INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book. These are also available as one exposure on a standard 35mm slide or as a 17" x 23" black and white photographic print for an additional charge.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Order Number 9000050

Theoretical studies of the energies and geometries of strained hydrocarbons

Miller, Mitchell Alan, Ph.D.

City University of New York, 1989

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

THEORETICAL STUDIES OF THE ENERGIES AND GEOMETRIES OF STRAINED HYDROCARBONS

by

MITCHELL A. MILLER

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

1989

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

12/29/88
date

Jerome M. Schulman
Chairperson of Examining Committee

1/3/89
date

Executive Officer

Arthur D Baker

Supervisory Committee

The City University of New York

Acknowledgements

The work involved in completing this thesis would have been impossible without the help of several people. I would like to acknowledge, first of all, the aid of my mentors, Drs. Jerome Schulman and Raymond Disch, whose help and guidance enabled me to complete this project with a minimum of wasted time and energy. Second, I thank the other members of my thesis committee, Drs. Baker and Dannenberg, not only for serving on the committee, but also for the valuable lessons I learned in their respective classes. It was Dr. Baker's Organic Chemistry lectures that first inspired me to study chemistry on an advanced level and Dr. Dannenberg's Quantum Organic class that induced me to switch from experimental research to theoretical explorations.

I would like to thank the staffs of the chemistry departments at both the Graduate Center and Queens College for their help in dealing with the bureaucracies of the two schools and also for their friendliness and warmth.

I am pleased to thank the staff of the Queens College Academic Computer Center for doing their damned best to provide me with access to state-of-the-art hardware and software. I gratefully thank Al 'AOPQC' Perez, Sal 'SLVQC' Saieva, as well as MMGQC, JONQC and many others for their answers to knotty programming question, constant willingness to increase my disk quota and for knowing when to bend the rules a bit. I also thank BIGCU and WGRCU for their as-

sistance in running large-scale batch jobs at UCC; HOEY@CORNELLD for her aid in finding explanations for the inexplicable; and RTT@CORNELLF for providing assistance above and beyond the call of duty of a sysop.

I thank my fellow students for their friendship and warmth which made the hard life of a graduate student a bit easier.

This research was supported, in part, by grants 666356, 667253 and 668248 of the PSC-CUNY Research Award Program of the City University of New York and several grants of computing time from the City University Committee on Research Computing. Part of this work was conducted, with vector programs developed by Dr. Raymond Disch (The Queens College Quantum Chemistry Package), using the Cornell National Supercomputer Facility, a resource of the Center for Theory and Simulation in Science and Engineering at Cornell University, which is funded in part by the National Science Foundation, New York State and the IBM Corporation and members of the Corporate Research Institute.

Perspective drawings were obtained with Chem-X, developed and distributed by Chemical Design, Ltd., Oxford, England.

Table of Contents

Acknowledgements iii

List of Tables viii

List of Figures x

1. GENERAL INTRODUCTION 1

Project I 1

Project II 3

Project III 4

Project IV 6

References 8

2. STUDIES OF CONCATENATED CYCLOBUTANES 9

Introduction 9

Computational Methods 11

Results for the [*n*]-Ladderanes 12

Results for the [*n*]-Prismanes 19

Results for the Asteranes: Helvetane and Israelane 25

References 30

3. ON THE HOMOAROMATIC CHARACTER OF TRIQUINACENE . . . 31

Introduction 31
Triquinacene 37
Dihydrotriquinacene 41
Tetrahydrotriquinacene 44
Hexahydrotriquinacene 47
Energetics 49
Heats of Hydrogenation 53
Conclusion 54
References 58

4. AB INITIO THERMOCHEMISTRY OF BARRELENE 60
Introduction 60
The Calculations 61
Energetics 69
Conclusion 75
References 76

5. A METHOD FOR SIMPLIFYING AB INITIO GEOMETRY OPTIMIZATIONS 77
Introduction 77
Conjugate-Gradient Optimization 80
The Algorithm 81
Testing the Algorithm 83
Results 86
Conclusion 88
References 96

BIBLIOGRAPHY 97

List of Tables

Table 2.1 Heats of Formation of the [*n*]-Ladderanes . . 13

Table 2.2 CC Bondlengths of the [*n*]-Ladderanes 18

Table 2.3 Geometric Parameters for the [*n*]-Prismanes . 21

Table 2.4 AM1 and MNDO Properties of the [*n*]-Prismanes 22

Table 2.5 AM1 and MM2 Geometric Parameters of Helvetane 28

Table 3.1 Selected Geometric Parameters of C_s Cyclopentene 34

Table 3.2 Selected Geometric Parameters of C_s Cyclopentane 35

Table 3.3 Ab Initio Energies, Zero-Point Energies and Thermal Enthalpy Corrections in the Triquinacene Series 36

Table 3.4 Selected Geometric Parameters and Vibrational Frequencies of C_{3v} Triquinacene 38

Table 3.5 Selected Geometric Parameters of C_1 Dihydrotriquinacene 43

Table 3.6 Selected Geometric Parameters of C_1 Tetrahydrotriquinacene 46

Table 3.7 Selected Geometric Parameters of C_3 Perhydrotriquinacene 48

Table 3.8 Heats of Reaction in the Triquinacene . . . 56

Table 3.9 Derived Heats of Formation in the Triquinacene Series 57

Table 4.1 Selected Geometric Parameters of D_{3h} Barrelene 63

Table 4.2 Selected Geometric Parameters of C_{2v} Dihydrobarrelene 64

Table 4.3 Selected Geometric Parameters of C_{2v} Tetrahydrobarrelene 65

Table 4.4 Selected Geometric Parameters of D_3 Bicyclooctane 66

Table 4.5 Ab Initio Energies, Zero-Point Energies and Thermal Enthalpy Corrections in the Barrelene Series 67

Table 4.6 Ab initio Enthalpies for Reactions in the Barrelene Series 72

Table 5.1 Results of Projected Optimizations Compared with Full Optimizations 91

List of Figures

Figure 2.1 Heats of Formation of the [*n*]-Ladderanes vs. *n* 14

Figure 2.2 MM2-optimized Structures of [10]-Ladderane 17

Figure 2.3 Heats of Formation of the [*n*]-Prismanes vs. *n* 23

Figure 2.4 Perspective Drawing of D_{2d} Helvetane . . . 27

Figure 3.1 Perspective Drawing of C_{3v} Triquinacene . . 37

Figure 3.2 Perspective Views of C_s and C_1 Forms of Dihydrotriquinacene 41

Figure 3.3 Perspective Views of C_s and C_1 Forms of Tetrahydrotriquinacene. 44

Figure 3.4 Perspective Views of C_3 and C_1 Forms of Hexahydrotriquinacene 47

1. GENERAL INTRODUCTION

This thesis, under the general title, 'Theoretical Studies of Energies and Geometries of Strained Cyclic Hydrocarbons,' consists of four projects. Although quite varied in theme, all use theoretical models to explore problems of interest to organic chemists. The first three projects apply existing methodologies to investigate a series of strained cyclic hydrocarbon molecules; the fourth concerns methodology.

Project I

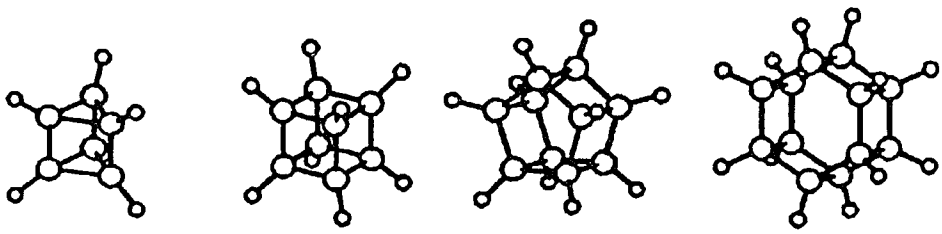
The first project is a study of concatenated cyclobutanes, using semiempirical molecular orbital methods. We have investigated the manner in which the strain inherent in the four-membered ring is affected when two or more such rings are fused together in a chain or a macrocycle. To this end, we performed AM1,[1] MNDO[2] and MM2[3] calculations on three sets of compounds, obtaining their optimized geometries, heats of formation and vibrational frequencies.

The first set, *anti*-linear concatenated cyclobutanes, for which we suggest the name "[*n*]-ladderanes," includes cyclobutane ([1]-ladderane, **I**), bicyclo[2.2.0]hexane ([2]-ladderane, **II**) and tricyclo[4.2.0.$0^{2,5}$]octane ([3]-ladderane, **III**).

I **II** **III**

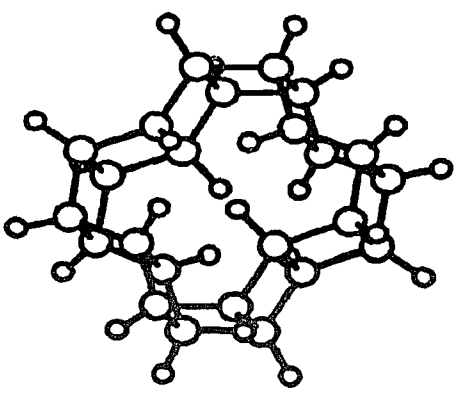
Their AM1 heats of formation increase with *n* by the nearly constant amount 21.7 kcal mol^{-1}; MM2 heats of formation increase by 19.9. The AM1 method furnishes conformations in which all 4-membered rings are planar, while MM2 predicts twisted-ribbon type structures. The MM2 energies for flattening are very small, however.

The second series of compounds included the [*n*]-prismanes, $C_{2n}H_{2n}$ macrocycles having the possibility of D_{nh} sym-

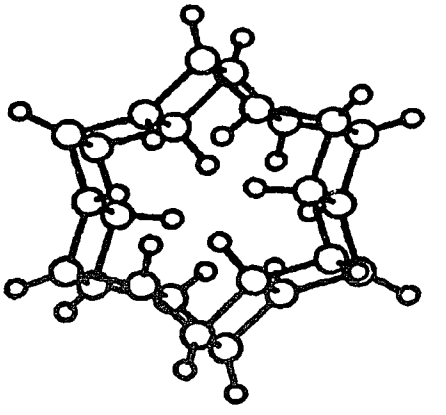


IV V VI VII

metry. The first three [*n*]-prismanes (**IV**), (**V**) and (**VI**) are known compounds having D_{nh} symmetry. We were interested in testing whether the [*n*]-prismanes would remain kinetically stable in their D_{nh} forms for larger *n*. Our results indicate that the [*n*]-prismanes through *n* = 12 have only real frequencies, confirming their D_{nh} symmetry. We have found [5]- and [6]-prismanes to be the most thermodynamically stable on a per carbon basis. The subsequent heats of formation increase rapidly for *n* greater than 7. The heats of formation do not show linear dependence on *n*, because angle-strain does not increase linearly with *n*.



VIII



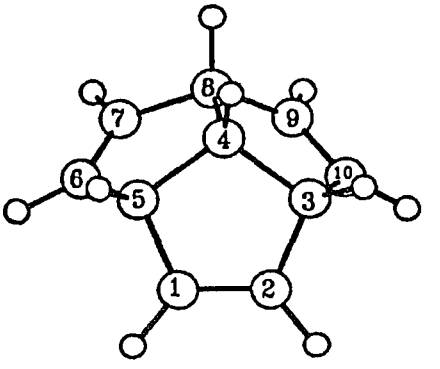
IX

Helvetane (**VIII**) and israelane (**IX**) are structural isomers of [12]-prismane, differing from it in their *anti* ring fusions. Helvetane was found to be the most stable of the three $C_{24}H_{24}$ isomers and israelane the least, due in part to substantial repulsions between its inward-pointing hydrogens. Helvetane was found to have D_{2d} symmetry and israelane D_{3d}, whereas previous calculations had assumed the two compounds to have D_{4h} and D_{6h} symmetry, respectively.[4]

Project II

The second project treats the question of the homo-aromatic character of triquinacene (**X**), a postulated special stability arising from its three proximal, suitably oriented double bonds. Evidence for this effect has been found in a calorimetric study.[5] We performed ab initio molecular orbital calculations on triquinacene and its di- (**XI**), tetra- (**XII**),

and hexahydro (**XIII**) derivatives (not shown). These included geometric optimizations at the STO-3G and 6-31G* SCF levels and single point calculations at the 6-31G* RMP2 and 6-31+G* SCF levels. From the total energies obtained from these calculations and zero point energies and thermal effects estimated using semiempirical and molecular mechanics methods, we have evaluated enthalpy changes for hypothetical reactions such as 1.1. At each level of theory, reaction 1.1 is essentially thermoneutral, in contrast with published thermochemical results which show a heat of reaction of 4.5 kcal mol^{-1}.[5] We find no evidence of special stability for triquinacene.

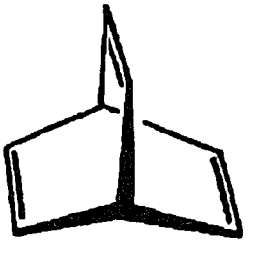


X

X + **XIII** ———> **XI** + **XII** (1.1)

Project III

The third project deals with the homoantiaromatic character of bicyclo-[2.2.2]octa-2,5,7-triene, (barrelene, **XIV**). While the three double bonds of barrelene are sufficiently close for interaction, their topology is such that the interaction should be destabilizing. Evidence for such destabilization has been found in calorimetric studies of the



XIV

heats of hydrogenation of barrelene and its hydrogenated derivatives, (not shown) bicyclo[2.2.2]octa-2,5-diene(**XV**), bicyclo[2.2.2]oct-2-ene (**XVI**), and bicyclo[2.2.2]-octane(**XVII**).[6,7] The ΔH_h of **XIV** → **XVII** (-93.78 ± 0.31 kcal mol^{-1}) was found to be lower than three times the ΔH_h of **XVI** → **XVII** (-28.25 ± 0.20 kcal mol^{-1}). We optimized geometries for the barrelene series of compounds at the 6-31G* SCF level and also obtained energies at the 6-31G** SCF and 6-31G* RMP2 levels.

The hypothetical reaction 1.2, which balances methines,

XIV + (3) **XVI** ---> (3) **XV** + **XVII** (1.2)

methylenes and double bonds, has an experimental ΔH of -9.9. From the ab initio total energies, zero-point energies and thermal effects, calculated by molecular mechanics, we obtained ΔH values for reaction 1.2 of 4.2, -2.2 and -1.2 kcal mol^{-1} at the 6-31G* SCF, 6-31G** SCF and 6-31G* RMP2 levels.

Our results support a destabilization of barrelene, but the effect is smaller in magnitude than obtained experimentally; we believe that the experimental heat of hydrogenation of **XV** → **XVII** is suspect.

Project IV

The fourth project involved the development of a scheme to reduce the cost of ab initio geometry optimizations in large basis sets using the eigenvectors of the force-constant matrix in a smaller basis. If the latter eigenvectors approximately diagonalize the force-constant matrix in the larger basis, optimization in this basis can be accomplished with as few as 3 or 4 gradient calculations. This is possible because the eigenvectors of the force-constant matrix define essentially uncoupled combinations of the parameters requiring optimization. The energy and gradient of a molecule, as functions of distortions ($\mathbf{q}$) from equilibrium of sets ("lists") of geometric parameters, are given by the expressions:

$$E = \tfrac{1}{2}\, \mathbf{q} \cdot \mathbf{F} \cdot \mathbf{q} \tag{1.3}$$

$$g_i = \sum_{j=1}^{N} F_{ij} q_j \tag{1.4}$$

where $\mathbf{F}$ is the force-constant matrix, $\mathbf{q}$ is the vector of displacements from equilibrium, g_i is the gradient on the i'th parameter list and q_i is the displacement of the i'th list from its equilibrium position. Unless second derivatives are computed, $N + 1$ gradient calculations are required in order to evaluate a force-constant matrix directly for N parameters. However, the expressions are greatly simplified when the parameter lists diagonalize $\mathbf{F}$:

$$E = \tfrac{1}{2}\Sigma F_{ii}Q_i^2 \tag{1.5}$$

$$g_i = F_{ii}Q_i \tag{1.6}$$

(Q_i represents the displacement of the i'th *diagonal* parameter list from its equilibrium position.) Since the force on any parameter list in a diagonal basis depends only on the displacement of that list from equilibrium, distortions may be applied simultaneously to all lists. Therefore, having optimized the geometry of a molecule in STO-3G, for example, one could perform a gradient calculation in 6-31G* at the STO-3G geometry, construct a single test point, and then, using the forces on these two structures, compute the force-constant matrix and obtain the equilibrium geometry. The process can be repeated in cases where refinement is desired or anharmonicity is encountered.

We have applied this method to 13 different strained molecules and found that it worked in every case. Energies and geometric parameters agreed with those obtained from complete optimizations to within the publishable cutoff (0.0001 a.u. for energies, 0.001 Å. for bondlengths and 0.1°, for angles).

References

1. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. J. Am. Chem. Soc. 1985, 107, 3902.

2. Dewar, M. J. S.; Thiel, W. J. Am. Chem. Soc. 1977, 99, 4899.

3. Allinger, N. L. J. Am. Chem. Soc. 1977, 99, 8127.

4. Li, W. K.; Luh, T. Y.; Chiu, S. W. Croat. Chem. Acta 1985, 58, 1.

5. Liebman, J. F., Paquette, L. A., Peterson, J. R.; D. W. Rogers, J. Am. Chem. Soc., 1986, 108, 8267.

6. Turner, R. B.; Meador, W. R.; Winkler, R. E. J. Am. Chem. Soc. 1957, 79, 4116.

7. Turner, R. B. J. Am. Chem. Soc. 1964, 86, 3586.

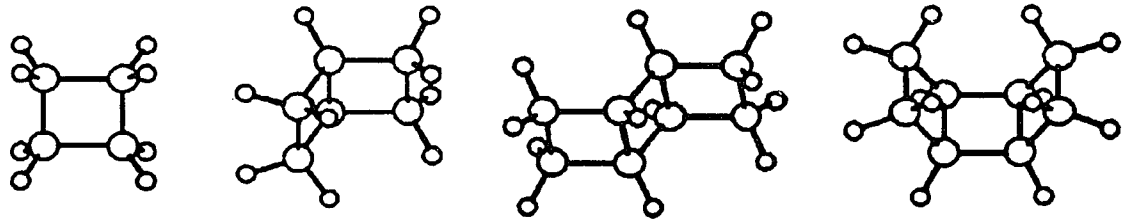
2. STUDIES OF CONCATENATED CYCLOBUTANES

Introduction

Compounds containing four-membered rings are of considerable interest with regard to their mechanisms of thermal bond cleavage, Cope rearrangements, factors leading to accelerated solvolysis rates, and potential functions for bond angle deformation. Unfortunately, molecular mechanics calculations, with force fields generally chosen to fit "normal" hydrocarbons, are unreliable for fused cyclobutane rings. Although it has been suggested[1] that ab initio molecular orbital calculations in extended basis sets containing polarization functions are the best method for obtaining information about such substances, these calculations can be quite costly.

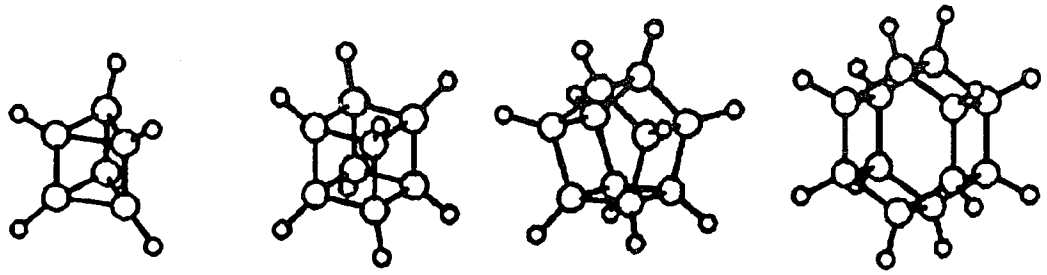
Semiempirical methods used previously, such as MINDO3[2] and MNDO,[3] gave large errors in the heats of formation of organic molecules containing four-membered rings. However, improved values are found with their successor, AM1.[4] For example, the substantial errors in the MINDO3- and MNDO-calculated heats of formation of cyclobutane (-11.9 and 18.7 kcal mol^{-1}) and cubane (-8.9 and 49.6 kcal mol^{-1})[3,5] are reduced to only -7.8 and 2.5 kcal mol^{-1}, respectively, with AM1.[4] Similarly, for [4.4.4.4]fenestrane we find the AM1 ΔH_f, 147 kcal mol^{-1}, to be in good agreement with ab initio estimates, 144.5 and 148 kcal mol^{-1}.[1,6]

To test the AM1 method further and to study cyclobutane-containing compounds of interest in their own right, calculations have been performed on a variety of condensed cyclobutanes, including: (1) *anti*-linear concatenated cyclobutanes, for which we suggest the name "[*n*]-ladderanes," and (2) the [*n*]-prismanes (*n* = 3 to 12). The first three members of the ladderane series are cyclobutane (**I**, *n* = 1), bicyclo[2.2.0]-



I II IIIa IIIb

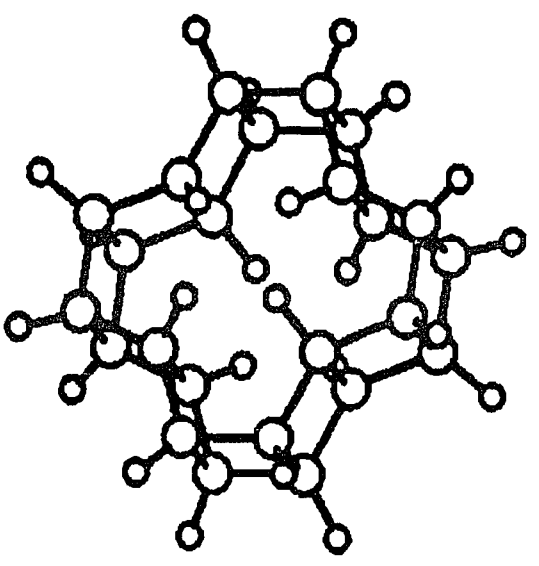
hexane (**II**, *n* = 2) and tricyclo[4.2.0.$0^{2,5}$]octane (**III**, *n* = 3). The first three prismanes are triprismane (**IV**), cubane (**V**),



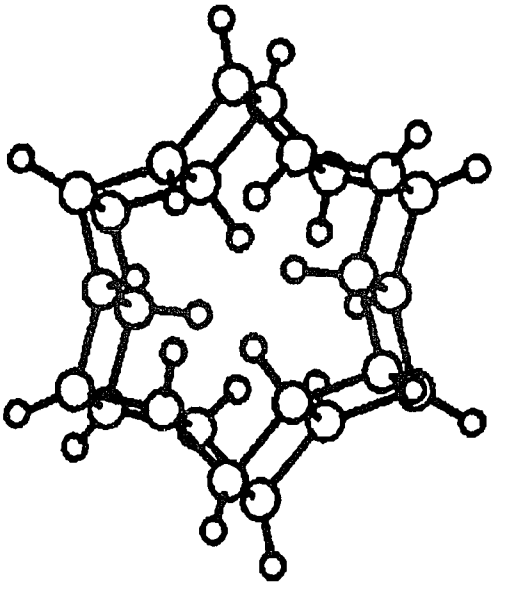
IV V VI VII

pentaprismane (**VI**) and hexaprismane (**VII**), a formal dimer of benzene. We also studied the two star-shaped $C_{24}H_{24}$

"asteranes", helvetane (**VIII**) and israelane (**IX**),[7] which are



VIII



IX

structural isomers of [12]-prismane.

Optimized geometries, heats of formation and vibrational frequencies for these systems were obtained. These are compared with experiment and other theoretical methods in several cases.

Computational Methods

The AMPAC program package[8] was used. Geometries were optimized for both MNDO and AM1 closed-shell singlet states using the (default) Davidon-Fletcher-Powell method with appropriate symmetry constraints. Vibrational frequencies were calculated for many of the structures in order to test their kinetic stabilities. Molecular mechanics calculations

were also made, using the MMP2 program,[9] after modifying it to allow for more than ten four-membered rings.

The heats of formation of the *n*-alkanes, which are known experimentally to increase linearly with *n*,[10] provided a test of AM1 and MM2 on a simple homologous series. Linear behavior was found with both the AM1 and the MM2 methods for all-*anti* conformations; the contributions per methylene unit: -6.85 kcal mol^{-1} (AM1) and -5.11 kcal mol^{-1} (MM2), are somewhat smaller than the experimental increment, -4.95 kcal mol^{-1}. A slight error arises from the fact that the AM1 calculations involve only the minimum-energy, all-*trans* conformation, while the molecules exist in a Boltzmann distribution of several conformers, including higher-energy *gauche* forms; MM2 makes some allowance for this distribution.

Results for the [*n*]-Ladderanes

Table 2.1 contains the heats of formation of the [*n*]-ladderanes. The AM1 heats of formation of the all-*anti* structures increase linearly with *n* by the nearly constant amount, 21.7 ± 0.1 kcal mol^{-1} (Figure 2.1); for MM2, the ΔH_f increment is 19.9 ± 0.1 kcal mol^{-1} per ring.

Table 2.1 Heats of Formation of the [*n*]-Ladderanes[a] (kcal mol^{-1})

n	AM1	MM2	Experiment	$\Delta H_f/n$ AM1	MM2
1	-1.0[b]	6.8	6.8[c]	-1.0	6.8
2	21.2	26.3	29.9[d]	10.6	13.2
3	42.9	46.4		14.3	15.5
4	64.5	66.4		16.1	16.6
5	86.2	86.4		17.2	17.3
6	107.9	106.3		18.0	17.7
7	129.7	126.2		18.5	18.0
8	151.3	146.1		18.9	18.3
9	173.0	166.0		19.2	18.4
10	194.4	186.0		19.4	18.6
11	216.4	205.9		19.7	18.7
12	238.1	225.8		19.8	18.8
13	259.8	245.7		20.0	18.9
14	281.4	265.6		20.1	19.0
15	303.1	285.5		20.2	19.0

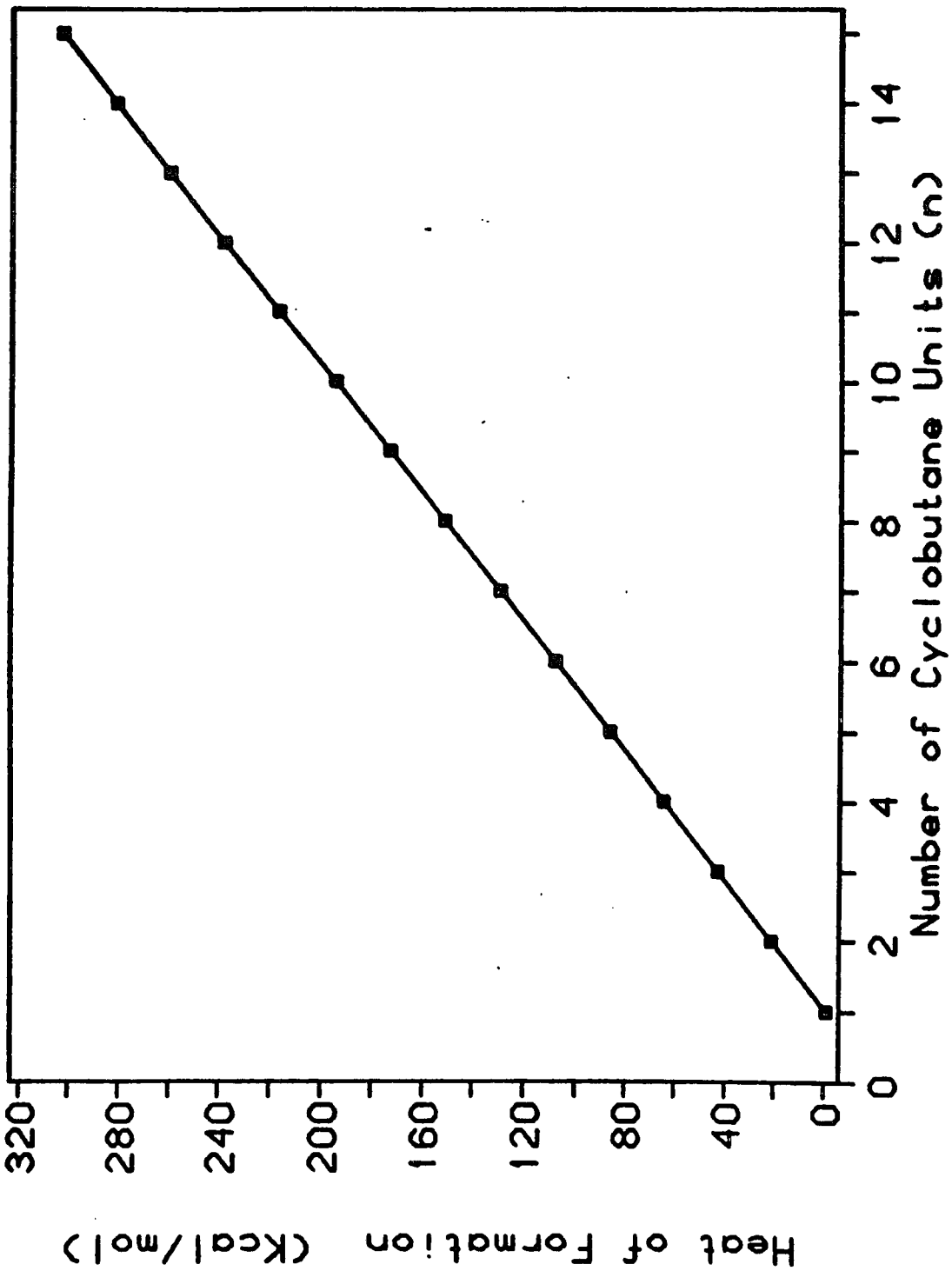
[a] [1]-ladderane = cyclobutane, [2]-ladderane = bicyclo-[2.2.0]hexane, etc.

[b] Reference 4 reports a value of 0.2 kcal/mol.

[c] Reference 10.

[d] Reference 11.

Figure 2.1 Heats of Formation of the [*n*]-Ladderanes vs. *n*



A comparison with experiment can be made for bicyclo-[2.2.0]hexane (**II**) whose heat of formation is known to be 29.9 kcal mol^{-1}.[11] The calculated AM1 heat of formation, 21.2 kcal mol^{-1}, is in error by 8.7 kcal mol^{-1}, essentially the AM1 error for cyclobutane (7.8 kcal mol^{-1}). The MM2 heat of formation of **II**, 26.3 kcal mol^{-1}, is in good agreement with experiment. On the other hand, the error in the MNDO heat of formation, 27.4 kcal mol^{-1}, is much greater. (Closest to experiment is an ab initio value, 29.8 kcal mol^{-1}, obtained from the 6-31G* (SCF) total energy and the methylene and methine group equivalents of Wiberg.[12])

AM1 calculations on [3]-ladderane (**IIIa**) and its *syn*-isomer (**IIIb**) furnish ΔH_f values of 47 and 43 kcal mol^{-1}, respectively. The 4 kcal mol^{-1} energy difference can be attributed largely to repulsions between the *endo* terminal hydrogens of **IIIb**, which are as close as 2.0 Å.

AM1 furnishes planar four-membered rings in all ladderanes, including cyclobutane, which is known to be puckered. MM2 predicts puckering if the starting geometry has puckered rings. The MM2 dihedral angle of cyclobutane, 20°, agrees with the experimental value; in **II** the dihedral angle about the CC central bond, 14°, is smaller, also in agreement with experiment.[13] It might be noted, however, that recent unpublished ab initio (6-31G*) calculations of R. L. Disch

show **II** to have C_{2v} symmetry, i.e. no puckering.

For the ladderanes with $n > 3$, the calculated dihedral angles $C_iC_{i'}C_{i'+1}C_{i+1}$ range from 8.0° to 10.7°, giving the molecules a twisted-ribbon structure (Figure 2.2a). For the outermost rings (i = 1 and n), the CCCC dihedral angle equals 10.6 ± 0.2°, while for the penultimate rings (i = 2 and n-1) the angle is equal to 9.5 ± 0.1°. Finally, the dihedral angles for the interior rings are 8.3 ± 0.3°. From this data, it can be computed that a full twist of 360° occurs in [21]-ladderane.

If MM2 calculations on the [n]-ladderanes start from structures containing only planar four-membered rings, the converged structures retain their planarity (Figure 2.2b). The heats of formation of the ladderanes are only about 0.3 kcal mol^{-1} higher than those of their twisted counterparts.

The salient geometric parameters of the ladderanes having planar rings are given in Table 2.2; transverse CC bonds are referred to as "rungs". The outer four-membered rings of the [n]-ladderanes for $n > 5$ are nearly trapezoids, the innermost rings rectangles. The CH bond lengths are 1.10 ± 0.1 Å and the HCC (rung) angles are 114° and 122° for the terminal and interior hydrogens, respectively.

Figure 2.2 MM2-optimized structures of [10]-ladderane. (a) The more stable structure containing puckered rings. (b) A slightly less stable structure containing planar rings.

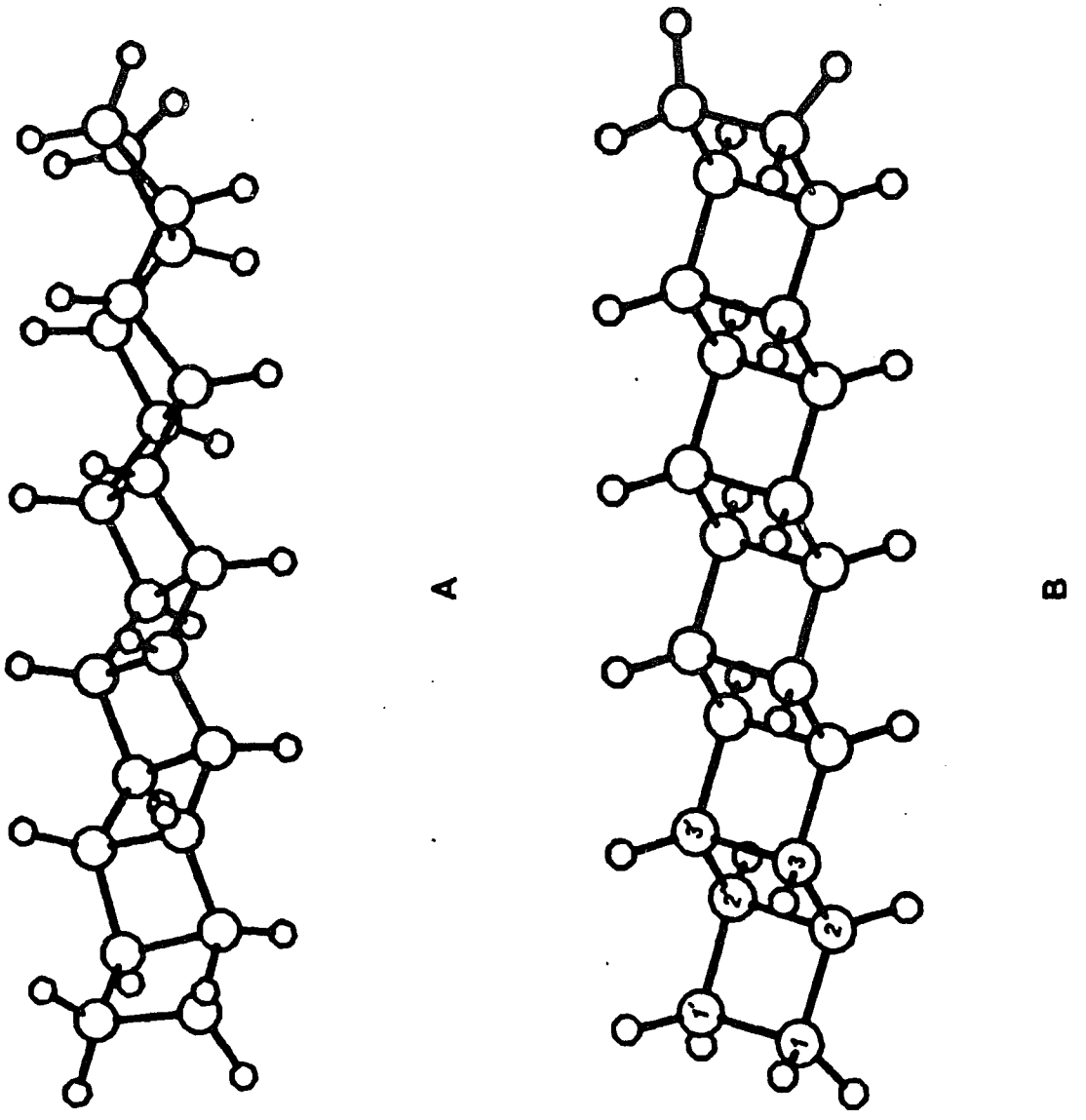


Table 2.2 CC Bondlengths of the [*n*]-Ladderanes[a] (Å)

n	Rung 1[b]	Rung 2	Rung 3	Side 1	Side 2	Side 3
1	1.543 (1.548)			1.543 (1.548)		
2	1.550 (1.542)	1.586 (1.579)		1.538 (1.541)		
3	1.549 (1.543)	1.595 (1.571)		1.538 (1.541)	1.532 (1.537)	
4	1.549 (1.543)	1.594 (1.572)	1.605 (1.564)	1.538 (1.541)	1.532 (1.536)	
≥5	1.549 (1.543)	1.594 (1.572)	1.604 (1.565)	1.538 (1.541)	1.532 (1.536)	1.531 (1.536)

[a] Geometries optimized by the AM1 and MM2 methods with MM2 values in parentheses.

[b] Rung 1 = $C_1C_{1'}$, Rung 2 = $C_2C_{2'}$, Side 1 = C_1C_2 Side 2 = C_2C_3, etc.

Results for the [*n*]-Prismanes

The [*n*]-ladderanes provided a point of departure for studies of the [*n*]-prismanes and the related compounds helvetane and israelane. The three smallest prismanes, triprismane, cubane and pentaprismane, are known compounds. Table 2.3 contains the geometric parameters of the [*n*]-prismanes (*n* = 3 to 12), optimized in D_{nh} symmetry. There are only two unique CC bond lengths, R_1 and R_2, for bonds between and within the *n*-membered rings, respectively. R_1 is found to increase monotonically from [3]-prismane to [7]-prismane, after which it remains constant at 1.610 ± 0.001 Å; the R_2 value, on the other hand, increases in going from [3]-prismane to [4]-prismane and then decreases to 1.523 ± 0.002 Å in the [*n*]-prismanes with *n* > 7.

The HCC angles involving C-C bonds parallel to the *n*-fold axes decrease monotonically from [3]-prismane to [12]-prismane, in response to the increase in the CCC angle, whose value is 180°-360°/*n*.

Table 2.4 contains the [*n*]-prismane heats of formation, ionization energies and lowest vibrational frequencies. As expected, the heats of formation do not increase linearly with *n* (Figure 2.3) due to non-linear angle-strain effects. Pentaprismane and hexaprismane are the most stable of the [*n*]-prismanes on a per ring basis, having energies of 11.8 and

11.7 kcal mol^{-1}, respectively. This is of interest because hexaprismane has yet to be synthesized.

Table 2.3 Geometric Parameters for the [*n*]-Prismanes[a,b] (Lengths in Å, Angles in degrees)

n	R_1	R_2	R_{CH}	HCC	HCC'
3	1.571 (1.554)	1.541 (1.552)	1.079 (1.076)	128.9 (129.3)	132.4 (132.1)
4	1.577 (1.571)	1.577 (1.571)	1.086 (1.084)	125.3 (125.3)	125.3 (125.3)
5	1.593 (1.580)	1.546 (1.559)	1.094 (1.091)	122.4 (123.1)	119.8 (119.5)
6	1.602 (1.585)	1.529 (1.547)	1.102 (1.097)	120.4 (121.5)	115.6 (115.2)
7	1.610 (1.589)	1.523 (1.540)	1.107 (1.102)	118.9 (120.2)	112.3 (112.0)
8	1.609 (1.591)	1.521 (1.536)	1.112 (1.106)	117.9 (119.3)	109.8 (109.5)
9	1.610 (1.592)	1.521 (1.535)	1.116 (1.110)	117.2 (118.7)	107.7 (107.5)
10	1.610 (1.592)	1.521 (1.535)	1.120 (1.112)	116.6 (118.2)	106.0 (105.8)
11	1.610 (1.592)	1.523 (1.536)	1.122 (1.115)	116.2 (117.8)	104.6 (104.4)
12	1.609 (1.592)	1.525 (1.525)	1.125 (1.117)	115.8 (117.5)	103.5 (103.3)

[a] Geometries optimized by the AM1 and MNDO methods; MNDO values are in parentheses.

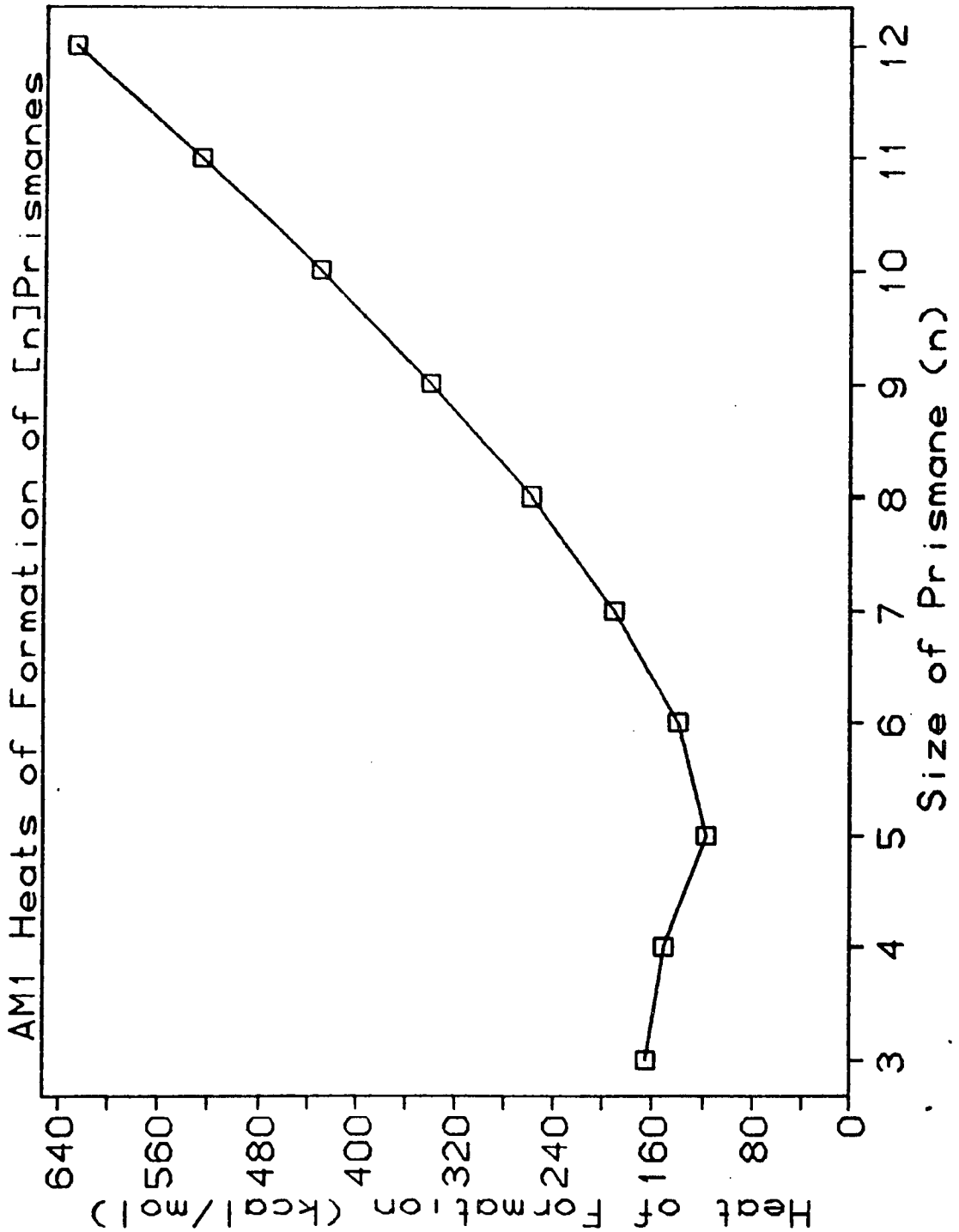
[b] R_1 and R_2 are CC bondlengths between and within *n*-membered rings, respectively. The carbons of HCC are those joining the *n*-membered rings, i. e., parallel to the *n*-fold axis; those of HCC' are within an *n*-membered ring.

Table 2.4 AM1 and MNDO Properties of the [*n*]-Prismanes[a]

n	Heat of Formation (kcal/mol)	Ionization potential (eV)	Zero-Point energy (kcal/mol)	Lowest AM1 frequencies (cm^{-1})	$\Delta H_f/2n$
3	165.0 (121.9)	10.0 (10.0)	63.5 (66.2)	570, 800, 809	27.5
4	151.2 (99.1)	10.5 (10.9)	87.3 (91.1)	571, 626, 813	18.9
5	117.7 (72.2)	10.2 (10.7)	111.9 (115.9)	549, 550, 623	11.8
6	139.9 (80.4)	9.6 (10.4)	135.3 (140.2)	411, 412, 478	11.7
7	191.0 (116.4)	9.7 (10.4)	157.7 (163.7)	300, 309, 347	13.6
8	259.2 (172.7)	9.4 (10.3)	180.3 (187.3)	234, 235, 271	16.2
9	340.6 (243.8)	9.5 (10.3)	202.3	166, 178, 206	18.9
10	430.9 (325.1)	9.4 (10.3)	224.5	133, 135, 174	21.5
11	527.6 (413.6)	9.4 (10.3)	246.4	84, 99, 137	24.0
12	629.3 (507.5)	9.4 (10.3)	268.4	67, 69, 121	26.2

[a] MNDO values are given in parentheses.

Figure 2.3 Heats of Formation of the [*n*]-Prismanes vs. *n*



An important issue is the kinetic stability of these compounds. A recent MM2 study by Jemmis and Reddy[14] found D_{nh} structures for [*n*]-prismanes (*n* = 5 to 7), but a D_{4d} structure for [8]-prismane, lower in energy than the D_{8h} form by 6.8 kcal mol^{-1}. In the present work, their D_{4d} structure was used as the starting point for an AM1 geometry optimization. This calculation led to a D_{8h} structure, suggesting that the AM1 D_{4d} form is not a minimum.

To further test kinetic stabilities, we applied small, random distortions to the cartesian coordinates of the AM1-optimized structures of the [*n*]-prismanes, and used these distorted coordinates to restart AMPAC optimizations without symmetry constraints. For each of the [*n*]-prismanes studied, (*n* = 3 to 12), this optimization furnished the same D_{nh} structure, once again. We examined the lowest AM1 vibrational frequencies of the [*n*]-prismanes. Their smallest AM1 frequencies (Table 2.4), while positive, are quite low for larger *n*, e.g. 67 cm^{-1} for *n* = 12. Thus, the prismanes with *n* > 7 are increasingly flexible.

It is interesting to compare the strain energies of the [*n*]-prismanes using Baeyer strain theory of cycloalkanes.[15] Saturated carbon atoms tend to have bond angles of 109.5°. Assuming a cyclic carbon compound to be planar, its CCC angles will be equal to those of the corresponding regular polygon: 60° for cyclopropane, 90° for cyclobutane, etc. Therefore,

every cyclic compound will exhibit a high degree of angle strain, except for cyclopentane, which would be almost strain-free, and cyclohexane, which would be only moderately strained.

While Baeyer's theory is incorrect for non-planar cycloalkanes, it can be applied to the [*n*]-prismanes since they have planar faces. The calculated energies of the prismanes bear out Baeyer's prediction in that [5]- and [6]-prismane are calculated to be most stable, while the [*n*]-prismane energies increase rapidly for larger *n*.

Results for the Asteranes: Helvetane and Israelane

The $C_{24}H_{24}$ molecules helvetane and israelane, suggested by Ginsburg,[7] are isomers of [12]-prismane and share with it a common chemical graph. Important structural differences between them and the completely *syn*-[12]-prismane are the combinations of *syn* and *anti* ring arrangements in **VIII** and **IX**; they lead to non-bonded interactions between inward-pointing carbons and hydrogens as well as severe deformations of the CCC angles. Earlier MNDO calculations[16] assumed D_{4h} symmetry for helvetane and D_{6h} symmetry for israelane; helvetane was found to be more stable by 383 kcal mol^{-1}. The present AM1 calculations show D_{4h} helvetane (ΔH_f = 400 kcal mol^{-1}) to be more stable than D_{6h} israelane (ΔH_f = 773 kcal mol^{-1}) by 373 kcal mol^{-1}. However, the AM1 force-constant matrices

of D_{4h} helvetane and D_{6h} israelane possess one and three negative eigenvalues, respectively. When slight distortions are applied to the coordinates of each and their geometries optimized without symmetry constraints, a D_{2d} structure is obtained for helvetane (Figure 2.4) and a D_{3d} structure for israelane. The force-constant matrices of both new structures have only positive eigenvalues. (The heats of formation of helvetane and israelane decreased by 4 and 23 kcal mol^{-1}.) The AM1 heats of formation of the $C_{24}H_{24}$ isomers are: (in kcal mol^{-1}) D_{2d} helvetane 396; D_{12h} [12]-prismane 629; and D_{3d} israelane 750. MM2 calculations on helvetane also furnished a D_{2d} structure; its ΔH_f was 356 kcal mol^{-1}. MM2 calculations on israelane failed to converge to any single geometry.

The AM1 and MM2 geometric parameters of helvetane are given in Table 2.5. The two σ_d planes contain C_3, C_{12}, C_{18}, C_{21} and C_6, C_9, C_{15}, C_{24} respectively, as well as their hydrogens. The cyclobutanes are slightly puckered; the two twelve-membered rings deviate from planarity with CCCC dihedral angles of 10° (at most) in AM1 and 30° in MM2. AM1 predicts inward-pointing distances H_3 - H_{24}, H_3 - H_6, H_6 - H_{24}, and H_3 - H_{21} of 1.695, 1.695, 1.713 and 2.654 Å, respectively.

Figure 2.4 Perspective Drawing of D_{2d} Helvetane

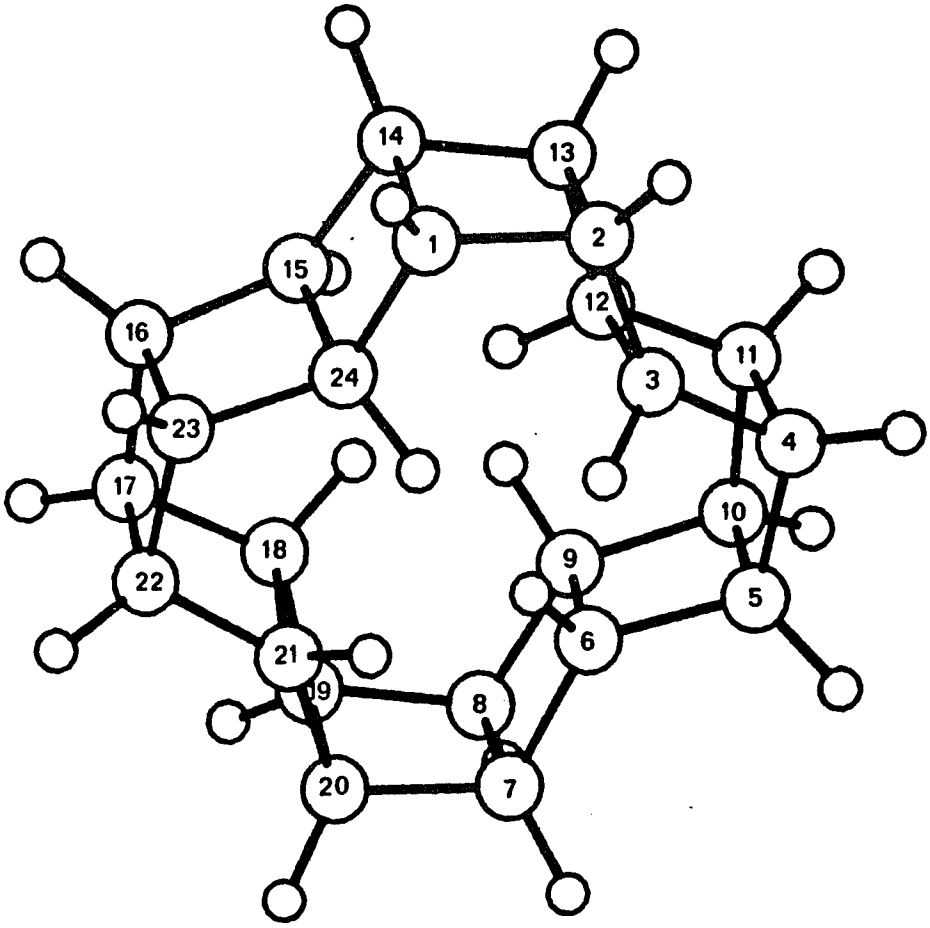


Table 2.5 AM1 and MM2[a] Geometric Parameters of Helvetane[b,c] (D_{2d} Symmetry)

bond lengths (Å)			
C_1H_1	1.097 (1.115)	C_1C_2	1.578 (1.581)
C_2H_2	1.097 (1.115)	C_2C_3	1.537 (1.555)
C_3H_3	1.110 (1.111)	C_1C_{14}	1.584 (1.556)
$C_{24}H_{24}$	1.088 (1.083)	$C_{12}C_{13}$	1.539 (1.536)
		C_3C_{12}	1.614 (1.595)
bond angles (degrees)			
$H_1C_1C_2$	116.3 (120.5)	$C_1C_2C_3$	111.3 (113.3)
$H_1C_1C_{14}$	122.1 (114.0)	$C_2C_3C_4$	138.8 (139.7)
$H_2C_2C_1$	115.9 (116.5)	$C_{13}C_{12}C_{11}$	130.7 (130.4)
$H_2C_2C_{13}$	122.1 (116.0)	$C_2C_{13}C_{12}$	88.8 (82.4)
$H_3C_3C_{12}$	131.7 (127.5)	$C_3C_{12}C_{13}$	90.9 (97.8)
$H_{24}C_{24}C_{15}$	121.2 (120.3)	$C_{24}C_1C_2$	114.1 (117.0)
dihedral angles (degrees)			
$C_1C_2C_{13}C_{14}$	7.0 (9.7)	$C_{24}C_1C_2C_3$	-9.8 (-27.2)
$C_1C_2C_3C_4$	169.7 (150.0)	$C_{14}C_{13}C_{12}C_{11}$	173.7 (160.7)
$H_1C_1C_{14}H_{14}$	8.8 (14.5)		

[a] MM2 values are in parentheses.

[b] See Figure 2.4 for atom numbering.

[c] helvetane, israelane and [12]-prismane share the IUPAC name tridecacyclo[12.10.0.$0^{2,13}$.$0^{3,12}$.$0^{4,11}$.$0^{5,10}$.$0^{6,9}$.$0^{7,20}$.-$0^{8,19}$.$0^{15,24}$.$0^{16,23}$.$0^{17,22}$.$0^{18,21}$]tetracosane

The following "homodesmic" reaction preserves the same

[*n* + 2]-ladderane ---> [*n*]-prismane + [2]-ladderane (2.1)

number of methylene and methine groups and provides a means of relating ladderane energies to those of the prismanes. For $n = 12$, the ΔH for reaction 2.1 is 369 kcal mol^{-1}. Reaction 2.2 is the analogue of 2.1 (for $n = 12$) with hel-

[14]-ladderane ---> helvetane + [2]-ladderane (2.2)

vetane in place of [12]-prismane; its ΔH is 136 kcal mol^{-1}. While this "extra energy" of the cyclic helvetane is large, it is only ca. 6 kcal mol^{-1} per methine, suggesting (along with the positive eigenvalues of its force-constant matrix) that helvetane may be capable of existence.

References

1. Wiberg, K. B.; Wendoloski, J. J. J. Am. Chem. Soc. 1982, 104, 5679.

2. Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. J. Am. Chem. Soc. 1975, 97, 1285.

3. Dewar, M. J. S.; Thiel, W. J. Am. Chem. Soc. 1977, 99, 4899.

4. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. J. Am. Chem. Soc. 1985, 107, 3902.

5. Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. J. Am. Chem. Soc. 1975, 97, 1294.

6. Schulman, J. M.; Disch, R. L.; Sabio, M. L. J. Am. Chem. Soc. 1983, 105, 743.

7. Dinsburg, G. (a.k.a. D. Ginsburg), Nouv. J. Chim. 1982, 6, 175.

8. The AMPAC program package, QCPE program 506.

9. Allinger, N. L. J. Am. Chem. Soc. 1977, 99, 8127.

10. Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York, 1970.

11. Roth, W. R.; Klarner, F. G.; Lennartz, H.-W. Chem. Ber. 1980, 113, 1818.

12. Wiberg, K. B. J. Comput. Chem. 1984, 5, 197.

13. Andersen, B.; Srinivasan, R. Acta Chem. Scand. 1972, 26, 3468.

14. Jemmis, E. D.; Reddy, V. P. Tetrahedron Lett. 1986, 27, 3771.

15. Morrison, R. T.; Boyd, R. N. *Organic Chemistry* (Third Edition), Allyn and Bacon, 1979.

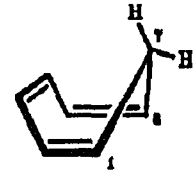
16. Li, W. K.; Luh, T. Y.; Chiu, S. W. Croat. Chem. Acta 1985, 58, 1.

3. ON THE HOMOAROMATIC CHARACTER OF TRIQUINACENE

Introduction

The concept of aromaticity is a central one in organic chemistry, explaining and tying together many phenomena. While aromaticity "was conceived as bound up with distinct types of reactivity and not with the properties of an isolated molecule in its ground state",[1] there are several properties associated with an aromatic molecule independent of any reactivity, among them NMR chemical shifts and exaltation of diamagnetic susceptibilities. Benzene, for example, has a proton chemical shift of 7.4 ppm.,[2] and an exaltation of its magnetic susceptibility of 13.7 x 10^{-6} cm^3 mol^{-1} [3] (compared to -0.7 x 10^{-6} for 1,3-cyclohexadiene).

The concept of homoaromaticity is newer than that of aromaticity. Winstein first used the term to account for the behavior of the bicyclo[3.1.0]hex-3-yl cation,[4] which contains a 3-membered cyclic π system separated by saturated carbons. Since then, considerable efforts have been made to find other homoaromatic systems.[5] One molecule that has been studied thoroughly is cycloheptatriene (I). The three double bonds of I are coupled by σ bonds while the termini, C_1 and C_6, are not. The C_1-C_6 distance, calculated to be 2.517 Å (STO-3G) (experiment places it between 2.35 Å and 2.65 Å[6]) is thought by some to be small enough to allow overlap



I

of the p-π orbitals in the non-planar boat form of the molecule, thereby enabling 'homo'-aromatic conjugation.[5] Proton NMR and diamagnetic susceptibility data (8.1×10^{-6} cm^3 mol^{-1}) provide some evidence of this;[2] moreover, a resonance energy of 6.7 kcal mol^{-1} can be ascribed to the compound.[7]

Triquinacene (**II**), possesses three double bonds separated by three saturated centers and is termed 'trishomoaromatic'.


II


III


IV


V

However, evidence against the homoaromatic nature of triquinacene has been adduced from NMR,[8] UV,[8] IR,[8] PES,[9] CD,[10] X-ray[11] and molecular mechanics[12] studies. Recently, a calorimetric study of the successive hydrogenations of its double bonds found evidence of a small extra stability for triquinacene[13] relative to its hydrogenated derivates dihydrotriquinacene (**III**), tetrahydrotriquinacene (**IV**) and perhydrotriquinacene (**V**). This stability can be seen in the following reaction:

II + **V** ----> **III** + **IV** (3.1)

The enthalpy change, ΔH, for reaction 3.1, derived from experimental heats of hydrogenation, is 4.5 kcal mol^{-1}; it is the first data in support of the homoaromatic character of triquinacene.

We undertook ab initio calculations on triquinacene and its hydrogenated derivatives in order to obtain accurate theoretical estimates of the ΔH of reaction 3.1. The geometries of **II-V**, as well as both planar and C_s forms of cyclopentene and cyclopentane, were optimized at both the STO-3G and 6-31G* SCF levels. Tables 3.1 and 3.2 list the optimized geometric parameters of C_s cyclopentene and cyclopentane in the two basis sets; the total energies of all six compounds are given in Table 3.3

Table 3.1 Selected Geometric Parameters of C_s Cyclopentene

Parameter	6-31G*	STO-3G	Exp.[a]	Parameter	6-31G*	STO-3G	Exp.
Bond lengths (Å)							
C_1C_2	1.318	1.308	1.342	C_2C_3	1.509	1.524	1.519
C_3C_4	1.549	1.556	1.546	C_1H_1	1.076	1.082	
C_3H_{3e}[b]	1.088	1.090		C_3H_{3i}	1.087	1.089	
C_4H_{4e}	1.084	1.087		C_4H_{4i}	1.084	1.087	
Bond angles (degrees)							
$C_1C_2C_3$	112.6	112.8	111.0	$C_2C_3C_4$	103.4	103.7	103.0
$C_3C_4C_5$	105.2	106.1		$C_2C_1H_1$	125.0	125.9	104.0
$C_4C_3H_{3e}$	112.2	111.5		$C_4C_3H_{3i}$	111.9	111.8	
$C_3C_4H_{4e}$	112.2	111.6		$C_3C_4H_{4i}$	109.7	110.1	
Dihedral angle between planes $C_5C_1C_2C_3$ and $C_3C_4C_5$ (degrees)							
	14.1	10.3	28.8				

[a] Davis, M. I.; Muecke, T. W. J. Phys. Chem. 1970, 74, 1104.

[b] 'e' refers to hydrogens external to the 'envelope;' 'i' to those inside the envelope.

Table 3.2 Selected Geometric Parameters of C_s Cyclopentane

Parameter	6-31G*	STO-3G	Exp.[a]	Parameter	6-31G*	STO-3G
Bond lengths (Å)						
C_1C_2	1.553	1.557		C_2C_3	1.542	1.550
C_3C_4	1.532	1.543	1.546	C_1H_{1e}[b]	1.085	1.087
C_1H_{1i}	1.085	1.087		C_3H_{3e}	1.087	1.088
C_3H_{3i}	1.085	1.087		C_4H_{4e}	1.085	1.087
C_4H_{4i}	1.088	1.088				
Bond angles (degrees)						
$C_1C_2C_3$	110.2	110.1		$C_2C_3C_4$	104.2	109.6
$C_3C_4C_5$	102.8	103.6		$C_2C_1H_{1e}$	112.2	111.7
$C_2C_1H_{1i}$	110.2	110.1		$C_4C_3H_{3e}$	109.3	109.6
$C_4C_3H_{3i}$	113.3	112.5		$C_3C_4H_{4e}$	113.2	112.6
$C_3C_4H_{4i}$	110.0	109.9				
Dihedral angle between planes $C_5C_1C_2C_3$ and $C_3C_4C_5$ (degrees)						
	40.1	36.5				

[a] Adams, W. J.; Giese, H. J.; Bartell, L. S. J. Am. Chem. Soc. 1970, 92, 5013.

[b] 'e' refers to hydrogens external to the 'envelope;' 'i' to those inside the envelope.

Table 3.3 Ab Initio Energies (a.u.), Zero-Point Energies (kcal mol^{-1}) and Thermal Enthalpy Corrections (kcal mol^{-1})[a] in the Triquinacene Series

	STO-3G SCF	6-31G* SCF	6-31+G*[b] SCF	6-31G* RMP2	Zero-Pt. Energy	$H_{298^\circ K} - H_{0^\circ K}$
triquinacene	-379.8427	-384.4515	-384.4609	-385.7198	105.4	5.0
dihydrotriquinacene	-381.0612	-385.6386	-385.6458	-386.9198	119.5	5.3
tetrahydrotriquinacene	-382.2805	-386.8250	-386.8302	-388.1178	113.7	5.7
hexahydrotriquinacene	-383.4994	-388.0105	-388.0138	-389.3160	148.1	5.5
cyclopentane	-192.8931	-195.1636	-191.1653	-195.8154	85.3[c]	3.60[d]
cyclopentene	-191.6736	-193.9772	-193.9811	-194.6164	71.1	3.46[d]

[a] Zero-point energies and values of $H_{298^\circ K} - H_{0^\circ K}$ were calculated by the method of Boyd, reference 23.

[b] 6-31+G* SCF and 6-31G* RMP2 energies were calculated at geometries optimized in 6-31G* SCF.

[c] Experimental value, Schulman, J. M.; Disch, R. L. Chem. Phys. Lett. 1985, 113, 291.

[d] Rossini, F. D.; Pitzer, K. S.; Arnett, R. C.; Braun, R. M; Pimentel, G. C. *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds;* Carnegie Press, Pittsburgh, 1953.

Triquinacene

An X-ray study of triquinacene found C_{3v} symmetry.[11] Moreover, the AM1 (C_{3v}) structure has only real frequencies and shows no tendency to distort. Finally, an MM2 search reveals no other low-energy conformations.

Automated conjugate-gradient geometric optimization was performed on the 11 independent geometrical parameters of triquinacene in C_{3v} symmetry in both the STO-3G and 6-31G* basis sets. Values of the parameters are given in Table 3.4 along with the vibrational frequencies for the totally symmetric modes. The parameters are in good agreement with both the X-ray values and the corresponding parameters of cyclopentene (given in Table 3.3): the triquinacene C=C bond lengths are 1.309 Å (STO-3G) and 1.318 Å (6-31G*); the X-ray C=C length is 1.319 Å. The calculated values for cyclopentene are 1.308 Å (STO-3G) and 1.318 Å (6-31G*). The lengths of the flanking C_2C_3 single bonds, 1.530 Å (STO-3G) and 1.514 Å (6-31G*), are also similar to their counterparts in cyclopentene, 1.524 Å (STO-3G) and 1.509 Å (6-31G*).

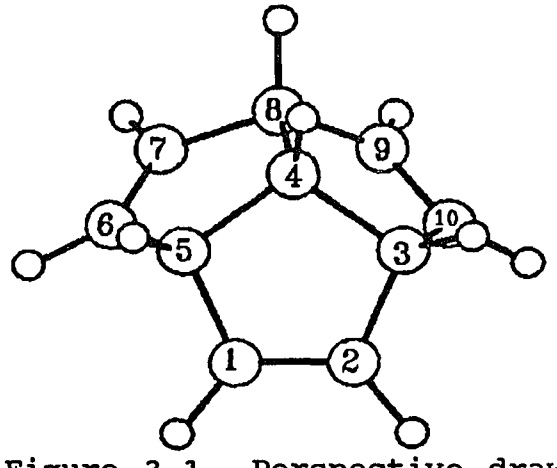


Figure 3.1 Perspective drawing of C_{3v} triquinacene

Table 3.4 Selected Geometric Parameters and Vibrational Frequencies of C_{3v} Triquinacene

Parameter[a]	6-31G*	STO-3G	Experiment[b]
Bond lengths (Å)			
C_1C_2	1.318	1.309	1.319
C_2C_3	1.514	1.530	1.511
C_3C_4	1.554	1.559	1.558
C_1H_1	1.076	1.082	
C_3H_3	1.088	1.092	
C_4H_4	1.082	1.087	
Bond angles (degrees)			
$C_1C_2C_3$	112.8	112.9	112.8
$C_2C_3C_4$	103.7	103.7	103.6, 103.9
$C_3C_4C_5$	106.8	106.6	106.5
$C_1C_5C_6$	114.4	114.1	113.8
$H_1C_1C_2$	124.9	125.8	
$H_3C_3C_4$	112.9	113.0	112.8
$H_4C_4C_3$	112.1	112.2	
Dihedral angles (degrees)			
$C_5C_1C_2C_3$	0.0	0.0	
$C_1C_2C_3C_4$	1.9	1.9	
$H_1C_1C_2C_3$	178.9	179.4	
$H_1C_1C_5H_5$	57.7	57.0	
$C_2C_1C_5C_6$	110.4	110.2	

Vibrational Frequencies for Totally Symmetric Modes (cm^{-1})
361.4, 830.8, 867.0, 952.2, 1088.0, 1254.0, 1462.9, 1850.7, 3182.0, 3272.3, 3379.2

[a] see Figure 3.1 for atom numbering.

[b] Stevens, E. D.; Kramer, J. D.; Paquette, L. A. J. Org. Chem. 1976, 41, 2266.

The degree of non-planarity in the five-membered rings of both triquinacene and cyclopentene was examined. A microwave investigation[14] of cyclopentene found an envelope (C_s) conformation, the angle (ϕ) between the planes $C_5C_1C_2C_3$ and $C_3C_4C_5$ being 22.3°. Ab initio SCF results in the STO-3G, a double-zeta basis (the (7,3) → <4,2> basis set of Roos and Siegbahn[15] for carbon atoms; Huzinaga's (4) → <2> basis[16] scaled by the factor 1.2[17] for hydrogen atoms)[18] and the 6-31G* basis sets give ϕ values of 10.3°, 13.6°, 14.1°, respectively. A planar cyclopentene is only 0.3 kcal mol^{-1} higher in energy at the 6-31G* SCF level (0.1 kcal mol^{-1} in the double-zeta basis);[18] changing the flap angle of the ring costs very little energy. The cyclopentene rings of triquinacene are nearly planar, the STO-3G and 6-31G* values of angle ϕ being 3.1° and 3.2°, respectively. The vinyl hydrogens of cyclopentene tilt to the side of the ring opposite C_4; the dihedral angle $H_1C_1C_2C_3$ is 179.3° (STO-3G) and 178.6° (6-31G*); the value of the angle in triquinacene is 179.4° (STO-3G) and 178.9° (6-31G*). This angle is of some interest as an indicator of rehybridization attending interaction of the non-bonded π orbitals of triquinacene, whose centers are separated by 2.545, 2.547 and 2.533 Å in the STO-3G, 6-31G* and x-ray structures, respectively.

The salient geometric parameters of triquinacene differ negligibly from those of cyclopentene itself. Three plausible manifestations of homoaromatic character do not appear: the five-membered rings do not flap inward, the lengths of the double bonds do not increase, and the vinyl carbons do not exhibit rehybridization.

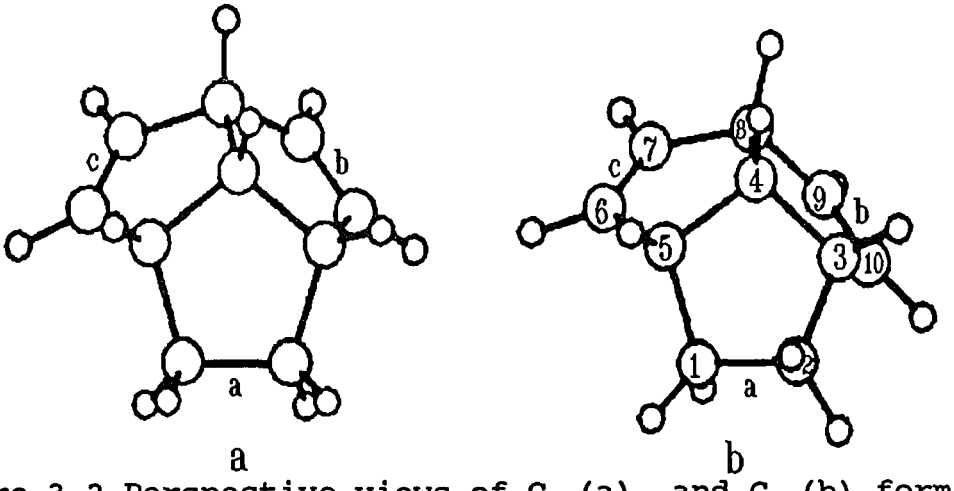
The highest occupied orbitals of triquinacene are its three π orbitals. The STO-3G orbital energies are (in a.u.) -0.2912 (e) and -0.3067 (a_1); the corresponding 6-31G* values are -0.3347 and -0.3560. Use of an empirical formula[19] for converting the 6-31G* orbital energies into vertical ionization energies gives a_1 and e ionization potentials of 9.46 and 9.92 eV, respectively. The observed values are 9.5 and 9.0 eV,[20] the latter broadened by ca. 0.2 eV due to the Jahn-Teller effect. The calculated splitting of 0.46 eV is in good agreement with experiment. The π orbitals contain a considerable admixture of methine CH orbitals, the extent being slightly larger for the a_1 orbitals. Mixing between the π orbitals and lower-lying σ orbitals of the same symmetry has been suggested[20] to play a role in the small a_1-e splitting insofar as it leads to a greater destabilization of the a_1 than of the e orbitals.

The next highest molecular orbitals of triquinacene are -0.4072 (e), -0.4087 (a_2) and -0.4420 (a_1) in STO-3G; the cor-

responding 6-31G* values are -0.4532 (e), -0.4641 (a_2) and -0.4830 (a_1). The 6-31G* values yield ionziation energies of 11.9, 12.2 and 12.3 eV, respectively.

Dihydrotriquinacene

Dihydrotriquinacene, **III**, has previously been reported to have C_s symmetry.[9] However, MM2 calculations predict a C_1 form lying 4.0 kcal mol^{-1} lower in energy. We performed



a b

Figure 3.2 Perspective views of C_s (a), and C_1 (b) forms of dihydrotriquinacene

automated conjugate-gradient geometric optimizations on both forms of **III** in the STO-3G basis set. The C_1 form (Figure 3.2b) was found to lie 2.0 kcal mol^{-1} lower than the C_s form at the STO-3G level and 3.3 kcal mol^{-1} lower at the 6-31G*//STO-3G level. We performed many 6-31G* calculations on this C_1 form, applying small adjustments to the geometric parameters until the gradients were very small. Final values for these parameters are listed in Table 3.5. The CCCC dihedral angles of **III** in the C_1 form, viewed along bonds labeled a, b and c in Figure 3.2, are -37.5, -1.3, -1.1°, respectively, at the 6-31G* SCF level; these angles in the C_s form are 0.0, -0.7 and 0.7°, respectively, in the STO-3G basis.

Table 3.5 Selected Geometric Parameters of C_1 Dihydrotriquinacene

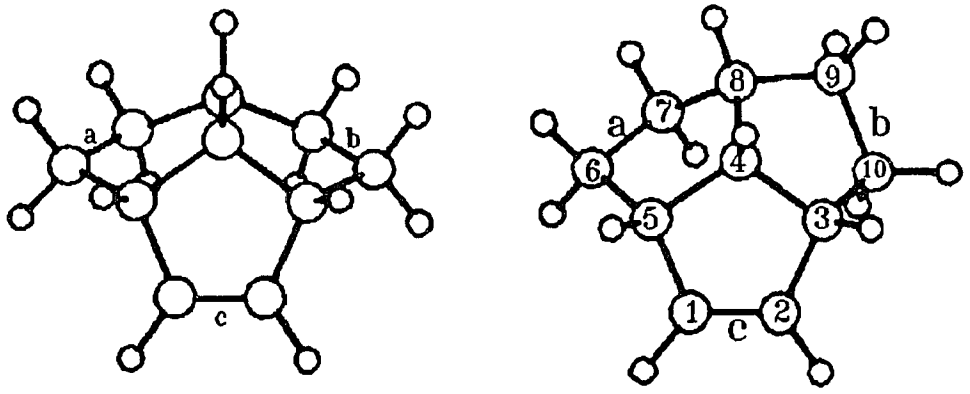
Parameter[a]	6-31G*	STO-3G	Parameter	6-31G*	STO-3G
Bond lengths (Å)					
C_1C_2	1.534	1.543	C_2C_3	1.539	1.550
C_3C_4	1.549	1.556	C_4C_5	1.553	1.561
C_5C_1	1.549	1.558	C_5C_6	1.510	1.526
C_6C_7	1.320	1.309	C_7C_8	1.515	1.529
C_8C_9	1.515	1.530	C_9C_{10}	1.320	1.309
C_3C_{10}	1.513	1.527	C_4C_8	1.552	1.559
C_1H_{1e}[b]	1.085	1.087	C_1H_{1i}	1.085	1.087
C_2H_{2e}	1.088	1.088	C_2H_{2i}	1.086	1.087
C_3H_3	1.087	1.091	C_4H_4	1.083	1.087
C_5H_5	1.087	1.090	C_6H_6	1.076	1.082
C_7H_7	1.077	1.082	C_8H_8	1.088	1.092
C_9H_9	1.076	1.082	$C_{10}H_{10}$	1.077	1.082
Bond angles (degrees)					
$C_1C_2C_3$	104.4	104.8	$C_5C_1C_2$	104.4	105.0
$C_2C_3C_4$	105.0	105.5	$C_3C_4C_5$	107.0	107.1
$C_4C_5C_6$	103.6	103.7	$C_4C_3C_{10}$	102.8	103.0
$C_3C_4C_8$	107.5	107.2	$C_4C_8C_9$	103.1	103.1
$C_8C_9C_{10}$	112.6	112.8	$C_9C_{10}C_3$	113.4	113.3
$C_5C_4C_8$	105.9	105.6	$C_5C_6C_7$	112.6	112.7
$C_6C_7C_8$	112.4	112.5	$C_7C_8C_4$	103.5	103.8
$C_1C_5C_4$	105.5	105.9			
Dihedral angles (degrees)					
$C_5C_1C_2C_3$	-37.5	-34.7	$C_3C_{10}C_9C_8$	-1.3	-0.8
$C_5C_6C_7C_8$	-1.1	-1.2			

[a] see Figure 3.2 for atom numbering.

[b] 'e' refers to hydrogens external to the cavity of the molecule; 'i' to those inside the cavity.

Tetrahydrotriquinacene

MM2 study of tetrahydrotriquinacene (IV) suggests three low energy forms, a C_1 form and two C_s forms. The two C_s forms differ in the values of their dihedral angles about the ethano bridges. The lower energy C_s form (ΔH_f = 5.56 kcal mol^{-1}) has dihedral angles of -35.0° and 35.0° about the CC bonds labeled a and b in Figure 3.3, respectively, whereas the coresponding dihedral angles in the higher energy form (ΔH_f = 6.50 kcal



a b

Figure 3.3 Perspective views of C_s (a), and C_1 (b) forms of tetrahydrotriquinacene. A second C_s form is not shown.

mol^{-1}) are 34.5° and -34.5°. The C_1 form, most stable of all, (ΔH_f = 5.34 kcal mol^{-1}) has dihedral angles of -39.2° and -32.9° about the two bonds.

AM1 geometric optimization starting from any of these three forms furnished a C_s form having dihedral angles of nearly 0° about both ethano bridges.

We started STO-3G optimizations from each of the three MM2 conformations of **IV**. The C_1 form and the lower of the two C_s forms yielded geometries whose gradients essentially vanished, while gradient optimization of the higher energy C_s form failed to converge. The C_1 form, lying 1.07 kcal mol^{-1} lower at the STO-3G level and 0.9 kcal mol^{-1} lower at the 6-31G*//STO-3G SCF level, was then adjusted until the 6-31G* gradients were quite small. The dihedral angles of this form are -37.0, -30.7 and -1.3°, for a, b, and c, respectively; the corresponding angles of the C_s form are -28.8, 28.8 and 0.0° (at the STO-3G level). Optimized values of other geometic parameters of this compound are given in Table 3.6.

Table 3.6 Selected Geometric Parameters of C_1 Tetrahydrotriquinacene

Parameter[a]	6-31G*	STO-3G	Parameter	6-31G*	STO-3G
Bond lengths (Å)					
C_1C_2	1.319	1.309	C_2C_3	1.509	1.525
C_3C_4	1.554	1.559	C_4C_5	1.556	1.560
C_5C_1	1.510	1.526	C_5C_6	1.514	1.553
C_6C_7	1.533	1.543	C_7C_8	1.540	1.550
C_8C_9	1.535	1.546	C_9C_{10}	1.539	1.547
C_3C_{10}	1.557	1.560	C_4C_8	1.545	1.553
C_1H_1	1.077	1.082	C_2H_2	1.077	1.082
C_3H_3	1.087	1.090	C_4H_4	1.084	1.087
C_5H_5	1.087	1.090	C_6H_{6e}[b]	1.087	1.088
C_6H_{6i}	1.086	1.087	C_7H_{7e}	1.086	1.087
C_7H_{7i}	1.087	1.082	C_8H_8	1.086	1.088
C_9H_{9e}	1.087	1.088	C_9H_{9i}	1.086	1.087
$C_{10}H_{10e}$	1.085	1.087	$C_{10}H_{10i}$	1.085	1.087
Bond angles (degrees)					
$C_1C_2C_3$	113.0	113.0	$C_5C_1C_2$	113.2	113.2
$C_2C_3C_4$	103.4	103.4	$C_3C_4C_5$	107.3	107.1
$C_4C_5C_6$	105.5	105.9	$C_4C_3C_{10}$	106.5	106.7
$C_3C_4C_8$	106.7	107.1	$C_4C_8C_9$	104.8	105.2
$C_8C_9C_{10}$	103.1	105.2	$C_9C_{10}C_3$	106.6	105.8
$C_5C_4C_8$	107.1	1.6	$C_5C_6C_7$	104.7	104.8
$C_6C_7C_8$	104.4	12.5	$C_7C_8C_4$	104.9	105.1
$C_1C_5C_4$	103.2	1.9			
Dihedral angles (degrees)					
$C_5C_1C_2C_3$	-1.3	-1.2	$C_3C_{10}C_9C_8$	-30.7	-29.5
$C_5C_6C_7C_8$	-37.0	-35.7.			

a see Figure 3.3 for atom numbering.

b 'e' refers to hydrogens external to the cavity of the molecule; 'i' to those inside the cavity.

Hexahydrotriquinacene

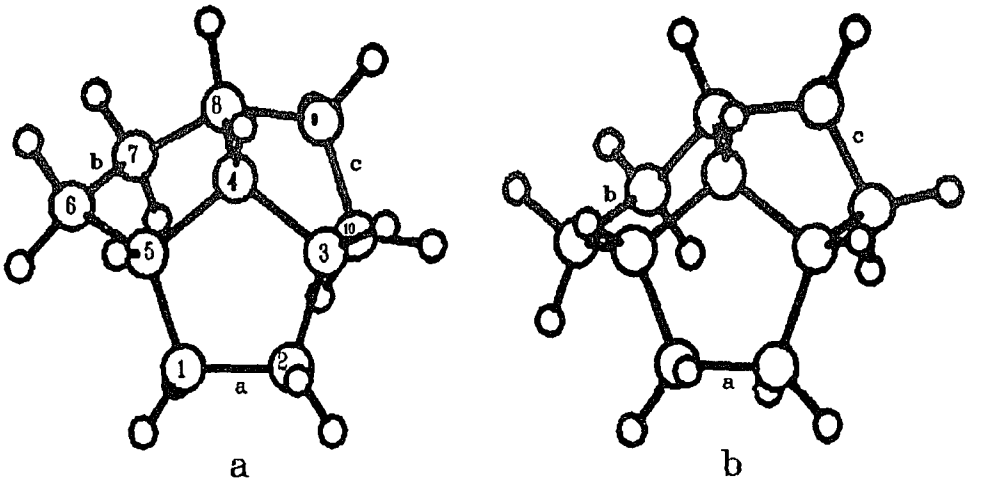


Figure 3.4 Perspective views of C_3 (a), and C_1 (b) forms of hexahydrotriquinacene

An MM2 study of hexahydrotriquinacene[21] (V) found the C_3 form to be the most stable, with a C_1 form about 2 kcal mol^{-1} higher in energy. The geometry of the C_3 conformer had been optimized previously[22] in the STO-3G basis set; we optimized the geometry of the C_1 form in this basis. STO-3G calculations also show that the C_3 form lies 2.0 kcal mol^{-1} below the C_1 form. At the 6-31G*//STO-3G SCF level, the C_3 form is more stable by 2.7 kcal mol^{-1}. The STO-3G values of the dihedral angles about the bonds labeled a, b and c in Figure 3.4b are 33.9°, -24.5° and -30.6°. We were able to adjust the C_3 6-31G* geometry until its gradients were very small. The dihedral angles about the ethano bridges are -36.5°; optimized values of other parameters are presented in Table 3.7.

Table 3.7 Selected Geometric Parameters of C_3 Perhydrotriquinacene

Parameter[a]	6-31G*	STO-3G[b]	Parameter	6-31G*	STO-3G
Bond lengths (Å)					
C_1C_2	1.533	1.544	C_2C_3	1.537	1.552
C_3C_4	1.551	1.557	C_4C_5	1.551	1.557
C_5C_1	1.543	1.547	C_1H_{1e}[c]	1.086	1.088
C_1H_{1i}	1.087	1.087	C_2H_{2e}	1.087	1.087
C_2H_{2i}	1.086	1.087	C_3H_3	1.086	1.088
C_4H_4	1.084	1.087			
Bond angles (degrees)					
$C_1C_2C_3$	104.5	104.6	$C_5C_1C_2$	104.0	105.0
$C_2C_3C_4$	105.1	105.6	$C_3C_4C_5$	107.4	107.3
$C_1C_5C_4$	105.5	107.4			
Dihedral angles (degrees)					
$C_5C_1C_2C_3$	-36.5	-35.5			

[a] see Figure 3.4 for atom numbering.

[b] STO-3G parameters from Schulman, J. M.; Disch, R. L. Tetrahedron Letters 1985, 26, 5647

[c] 'e' refers to hydrogens external to the cavity of the molecule; 'i' to those inside the cavity.

Energetics

The ab initio energies of the most stable conformers of cyclopentane, cyclopentene and **II-V** are given in Table 3.3, along with zero-point energies and thermal effects on the enthalpy computed by Boyd's molecular mechanics method.[23] We used these energies to evaluate ΔH of reaction 3.1, as well as that of reaction 3.2 from which triquinacene is absent. The

III + **V** ---> (2) **IV** (3.2)

zero-point energy difference obtained from AM1 calculations is 0.0 kcal mol^{-1}, as expected, since zero-point energies are closely related to stoichiometry.[24]

The computed enthalpy change of reaction 3.1 is -0.8 and -0.9 kcal mol^{-1} at the 6-31G* (SCF) and (RMP2) levels; the experimental value is +4.5 ± 1.2 kcal mol^{-1}. In contrast, the calculated ΔH's for 3.2, -0.2 and 0.5 kcal mol^{-1}, are in good agreement with experiment, 0.0 ± 1.0 kcal mol^{-1}. That both reactions are essentially thermoneutral is due to the nearly identical differences in total energies of **II** → **III**, **III** → **IV**, and **IV** → **V**, 1.1863 ± 0.0008 and 1.1990 ± 0.001 a.u. at the two levels, which are essentially the same as the energy differences between cyclopentene and cyclopentane, 1.1864 and 1.1990 a.u.

It is possible that π interactions between nonbonded carbons 2.533 Å apart are not treated adequately in the 6-31G* basis. The 6-31+G* basis, which contains a diffuse sp shell of exponent 0.0438 on carbon, should be sufficient, since the diffuse atomic orbitals have maxima at ca. 1.8 Å from their atomic centers. We therefore calculated the SCF energies of **II**, **III**, **IV**, and **V**, cyclopentene and cyclopentane in the 6-31+G* basis[25] using the 6-31G* geometries; the resulting energies are given in Table 3.3. The 6-31+G* ΔH values obtained for 3.1 and 3.2 are -0.6 and -0.1 kcal mol^{-1}, virtually the same as the 6-31G* SCF values. The differences in total energies of **II** → **III**, **III** → **IV**, and **IV** → **V** are 1.1843 ± 0.0007 a.u. with that of **II** → **III**, 1.1849 a.u., the largest. The difference in total energies of cyclopentene and cyclopentane is 1.1842 a.u.

Reaction 3.1 may be combined with various multiples of 3.2 to yield other homodesmic reactions (e.g. 3.1 + 3.2) from which either **III**, **IV** or **V** is absent; the enthalpy changes for all of these are nearly zero by calculation and +4.5 kcal

II + (3) **V** ----> **V** + (3) **IV** (3.3)

mol^{-1} according to experiment. For example, reaction 3.3, used by Liebman et al.[13] to justify the homoaromatic stabilization of triquinacene, has a ΔH of -0.1, -0.7 and -0.4 kcal mol^{-1} at the 6-31G* SCF, 6-31+G* SCF and the 6-31G* RMP2 levels, respectively. (This reaction compares the ΔH of **II** → **V** with three times that of **IV** → **V** and is therefore redundant.) The experimental value was 4.5 kcal mol^{-1}.

The AM1 method leads to heats of reaction almost identical to the ab initio values, namely, -0.5 and -0.1 kcal mol^{-1} for 3.1 and 3.2, respectively. The thermoneutrality of the two reactions is also predicted by the molecular mechanics method of Boyd and by MM2 and MMP2, even though a previous MMP2 investigation found a 1.28 kcal mol^{-1} stabilization of **II**.[26] A POAV/3D-HMO analysis of triquinacene gives a value of 0.200 for ρ^8 which is just equal to the threshold of nonbonded π interactions in the 3D-HMO method. Thus, none of the theoretical models applied here indicates special stability for **II**. This is the principal result of this study.

While there is an apparent conflict between experiment and theory, we cannot say where the problem lies. It is possible that the inclusion of higher orders in the perturbation expansion of the correlation energy and/or use of larger basis sets would furnish a ΔH for 3.1 closer to the experimental value while retaining the good agreement for 3.2.

Also, were it within our means, geometric optimization at the 6-31+G* SCF or 6-31G* RMP2 levels would have been undertaken. An important reason for considering the role of correlation effects here is the error in the calculated heat of reaction 3.4 (including zero-point and thermal effects) 3.7 and 7.9

benzene + (3) **ethylene** ----> (3) **butadiene** (3.4)

kcal mol^{-1} at the 6-31G* SCF and RMP2 levels, respectively.[27] (The error at the RMP4 level can be estimated to be 3.3 kcal mol^{-1}.[28]) However, both levels err in overestimating the stability of the aromatic system, while a reconciliation of the calculated heat of reaction 3.1 with experiment requires an error of underestimation. Moreover, the errors for benzene apply to an aromatic system and smaller errors would reasonably be expected for a homoaromatic system. Finally, whereas for benzene there is a large disparity in the heat of reaction at the SCF and RMP2 levels, suggestive of additional correlation effects, these two levels of theory furnish almost identical values of ΔH for reaction 3.1.

It is also possible that the 4.5 kcal mol^{-1} discrepancy between theory and experiment may not be statistically significant. Moderately small errors in individually measured quantities, either theoretical or experimental, become larger when the quantities are summed, as is the case here. It is possible that our result and that of Liebman et al.[13] are

simply on opposite ends of the same error brackets.

Heats of Hydrogenation

The heats of homodesmic reactions 3.1 and 3.2 can be calculated with greater accuracy than the heats of hydrogenation of **II**, **III** and **IV** to **V**, which require reference molecules outside the series. With this caveat, we turn to a brief discussion of the heats of hydrogenation in the 6-31G* basis. (All energies are in kcal mol^{-1}, with the RMP2-derived values in parentheses.)

The heat of hydrogenation of triquinacene to hexahydrotriquinacene can be estimated from homodesmic reaction 3.5

II + (3) **cyclopentane ---> V** + (3) **cyclopentene** (3.5)

The 6-31G* ab initio enthalpy change for this reaction, when combined with the zero-point and thermal effects on ΔH, is 0.3 (0.7). The heat of hydrogenation of cyclopentene to cyclopentane, measured in the vapor phase at 355 K[29] and corrected, as an ideal gas, to 298 K is -26.67 kcal mol^{-1}.[30] (A value of -26.94 for the heat of hydrogenation of cyclopentene in hexane is reported in reference 13.) From these data, the enthalpy difference between hexahydrotriquinacene and triquinacene at the 6-31G* level is -79.7 (-79.3), in fair agreement with the experimental value, -78.0 ± 0.5.

Using a reaction analogous to 3.5 for dihydrotriquinacene, we find the heat of reaction to be 0.7 (1.3), which

III + (2) **cyclopentane** ---> **V** + (2) **cyclopentene** (3.6)

leads to a calculated heat of hydrogenation for **III** → **V** of -52.7 (-52.1); the experimental value is -55.0 ± 0.4. Finally, for reaction 3.7, the 6-31G* heat of reaction is 0.4

IV + **cyclopentane** ---> **V** + **cyclopentene** (3.7)

(0.4), leading to a calculated heat of hydrogenation for **IV** → **V** of -26.3 (-26.3). The experimental value is -27.5 ± 0.3.

Conclusion

Comparison of the three heats of hydrogenation with their experimental counterparts (Table 3.8) exhibits disagreement, especially for **III** → **V**. More important, for the successive hydrogenations **II** → **III**, **III** → **VI** and **IV** → **V**, the computed values are -27.0 (-27.2), -26.4 (-25.8), and -26.3 (-26.3), compared with the experimental values of -23.0, -27.5 and -27.5. The experimentally derived result for **II** → **III** indicates the special stability of triquinacene attributed to homoaromatic character. We find no theoretical conformation of this result; indeed, this reaction is predicted to be the most exothermic of the three. Moreover, the thermoneutrality of 3.2 (as well as of 3.1) argues against the presence even of (linear) homoconjugation, as distinct from (cyclic)

homoaromatic conjugation.

Using -79.7 (-79.3) for the enthalpy change of **II** → **V** and -22.7 for the heat of formation of hexahydrotriquinacene, we predict ΔH_f of triquinacene to be ca. 57.0 (56.6). For comparison, the empirical method of Ibrahim et al.[31] (with our 6-31G* SCF energy) gives a ΔH_f of 53.0; however, it furnishes a ΔH_f for cyclopentene, too low by 1.4. Using -22.7 and the heats of hydrogenation (Table 3.8), the heats of formation of **III** and **IV** are estimated to be 30.0 (29.4) and 3.6 (3.6), respectively. These results are collected in Table 3.9. The respective MM2 enthalpies of formation of **II**, **III**, **IV** and **V** are 59.8, 32.2, 5.3 and -22.1 kcal mol^{-1}, in reasonable agreement with the ab initio results.

Table 3.8 Heats of Reaction[a] in the Triquinacene Series

Reaction[b]	ΔH (kcal mol^{-1})				
	STO-3G	6-31G* SCF	6-31+G* SCF	6-31G* RMP2	expt.[c]
3.1	0.5	-0.8	-0.6	-0.9	4.5 ± 1.2
3.2	0.2	-0.2	-0.1	0.5	0.0 ± 1.0
3.3	1.0	-0.1	0.7	-0.4	4.5 ± 1.4
II → V	-78.7	-79.7	-80.0	-79.3	-78.0 ± 0.5
III → V	-52.7	-52.7	-53.0	-52.1	-55.0 ± 0.4
IV → V	-26.4	-26.3	-26.4	-26.3	-27.5 ± 0.3

[a] Zero-point energies and thermal corrections are included.

[b] These reaction are not all independent.

[c] Reference 13.

Table 3.9 Derived Heats of Formation in the Triquinacene Series[a]

molecule	ΔH_f (kcal mol^{-1}) 6-31G* SCF	6-31G* RMP2	expt.
II	57.0	56.6	53.5[b]
III	30.0	29.4	30.5[b]
IV	3.3	3.6	3.0[b]
V	-22.7		-24.5 ± 0.9[c]

[a] The heat of formation of **V**, calculated as described in the text, and the heats of formation of **II**, **III** and **IV** derived from that of **V** and the 6-31G* SCF and RMP2 heats of hydrogenation, Table 3.8.

[b] Calculated from the experimental heat of formation of **V** and the experimental heat of hydrogenation, Reference 13.

[c] From Clark, T; Knox, T. McO.; McKervey M. A.; Mackle, H; Rooney, J. J. J. Am. Chem. Soc. 1979, 101, 2404.

References

1. Craig, D. P. 'Aromaticity,' in *Non-Benzenoid Aromatic Compounds*, D. Ginsburg, Ed., Interscience Publishers, Inc. 1959.

2. Pouchert, C. J.; Campbell, J. R. *The Aldrich Library of NMR Spectra*, 1974, vol. IV, p. 1.

3. Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. J. Am. Chem. Soc. 1969, 91, 1991.

4. Winstein, S. J. Am. Chem. Soc. 1959, 81, 6524.

5. Paquette, L. A. Angew. Chem., Int. Ed. Engl. 1978, 17, 106.

6. Traetterberg, M. J. Am. Chem. Soc. 1964, 86, 4265.

7. Conn, J. B.; Kistiakowsky, G. B.; Smith, E. A. J. Am. Chem. Soc. 1939, 61, 1868.

8. Woodward, R. B.; Fukunaga, T.; Kelly, R. C. J. Am. Chem. Soc. 1964, 86, 3162.

9. Bishof, P.; Bosse, D.; Gleiter, R.; Kukla, M. J.; de Meijere, A.; Paquette, L. A. Chem. Ber. 1975, 108, 1218.

10. Paquette, L. A.; Kearney, F. R.; Drake, A. F.; Mason, S. F. J. Am. Chem. Soc. 1981, 103, 5064.

11. Stevens, E. D.; Kramer, J. D.; Paquette, L. A. J. Org. Chem. 1976, 41, 2266.

12. McEwen, A. B.; Schleyer, P. v. R. J. Org. Chem. 1986, 51, 4357.

13. Liebman, J. F., Paquette, L. A., Peterson, J. R.; D. W. Rogers, J. Am. Chem. Soc. 1986, 108, 8267.

14. Rathjens, G. W., Jr. J. Chem. Phys. 1962, 36, 2401.

15. Roos, B.; Siegbahn, P. Theor. Chim. Acta. 1970, 19, 209.

16. Huzinaga, S. J. Chem. Phys. 1965, 42, 1293.

17. Dunning, T. H., Jr. J. Chem. Phys. 1970, 53, 2823.

18. Saebϕ, S.; Cordell, F. R.; Boggs, J. E. J. Mol. Struct. (Theochem) 1983, 104, 221.

19. Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J.; Brundle, C. R.; Kuebler, N. A. J. Am. Chem. Soc. 1976, 98, 7179.

20. Bünzli, J. C.; Frost, D. C.; Weiler, L. Tetrahedron Lett. 1973, 1159.

21. Osawa, E. J. Am. Chem. Soc. 1979, 101, 5523.

22. Schulman, J. M.; Disch, R. L. Tett. Lett. 1985, 26, 5647.

23. Boyd, R. H.; Sanwal, S. N.; Shakrokh-Tehrany, S.; McNally, D. J. Phys. Chem. 1971, 75, 1264.

24. Schulman, J. M.; Disch, R. L. Chem. Phys. Lett. 1985, 113, 291.

25. Clark, T.; Chandrasekhar, J. Spitznagel, G. W.; Schleyer, P. v. R. J. Comput. Chem. 1983, 4, 294.

26. McEwen, A. B.; Schleyer, P. v. R. J. Org. Chem. 1986, 51, 4357.

27. Disch, R. L.; Schulman, J. M.; Sabio, M. L. J. Am. Chem. Soc. 1985, 107, 1904.

28. Haddon, R. C.; Raghavachari, K. J. Am. Chem. Soc. 1985, 107, 289.

29. Dolliver, M. A.; Gresham, T. L.; Kistiakowsky, G. B.; Vaughan, W. E. J. Am. Chem. Soc. 1937, 59, 831.

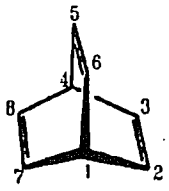
30. Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds,* Academic Press, New York, 1970.

31. Ibrahim, M. R.; Schleyer, P. v. R. J. Comput. Chem. 1985, 6, 157.

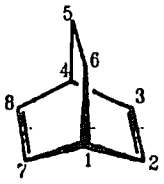
4. AB INITIO THERMOCHEMISTRY OF BARRELENE

Introduction

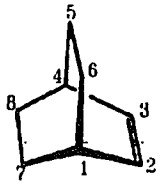
The molecule bicyclo[2.2.2]octa-2,5,7-triene (barrelene) (**I**) has been the subject of much theoretical investigation because of the unique arrangement of its three double bonds.[1,2,3] The interaction of the p-π orbitals head-to-tail, is such that there is a net destabilization of these orbitals relative to the π bonds of isolated ethylene units.[2] The molecule has been termed 'homo-antiaromatic' and this nature has been observed in the heats of hydrogenation of barrelene



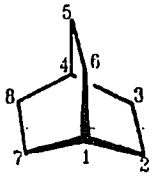
I



II



III



IV

relative to its hydrogenated derivatives, bicyclo[2.2.2]octa-2,5-diene (**II**), bicyclo[2.2.2]oct-2-ene (**III**) and bicyclo-[2.2.2]octane (**IV**), as measured by Turner et al.[4,5] The measured enthalpies of hydrogenation (in kcal mol^{-1}), -93.78 ± 0.31 (**I** → **IV**), -56.21 ± 0.10 (**II** → **IV**), and -28.25 ± 0.20 (**III** → **IV**), indicate a destabilization of **I** as its ΔH_h is greater than three times the ΔH_h of **III**. The heats of formation of **III** and **IV** have been obtained by Wong and Westrum[6] and their difference gives an enthalpy of hydrogen-

ation for **III** → **IV** of -28.55 ± 0.42 kcal mol^{-1}, in good agreement with Turner's result. The enthalpy change for **III** → **IV** is similar to that for cyclohexene → cyclohexane, -28.42.[7] On the other hand, the monohydrogenation of barrelene (**I**) is much more exothermic, -37.57 ± 0.41 kcal mol^{-1}. This larger magnitude could arise from destabilization of barrelene due to strain in its σ system, repulsions of the π electrons of its double bonds and/or homoantiaromatic character as discussed by Goldstein and Hoffmann.[2]

The nearly identical enthalpies of hydrogenation for **II** → **III** and **III** → **IV**, -27.96 and -28.25 (or -28.55) kcal mol^{-1}, respectively, are surprising; one might have expected the strain energies in the series to increase with increasing numbers of double bonds, which would have made the heat of hydrogenation for **II** → **III** more negative than that of **III** → **IV**.

The Calculations

In light of the interesting experimental results, we undertook ab initio calculations of the thermochemistry of the molecules in the barrelene series. The geometries of **I-IV** were optimized at the RHF-SCF STO-3G, 3-21G and 6-31G* levels and single point 6-31G* RMP2 (frozen core) and 6-31G** SCF calculations were performed at the 6-31G* SCF geometries. D_{3h} symmetry was assumed for barrelene, C_{2v} symmetry for **II** and **III**. For **IV**, both D_{3h} and D_3 forms were investigated. The

geometric parameters of compounds **I-IV** are given in Tables 4.1-4.4; Table 4.5 contains the energies of the compounds in the barrelene series.

Table 4.1 Selected Geometric Parameters of D_{3h} Barrelene

Parameter[a]	6-31G*	3-21G	STO-3G	Parameter	6-31G*	3-21G	STO-3G
Bond lengths (Å)							
C_1C_2	1.538	1.543	1.545	C_2C_3	1.314	1.313	1.308
C_1H_1	1.081	1.077	1.087	C_2H_2	1.074	1.070	1.081
Bond angles (degrees)							
$C_1C_2C_3$	113.0	113.3	113.2	$C_3C_4C_5$	105.8	105.4	105.5
$H_1C_1C_2$	113.0	113.3	113.2	$H_2C_2C_3$	125.8	125.8	126.3

[a] see figure 4.1 for atom numbering.

Table 4.2 Selected Geometric Parameters of C_{2v} Dihydrobarrelene

Parameter[a]	6-31G*	3-21G	STO-3G	Parameter	6-31G	3-21G	STO-3G
Bond lengths (Å)							
C_1C_2	1.520	1.523	1.532	C_2C_3	1.318	1.317	1.310
C_1C_7	1.562	1.574	1.567	C_7C_8	1.549	1.558	1.555
C_1H_1	1.083	1.079	1.087	C_2H_2	1.075	1.071	1.081
C_7H_7	1.085	1.082	1.087				
Bond angles (degrees)							
$C_1C_2C_3$	113.8	114.1	113.9	$C_3C_4C_5$	108.7	108.6	107.8
$C_1C_7C_8$	108.6	108.6	110.7	$C_2C_1C_7$	105.7	105.4	106.1
$H_1C_1C_7$	111.1	113.2	111.1	$H_2C_2C_3$	124.7	124.8	125.5
$H_7C_7C_8$	110.9	110.7	110.7				

[a] see figure 4.1 for atom numbering.

Table 4.3 Selected Geometric Parameters of C_{2v} Tetrahydrobarrelene

Parameter[a]	6-31G*	3-21G	STO-3G	Parameter	6-31G*	3-21G	STO-3G
Bond lengths (Å)							
C_1C_2	1.513	1.514	1.525	C_2C_3	1.321	1.319	1.310
C_1C_7	1.545	1.553	1.555	C_7C_8	1.550	1.560	1.555
C_1H_1	1.085	1.082	1.088	C_2H_2	1.076	1.072	1.082
C_7H_{7d}[b]	1.085	1.083	1.087	C_7H_{7s}	1.087	1.085	1.087
Bond angles (degrees)							
$C_1C_2C_3$	114.3	114.6	115.5	$C_3C_4C_5$	108.0	108.0	108.0
$C_1C_7C_8$	109.2	109.2	109.2	$C_6C_1C_7$	107.9	107.5	107.9
$H_1C_1C_2$	112.0	112.1	112.0	$H_2C_2C_3$	124.0	124.1	124.9
$H_{7d}C_7C_8$	110.7	110.4	110.5	$H_{7s}C_7C_8$	110.9	110.6	110.6

[a] see figure 4.1 for atom numbering.

[b] 'd' denotes hydrogen pointing toward olefin; 's' hydrogen pointing toward ethano bridge.

Table 4.4 Selected Geometric Parameters of D_3 Bicyclooctane

Parameter[a]	6-31G*	3-21G	STO-3G	Parameter	6-31G*	3-21G	STO-3G
Bond lengths (Å)							
C_1C_2	1.535	1.541	1.547	C_2C_3	1.552	1.561	1.555
C_1H_1	1.087	1.084	1.089	C_2H_{2a}	1.087	1.085	1.087
C_2H_{2b}	1.086	1.084	1.087				
Bond angles (degrees)							
$C_1C_2C_3$	109.7	109.7	109.7	$C_3C_4C_5$	109.2	109.2	109.2
$H_1C_1C_2$	109.8	109.8	109.7	$H_{2a}C_2C_3$	110.6	110.4	110.4
$H_{2b}C_2C_3$	110.7	110.4	110.4				
Dihedral angle $C_1C_2C_3C_4$ (degrees)							
	3.9	5.7	2.4				

[a] see figure 4.1 for atom numbering.

Table 4.5 Ab initio energies (a.u.), Zero-Point Energies (kcal mol^{-1}) and Thermal Enthalpy Corrections (kcal mol^{-1}) in the Barrelene Series

	STO-3G SCF	3-21G SCF	6-31G* SCF	6-31G**[a] SCF	6-31G* RMP2	Zero-Point Energy	$H_{298\ K} - H_{0\ K}$
barrelene	-303.8075	-305.8105	-307.5093	-307.5235	-308.5325	82.3	4.4
dihydrobarrelene	-305.0375	-307.0128	-308.7159	-308.7323	-309.7444	97.4	4.4
tetrahydrobarrelene	-306.2633	-308.2053	-309.9124	-309.9311	-310.9481	110.3	4.9
bicyclooctane	-307.4866	-307.3926	-311.1036	-311.1247	-312.1483	124.1	4.7
cyclohexane	-231.4827	-232.9169	-234.2080	-234.2263	-234.9916	103.2	4.4
cyclohexene	-230.2611	-231.7292	-233.0197	-233.0355	-233.7901	89.1	4.1

[a] 6-31G** SCF and 6-31G* RMP2 energies were calculated at geometries optimized in 6-31G* SCF.

Previous ab initio calculations[8] using optimizations in the 3-21G basis found the D_3 form of **IV**, with dihedral angles of 5.2° about the ethano bridges, to be more stable than the D_{3h} form by 4 cal mol^{-1}. According to our 3-21G results, the D_3 form having dihedral angles of 5.7° about the ethano bridges is 3.4 cal mol^{-1} more stable than the D_{3h} form. Increasing this dihedral angle costs very little energy; we performed optimizations on D_3 bicyclooctane with the ethano dihedral angle constrained to 14.9°, 19.1° and 24.4° and obtained structures only 0.1, 0.4 and 1.3 kcal mol^{-1} higher in energy than the equilibrium geometry. At the 6-31G* SCF level, however, the energies of the D_{3h} form and a D_3 form having dihedral angles of 3.9° about the ethano bridges are identical to five decimal places in atomic units.

The highest 6-31G* occupied molecular orbitals of barrelene are (in eV) 8.08 (a'_2), 9.97 (e'), 12.37 (e'') and 13.01 ($a'1$). Calculations have been reported at the 6-31G*//3-21 level[8] and in a double-zeta basis set (using a (9,5) → <4,2> Gaussian contraction for carbon atoms and a (4) → <2> contraction for hydrogen atoms[9,10])[3] furnishing orbital energies of 8.10, 9.96, 12.32 and 13.09 eV and 8.33, 10.17, 12.61 and 13.20 eV, for the same set of orbitals. PES values are 8.23, 9.65, 11.25 and 12.0 eV.

Energetics

To provide a means of comparing theoretical total energies of compounds **I-IV** to the experimental enthalpies of hydrogenation, we used several hypothetical reactions which

I + (3) **IV** ---> **IV** + (3) **III** (4.1)

conserve the same number of double bonds, methylenes and methines in reactants and products. From the experimental heats of hydrogenation, we obtained a ΔH of -9.1 ± 0.91 kcal mol^{-1} for reaction 4.1. Using ab initio total energies and zero-point energies and thermal corrections to the enthalpy computed by the molecular mechanics method of Boyd et al.[11] we obtain heats of reaction (in kcal mol^{-1}) -4.5, -11.4, -11.8, -11.6 and -8.2 at the STO-3G, 3-21G, 6-31G* SCF, 6-31G** and 6-31G* RMP2 levels. The RMP2 value agrees with the experimental value within the latter's error limits, while the values obtained in 3-21G SCF, 6-31G* SCF and 6-31G** are further (ca. 2.5 kcal mol^{-1}) from experiment, although they are internally consistent. From the discrepancy between 6-31G* RMP2 and 6-31G* SCF (3.6 kcal mol^{-1}), it can be estimated that the inclusion of second order correlation energy lowers the energy of a compound containing parallel, proximal double bonds by 1.2 kcal mol^{-1} per pair of such double bonds.

Reaction 4.2 offers another possible means of relating ab initio total energies to experimental enthalpies of

I + (3) III ---> IV + (3) II (4.2)

hydrogenation and preserves not only the number of methines, methylenes and double bonds, but also the same number of intramolecular interactions between pairs of double bonds (3), double bonds and ethano bridges (6) and pairs of ethano bridges (3). From the values given in Table 4.5, we obtain an ab initio heat of reaction of 0.8, -1.0, -1.1, -0.9 and -1.1 kcal mol^{-1} at the STO-3G, 3-21G, 6-31G* SCF, 6-31G** and 6-31G* RMP2 levels. With the exception of STO-3G, the values are remarkably consistent, despite the very different levels of calculation. The experimental heat of reaction 4.2, calculated from the enthalpy changes for **I → IV** plus three times **III → IV** minus three times **II → IV**, is -9.9 ± 1.1 kcal mol^{-1}. The difference between theory and experiment of almost 9 kcal mol^{-1} is surprising in light of the agreement for reaction 4.1.

Similar disagreement exists between theory and experiment

I + IV ---> II + III (4.3)

for reaction 4.3, the barrelene analogue of reaction 3.1. The experimental energy change for this reaction is -9.3 ± 0.6 kcal mol^{-1}. The theoretical values of ΔH are -2.7, -7.9, -8.2, -8.0 and -5.8 kcal mol^{-1} in STO-3G, 3-21G, 6-31G*,

6-31G** and 6-31G* RMP2. As was found for reaction 4.1, the values obtained from SCF calculations using the three split valence basis sets agree among themselves, but are about 2.4 kcal mol^{-1} (2 x 1.2 kcal mol^{-1} per pair of double bonds) lower than the RMP2 value.

In light of these discrepancies, it is useful to consider another reaction, 4.4; we obtain ab initio heats of reaction

II + **IV** ---> (2) **III** (4.4)

of -1.8, -3.4, -3.6, -3.6 and -2.4 kcal mol^{-1} at the STO-3G, 3-21G, 6-31G* SCF, 6-31G** and 6-31G* RMP2. The experimental value, based upon the enthalpy of hydrogenation of **II** minus twice the enthalpy of hydrogenation of **III**, is 0.3 ± 0.5 kcal mol^{-1}. There is again a discrepancy between theory and experiment, although less serious than that for reactions 4.2 and 4.3.

Reaction 4.4 belongs to a family of hydrogen transfer reaction which include reaction 4.4a and 4.4b. Experimental

norbornadiene + norbornane ---> (2) norbornene (4.4a)

Dewar benzene + bicyclo[2.2.0]hexane --->
(2) bicyclo[2.2.0]hex-2,3-ene (4.4b)

and theoretical enthalpy changes for reactions 4.4, 4.4a and 4.4b are given in Table 4.6. The calculated ΔH values are all negative, and the experimental value for 4.4a is also negative.

Table 4.6 Ab initio Enthalpies for Reactions in the Barrelene Series (kcal mol^{-1})

Reaction	STO-3G SCF	321G SCF	6-31G* SCF	6-31G** SCF	6-31G* RMP2	Expt.[a]	Corr. Expt.[b]
I + (3) IV → IV + (3) III	-4.5	-11.4	-11.8	-11.6	-8.2	-9.0	
I + (3) III → IV + (3) II	0.8	-1.0	-1.1	-0.9	-1.1	-9.9	-0.6
I + IV → II + III	-2.7	-7.9	-8.2	-8.0	-5.8	-9.3	-6.2
II + IV → (2) III	-1.8	-3.4	-3.6	-3.6	-2.4	0.3	-2.8
I + $3H_2$ → IV[c]	-95.3	-98.3	-104.8	-104.4	-93.5	-93.8	
II + $2H_2$ → IV[d]	-62.4	-61.4	-65.6	-65.4	-59.3	-56.2	
III + H_2 → IV[e]	-30.3	-29.0	-31.0	-31.0	-28.5	-28.3	

[a] Derived from experimental heats of hydrogenation in references 4 and 5.

[b] Reactions involving dihydrobarrelene (II) have been corrected by 3.1 kcal mol^{-1} per molecule of II, as discussed on page 74.

[c] Theoretical values were obtained using homodesmic reaction 4.5.

[d] Theoretical values were obtained using homodesmic reaction 4.6.

[e] Theoretical values were obtained using homodesmic reaction 4.7.

Of the four reactions, 4.1, 4.2, 4.3 and 4.4, the first is the one for which experiment and theory are in best agreement. This is also the only reaction from which **II** is absent. It therefore seems possible that the experimental heat of hydrogenation for **II** is in error. It has been reported that the purification of this compound is difficult.[8]

To investigate the possibility that the experimental heat of perhydrogenation of **II** is in error, we have computed the heats of hydrogenation for compounds **I-IV** using homodesmic cycles similar to those used in the preceding chapter for the molecules in the triquinacene series. Heats of hydrogenation were obtained using 6-31G* RMP2 total energies including zero-point and thermal effects (6-31G* SCF values are in parentheses); units are kcal mol^{-1}. Reaction 4.5 relates the heat of hydrogenation of barrelene to that of cyclohexene; it has

I + (3) **cyclohexane** --> **IV** + (3) **cyclohexene** (4.5)

a ΔH of -8.28 (-19.58). Using -28.42 as the enthalpy of hydrogenation of cyclohexene → cyclohexane,[7] we computed the heat of hydrogenation of **I** → **IV** to be -93.54 (-104.84), only 0.24 kcal mol^{-1} higher than the experimental.

Reaction 4.6 is the analogue of 4.5 for compound **II**.

II + (2) **cyclohexane** ---> **IV** + (2) **cyclohexene** (4.6)

Its calculated enthalpy of reaction is -2.44 (-8.74). The heat of hydrogenation of **II** → **IV** is thus -59.28 (-65.58), ca. 3 kcal mol^{-1} greater than the experimental value, -56.21. To evaluate the enthalpy of hydrogenation of tetrahydrobarrelene, we used reaction 4.7, whose ΔH, -0.04 (-2.60), furnishes a ΔH_h for **III** → **IV** of -28.46 (-31.02), in good agreement with the

III + **cyclohexane** --> **IV** + **cyclohexene** (4.7)

experimental value, -28.25.

In light of the close agreement seen for reactions 4.5 and 4.7 and the disagreement over reaction 4.6, it seems possible that the experimental heat of hydrogenation of **II** is in error by about 3.1 kcal mol^{-1}. When this correction is applied to the experimental enthalpy of reaction 4.2, the value -0.6 kcal mol^{-1} is obtained, in good agreement with our RMP2 value. For reaction 4.4, a similar correction yields a ΔH of -2.8, again in good agreement with the RMP2 value.

Assuming the theoretical and experimental enthalpies of hydrogenation to be valid (including that of **II** as corrected), it appears that barrelene is destablized relative to three isolated double bonds as in bicyclo[2.2.2]oct-2-ene. This can be seen in the negative ΔH of reaction 4.1 (-9.1 ± 0.9 kcal mol^{-1}). However, the question remains as to whether this

destabilization is caused by a homo-antiaromatic effect or is simply due to the repulsion between 3 pairs of double bonds in close proximity. If we take the corrected value of the ΔH of reaction 4.4 as mentioned in the preceding paragraph, a 2.8 kcal mol^{-1} destablization can be attributed to the repulsion between the neighboring double bonds of compound **II** (in which homo-aromaticity is clearly absent). The destabilization of **I** is only 0.7 kcal mol^{-1} greater than three times the destabilization of **II**, thus the issue of homo-aromaticity cannot be resolved at this time.

Conclusion

The theoretical energies obtained using second-order estimates of electron-correlation energy are in good agreement with the experimental values except for the one case pointed out, where it appears plausible that the experimental value is in error. This argues for the usefulness of such methods as predictors of enthalpies of reaction.

References

1. Zimmerman, H. E.; Grunewald, G. L.; Paufler, R. M.; Sherwin, M. A. J. Am. Chem. Soc. 1969, 91, 2330.

2. Goldstein, M. J.; Hoffmann, R. J. Am. Chem. Soc. 1971, 93, 6193.

3. Palmer, M. H. J. Mol. Str. 1987, 161, 333.

4. Turner, R. B.; Meador, W. R.; Winkler, R. E. J. Am. Chem. Soc. 1957, 79, 4116.

5. Turner, R. B. J. Am. Chem. Soc. 1964, 86, 3586.

6. Wong, S. S.; Westrum, E. F. J. Am. Chem. Soc. 1971, 93, 5317.

7. Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*, pp. 148-149, Academic Press, New York 1970.

8. Schmitz, L. R.; Allinger, N. L.; Flurchick, K. M J. Comput. Chem. 1988, 9, 281.

9. Huzinaga, S. J. Chem. Phys. 1965, 42, 1293.

10. Dunning, T. H. J. Chem. Phys. 1970, 53, 1970.

11. Boyd, R. H.; Sanwal, S. N.; Shakrokh-Tehrany, S.; McNally, D. J. Phys. Chem. 1971, 75, 1264.

5. A METHOD FOR SIMPLIFYING AB INITIO GEOMETRY OPTIMIZATIONS

Introduction

Optimization of the geometry of an N-atomic molecule is the determination of a molecular configuration for which the forces on all N nuclei vanish, i.e. the derivatives $-\mathbf{f}_\alpha = \partial E/\partial \mathbf{r}_\alpha = 0$ for all α, where $\mathbf{r}_\alpha$ is a radius vector locating nucleus α, and the force $\mathbf{f}_\alpha$ is a 3-vector. This configuration, which is at an extremum on the energy surface, is referred to as the optimized geometry. The extremum is not necessarily a minimum; even if it is, it need not be the global minimum of the potential energy surface. The nature of an extremum can be determined from the eigenvalues of the second derivative matrix, $\partial^2 E/\partial \mathbf{r}_\alpha \partial \mathbf{r}_\beta$, after discarding the lowest 6 eigenvalues (5 for a linear molecule). All positive eigenvalues signal a minimum, a single negative eigenvalue a transition state.

Several schemes have been developed for efficient geometry optimization, all of which rely upon the computation of the $\mathbf{f}_\alpha$ using an analytical formula, some of which even compute the second derivatives of E with an analytical formula. These methods exploit the fact that near an extremum virtually any function of many variables (x_i) is accurately represented by a Taylor expansion truncated after the second-

$$E - E_0 = \tfrac{1}{2}\sum_i \sum_j q_i \cdot (\partial^2 E/\partial x_i \partial x_j) \cdot q_j \qquad (5.1)$$

order term, i.e. $E-E_0$ is given by a quadratic form in the displacements ($q_i = x_i - x_{i0}$) from their equilibrium values x_{i0} of the geometrical parameters to be optimized. Note that, since the Taylor expansion is about the geometry of the extremum (of energy E_0), the first derivatives $-f_i$ vanish and the first-order term in the Taylor expansion is absent. For optimization of N independent internal coordinates, the quantities $(\partial^2 E/\partial x_i \partial x_j)$ constitute a symmetrical N x N matrix known as the force-constant matrix (F).

Newton and quasi-Newton methods of molecular geometry optimization use the matrix F as well as analytical SCF gradients, g, ($g_\alpha = -f_\alpha$).[12,13] The gradient at some geometry $\mathbf{x}$, at a displacement $\mathbf{q}$ from equilibrium is expressed by equation 5.2,

$$\mathbf{g}(\mathbf{x}) = \mathbf{F} \cdot \mathbf{q} \tag{5.2}$$

which is derived by differentiation of the truncated Taylor series expansion (5.1) The vector $\mathbf{q}$ can be found from equation 5.3 if F is known: $-\mathbf{q}$ is a vector in the conjugate direction,

$$-\mathbf{q} = -\mathbf{F}^{-1}\mathbf{g}(\mathbf{x}) \tag{5.3}$$

i.e. it points to the equilibrium geometry.

There are several ways of obtaining F, including direct analytical calculation (usually quite expensive since the calculation not only requires much CPU time, but also access to secondary storage devices containing the two-electron integrals), finite differences of analytically calculated gradients and estimation by various means. Most optimization al-

gorithms using an estimated F start with a guess, based either on intuition or some empirical calculation[13] and then update F according to one of several procedures[14,15] using information gleaned from several cycles of gradient calculations. Provided one begins with a geometry within the quadratic region, it can be shown that an N x N second-derivative matrix can be obtained correctly after at most N cycles.

Although an N-atomic molecule is described by 3N-6 internal coordinates, not all of these in general require optimization. If there is good reason to expect that the optimized configuration has elements of symmetry, the optimization may usefully and economically be limited to that subset of these parameters which preserve that symmetry. They are identical in number to those genuine normal modes of vibration which belong to the totally symmetric irreducible representation of the molecular point symmetry group. The optimization must span all these parameters. Note that, even when the structure has not been optimized with respect to the totally symmetric parameters, the forces on all non-totally symmetric parameters, i.e. those which would reduce the molecular symmetry, vanish because they are transformed by symmetry operations in the same manner as those parameters.

Conjugate-Gradient Optimization

To obtain F by finite differences of analytical gradients, one typically designates sets of Z-matrix parameters ('lists,' L_j) that span the space of all totally symmetric

$$L_j = \{Z_a, Z_b, Z_c, \ldots\} \tag{5.4}$$

distortions of the molecule. It is not necessary that the lists be entirely linearly independent of one another, but they must not contain any redundancies, i.e. there must be no linear combinations of the lists that fail to produce internal distortion of the molecule.

Before beginning the process, it is desirable to ascertain that the geometry is already within the quadratic region. Then gradients are computed for the initial ('reference') structure. This gradient calculation, as well as each of the ensuing gradient calculations, includes the computation of two-electron and one-electron integrals, an SCF procedure and computation of the analytical first derivatives of the energy with respect to the 3N cartesian coordinates of the molecule (the cartesian gradients). This is the step requiring by far the most time. Once obtained, the cartesian gradients are referred to the Z-matrix (equation 5.5) and gradients with respect to the lists are obtained by summing the gradients

$$g_{Z_i} = (\partial E/\partial Z_i)_{Z_{j\neq i}} = \sum_{\alpha=1} (\partial E/\partial r_\alpha)\cdot(\partial r_\alpha/\partial Z_i) \tag{5.5}$$

on those parameters of the Z-matrix in each list (equation

$$g_{L_j} = \sum_{i \epsilon L_j} g_{Z_i} \tag{5.6}$$

5.6). The set of gradients with respect to lists at the reference geometry are here designated reference gradients.

A test point is obtained for each of the *N* lists to be optimized by changing its constituent Z-matrix parameters by some (small) amount. Gradients with respect to lists are then obtained for the test point. Comparison of these gradients with the reference gradients allows the computation of one column of **F** from each test point. When all the test-point calculations are complete, the second derivative matrix is inverted and multiplied by the reference gradients (equation 5.3). This provides $-\mathbf{q}$, a vector of increments to be applied to the lists to reach the equilibrium geometry for the molecule, i.e. a vector in the conjugate direction.

The Algorithm

The foregoing process requires a total of $N + 1$ gradient calculations to obtain an equilibrium geometry with respect to *N* parameters. If, however, the **eigenvectors** (V_{ij}) of the second derivative matrix are known even approximately, before the optimization is begun, the procedure can be greatly simplified.

If these eigenvectors approximately diagonalize the force-constant matrix, optimization on *all lists simul-*

taneously can be accomplished with as few as 3 or 4 gradient calculations. This is possible because the eigenvectors of the force-constant matrix define essentially uncoupled linear combinations of the lists ('superlists,' $Q_j = \Sigma\ V_{ij}q_i$) for optimization. The energy and gradient of a molecule near its minimum-energy geometry are given by the following expressions:

$$E = \tfrac{1}{2}\ \mathbf{q}\cdot\mathbf{F}\cdot\mathbf{q} \tag{5.7}$$

$$g_i = \sum_{j=1}^{N} F_{ij}q_j \tag{5.8}$$

where $\mathbf{F}$ is the force-constant matrix referred to lists, $\mathbf{q}$ is the vector of displacements of the parameter lists from equilibrium and g_i is the gradient on the i'th parameter list. Unless analytical second derivatives are computed, $N + 1$ gradient calculations would normally be required to evaluate the force-constant matrix directly for N parameters. However, the expressions are greatly simplified for parameter lists that diagonalize $\mathbf{F}$:

$$E = \tfrac{1}{2}\Sigma\ F_{ii}Q_i^2 \tag{5.9}$$

$$g_i = F_{ii}Q_i \tag{5.10}$$

Since the force on any superlist in a diagonal basis depends only on the displacement of that list from equilibrium, distortions may be applied simultaneously to all superlists.

One method of obtaining approximate eigenvectors of a

force-constant matrix for an ab intio calculation is from a previous conjugate-gradient optimization in a smaller basis set. The force-constant matrix itself is not generally transferable from one basis to another since the eigenvalues (force constants) are very basis dependent; optimizations would be even further simplified if the force-constant matrix were transferable. The eigenvectors, however, which reflect the interactions among Z-matrix parameter lists, are assumed here to be independent of basis.

Having optimized the geometry of a molecule in STO-3G, for example, one could perform a gradient calculation in 6-31G* at the STO-3G geometry, construct a single test point, and then, using the forces on these two structures, compute the force-constant matrix and obtain the equilibrium geometry. The process could be repeated in cases where refinement is desired or anharmonicity is encountered.

Testing the Algorithm

Thirteen cyclic hydrocarbon molecules were selected, most of them strained, in keeping with the general theme of this thesis. Complete conjugate-gradient geometric optimizations were performed for all 13 molecules at the STO-3G, 3-21G and 6-31G* (SCF) levels of theory, using gradients obtained on an IBM 3090 or 3081 mainframe. Parameter lists for optimization were chosen to preserve particular molecular symmetries. The eigenvectors of the force-constant matrix from each of the

optimizations in STO-3G and 3-21G were preserved on disk for later use.

Projections were performed from each of the two smaller bases above to each of the two larger bases, i.e. STO-3G eigenvectors were used to simplify both 3-21G and 6-31G* optimizations and 3-21G eigenvectors were used for 6-31G* optimizations.

The procedure used is as follows. First, a gradient calculation is performed in the higher basis using the equilibrium geometry of the lower basis. If the gradient on any parameter appears to lie outside the quadratic region (approximately greater than 0.01 a.u. per bohr or radian), the Z-matrix is adjusted to bring it within the quadratic region and another gradient calculation is performed on this modified Z-matrix. In most cases, preadjustment is not necessary.

Next, the appropriate initial Z-matrix is submitted to a program running on a VAX 8600 together with the parameter lists, the cartesian gradients in the larger basis and the eigenvectors V_{ji} from the smaller-basis optimization. After reading and verifying the input data and computing the forces with respect to optimization lists, this program uses the eigenvectors to obtain forces with respect to the linear

$$f_i = \sum_{j=1}^{N} f_{L_j} V_{ji} \qquad (5.11)$$

combinations of the lists defined by the matrix **V** ('superlists', equation 5.11). Then, test increments are chosen for each of the superlists (vide infra) and the Z-matrix is edited to reflect simultaneous distortions of all the superlists. The edited Z-matrix is submitted to the ab initio program for a gradient calculation.

When the gradients on the test point are available, the program on the VAX is again entered to read these gradients and to compute the force constant for each of the superlists and the displacement of each superlist from equilibrium. The force constants are then back-transformed, using the matrix **V**, to the force-constant matrix with respect to lists, which is used to compute approximate vibrational frequencies in the new basis. The vector of displacements furnishes a projected equilibrium Z-matrix, which is then submitted to the ab initio program for a gradient calculation. In almost all cases, a significant improvement over the initial geometry is found in both the energy and the gradient. Further improvement is generally obtained by treating the projected equilibrium Z-matrix as a second test point and using its gradients to compute a second equilibrium Z-matrix, which is then submitted for a gradient calculation. At this point, force constants and frequencies are recomputed and found to match more closely those produced by complete optimization.

Results

The results of applying this method to the 13 hydrocarbons are displayed in Table 5.1. The sixth column of the table ('No. of Grad. Cal'ns') gives the total number of calculations in the new basis set, including any pre-adjustments. As can be seen, the method is generally quite successful for simplifying optimizations. There were only a few cases where the process had to be repeated to obtain satisfactory results. It should be noted, however, that even multiple applications of the projection algorithm are generally less costly than a single complete optimization. Geometric parameters from the projections were found to agree with those from complete optimizations to within the publishable cutoff. We note that eigenvectors from STO-3G optimizations are often more accurate in 6-31G* calculations than those from 3-21G. This is somewhat suprising since 3-21G, having a split-valence shell, generally provides geometries and energies closer to those of 6-31G*.

This method was not found to be reliable as a predictor of vibrational frequencies. Although in many cases, frequencies obtained using the projection method closely matched those obtained from conjugate-gradient optimizations, there were some cases in which there were large discrepancies (5000 cm^{-1} in one instance); the average RMS discrepancy was 191 cm^{-1}.

Three additional projections were attempted using eigenvectors from STO-2G optimizations. These were found to perform quite well, which is fortunate since STO-2G optimizations run quickly and cost little. It is thought that eigenvectors from force-constant matrices derived from semiempirical molecular orbital calculations might be useful and, of course, are much less costly still.

To test the projection method on a very large basis set, we performed a projection-optimization on cyclopentane at the 6-311G** level using eigenvectors obtained from an STO-3G optimization. While we have no complete optimization in 6-311G** to compare our results to, after only four gradient calculations, we obtained a 6-311G** cyclopentane geometry for which the RMS gradient was 0.000137 au.

One factor in these projection calculations that has not yet been settled conclusively is how to choose the test increments for the superlists when the calculations are begun. Two methods that were found to give satisfactory results were (1) setting the test increments for each superlist equal to a constant (most often 0.8333) times the force on that superlist and (2) setting all the test increments to some constant value (e.g. 0.001). The first method is better suited to cases of large initial gradients while the second method appears to be preferable for small molecules with many parameters. Irrespective of method, it is thought wise to have the program examine any computer-generated test-point Z-

matrix thoroughly to ascertain that no atom has been shifted by too large an amount: the molecule must remain in the quadratic region of its potential energy surface.

Conclusion

The method of transporting eigenvectors from one basis to another has been found to reduce dramatically the number of gradient calculations needed to obtain an opimized geometry in the 3-21G and 6-31G* basis sets. The full set of $N + 1$ gradient calculations to obtain the force-constant matrix is carried out in a small basis set, in which these calculations are relatively inexpensive. (Alternatively, analytical calculation of the force-constant matrix may be performed.) Then the eigenvectors of this matrix provide a means of obtaining a geometry with low gradients after as few as 3 or 4 gradient calculations in an extended basis set, *independent of the number of geometric parameters requiring optimization*. For a molecule such as cyclopentane, which has 21 geometric parameters within C_s symmetry, a total of 23 gradient calculations would be required in a complete geometry optimization (21 + 1 to obtain the equilibrium geometry plus one additional calculation to evaluate it). Using the projection algorithm, only 4 gradient calculations are necessary, a saving of a factor greater than 5 (assuming no editing of two-electron integrals).

Calculations on cyclohexane and 3-methylcyclobutene serve as examples of the minimal and maximal savings that can be expected of this method. D_{3d} cyclohexane has only six parameters requiring optimization. Conjugate-gradient optimizations in STO-3G and 3-21G, using the method discussed earlier in this chapter, required 5.6 and 13.7 min. on an IBM 3090-600E. Projection-optimizations in 6-31G* using eigenvectors from STO-3G and 3-21G required 4 gradient calculations each, taking 66.5 and 66.7 min., respectively, on the same machine. A complete conjugate-gradient optimization in 6-31G* required 131.3 min., almost twice the CPU time required for the STO-3G projection which yielded essentially the same geometry.

Calculations on 3-methylcyclobutene, an asymmetric molecule, provide an example of more dramatic savings. Since there are 13 atoms in this molecule, a total of 33 parameters require optimization (3N-6). A complete optimization in 6-31G* required 287.4 min. on the IBM 3090. Five gradient calculations (a pre-adjustment was required) using the projection method and eigenvectors from an optimization in 3-21G required 77.4 min.. Using STO-3G eigenvectors proved less costly; only 4 gradient calculations were necessary (61.2 min.). The STO-3G optimization itself only required 13.1 min. Thus, in a total of 74.3 min., we were able to obtain the same 6-31G* geomtry as a conjugate-gradient optimization costing

almost 4 times as much. The advantages of our method are apparent.

Table 5.1 Results of Projected Optimizations Compared with Full Optimizations

Molecule	Symmetry Group	No. of Geom. Param. (N)	Basis Set	Source of Eigen-vectors	No. of Grad. Cal'ns	Best Force Obtained (a.u.)	Initial RMS Force (a.u.)	RMS Error in Frequencies (cm^{-1})
barrelene	D_{3h}	6	6-31G*	STO-3G	4	0.000009	0.004237	64.2
barrelene	D_{3h}	6	6-31G*	3-21G	4	0.000003	0.003243	48.2
barrelene	D_{3h}	6	3-21G	STO-2G	4	0.000010	0.001926[a]	60.8
barrelene	D_{3h}	6	3-21G	STO-3G	4	0.000022	0.005572	19.9
bicyclooctane	D_3	11	6-31G*	STO-3G	4	0.000022	0.002261	225.8
bicyclooctane	D_3	11	6-31G*	3-21G	4	0.000006	0.002642	79.5
bicyclooctane	D_3	11	3-21G	STO-3G	4	0.000080	0.001741	1705.2
bicyclopentane	C_s	18	6-31G*	STO-3G	4	0.000163	0.001447[a]	283.4

[a] Previous adjustment(s) in the larger basis have been made before applying the algorithm.

Table 5.1 (cont.) Results of Projected Optimizations Compared with Full Optimizations

Molecule	Symmetry Group	No. of Geom. Param. (*N*)	Basis Set	Source of Eigen-vectors	No. of Grad. Cal'ns	Best Force Obtained (a.u.)	Initial RMS Force (a.u.)	RMS Error in Frequencies (cm^{-1})
bicyclopentane	C_s	18	6-31G*	3-21G	4	0.000084	0.002917[a]	26.1
bicyclopentane	C_s	18	3-21G	STO-3G	4	0.000033	0.003104[a]	87.6
bicyclopentene	C_s	15	6-31G*	STO-3G	4	0.000047	0.004517	48.8
bicyclopentene	C_s	15	6-31G*	3-21G	4	0.000432	0.005851[a]	393.9
bicyclopentene	C_s	15	3-21G	STO-3G	4	0.000332	0.006303[a]	44.6
cyclohexadiene	D_{2h}	7	6-31G*	STO-3G	5	0.000034	0.003475[a]	35.5
cyclohexadiene	D_{2h}	7	6-31G*	3-21G	4	0.000012	0.002806	38.3
cyclohexadiene	D_{2h}	7	3-21G	STO-3G	4	0.000400	0.005477	68.0
cyclohexane	D_{3d}	6	6-31G*	STO-3G	4	0.000032	0.003170	297.9
cyclohexane	D_{3d}	6	6-31G*	3-21G	4	0.000014	0.003325	201.1
cyclohexane	D_{3d}	6	3-21G	STO-3G	4	0.000172	0.00811	292.2
cyclohexene	C_2	22	6-31G*	STO-3G	4	0.000023	0.004438[a]	56.0

Table 5.1 (cont.) Results of Projected Optimizations Compared with Full Optimizations

Molecule	Symmetry Group	No. of Geom. Param. (N)	Basis Set	Source of Eigen-vectors	No. of Grad. Cal'ns	Best Force Obtained (a.u.)	Initial RMS Force (a.u.)	RMS Error in Frequencies (cm^{-1})
cyclohexene	C_2	22	6-31G*	3-21G	4	0.000077	0.003266	50.2
cyclohexene	C_2	22	3-21G	STO-3G	7	0.000066	0.000956[b]	410.8
cyclopentane	C_s	21	6-311G**	STO-3G	4	0.000137	0.002158	[c]
cyclopentane	C_s	21	6-31G*	STO-3G	4	0.000078	0.004386	215.7
cyclopentane	C_s	21	6-31G*	3-21G	4	0.000031	0.002878[a]	116.1
cyclopentane	C_s	21	6-31G*	STO-2G	4	0.000137	0.001164[a]	46.5
cyclopentane	C_s	21	3-21G	STO-3G	3	0.000428	0.001168[a]	215.7
cyclopentane	C_s	21	3-21G	STO-2G	4	0.000171	0.004866	415.8
cyclopentene	C_s	18	6-31G*	3-21G	4	0.000041	0.004508	103.4

[b] This is the result of a previous application of the algorithm to the molecule.

[c] This molecule was not optimized directly in the larger basis set; no frequencies are available for comparison.

Table 5.1 (cont.) Results of Projected Optimizations Compared with Full Optimizations

Molecule	Symmetry Group	No. of Geom. Param. (*N*)	Basis Set	Source of Eigen-vectors	No. of Grad. Cal'ns	Best Force Obtained (a.u.)	Initial RMS Force (a.u.)	RMS Error in Frequencies (cm^{-1})
dihydro-barrelene	C_{2v}	14	6-31G*	STO-3G	5	0.000055	0.002130[a]	295.7
dihydro-barrelene	C_{2v}	14	6-31G*	3-21G	4	0.000001	0.003086	[d]
dihydro-barrelene	C_{2v}	14	3-21G	STO-3G	4	0.000082	0.004113	74.8
3-methyl-cyclobutene	C_1	33	6-31G*	STO-3G	4	0.000038	0.004523	187.9
3-methyl-cyclobutene	C_1	33	6-31G*	3-21G	5	0.000031	0.004738[a]	176.1
3-methyl-cyclobutene	C_1	33	3-21G	STO-3G	5	0.000164	0.004098[a]	118.4
tetrahydro-barrelene	C_{2v}	16	6-31G*	STO-3G	3	0.000283	0.001512[a]	85.6

[d] This projection was run before the code that estimates frequencies was working properly.

Table 5.1 (cont.) Results of Projected Optimizations Compared with Full Optimizations

Molecule	Symmetry Group	No. of Geom. Param. (N)	Basis Set	Source of Eigen-vectors	No. of Grad. Cal'ns	Best Force Obtained (a.u.)	Initial RMS Force (a.u.)	RMS Error in Frequencies (cm^{-1})
tetrahydro-barrelene	C_{2v}	16	6-31G*	3-21G	3	0.000283	0.002828	20.8
tetrahydro-barrelene	C_{2v}	16	3-21G	STO-3G	4	0.000175	0.001511[a]	231.1
toluene	C_s	22	6-31G*	STO-3G	4	0.000236	0.002762	166.2
toluene	C_s	22	6-31G*	3-21G	3	0.000100	0.001648	109.7
toluene	C_s	22	3-21G	STO-3G	4	0.000080	0.003005	154.8
triquinacene	C_{3v}	11	6-31G*	STO-3G	4	0.000059	0.003454[a]	151.3
triquinacene	C_{3v}	11	6-31G*	3-21G	4	0.000064	0.004094	[d]
triquinacene	C_{3v}	11	3-21G	STO-3G	4	0.000632	0.003399[b]	[e]
vinylbutadienyl borane	C_s	29	6-31G*	STO-3G	4	0.000045	0.003139[a]	[c]

[e] The output from the complete optimization was lost before the frequencies could be recorded.

References

12. Head, J. D.; Weiner, B.; Zerner, M. C. Int. J. Quantum Chem. 1988, 33, 177.

13. Schlegel, H. B. J. Comput. Chem. 1982, 3, 214.

14. Head, J. D.; Zerner, M. C. Chem. Phys. Lett. 1985, 122, 264.

15. Murtagh, B. A.; Sargent, R. W. H. Comp. J. 1970, 13, 185.

BIBLIOGRAPHY

1. Allinger, N. L. J. Am. Chem. Soc. 1977, 99, 8127.

2. The AMPAC program package, QCPE program 506.

3. Andersen, B.; Srinivasan, R. Acta Chem. Scand. 1972, 26, 3468.

4. Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. J. Am. Chem. Soc. 1975, 97, 1285.

5. Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. J. Am. Chem. Soc. 1975, 97, 1294.

6. Bishof, P.; Bosse, D.; Gleiter, R.; Kukla, M. J.; de Meijere, A.; Paquette, L. A. Chem. Ber. 1975, 108, 1218.

7. Boyd, R. H.; Sanwal, S. N.; Shakrokh-Tehrany, S.; McNally, D. J. Phys. Chem. 1971, 75, 1264.

8. Bünzli, J. C.; Frost, D. C.; Weiler, L. Tetrahedron Lett. 1973, 1159.

9. Clark, T.; Chandrasekhar, J. Spitznagel, G. W.; Schleyer, P. v. R. J. Comput. Chem. 1983, 4, 294.

10. Conn, J. B.; Kistiakowsky, G. B.; Smith, E. A. J. Am. Chem. Soc. 1939, 61, 1868.

11. Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York, 1970.

12. Craig, D. P. 'Aromaticity,' in *Non-Benzenoid Aromatic Compounds*, D. Ginsburg, Ed., Interscience Publishers, Inc. 1959.

13. Dauben, H. J. Jr.; Wilson, J. D.; Laity, J. L. J. Am. Chem. Soc. 1969, 91, 1991.

14. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. J. Am. Chem. Soc. 1985, 107, 3902.

15. Dewar, M. J. S.; Thiel, W. J. Am. Chem. Soc. 1977, 99, 4899.

16. Dinsburg, G. (a.k.a. D. Ginsburg), Nouv. J. Chim. 1982, 6, 175.

17. Disch, R. L.; Schulman, J. M.; Sabio, M. L. J. Am. Chem. Soc. 1985, 107, 1904.

18. Dolliver, M. A.; Gresham, T. L.; Kistiakowsky, G. B.; Vaughan, W. E. J. Am. Chem. Soc. 1937, 59, 831.

19. Dunning, T. H., Jr. J. Chem. Phys. 1970, 53, 2823.

20. Goldstein, M. J.; Hoffmann, R. J. Am. Chem. Soc. 1971, 93, 6193.

21. Haddon, R. C.; Raghavachari, K. J. Am. Chem. Soc. 1985, 107, 289.

22. Head, J. D.; Weiner, B.; Zerner, M. C. Int. J. Quantum Chem. 1988, 33, 177.

23. Head, J. D.; Zerner, M. C. Chem. Phys. Lett. 1985, 122, 264.

24. Huzinaga, S. J. Chem. Phys. 1965, 42, 1293.

25. Ibrahim, M. R.; Schleyer, P. v. R. J. Comput. Chem. 1985, 6, 157.

26. Jemmis, E. D.; Reddy, V. P. Tetrahedron Lett. 1986, 27, 3771.

27. Li, W. K.; Luh, T. Y.; Chiu, S. W. Croat. Chem. Acta 1985, 58, 1.

28. Liebman, J. F., Paquette, L. A., Peterson, J. R.; D. W. Rogers, J. Am. Chem. Soc. 1986, 108, 8267.

29. McEwen, A. B.; Schleyer, P. v. R. J. Org. Chem. 1986, 51, 4357.

30. Morrison, R. T.; Boyd, R. N. *Organic Chemistry* (Third Edition), Allyn and Bacon, 1979.

31. Murtagh, B. A.; Sargent, R. W. H. Comp. J. 1970, 13, 185.

32. Osawa, E. J. Am. Chem. Soc. 1979, 101, 5523.

33. Palmer, M. H. J. Mol. Str. 1987, 161, 333.

34. Paquette, L. A. Angew. Chem., Int. Ed. Engl. 1978, 17, 106.

35. Paquette, L. A.; Kearney, F. R.; Drake, A. F.; Mason, S. F. J. Am. Chem. Soc. 1981, 103, 5064.

36. Pouchert, C. J.; Campbell, J. R. *The Aldrich Library of NMR Spectra*: 1974, vol. IV, p. 1.

37. Rathjens, G. W., Jr. J. Chem. Phys. 1962, 36, 2401.

38. Roos, B.; Siegbahn, P. Theor. Chim. Acta. 1970, 19, 209.

39. Roth, W. R.; Klarner, F. G.; Lennartz, H.-W. Chem. Ber. 1980, 113, 1818.

40. Saebϕ, S.; Cordell, F. R.; Boggs, J. E. J. Mol. Struct. (Theochem) 1983, 104, 221.

41. Schlegel, H. B. J. Comput. Chem. 1982, 3, 214.

42. Schmitz, L. R.; Allinger, N. L.; Flurchick, K. M J. Comput. Chem. 1988, 9, 281.

43. Schulman, J. M.; Disch, R. L. Chem. Phys. Lett. 1985, 113, 291.

44. Schulman, J. M.; Disch, R. L. Tett. Lett. 1985, 26, 5647.

45. Schulman, J. M.; Disch, R. L.; Sabio, M. L. J. Am. Chem. Soc. 1983, 105, 743.

46. Stevens, E. D.; Kramer, J. D.; Paquette, L. A. J. Org. Chem. 1976, 41, 2266.

47. Traetterberg, M. J. Am. Chem. Soc. 1964, 86, 4265.

48. Turner, R. B. J. Am. Chem. Soc. 1964, 86, 3586.

49. Turner, R. B.; Meador, W. R.; Winkler, R. E. J. Am. Chem. Soc. 1957, 79, 4116.

50. Wiberg, K. B. J. Comput. Chem. 1984, 5, 197.

51. Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J.; Brundle, C. R.; Kuebler, N. A. J. Am. Chem. Soc. 1976, 98, 7179.

52. Wiberg, K. B.; Wendoloski, J. J. J. Am. Chem. Soc. 1982, 104, 5679.

53. Winstein, S. J. Am. Chem. Soc. 1959, 81, 6524.

54. Wong, S. S.; Westrum, E. F. J. Am. Chem. Soc. 1971, 93, 5317.

55. Woodward, R. B.; Fukunaga, T.; Kelly, R. C. J. Am. Chem. Soc. 1964, 86, 3162.

56. Zimmerman, H. E.; Grunewald, G. L.; Paufler, R. M.; Sherwin, M. A. J. Am. Chem. Soc. 1969, 91, 2330.