

Table 8-459. Final Anisotropic Thermal Parameters (U's) for MC-3 at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O2	0.0657(7)	0.0531(9)	0.0984(9)	-0.0216(7)	0.0354(6)	-0.0041(8)
O7	0.0840(9)	0.0603(9)	0.0717(8)	0.0029(8)	0.0272(6)	0.0259(7)
C1	0.0393(7)	0.037(1)	0.0397(8)	-0.0004(7)	0.0175(6)	-0.0017(8)
C2	0.0421(8)	0.047(1)	0.0476(9)	-0.0037(9)	0.0141(7)	-0.0044(9)
C3	0.0388(8)	0.041(1)	0.061(1)	-0.0002(8)	0.0146(7)	0.0059(9)
C4	0.0449(8)	0.051(1)	0.0608(9)	-0.0052(8)	0.0280(6)	-0.0031(9)
C5	0.0394(7)	0.036(1)	0.0524(8)	0.0013(7)	0.0235(6)	-0.0008(8)
C6	0.0522(9)	0.045(1)	0.068(1)	0.0094(9)	0.0253(7)	0.008(1)
C7	0.0527(9)	0.042(1)	0.0505(9)	-0.0067(9)	0.0137(7)	0.0029(9)
C8	0.0486(8)	0.048(1)	0.0481(8)	0.0000(9)	0.0241(6)	0.0056(9)
C9	0.0378(7)	0.037(1)	0.0453(8)	-0.0010(7)	0.0204(6)	0.0008(8)
C10	0.0480(8)	0.045(1)	0.0625(9)	0.0032(9)	0.0285(6)	-0.0036(9)
C11	0.0561(9)	0.046(1)	0.084(1)	0.0103(9)	0.0383(7)	0.008(1)
C12	0.057(1)	0.060(1)	0.077(1)	0.017(1)	0.0299(8)	0.024(1)
C13	0.055(1)	0.063(1)	0.0510(9)	0.004(1)	0.0154(8)	0.014(1)
C14	0.0431(8)	0.043(1)	0.0425(8)	-0.0024(8)	0.0191(6)	0.0044(8)
C15	0.0505(8)	0.047(1)	0.0401(7)	-0.0105(8)	0.0223(6)	-0.0025(8)
C16	0.072(1)	0.064(1)	0.0485(9)	-0.022(1)	0.0240(8)	-0.008(1)
C17	0.093(1)	0.078(2)	0.064(1)	-0.038(1)	0.0436(8)	-0.029(1)
C18	0.093(1)	0.069(1)	0.094(1)	-0.028(1)	0.0626(8)	-0.041(1)
C19	0.0670(9)	0.052(1)	0.089(1)	-0.009(1)	0.0478(7)	-0.024(1)
C20	0.0504(8)	0.041(1)	0.0546(8)	-0.0090(8)	0.0316(6)	-0.0088(8)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-460. Bond Distances (Å) for MC-3 at **295 K**

O2	C3	1.212(2)	C9	C10	1.394(3)
O7	C7	1.207(3)	C9	C14	1.400(2)
C1	C2	1.544(2)	C10	C11	1.382(2)
C1	C5	1.569(3)	C11	C12	1.378(3)
C1	C8	1.534(3)	C12	C13	1.374(3)
C1	C9	1.514(2)	C13	C14	1.396(2)
C2	C3	1.502(3)	C14	C15	1.478(3)
C3	C4	1.500(3)	C15	C16	1.401(2)
C4	C5	1.539(3)	C15	C20	1.400(2)
C5	C6	1.541(3)	C16	C17	1.383(3)
C5	C20	1.517(2)	C17	C18	1.376(3)
C6	C7	1.508(3)	C18	C19	1.381(3)
C7	C8	1.499(3)	C19	C20	1.396(3)

Table 8-461. Bond Angles (°) for MC-3 at **295 K**

C2	C1	C5	101.6(1)	C1	C8	C7	104.3(2)
C2	C1	C8	112.7(1)	C1	C9	C10	120.4(1)
C2	C1	C9	111.8(1)	C1	C9	C14	120.6(2)
C5	C1	C8	104.2(1)	C10	C9	C14	119.0(1)
C5	C1	C9	113.3(1)	C9	C10	C11	121.5(2)
C8	C1	C9	112.4(1)	C10	C11	C12	119.3(2)
C1	C2	C3	104.9(1)	C11	C12	C13	120.0(2)
O2	C3	C2	125.2(2)	C12	C13	C14	121.6(2)
O2	C3	C4	125.1(2)	C9	C14	C13	118.4(2)
C2	C3	C4	109.6(2)	C9	C14	C15	120.4(1)
C3	C4	C5	105.2(2)	C13	C14	C15	121.2(1)
C1	C5	C4	104.0(1)	C14	C15	C16	120.8(2)
C1	C5	C6	101.7(1)	C14	C15	C20	120.4(1)
C1	C5	C20	113.1(1)	C16	C15	C20	118.8(2)
C4	C5	C6	112.9(1)	C15	C16	C17	121.2(2)
C4	C5	C20	111.7(2)	C16	C17	C18	119.8(2)
C6	C5	C20	112.8(1)	C17	C18	C19	119.9(2)
C5	C6	C7	106.0(2)	C18	C19	C20	121.3(2)
O7	C7	C6	124.6(2)	C5	C20	C15	120.3(2)
O7	C7	C8	125.8(2)	C5	C20	C19	120.6(1)
C6	C7	C8	109.6(2)	C15	C20	C19	119.0(1)

Table 8-462 Root-Mean-Square Amplitudes of Thermal Vibration (Å) for MC-3 at **295 K**

Atom	Min.	Int'med.	Max.
O2	0.187	0.280	0.315
O7	0.196	0.290	0.306
C1	0.183	0.191	0.206
C2	0.199	0.216	0.228
C3	0.196	0.198	0.254
C4	0.187	0.224	0.253
C5	0.177	0.193	0.232
C6	0.196	0.229	0.266
C7	0.196	0.220	0.250
C8	0.188	0.219	0.235
C9	0.177	0.194	0.217
C10	0.188	0.219	0.254
C11	0.194	0.222	0.298
C12	0.201	0.232	0.308
C13	0.204	0.240	0.271
C14	0.181	0.212	0.217
C15	0.179	0.202	0.244
C16	0.211	0.218	0.300
C17	0.202	0.229	0.360
C18	0.190	0.234	0.375
C19	0.188	0.226	0.325
C20	0.179	0.192	0.258

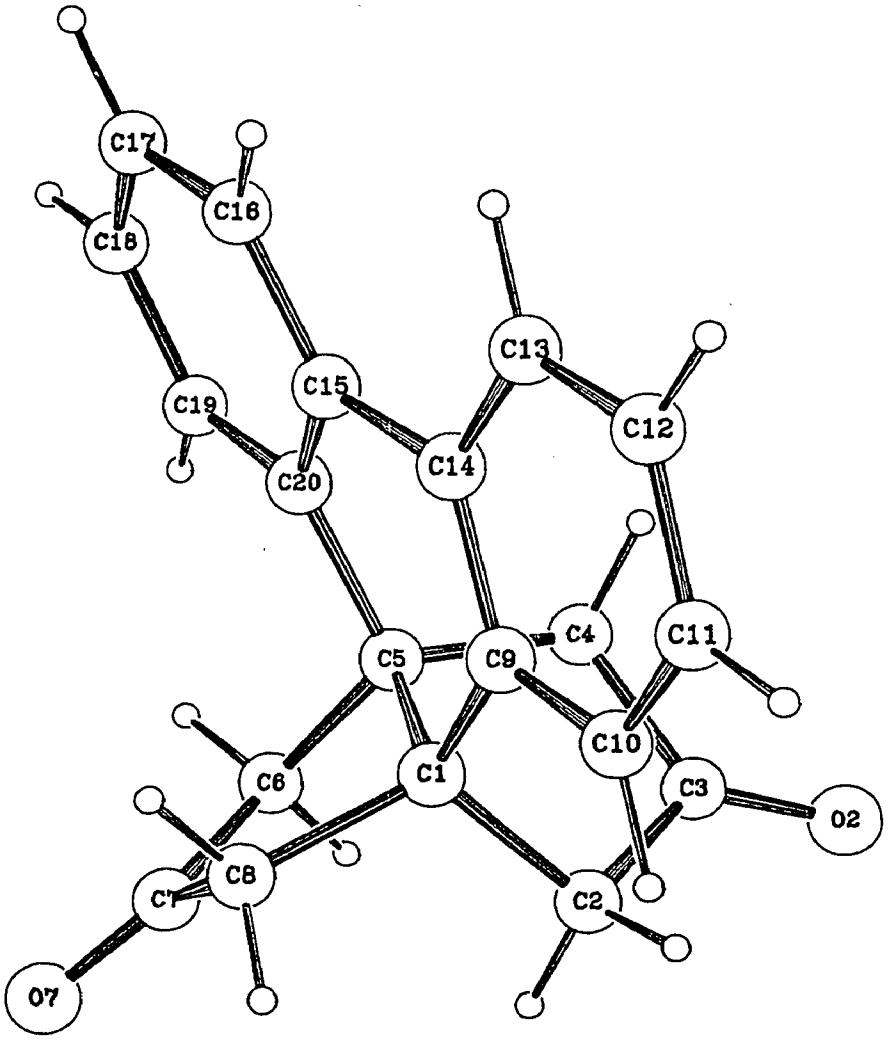
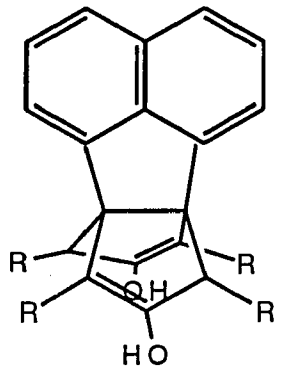


Figure 8–22. *ORTEP* drawing of MC-3 at **295 K.**



R = $COOCH_3$

1,5-(1,2-acenaphtho)-2,4,6,8-tetracarbomethoxybicyclo[3.3.0]octa-2,6-diene-3,7-diol
(Acenaphtho-Weiss)
(MC-4)

Table 8–463. X-ray Crystal Data for MC-4 at **295 K**

Formula	$C_{26}H_{22}O_{10}$
Formula weight	494.46
Melting point (°C)	209–211
Crystal size (mm)	0.28 x 0.29 x 0.33
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.283(4)
b (Å)	12.218(3
c (Å)	17.217(3)
β (°)	95.79(2)
Cell volume ($Å^3$)	2361.34(5.62)
Z	4
d_{calc} (g cm^{-3})	1.391
μ(Cu $K\alpha$) (cm^{-1})	8.70
Maximum θ(°)	75
Unique reflections	4854
Observed reflections [$I > 3.0\sigma(I)$]	2901
Number of variables	325
R	0.051
R_w	0.059
$(\Delta\rho)_{max}$ (e $Å^{-3}$)	0.21
$(\Delta\rho)_{min}$ (e $Å^{-3}$)	-0.27

Table 8-464. Final Atomic Parameters for MC-4 at **295 K**

Atom	x	y	z	B(Å^2)
O3	-0.0125(2)	0.1343(2)	0.4749(1)	4.21(5)
O7	0.1037(2)	0.5972(2)	0.5739(1)	3.44(4)
O19	0.0375(2)	0.2297(2)	0.7092(1)	3.62(5)
O20	0.2677(2)	0.0924(2)	0.4698(1)	4.26(5)
O21	0.2172(2)	0.4676(2)	0.3685(1)	3.71(5)
O22	0.2106(2)	0.4286(2)	0.7674(1)	4.86(6)
O23	-0.0709(2)	0.1271(2)	0.6200(1)	4.54(5)
O24	0.2541(2)	0.1733(2)	0.3529(1)	5.06(6)
O25	0.1350(2)	0.6111(2)	0.4249(1)	3.39(4)
O26	0.3287(2)	0.5154(2)	0.6904(2)	5.20(6)
C1	0.1930(2)	0.3092(2)	0.5981(1)	2.10(5)
C2	0.0902(2)	0.2307(2)	0.5826(2)	2.41(5)
C3	0.0718(2)	0.2026(2)	0.5076(2)	2.70(5)
C4	0.1548(2)	0.2539(2)	0.4557(2)	2.53(5)
C5	0.2273(2)	0.3373(2)	0.5121(1)	2.14(5)
C6	0.1825(2)	0.4529(2)	0.4997(2)	2.30(5)
C7	0.1464(2)	0.4960(2)	0.5648(2)	2.51(5)
C8	0.1542(2)	0.4207(2)	0.6329(2)	2.47(5)
C9	0.3074(2)	0.2622(2)	0.6395(2)	2.33(5)
C10	0.3331(3)	0.2170(2)	0.7119(2)	3.05(6)
C11	0.4536(3)	0.1886(3)	0.7360(2)	3.82(7)
C12	0.5436(3)	0.2070(3)	0.6902(2)	3.84(7)
C13	0.5193(3)	0.2523(2)	0.6148(2)	3.01(6)
C14	0.6023(3)	0.2771(3)	0.5612(2)	3.80(7)
C15	0.5667(3)	0.3257(3)	0.4909(2)	3.84(7)
C16	0.4439(3)	0.3501(3)	0.4683(2)	3.14(6)
C17	0.3619(2)	0.3248(2)	0.5183(2)	2.44(5)
C18	0.3998(2)	0.2779(2)	0.5912(2)	2.49(5)
C19	0.0109(3)	0.1900(2)	0.6378(2)	3.11(6)
C20	0.2305(3)	0.1703(3)	0.4185(2)	3.15(6)
C21	0.1759(2)	0.5176(2)	0.4289(2)	2.71(5)
C22	0.2417(3)	0.4621(2)	0.6989(2)	3.38(6)
C23	-0.0372(3)	0.1952(4)	0.7683(2)	5.46(9)
C24	0.3421(4)	0.0091(3)	0.4407(3)	7.0(1)
C25	0.2164(4)	0.5307(3)	0.2969(2)	4.87(9)
C26	0.2959(5)	0.4494(4)	0.8358(2)	7.6(1)
HO3	-0.054	0.114	0.515	4.9
HO7	0.103	0.628	0.526	4.0
H4	0.114	0.291	0.409	3.0
H8	0.078	0.414	0.657	2.9
H10	0.269	0.204	0.747	3.6
H11	0.473	0.154	0.788	4.5
H12	0.627	0.188	0.710	4.5
H14	0.688	0.259	0.575	4.5
H15	0.628	0.345	0.455	4.5
H16	0.419	0.385	0.417	3.7
H23A	-0.009	0.230	0.819	6.5
H23B	-0.122	0.218	0.752	6.5
H23C	-0.033	0.114	0.774	6.5
H24A	0.365	-0.045	0.483	8.3
H24B	0.297	-0.029	0.395	8.3
H24C	0.415	0.044	0.423	8.3
H25A	0.249	0.485	0.256	5.8
H25B	0.133	0.553	0.279	5.8
H25C	0.266	0.598	0.307	5.8
H26A	0.264	0.421	0.884	9.0
H26B	0.373	0.411	0.829	9.0
H26C	0.311	0.530	0.841	9.0

Table 8-465. Final Anisotropic Thermal Parameters (U's) for MC-4 at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O3	0.049(1)	0.061(1)	0.049(1)	-0.023(1)	-0.002(1)	-0.013(1)
O7	0.050(1)	0.033(1)	0.048(1)	0.0142(9)	0.006(1)	-0.0011(9)
O19	0.047(1)	0.057(1)	0.035(1)	-0.003(1)	0.0160(8)	0.004(1)
O20	0.062(1)	0.043(1)	0.056(1)	0.017(1)	0.004(1)	-0.007(1)
O21	0.067(1)	0.042(1)	0.033(1)	0.004(1)	0.0107(9)	0.0089(9)
O22	0.098(2)	0.056(1)	0.027(1)	0.001(1)	-0.011(1)	-0.004(1)
O23	0.046(1)	0.057(1)	0.071(1)	-0.021(1)	0.014(1)	-0.001(1)
O24	0.081(2)	0.073(2)	0.042(1)	-0.000(1)	0.026(1)	-0.014(1)
O25	0.039(1)	0.037(1)	0.053(1)	0.0077(9)	0.0033(9)	0.0142(9)
O26	0.060(1)	0.060(1)	0.073(2)	-0.016(1)	-0.015(1)	-0.009(1)
C1	0.027(1)	0.028(1)	0.025(1)	0.001(1)	0.0027(9)	0.001(1)
C2	0.031(1)	0.028(1)	0.033(1)	-0.001(1)	0.005(1)	0.002(1)
C3	0.031(1)	0.035(1)	0.036(1)	-0.001(1)	-0.000(1)	-0.002(1)
C4	0.036(1)	0.034(1)	0.026(1)	-0.000(1)	0.000(1)	-0.001(1)
C5	0.028(1)	0.028(1)	0.025(1)	0.002(1)	0.000(1)	0.000(1)
C6	0.024(1)	0.031(1)	0.032(1)	0.001(1)	0.001(1)	0.004(1)
C7	0.030(1)	0.028(1)	0.037(1)	0.004(1)	0.000(1)	0.001(1)
C8	0.032(1)	0.034(1)	0.028(1)	0.001(1)	0.002(1)	-0.003(1)
C9	0.030(1)	0.029(1)	0.028(1)	0.001(1)	-0.002(1)	0.001(1)
C10	0.041(1)	0.039(1)	0.036(1)	0.002(1)	-0.001(1)	0.006(1)
C11	0.051(2)	0.048(2)	0.044(2)	0.005(2)	-0.011(1)	0.013(1)
C12	0.039(2)	0.047(2)	0.057(2)	0.004(1)	-0.011(1)	0.008(2)
C13	0.030(1)	0.034(1)	0.049(2)	0.001(1)	-0.003(1)	-0.000(1)
C14	0.028(1)	0.049(2)	0.068(2)	0.000(1)	0.006(1)	-0.002(2)
C15	0.036(1)	0.052(2)	0.060(2)	-0.001(1)	0.017(1)	-0.001(2)
C16	0.035(1)	0.046(2)	0.040(1)	-0.001(1)	0.010(1)	-0.001(1)
C17	0.030(1)	0.029(1)	0.034(1)	0.003(1)	0.003(1)	-0.002(1)
C18	0.030(1)	0.030(1)	0.034(1)	0.001(1)	0.001(1)	-0.000(1)
C19	0.037(1)	0.039(1)	0.043(1)	0.000(1)	0.007(1)	0.002(1)
C20	0.041(2)	0.043(2)	0.035(1)	-0.005(1)	0.004(1)	-0.011(1)
C21	0.030(1)	0.035(1)	0.038(1)	-0.004(1)	0.001(1)	0.003(1)
C22	0.053(2)	0.034(1)	0.039(1)	0.006(1)	-0.007(1)	-0.006(1)
C23	0.072(2)	0.087(3)	0.054(2)	0.001(2)	0.038(1)	0.017(2)
C24	0.081(3)	0.066(2)	0.118(3)	0.039(2)	0.006(2)	-0.024(2)
C25	0.096(3)	0.054(2)	0.035(2)	-0.002(2)	0.011(2)	0.016(2)
C26	0.158(4)	0.076(3)	0.043(2)	-0.001(3)	-0.050(2)	-0.005(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-466. Bond Distances (') for MC-4 at **295 K**

O3	C3	1.345(3)	C3	C4	1.495(4)
O7	C7	1.342(3)	C4	C5	1.579(4)
O19	C19	1.327(3)	C4	C20	1.514(4)
O19	C23	1.448(4)	C5	C6	1.509(4)
O20	C20	1.337(4)	C5	C17	1.520(4)
O20	C24	1.441(5)	C6	C7	1.338(4)
O21	C21	1.329(4)	C6	C21	1.449(4)
O21	C25	1.453(4)	C7	C8	1.485(4)
O22	C22	1.330(4)	C8	C22	1.515(4)
O22	C26	1.466(5)	C9	C10	1.367(4)
O23	C19	1.216(4)	C9	C18	1.410(4)
O24	C20	1.188(4)	C10	C11	1.424(4)
O25	C21	1.232(3)	C11	C12	1.366(5)
O26	C22	1.199(4)	C12	C13	1.411(4)
C1	C2	1.508(4)	C13	C14	1.413(4)
C1	C5	1.604(4)	C13	C18	1.404(4)
C1	C8	1.568(4)	C14	C15	1.372(5)
C1	C9	1.523(3)	C15	C16	1.432(4)
C2	C3	1.333(4)	C16	C17	1.361(4)
C2	C19	1.458(4)	C17	C18	1.406(4)

Table 8-467. Bond Angles (') for MC-4 at **295 K**

C19	O19	C23	116.8(2)	C1	C8	C22	113.0(2)
C20	O20	C24	115.4(3)	C7	C8	C22	111.5(2)
C21	O21	C25	116.6(2)	C1	C9	C10	132.1(2)
C22	O22	C26	116.6(3)	C1	C9	C18	108.3(2)
C2	C1	C5	103.0(2)	C10	C9	C18	119.4(2)
C2	C1	C8	112.4(2)	C9	C10	C11	118.2(3)
C2	C1	C9	116.3(2)	C10	C11	C12	122.3(3)
C5	C1	C8	105.6(2)	C11	C12	C13	120.6(3)
C5	C1	C9	103.9(2)	C12	C13	C14	127.2(3)
C8	C1	C9	113.9(2)	C12	C13	C18	116.4(3)
C1	C2	C3	112.2(2)	C14	C13	C18	116.3(3)
C1	C2	C19	127.9(2)	C13	C14	C15	121.0(3)
C3	C2	C19	119.9(2)	O20	C20	C4	110.7(2)
O3	C3	C2	126.8(3)	O24	C20	C4	124.9(3)
O3	C3	C4	118.0(2)	O21	C21	O25	122.8(3)
C2	C3	C4	115.2(2)	O21	C21	C6	114.6(2)
C3	C4	C5	102.7(2)	O25	C21	C6	122.6(3)
C3	C4	C20	112.6(2)	O22	C22	O26	124.7(3)
C5	C4	C20	114.6(2)	O22	C22	C8	110.6(3)
C1	C5	C4	105.8(2)	O26	C22	C8	124.7(3)
C1	C5	C6	102.8(2)	C14	C15	C16	121.2(3)
C1	C5	C17	104.3(2)	C15	C16	C17	118.8(3)
C4	C5	C6	111.8(2)	C5	C17	C16	132.1(2)
C4	C5	C17	115.5(2)	C5	C17	C18	108.3(2)
C6	C5	C17	115.0(2)	C16	C17	C18	119.5(2)
C5	C6	C7	112.1(2)	C9	C18	C13	122.9(2)
C5	C6	C21	128.1(2)	C9	C18	C17	114.0(2)
C7	C6	C21	119.8(2)	C13	C18	C17	123.1(3)
O7	C7	C6	127.1(2)	O19	C19	O23	124.1(3)
O7	C7	C8	118.1(2)	O19	C19	C2	112.5(2)
C6	C7	C8	114.8(2)	O23	C19	C2	123.4(3)
C1	C8	C7	103.5(2)	O20	C20	O24	124.4(3)

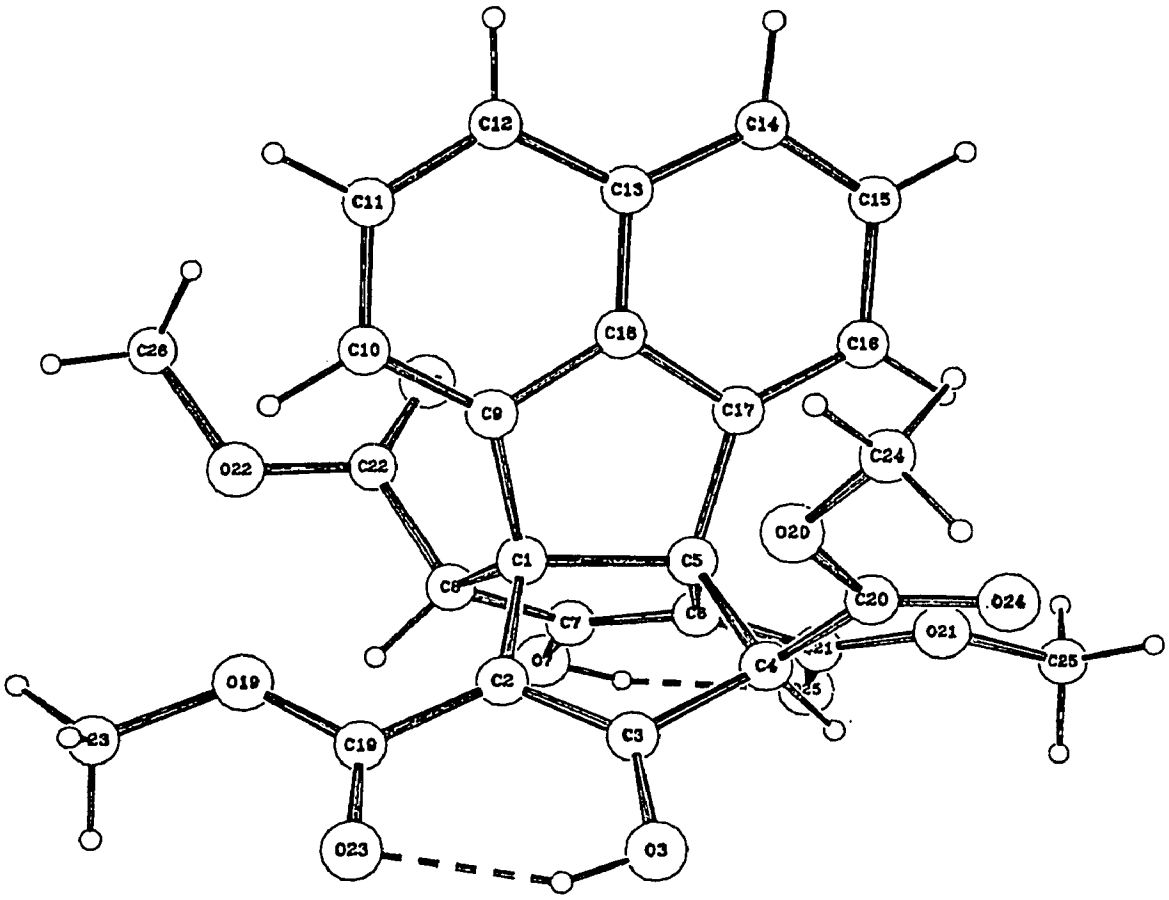
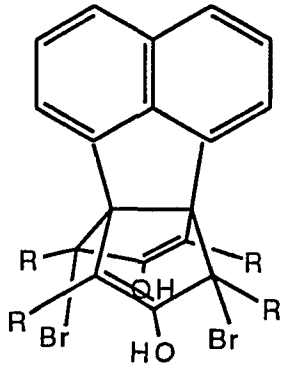


Figure 8–23. *ORTEP* drawing of MC-4 at **295 K.**



R = $COOCH_3$

Acenaphtho-3,7-enol-tetraester
(MC-5)

Table 8–468. X-ray Crystal Data for MC-5 at **295 K**

Formula	$C_{26}H_{20}Br_2O_{10}$
Formula weight	652.26
Melting point (°C)	
Crystal size (mm)	0.09 x 0.14 x 0.44
Crystal system	monoclinic
Space group	$P2_1/a$
a (Å)	17.995(3)
b (Å)	9.738(8)
c (Å)	19.166(3)
β (°)	112.42(1)
Cell volume (Å^3)	3104.95(18.37)
Z	4
d_{calc} (g cm^{-3})	1.395
μ(Cu $K\alpha$) (cm^{-1})	7.48
Maximum θ (°)	60
Unique reflections	4592
Observed reflections [$I > 3.0\sigma(I)$]	3837
Number of variables	397
R	0.039
R_w	0.049
$(\Delta\rho)_{max}$ (e Å^{-3})	0.56
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.61

Table 8-469. Final Atomic Parameters for MC-5 at **295 K**

Atom	x	y	z	B(Å^2)
Br1	0.18267(2)	0.89715(5)	0.91074(2)	3.153(9)
Br2	0.01289(2)	0.95846(5)	0.69837(2)	3.41(1)
O3	0.2820(1)	0.8903(3)	0.8026(1)	3.16(6)
O7	-0.0814(1)	0.7561(3)	0.7705(1)	3.49(6)
O22	0.2202(2)	0.9263(3)	0.6564(2)	4.18(7)
O23	0.1055(2)	0.8157(3)	0.5884(1)	3.43(6)
O24	0.2977(2)	0.6577(4)	0.9718(1)	4.34(8)
O25	0.3149(2)	0.6127(3)	0.8643(1)	3.47(7)
O26	-0.0166(1)	0.6754(4)	0.9122(1)	4.19(7)
O27	0.1126(1)	0.6103(3)	0.9584(1)	3.28(6)
O28	-0.0723(2)	0.7651(3)	0.5709(1)	4.03(7)
O29	-0.0865(2)	0.5920(3)	0.6419(1)	3.60(7)
C1	0.0956(2)	0.6894(4)	0.7240(2)	2.01(7)
C2	0.1600(2)	0.7838(4)	0.7195(2)	2.21(8)
C3	0.2169(2)	0.8118(4)	0.7874(2)	2.22(7)
C4	0.2032(2)	0.7467(4)	0.8524(2)	2.21(8)
C5	0.1277(2)	0.6523(4)	0.8128(2)	1.99(7)
C6	0.0546(2)	0.6792(4)	0.8318(2)	2.34(8)
C7	-0.0082(2)	0.7278(4)	0.7729(2)	2.44(8)
C8	0.0101(2)	0.7575(4)	0.7046(2)	2.26(8)
C9	0.0936(2)	0.5505(4)	0.6855(2)	2.11(7)
C10	0.0700(2)	0.5134(4)	0.6113(2)	2.70(8)
C11	0.0798(2)	0.3752(5)	0.5941(2)	3.4(1)
C12	0.1113(2)	0.2777(4)	0.6480(2)	3.4(1)
C12A	0.1354(2)	0.3119(4)	0.7256(2)	2.73(8)
C13	0.1684(3)	0.2223(4)	0.7877(2)	3.5(1)
C14	0.1881(3)	0.2714(4)	0.8599(2)	3.4(1)
C15	0.1782(2)	0.4106(4)	0.8751(2)	2.80(8)
C16	0.1474(2)	0.4996(4)	0.8161(2)	2.17(7)
C16A	0.1257(2)	0.4507(4)	0.7420(2)	2.24(8)
C22	0.1657(2)	0.8480(4)	0.6528(2)	2.87(8)
C23	0.1062(3)	0.8822(6)	0.5200(2)	5.9(1)
C24	0.2774(2)	0.6694(4)	0.9055(2)	2.73(9)
C25	0.3819(3)	0.5221(6)	0.9049(3)	5.4(1)
C26	0.0465(2)	0.6548(4)	0.9041(2)	2.82(8)
C27	0.1093(3)	0.5863(6)	1.0320(2)	4.9(1)
C28	-0.0546(2)	0.7084(4)	0.6303(2)	2.71(8)
C29	-0.1457(3)	0.5288(6)	0.5744(3)	5.0(1)
O31	0.1561(3)	0.8509(5)	0.2748(3)	10.0(2)
O32	0.1892(3)	0.8131(6)	0.3954(3)	10.8(2)
C31	0.1881(3)	0.8912(7)	0.3460(3)	7.0(2)
C32	0.2162(3)	1.0279(8)	0.3550(4)	8.3(2)
C33	0.1314(7)	0.706(1)	0.2487(6)	16.3(4)
C34	0.0516(5)	0.706(1)	0.2188(7)	19.9(4)

Table 8-469 (cont.). Final Atomic Parameters for MC-5 at **295 K**

Atom	x	y	z	B(Å^2)
HO3	0.278	0.922	0.757	3.7
HO7	-0.079	0.737	0.817	4.2
H10	0.047	0.583	0.570	3.2
H11	0.062	0.348	0.540	4.1
H12	0.118	0.181	0.633	4.1
H13	0.178	0.124	0.779	4.3
H14	0.210	0.206	0.903	4.1
H15	0.194	0.444	0.928	3.4
H23A	0.058	0.851	0.475	7.1
H23B	0.103	0.985	0.525	7.1
H23C	0.156	0.858	0.513	7.1
H25A	0.406	0.485	0.870	6.4
H25B	0.424	0.575	0.946	6.4
H25C	0.362	0.444	0.927	6.4
H27A	0.163	0.554	1.068	5.8
H27B	0.095	0.675	1.051	5.8
H27C	0.067	0.516	1.027	5.8
H29A	-0.166	0.442	0.589	6.0
H29B	-0.191	0.594	0.551	6.0
H29C	-0.120	0.507	0.538	6.0
H32A	0.240	1.052	0.410	10.0
H32B	0.259	1.038	0.334	10.0
H32C	0.171	1.092	0.328	10.0
H33A	0.151	0.644	0.294	18.6
H33B	0.155	0.678	0.213	18.6
H34A	0.033	0.610	0.201	23.4
H34B	0.029	0.736	0.256	23.4
H34C	0.033	0.770	0.174	23.4

The parameters of the hydrogen atoms were not refined.

Table 8-470. Final Anisotropic Thermal Parameters (U's) for MC-5 at 295 K

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Br1	0.0558(2)	0.0278(2)	0.0383(2)	-0.0034(2)	0.0202(1)	-0.0098(2)
Br2	0.0494(2)	0.0270(2)	0.0534(2)	0.0064(2)	0.0197(2)	0.0042(2)
O3	0.039(1)	0.039(2)	0.040(1)	-0.012(1)	0.0128(9)	0.000(1)
O7	0.036(1)	0.064(2)	0.039(1)	0.009(1)	0.0205(8)	0.006(1)
O22	0.058(1)	0.059(2)	0.047(1)	-0.019(1)	0.025(1)	0.010(1)
O23	0.051(1)	0.049(2)	0.028(1)	-0.007(1)	0.0125(9)	0.009(1)
O24	0.061(2)	0.064(2)	0.028(1)	0.008(2)	0.004(1)	0.005(1)
O25	0.044(1)	0.040(2)	0.046(1)	0.014(1)	0.016(1)	0.006(1)
O26	0.046(1)	0.082(2)	0.040(1)	0.009(1)	0.0264(9)	0.012(1)
O27	0.045(1)	0.054(2)	0.028(1)	-0.001(1)	0.0166(8)	0.006(1)
O28	0.062(2)	0.054(2)	0.028(1)	0.004(2)	0.008(1)	0.006(1)
O29	0.045(1)	0.052(2)	0.037(1)	-0.018(1)	0.012(1)	-0.006(1)
C1	0.031(1)	0.025(2)	0.021(1)	-0.000(1)	0.010(1)	0.003(1)
C2	0.033(2)	0.023(2)	0.029(1)	-0.001(2)	0.012(1)	0.003(1)
C3	0.033(2)	0.018(2)	0.035(2)	0.002(1)	0.015(1)	0.001(1)
C4	0.034(2)	0.023(2)	0.026(1)	-0.000(2)	0.011(1)	-0.002(1)
C5	0.032(1)	0.022(2)	0.021(1)	-0.002(1)	0.010(1)	-0.000(1)
C6	0.036(2)	0.028(2)	0.029(1)	-0.002(2)	0.016(1)	-0.001(2)
C7	0.035(2)	0.030(2)	0.030(1)	-0.001(2)	0.017(1)	-0.001(2)
C8	0.032(2)	0.022(2)	0.030(2)	-0.001(2)	0.009(1)	0.002(2)
C9	0.030(1)	0.024(2)	0.025(1)	-0.001(1)	0.010(1)	-0.002(1)
C10	0.042(2)	0.031(2)	0.029(2)	-0.000(2)	0.013(1)	-0.003(2)
C11	0.053(2)	0.044(3)	0.033(2)	-0.003(2)	0.016(1)	-0.015(2)
C12	0.056(2)	0.031(2)	0.043(2)	0.000(2)	0.018(2)	-0.010(2)
C12A	0.045(2)	0.024(2)	0.036(2)	-0.003(2)	0.016(1)	-0.005(2)
C13	0.065(2)	0.021(2)	0.045(2)	0.001(2)	0.017(2)	0.000(2)
C14	0.060(2)	0.024(2)	0.043(2)	0.004(2)	0.015(2)	0.006(2)
C15	0.049(2)	0.028(2)	0.027(2)	0.003(2)	0.011(1)	0.004(2)
C16	0.034(2)	0.021(2)	0.028(1)	-0.003(2)	0.011(1)	0.001(1)
C16A	0.035(2)	0.022(2)	0.029(1)	-0.002(2)	0.013(1)	0.000(1)
C22	0.042(2)	0.034(2)	0.036(2)	0.004(2)	0.018(1)	0.007(2)
C23	0.099(3)	0.090(4)	0.030(2)	-0.019(3)	0.019(2)	0.019(2)
C24	0.038(2)	0.026(2)	0.034(2)	-0.006(2)	0.008(1)	-0.001(2)
C25	0.054(2)	0.063(3)	0.085(3)	0.026(2)	0.021(2)	0.018(3)
C26	0.043(2)	0.036(2)	0.030(2)	-0.004(2)	0.015(1)	0.001(2)
C27	0.067(2)	0.093(4)	0.029(2)	-0.001(3)	0.022(1)	0.014(2)
C28	0.034(2)	0.039(2)	0.030(2)	0.004(2)	0.011(1)	-0.002(2)
C29	0.055(2)	0.082(4)	0.050(2)	-0.033(2)	0.015(2)	-0.020(3)
O31	0.189(4)	0.088(3)	0.095(3)	0.030(3)	0.045(3)	0.015(3)
O32	0.196(4)	0.106(4)	0.135(3)	0.002(3)	0.094(2)	0.024(3)
C31	0.086(3)	0.090(4)	0.102(3)	0.020(3)	0.051(2)	0.028(3)
C32	0.057(3)	0.098(5)	0.145(6)	0.000(3)	0.023(3)	0.028(4)
C33	0.29(1)	0.116(8)	0.240(9)	0.051(8)	0.137(7)	0.050(7)
C34	0.210(5)	0.104(7)	0.55(1)	-0.033(5)	0.267(5)	-0.020(8)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-471. Bond Distances (Å) for MC-5 at **295 K**

Br1	C4	1.962(4)
Br2	C8	1.962(4)
O3	C3	1.334(4)
O7	C7	1.328(5)
O22	C22	1.224(5)
O23	C22	1.332(4)
O23	C23	1.467(6)
O24	C24	1.186(5)
O25	C24	1.339(5)
O25	C25	1.456(5)
O26	C26	1.218(5)
O27	C26	1.320(4)
O27	C27	1.453(5)
O28	C28	1.194(5)
O29	C28	1.328(5)
O29	C29	1.462(5)
C1	C2	1.508(5)
C1	C5	1.616(4)
C1	C8	1.584(5)
C1	C9	1.533(5)
C2	C3	1.341(4)
C2	C22	1.461(6)
C3	C4	1.499(5)
C4	C5	1.576(5)
C4	C24	1.533(5)
C5	C6	1.515(5)
C5	C16	1.524(5)
C6	C7	1.342(4)
C6	C26	1.469(5)
C7	C8	1.494(6)
C8	C28	1.533(4)
C9	C10	1.370(5)
C9	C16A	1.404(5)
C10	C11	1.413(6)
C11	C12	1.357(6)
C12	C12A	1.421(5)
C12A	C13	1.412(5)
C12A	C16A	1.413(5)
C13	C14	1.376(6)
C14	C15	1.412(6)
C15	C16	1.365(5)
C16	C16A	1.405(5)
O31	C31	1.323(7)
O31	C33	1.51(1)
O32	C31	1.208(9)
C31	C32	1.41(1)
C33	C34	1.33(1)

Table 8-472. Bond Angles in Degrees for MC-5 at **295 K**

C22	O23	C23	116.3(3)	C1	C8	C28	114.3(3)
C24	O25	C25	115.8(3)	C7	C8	C28	114.3(3)
C26	O27	C27	117.4(3)	C1	C9	C10	132.3(3)
C28	O29	C29	115.2(3)	C1	C9	C16A	108.3(3)
C2	C1	C5	102.8(2)	C10	C9	C16A	119.4(3)
C2	C1	C8	115.5(3)	C9	C10	C11	118.5(3)
C2	C1	C9	112.8(3)	C10	C11	C12	122.8(4)
C5	C1	C8	105.4(3)	C11	C12	C12A	120.3(4)
C5	C1	C9	104.0(3)	C12	C12A	C13	126.9(4)
C8	C1	C9	114.5(2)	C12	C12A	C16A	116.2(3)
C1	C2	C3	112.8(3)	C13	C12A	C16A	116.8(3)
C1	C2	C22	128.5(3)	C12A	C13	C14	119.8(4)
C3	C2	C22	118.7(3)	C13	C14	C15	122.5(4)
O3	C3	C2	127.5(4)	C14	C15	C16	118.8(3)
O3	C3	C4	118.0(3)	C5	C16	C15	131.9(3)
C2	C3	C4	114.5(3)	C5	C16	C16A	108.6(3)
Br1	C4	C3	106.5(3)	C15	C16	C16A	119.4(3)
Br1	C4	C5	113.3(3)	C9	C16A	C12A	122.7(3)
Br1	C4	C24	107.1(2)	C9	C16A	C16	114.7(3)
C3	C4	C5	103.4(2)	C12A	C16A	C16	122.6(3)
C3	C4	C24	112.4(3)	O22	C22	O23	123.3(4)
C5	C4	C24	114.0(3)	O22	C22	C2	122.7(3)
C1	C5	C4	105.9(3)	O23	C22	C2	114.0(3)
C1	C5	C6	102.7(2)	O24	C24	O25	125.0(3)
C1	C5	C16	104.2(3)	O24	C24	C4	126.4(4)
C4	C5	C6	116.8(3)	O25	C24	C4	108.6(3)
C4	C5	C16	113.9(3)	O26	C26	O27	123.9(4)
C6	C5	C16	111.7(3)	O26	C26	C6	121.7(3)
C5	C6	C7	112.9(3)	O27	C26	C6	114.4(3)
C5	C6	C26	127.4(3)	O28	C28	O29	125.5(3)
C7	C6	C26	119.7(3)	O28	C28	C8	125.0(4)
O7	C7	C6	127.5(4)	O29	C28	C8	109.5(3)
O7	C7	C8	118.3(3)	C31	O31	C33	125.3(6)
C6	C7	C8	114.1(3)	O31	C31	O32	119.6(6)
Br2	C8	C1	112.8(2)	O31	C31	C32	113.6(6)
Br2	C8	C7	105.4(3)	O32	C31	C32	126.9(6)
Br2	C8	C28	106.4(2)	O31	C33	C34	105.8(9)
C1	C8	C7	103.4(3)				

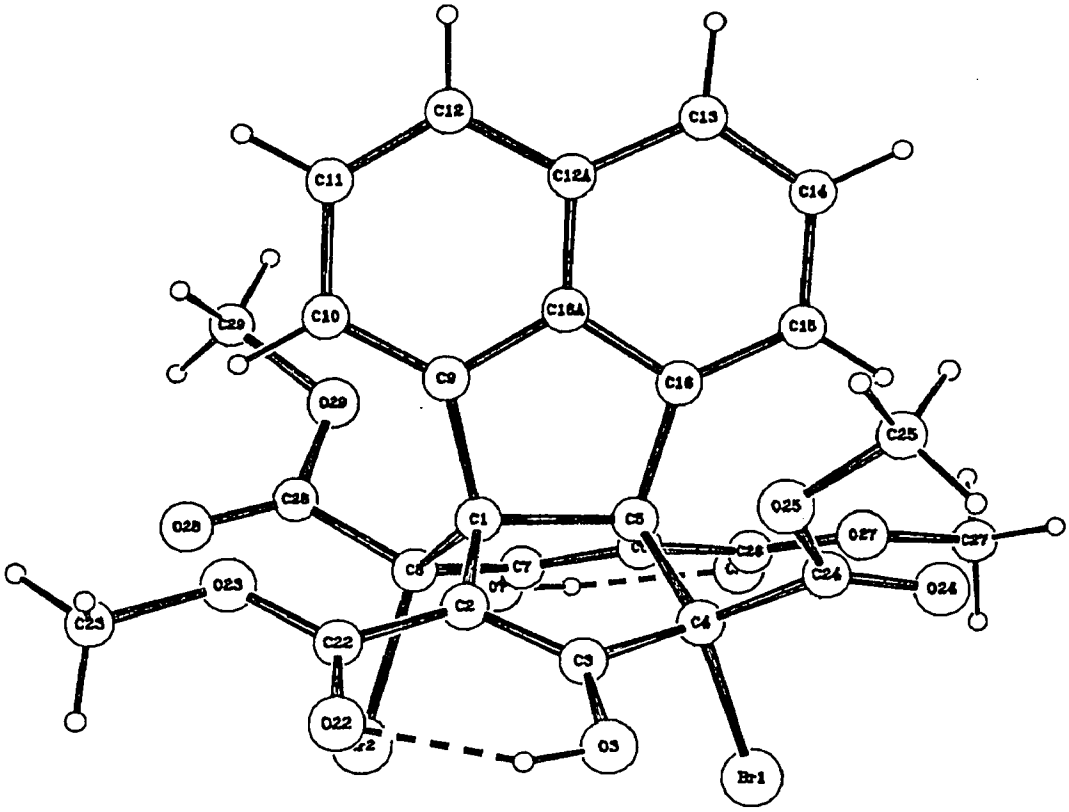
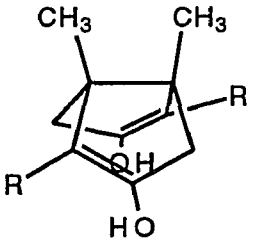


Figure 8–24. *ORTEP* drawing of MC-5 at **295 K.**



R = $COOCH_3$

1,5-Dimethyl-2,6-dicarbomethoxybicyclo[3.3.0]octa-2,6-diene-3,7-diol
(Diester Weiss)
(MC-6)

Table 8–473. X-ray Crystal Data for MC-6 at **115 K**

Formula	$C_{14}H_{18}O_6$
Formula weight	282.30
Melting point (°C)	138–140
Crystal size (mm)	0.08 x 0.20 x 0.30
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	17.936(2)
b (Å)	7.079(2)
c (Å)	10.734(2)
β (°)	95.84(1)
Cell volume (Å^3)	1355.71(1.67)
Z	4
d_{calc} (g cm^{-3})	1.383
μ(Cu $K\alpha$) (cm^{-1})	8.70
Maximum θ (°)	75
Unique reflections	2786
Observed reflections [$I > 3.0\sigma(I)$]	2222
Number of variables	181
R	0.041
R_w	0.053
$(\Delta\rho)_{max}$ (e Å^{-3})	0.26
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.24

Table 8-474. Final Atomic Parameters for MC-6 at **115 K**

Atom	x	y	z	B(Å^2)
O1	0.09282(6)	0.5771(2)	0.4263(1)	1.61(2)
O2	0.07112(7)	0.2656(2)	0.3986(1)	2.00(2)
O3	0.14573(7)	0.0287(2)	0.5532(1)	1.95(2)
O5	0.40901(7)	0.1219(2)	0.6825(1)	1.77(2)
O6	0.45360(7)	0.2954(2)	0.5307(1)	1.74(2)
O7	0.37288(6)	0.5902(2)	0.4412(1)	1.84(2)
C1	0.21646(8)	0.5080(2)	0.6254(1)	1.13(2)
C2	0.16790(9)	0.3640(2)	0.5499(1)	1.25(3)
C3	0.18131(9)	0.1867(2)	0.5935(2)	1.42(3)
C4	0.24154(9)	0.1785(2)	0.6992(2)	1.44(3)
C5	0.27890(8)	0.3752(2)	0.6952(1)	1.14(3)
C6	0.33958(8)	0.3846(2)	0.6058(1)	1.20(3)
C7	0.32860(8)	0.5325(2)	0.5266(1)	1.27(3)
C8	0.25907(9)	0.6402(2)	0.5428(2)	1.33(3)
C9	0.17009(9)	0.6178(2)	0.7123(2)	1.47(3)
C10	0.30970(9)	0.4428(3)	0.8254(2)	1.57(3)
C21	0.10732(9)	0.3953(2)	0.4526(2)	1.40(3)
C22	0.0316(1)	0.6130(3)	0.3305(2)	2.03(3)
C61	0.40522(9)	0.2671(2)	0.6019(1)	1.37(3)
C62	0.4700(1)	-0.0106(3)	0.6732(2)	2.42(3)
HO3	0.112	0.067	0.491	2.3
HO7	0.411	0.508	0.448	2.2
H4A	0.278	0.076	0.686	1.7
H4B	0.220	0.158	0.781	1.7
H8A	0.271	0.763	0.586	1.6
H8B	0.229	0.664	0.460	1.6
H9A	0.132	0.697	0.661	1.8
H9B	0.144	0.527	0.764	1.8
H9C	0.204	0.701	0.768	1.8
H10A	0.348	0.352	0.862	1.9
H10B	0.333	0.570	0.819	1.9
H10C	0.268	0.451	0.880	1.9
H22A	0.025	0.752	0.318	2.4
H22B	0.043	0.553	0.250	2.4
H22C	-0.016	0.559	0.357	2.4
H62A	0.468	-0.113	0.737	2.9
H62B	0.465	-0.068	0.588	2.9
H62C	0.519	0.057	0.689	2.9

The parameters of the hydrogen atoms were not refined.

Table 8-475. Final Anisotropic Thermal Parameters (U's) for MC-6 at **115 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0164(5)	0.0208(5)	0.0235(5)	0.0009(5)	-0.0013(4)	0.0044(5)
O2	0.0244(6)	0.0244(6)	0.0261(6)	-0.0045(5)	-0.0019(5)	-0.0025(5)
O3	0.0270(6)	0.0149(5)	0.0318(6)	-0.0055(5)	0.0015(5)	-0.0012(5)
O5	0.0218(5)	0.0226(6)	0.0234(5)	0.0105(5)	0.0054(4)	0.0046(5)
O6	0.0177(5)	0.0249(6)	0.0247(5)	0.0027(5)	0.0083(4)	-0.0003(5)
O7	0.0203(5)	0.0237(6)	0.0277(5)	0.0018(5)	0.0116(4)	0.0071(5)
C1	0.0135(6)	0.0132(6)	0.0165(6)	0.0010(5)	0.0032(5)	0.0005(5)
C2	0.0146(6)	0.0162(7)	0.0173(6)	-0.0002(6)	0.0042(5)	-0.0009(6)
C3	0.0176(7)	0.0152(7)	0.0219(7)	-0.0018(6)	0.0063(6)	-0.0015(6)
C4	0.0185(7)	0.0142(7)	0.0225(7)	0.0008(6)	0.0041(6)	0.0037(6)
C5	0.0148(6)	0.0129(6)	0.0163(6)	0.0025(6)	0.0039(5)	0.0013(5)
C6	0.0137(6)	0.0150(7)	0.0173(6)	0.0002(6)	0.0035(5)	-0.0010(6)
C7	0.0147(6)	0.0162(7)	0.0181(6)	-0.0015(6)	0.0046(5)	-0.0008(6)
C8	0.0160(6)	0.0141(7)	0.0211(7)	0.0012(6)	0.0054(5)	0.0030(6)
C9	0.0188(7)	0.0181(7)	0.0197(7)	0.0047(6)	0.0052(5)	-0.0023(6)
C10	0.0199(7)	0.0225(8)	0.0174(7)	0.0031(6)	0.0023(6)	0.0004(6)
C21	0.0153(6)	0.0194(7)	0.0193(7)	-0.0002(6)	0.0046(5)	0.0002(6)
C22	0.0172(7)	0.0312(9)	0.0274(8)	-0.0005(7)	-0.0033(6)	0.0089(7)
C61	0.0174(7)	0.0170(7)	0.0177(7)	0.0011(6)	0.0016(6)	-0.0020(6)
C62	0.0274(8)	0.0312(9)	0.0343(9)	0.0168(7)	0.0078(7)	0.0059(8)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table 8-476. Bond Distances (Å) for MC-6 at **115 K**

O1	C21	1.337(2)	C1	C9	1.524(2)
O1	C22	1.449(2)	C2	C3	1.352(2)
O2	C21	1.234(2)	C2	C21	1.446(2)
O3	C3	1.337(2)	C3	C4	1.486(2)
O5	C61	1.341(2)	C4	C5	1.547(2)
O5	C62	1.451(2)	C5	C6	1.524(2)
O6	C61	1.229(2)	C5	C10	1.526(2)
O7	C7	1.336(2)	C6	C7	1.351(2)
C1	C2	1.520(2)	C6	C61	1.446(2)
C1	C5	1.590(2)	C7	C8	1.487(2)
C1	C8	1.544(2)			

Table 8-477. Bond Angles (°) for MC-6 at **115 K**

C21	O1	C22	115.8(1)	C1	C5	C10	114.7(1)
C61	O5	C62	116.1(1)	C4	C5	C6	113.3(1)
C2	C1	C5	101.1(1)	C4	C5	C10	112.0(1)
C2	C1	C8	113.0(1)	C6	C5	C10	110.3(1)
C2	C1	C9	110.4(1)	C5	C6	C7	111.3(1)
C5	C1	C8	105.3(1)	C5	C6	C61	129.0(1)
C5	C1	C9	114.5(1)	C7	C6	C61	119.6(1)
C8	C1	C9	112.0(1)	O7	C7	C6	127.6(1)
C1	C2	C3	111.5(1)	O7	C7	C8	119.2(1)
C1	C2	C21	129.1(1)	C6	C7	C8	113.2(1)
C3	C2	C21	119.1(1)	C1	C8	C7	103.1(1)
O3	C3	C2	127.0(1)	O1	C21	O2	122.3(1)
O3	C3	C4	120.0(1)	O1	C21	C2	114.6(1)
C2	C3	C4	112.9(1)	O2	C21	C2	123.1(2)
C3	C4	C5	103.1(1)	O5	C61	O6	122.2(1)
C1	C5	C4	105.0(1)	O5	C61	C6	114.2(1)
C1	C5	C6	101.0(1)	O6	C61	C6	123.6(1)

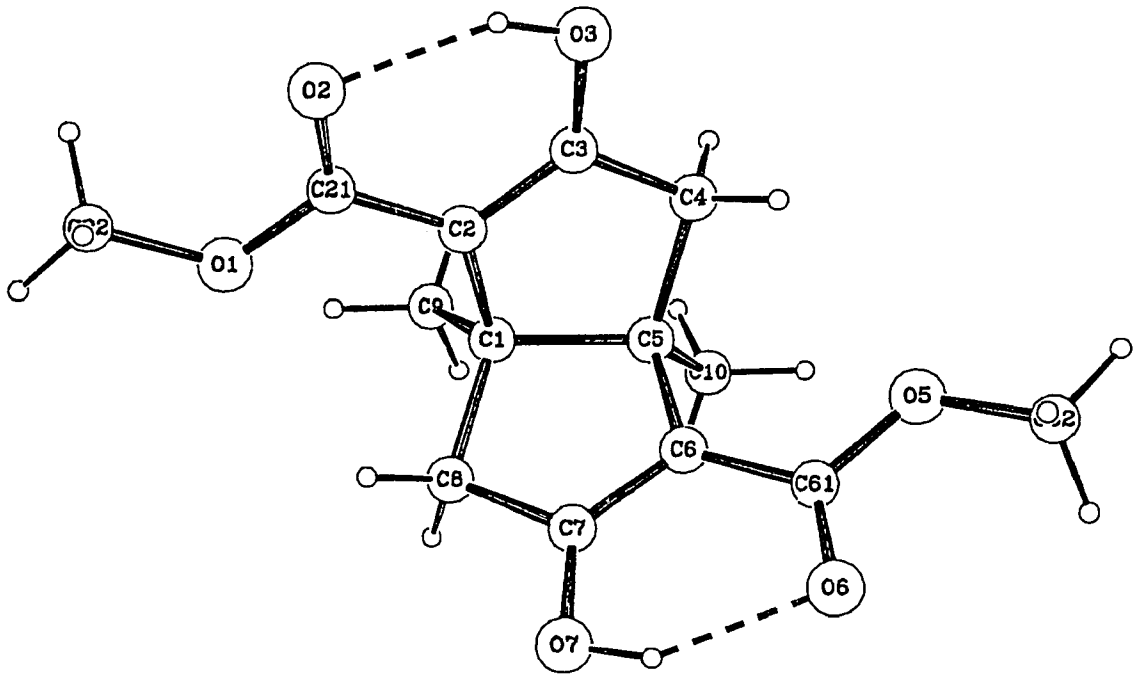
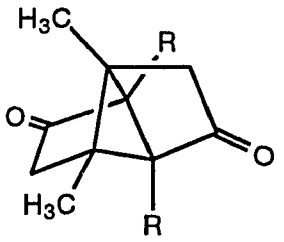


Figure 8–25. *ORTEP* drawing of MC-6 at **115 K.**



R = $COOCH_3$

1,5-Dimethyl-2,6-dicarbomethoxytricyclo[3.3.0.0^{2,6}]octane-3,7-dione
(MC-7)

Table 8–478. X-ray Crystal Data for MC-7 at **295 K**

Formula	$C_{14}H_{16}O_6$
Formula weight	280.28
Melting point (°C)	
Crystal size (mm)	0.55 x 0.77 x 0.89
Crystal system	orthorhombic
Space group	*Pbca*
a (Å)	10.611(1)
b (Å)	13.282(1)
c (Å)	19.838(4)
Cell volume (Å^3)	2796.01(0.67)
Z	8
d_{calc} (g cm^{-3})	1.332
μ(Cu $K\alpha$) (cm^{-1})	8.432
Maximum θ (°)	75
Unique reflections	2881
Observed reflections [$I > 3.0\sigma(I)$]	2383
Number of variables	181
R	0.057
R_w	0.077
$(\Delta\rho)_{max}$ (e Å^{-3})	0.19
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.38

Table 8-479. Final Atomic Parameters for MC-7 at **295 K**

Atom	x	y	z	B(Å^2)
O3	0.1088(1)	0.2164(1)	0.33199(8)	5.47(4)
O7	0.6287(1)	0.1769(1)	0.42383(7)	5.01(3)
O11	0.4153(2)	0.0526(1)	0.30581(8)	5.93(4)
O12	0.2685(2)	0.0928(2)	0.46361(9)	7.83(4)
O13	0.3193(1)	0.1546(1)	0.23232(6)	4.29(3)
O14	0.4214(1)	0.1626(1)	0.52354(7)	5.32(3)
C1	0.4075(2)	0.3181(1)	0.33382(8)	3.03(3)
C2	0.3385(2)	0.2125(1)	0.34194(8)	2.80(3)
C3	0.2047(2)	0.2460(2)	0.35697(9)	3.53(3)
C4	0.2242(2)	0.3298(2)	0.40806(9)	3.81(4)
C5	0.3679(2)	0.3298(1)	0.40970(8)	3.00(3)
C6	0.4035(2)	0.2132(1)	0.41220(8)	2.74(3)
C7	0.5430(2)	0.2173(1)	0.39538(8)	3.31(3)
C8	0.5465(2)	0.2885(2)	0.33595(9)	3.77(4)
C9	0.3665(2)	0.3914(2)	0.2798(1)	4.64(4)
C10	0.4317(2)	0.4036(2)	0.4562(1)	4.66(4)
C11	0.3616(2)	0.1294(1)	0.29289(9)	3.49(3)
C12	0.3567(2)	0.1479(2)	0.46794(9)	3.74(4)
C13	0.3428(3)	0.0838(2)	0.1781(1)	5.14(5)
C14	0.3846(3)	0.1046(3)	0.5819(1)	7.52(7)
H4A	0.1868	0.3129	0.4529	4
H4B	0.1893	0.3955	0.3919	4
H8A	0.6023	0.3477	0.3445	4
H8B	0.5738	0.2538	0.2936	4
H9A	0.4199	0.4533	0.2821	5
H9B	0.3761	0.3594	0.2345	5
H9C	0.2762	0.4100	0.2871	5
H10A	0.3927	0.3992	0.5020	5
H10B	0.5235	0.3871	0.4593	5
H10C	0.4212	0.4733	0.4381	5
H13A	0.3068	0.1108	0.1351	6
H13B	0.4357	0.0739	0.1727	6
H13C	0.3021	0.0178	0.1889	6
H14A	0.4403	0.1221	0.6207	9
H14B	0.2950	0.1201	0.5936	9
H14C	0.3928	0.0311	0.5715	9

The parameters of the hydrogen atoms were not refined.

Table 8-480. Bond Distances (Å) for MC-7 at **295 K**

O3	C3	1.198(2)	C1	C9	1.512(3)
O7	C7	1.197(2)	C2	C3	1.518(2)
O11	C11	1.196(2)	C2	C6	1.555(2)
O12	C12	1.191(3)	C2	C11	1.492(2)
O13	C11	1.326(2)	C3	C4	1.520(3)
O13	C13	1.451(3)	C4	C5	1.526(3)
O14	C12	1.314(2)	C5	C6	1.595(2)
O14	C14	1.444(3)	C5	C10	1.507(3)
C1	C2	1.589(2)	C6	C7	1.519(2)
C1	C5	1.570(2)	C6	C12	1.490(2)
C1	C8	1.528(3)	C7	C8	1.512(3)

Table 8-481. Bond Angles (°) for MC-7 at **295 K**

C11	O13	C13	116.8(2)	C1	C5	C10	122.1(2)
C12	O14	C14	116.9(2)	C4	C5	C6	103.7(1)
C2	C1	C5	82.4(1)	C4	C5	C10	117.5(2)
C2	C1	C8	102.4(1)	C6	C5	C10	120.5(1)
C2	C1	C9	120.5(2)	C2	C6	C5	82.7(1)
C5	C1	C8	104.9(1)	C2	C6	C7	103.6(1)
C5	C1	C9	122.6(2)	C2	C6	C12	121.0(1)
C8	C1	C9	117.6(2)	C5	C6	C7	100.9(1)
C1	C2	C3	101.1(1)	C5	C6	C12	120.6(1)
C1	C2	C6	83.2(1)	C7	C6	C12	120.6(1)
C1	C2	C11	120.7(1)	O7	C7	C6	128.4(2)
C3	C2	C6	103.7(1)	O7	C7	C8	129.0(2)
C3	C2	C11	119.9(1)	C6	C7	C8	102.6(1)
C6	C2	C11	121.1(1)	C1	C8	C7	99.1(1)
O3	C3	C2	128.1(2)	O11	C11	O13	124.8(2)
O3	C3	C4	129.2(2)	O11	C11	C2	124.7(2)
C2	C3	C4	102.6(1)	O13	C11	C2	110.4(1)
C3	C4	C5	98.6(1)	O12	C12	O14	124.2(2)
C1	C5	C4	104.3(1)	O12	C12	C6	124.4(2)
C1	C5	C6	82.6(1)	O14	C12	C6	111.3(2)

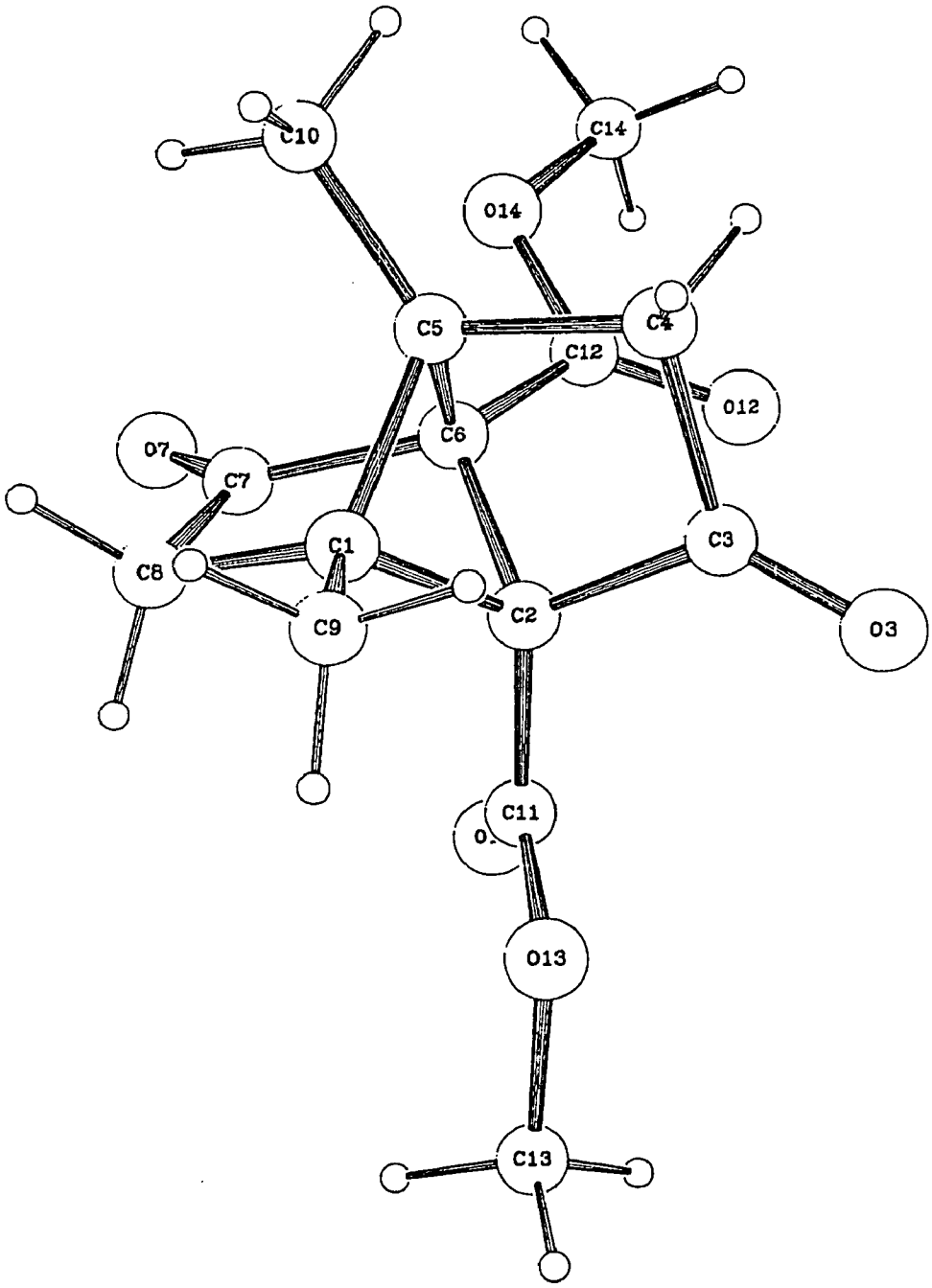


Figure 8–26. *ORTEP* drawing of MC-7 at **295 K.**

APPENDIX

DERIVATION OF THE VAN'T HOFF EQUATION

The van't Hoff equation relates the equilibrium constant, K, to the absolute temperature, T, and the overall enthalpy change, ΔH, of a reaction at constant pressure, P. This equation is

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H}{RT^2}$$

in which R is the gas constant. If constant pressure is understood, the van't Hoff equation is written as

$$\frac{d \ln k}{dT} = \frac{\Delta H}{RT^2}$$

To prove the van't Hoff equation, we begin with the definition of enthalpy,

$$H \equiv U + PV$$

where H is enthalpy, U is internal energy, P is pressure, and V is volume. For a change from state A to B, we write

$$\Delta H \equiv \Delta U + \Delta PV$$

Since the change occurs at constant pressure,

$$\Delta H \equiv \Delta U + P\Delta V$$

The **first law of thermodynamics** states that

$$\Delta U = q + w$$

in which ΔU is the change in internal energy, q is heat, and w is work. If there is only pressure-volume work,

$$w = -\int_{V_A}^{V_B} P dV$$

$$\Delta U = q - \int_{V_A}^{V_B} P dV$$

Since the pressure is constant,

$$\Delta U = q - P\int_{V_A}^{V_B} dV$$

or

$$\Delta U = q - P\Delta V$$

Thus,

$$\begin{aligned} \Delta H &\equiv \Delta U + P\Delta V \\ &\equiv (q - P\Delta V) + P\Delta V \\ \Delta H &= q \end{aligned}$$

Differentiating both sides with respect to T,

$$\frac{d\Delta H}{dT} = \frac{dq}{dT}$$

or

$$\frac{dq}{dT} = \frac{d\Delta H}{dT}$$

According to the definition of entropy, the change in entropy, ΔS, from state A to state B is

$$\Delta S = \int_A^B \left(\frac{1}{T}\right) dq$$

which implies, according to the **fundamental theorem of integral calculus**, that

$$\frac{d\Delta S}{dq} = \frac{1}{T}$$

Applying the chain rule,

$$\frac{d\Delta S}{dT} = \frac{d\Delta S}{dq}\frac{dq}{dT}$$

But from above,

$$\frac{d\Delta S}{dq} = \frac{1}{T}$$

$$\frac{dq}{dT} = \frac{d\Delta H}{dT}$$

Thus,

$$\frac{d\Delta S}{dT} = \frac{1}{T}\frac{d\Delta H}{dT}$$

Anticipating future needs, we differentiate the ratio $\Delta H/T$ with respect to T:

$$\frac{d(\Delta H/T)}{dT} = \frac{d\left(T^{-1}\Delta H\right)}{dT}$$

$$= \Delta H\frac{dT^{-1}}{dT} + T^{-1}\frac{d\Delta H}{dT}$$

$$\frac{d(\Delta H/T)}{dT} = -\frac{\Delta H}{T^2} + \frac{1}{T}\frac{d\Delta H}{dT}$$

We also need to differentiate the ratio $\Delta G/T$ with respect to T, where ΔG is the change of Gibbs free energy from state A to state B. We begin with the well-known thermodynamic relation,

$$\Delta G = \Delta H - T\Delta S$$

We now divide both sides by T and then differentiate with respect to T:

$$\Delta G = \Delta H - T\Delta S$$

$$\frac{\Delta G}{T} = \frac{\Delta H}{T} - \Delta S$$

$$\frac{d(\Delta G/T)}{dT} = \frac{d(\Delta H/T)}{dT} - \frac{d\Delta S}{dT}$$

But from above,

$$\frac{d(\Delta H/T)}{dT} = -\frac{\Delta H}{T^2} + \frac{1}{T}\frac{d\Delta H}{dT}$$

$$\frac{d\Delta S}{dT} = \frac{1}{T}\frac{d\Delta H}{dT}$$

After substitutions,

$$\frac{d(\Delta G/T)}{dT} = \left(-\frac{\Delta H}{T^2} + \frac{1}{T}\frac{d\Delta H}{dT}\right) - \frac{1}{T}\frac{d\Delta H}{dT}$$

or

$$\frac{d(\Delta G/T)}{dT} = -\frac{\Delta H}{T^2}$$

Another well-known thermodynamic relation which relates ΔG and the equilibrium constant, K, is

$$\Delta G = -RT \ln K$$

Again, dividing both sides by T and then differentiating with respect to T, we have

$$\Delta G = -RT \ln K$$

$$\frac{\Delta G}{T} = -R \ln K$$

$$\frac{d(\Delta G/T)}{dT} = -R \frac{d \ln K}{dT}$$

Therefore,

$$-R \frac{d \ln K}{dT} = -\frac{\Delta H}{T^2}$$

At last, after dividing both sides by $-R$, we have the van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

Remark!

This remark gives me the opportunity to take off my chest something which has been bothering me for a long time. The unique and redeeming feature of this proof is that it is *completely free* of *distasteful differentials*. The derivative symbol

$$\frac{df(x)}{dx}$$

is properly defined as the limit of a ratio,

$$\frac{df(x)}{dx} \equiv \lim_{\Delta x \to 0} \frac{f(x + \Delta x) - f(x)}{\Delta x}$$

In turn, the concept of a *limit* is rigorously cast in terms of δ's and ε's. When the symbols, $df(x)$ and dx, are used separately, they become totally meaningless! Still, erudite authors explain ingenious and aesthetic scientific principles by filling pages and

pages with cryptic nonsense like dG, dH, dT, in a harun-scarum fashion. To add insults to injuries, these same authors insist to cruelly differentiate, in cold blood, integral variables without any remorse of conscience. What atrocities committed in the name of expediency! They will forever and ever inundate the literature with these asinine antics, and they will continue to make my life very miserable with such irritating gibberish! It's heartening, however, to know that there are a few good men who not only recognize these pervasive, insidious, and obnoxious practices in the scientific community but also are willing to go out of their way to correct the ingrown bad habits by lighting up the righteous path with their own good examples. Case in point is the elegant *Derivation of a Statistical Mechanical Distribution Function by a Method of Inequalities* by W. L. Clinton and L. J. Massa, who meticulously avoid differentiating discrete variables.[1]

End of Remark!

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