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TRIPTYCENES.

The City University of New York
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RESTRICTED ROTATION BETWEEN Sp^3 HYBRIDIZED CARBON ATOMS.
9-SUBSTITUTED TRIPTYCENES.

by

Jill H. Paul

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.

1976

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.

1/12/76
date

Leonard H. Schwartz
Chairman of Examining Committee

1/12/76
date

Leonard H. Schwartz
Executive Officer

Neil McKelvie

W F Berkowitz

The City University of New York

TO MY LOVE, for whom there are neither ample nor
adequate words to express the joy,
the tenderness and the pleasure you
give to me.

To my family, whom I adore, and especially to my mother, whose love, friendship and understanding I will always remember.

Acknowledgements

I wish to give a special acknowledgement to Prof. Leonard H. Schwartz for his superb guidance, understanding, encouragement and patience. Prof. Schwartz truly possesses a gift for imparting his knowledge and his enthusiasm to his students. I am deeply appreciative of the important influence he has had on my life and as a result of his devoted and skillful training, I feel confident that my future in chemistry will be a successful one.

I am very grateful to Professors Samuel Wilen, Neil McKelvie and William Berkowitz for their continued interest and thought provoking suggestions as members of my Thesis Committee.

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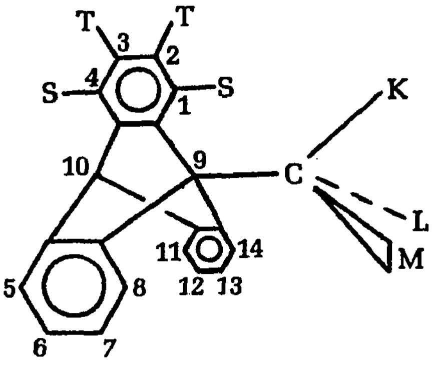
Abstract

The following substituted 9-isopropyltriptycenes were synthesized, as the skew conformers, by the addition of the appropriately substituted benzyne to 9-isopropylanthracene: 1,2,3,4-tetrachloro-, 1,2,3,4-tetrabromo-, 1,4-dichloro-, 1,4-dibromo. The addition of tetrafluorobenzyne to 9-isopropylanthracene yielded 1,2,3,4-tetrafluoro-9-isopropyltriptycene as a mixture of approximately equal parts of skew and anti conformers. Rotational barriers of the above skew conformers in deuterionitrobenzene are all approximately equal within experimental error. This suggests that the major interactions in the rotational transition states do not involve the halogen atoms. An attempt to verify this conclusion by studying the magnitude of the rotational barriers of 1,2,3,4-tetrabromo-9-(1,1,1-trideuterio-2-propyl) triptycene and 1,2,3,4-tetrabromo-9-(2-deuterio-2-propyl)triptycene was inconclusive.

No interconversion of the skew and anti conformers of 1,2,3,4-tetrafluoro-9-isopropyltriptycene was observed at 183.5°, the highest attainable temperature in our nmr spectrometer. It is concluded from this result, that the pathway for the interconversion of the two skew conformers, in each of the above-mentioned triptycenes, involves a back and forth motion in which the isopropyl-hydrogen passes the halogen-substituted aryl ring.

I Introduction

This thesis focuses on the rotational barriers of System I. It was expected that compounds of this general structure



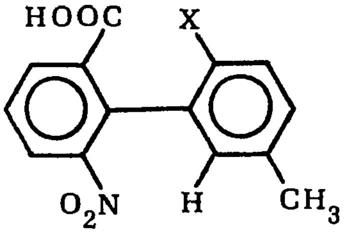
I

S = halogen
T = H or halogen
K = H or D
L,M = H, CH_3, or CD_3

would exhibit rather high rotational barriers between the ethane carbons, defined by the bridgehead carbon atom and the first carbon of the 9-substituent. It was felt that because of the high barriers, this system would allow us to study various phenomena related to steric effects in a more advantageous manner compared to previous studies with hindered ethanes, which involved relatively low barriers. Specifically, we proposed to study the following: (1) the effect of van der Waals radii on rotational barriers, (2) compounds exhibiting a conformationally stable methyl group, and (3) steric isotope effects.

Restricted rotation between singly bonded carbon atoms has been the subject of numerous past investigations. In the case of the biphenyls, where we are dealing with restricted rotation between two sp^2 hybridized carbon atoms, large rotational barriers have often been observed, and the isolation of enantiomeric conformers has been accomplished in many instances.

A number of systematic studies have been carried out with the biphenyls. It has been observed that the rotational barriers reflect the size of the interfering groups involved, as measured by their van der Waals radii. For example, it was found that the compounds of system II exhibited the half lives of racemization as shown in Table I.[1]



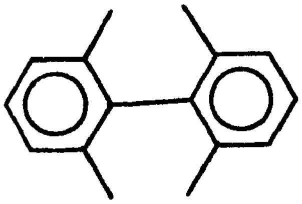
II

Table I. Racemization Half Lives of II

X	$t_{\frac{1}{2}}$ (118°C)
Br	3240 min.
Cl	154 min.
F	cannot be resolved

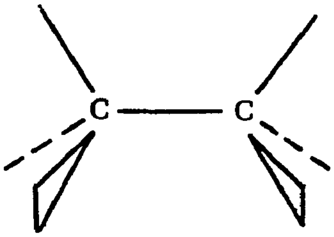
In general, for biphenyls, the capacity of the ortho substituents to interfere with one another is $Br \gg CH_3 > Cl > NO_2 > COOH \gg OCH_3 > F$.[2] The fact that there is a rather good agreement between the magnitude of the rotational barrier and the size of the ortho substituents, as measured by their van der Waals radii, can be explained in terms of the commonly pictured planar rotational transition state, for such species. Fig. I, which depicts this transition state, indicates that

Fig. I



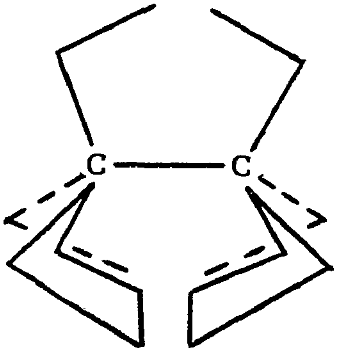
the interfering groups are partially directed towards each other. As a result of this orientation, the opposing groups are brought in close proximity to one another, such that their van der Waals radii tend to interpenetrate. By comparison, hindered systems involving rotation about two sp^3 hybridized carbon atoms (substituted ethanes), with the same interfering groups as in the biphenyls, have been found to exhibit much lower rotational barriers. An explanation for this can be found by inspection of the rotational transition state for the ethane system, as illustrated in Fig. II. Although the

Fig. II



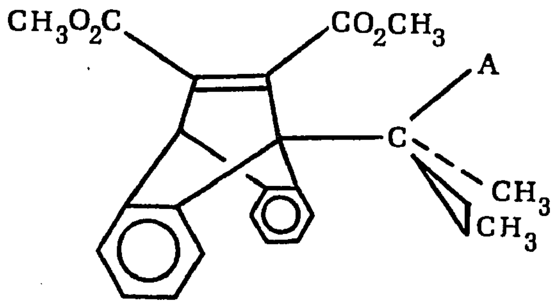
same interfering groups may be involved in the rotational transition states of both a biphenyl and an ethane, the orientation of these groups in the two cases are very different. The opposing groups in the planar transition state of the biphenyls (Fig. I) are partially directed towards each other. On the other hand, the same substituents in the eclipsed form of an ethane are pointed away from one another. Thus, in order to achieve the same degree of steric hindrance as present in the biphenyls, much larger groups would be necessary for the ethane system. The approach of utilizing increasingly bulkier groups in an effort to obtain large rotational barriers in simple ethanes would not be very fruitful, due to the eventual severity of the geminal interactions, rendering the syntheses of such compounds impossible. We anticipated that a far more productive approach would be the use of a special type of hindering group, one that has directional hindrance rather than uniform bulkiness in all directions. Figure III illustrates the kind of orientation that substituents would have to assume in order to exhibit this directional hindrance in an ethane system.

<u>Figure III</u>



In the case of our proposed system (1), we have an example of such directional hindrance between ethane carbon atoms. One side of the ethane system projects directly back towards the opposite ethane atom, i.e., referring to system I (pg. 1), substituent S is oriented towards groups K, L and M.

The expectation for high rotational barriers in systems such as I was based upon recent reports in the chemical literature. In 1971, M. Oki and M. Suda found a rotational barrier of 17.7 kcal/mole for compound IIIa and a barrier of greater than 25 kcal/mole for IIIb.[3] In 1972, Oki and G. Yamamoto found a barrier of 33 kcal/mole for IIIc.[4,*]



IIIa, A = H
IIIb, A = CH_3
IIIc, A = $CH_2C_6H_5$

Sergeyev and coworkers found a barrier of 16 kcal/mole for compound IV.[6]

These compounds show rotational barriers considerably larger than those previously found in studies of highly substituted ethanes. Based upon the similarity of these structures and that of system I, we felt confident that high

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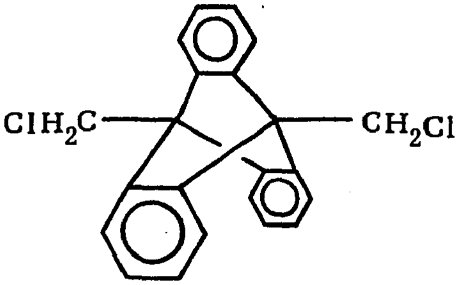
[*] In terms of energy a barrier of approximately 20 kcal/mole is necessary for the isolation of stable conformers at room temperature.[5]



IV

rotational barriers would be found in our system.

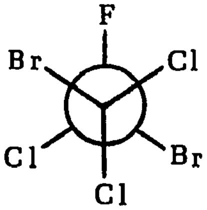
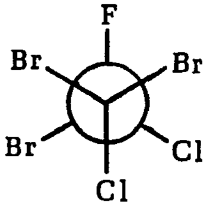
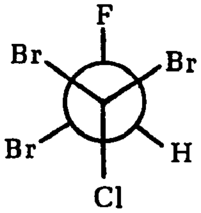
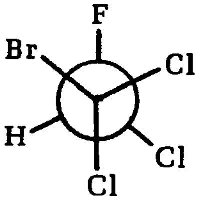
A major aim of this research is to study the effect of the individual halogens on rotational barriers, the goal being to gain information on the relationship between van der Waals radius and steric size. A system used in such a study should exhibit large rotational barriers in order to insure that steric (bulk) effects will be the main contributor to the overall barrier, rather than secondary effects not necessarily related to the volume of an atom. It has been demonstrated, particularly in the studies of rotational barriers of halogenated ethanes, where rather low barriers were obtained (3-14 kcal/mole), that such barriers were not always in a direction consistent with the van der Waals radii of the halogens. The following investigations illustrate this point. C.R. Ward and C.H. Ward reported that rotational barriers for compounds of structure CF_3CH_2X were in the order $X=I > X=Br > X=Cl > X=F$, however, for compounds of structure CF_3CF_2X the order was $X=I < X=Br > X=Cl > X=F$.[7]

J.P. Lowe found that the rotational barriers for the ethyl halides were in the order $X=I < X=Br \approx X=Cl > X=F > X=H$,[8] a rather anomalous result in terms of what one would expect based upon the differences in van der Waals radii of the halogens.

In a study of conformational preferences and rotational barriers of polyhalogenated ethanes by J.D. Roberts and co-workers,[9] it was observed, for example, that the barrier heights between compounds V and VI as well as between compounds VII and VIII (Table II) were strikingly similar, in contrast to what would be expected from a consideration of van der Waals radii.

If the magnitude of the rotational barriers for the haloethanes cited above [7,8,9] are any indication of the steric size of the halogens, then it appears that one must define steric size in broader terms than just their van der Waals radii. A number of factors may contribute to the steric size of the halogens, such as van der Waals radii, electrostatic interactions, bond bending and stretching force constants, electronegativity, polarizability, and London dispersion forces. A close balance may exist between all of these forces, which together constitute a more total picture of what is meant by the steric size of a group or atom. The contribution to a rotational barrier due to van der Waals radii may not necessarily dominate the final result. In particular this is expected to be the case in dealing with the rather low barriers of the halogenated ethanes mentioned above,[7,8,9] where opposing groups in the rotational transition state are not in as close proximity with one another, as would be the case if the same substituents were part of a molecule exhibiting directional hindrance.

Table II. Free Energies of Activation for Interconversion of Rotational Isomers of Halogenated Ethanes[9]

Most Stable Conformation	$\Delta G^{\ddagger}$[a,b] 0-120°	$\Delta G^{\ddagger}$[a,b] 120-240°	$\Delta G^{\ddagger}$[a,b] 240-360°
V 	13.8	14.5	14.2
VI 	13.9	14.7	14.0
VII 	9.6	10.2	10.0
VIII 	9.0	9.4	9.1

[a] Angle of clockwise rotation of the rear carbon with respect to the front carbon. [b] Energy in kcal/mole

Examples may be found in the chemical literature where the steric requirement of the halogens appears to be governed by mainly one or a combination of these factors. It was suggested by J. Dale[10] in 1966 that the polarizability of the carbon-halogen bond makes a contribution to the total steric effect of the halogens and such polarization will have a definite influence upon rotational barriers. The author stated that the polar character of the carbon-halogen bond will tend to reduce the steric requirement of the halogen, due to a contraction of the geminal bond angles, in ethanes containing two or three halogens on a single carbon atom. This in turn will lead to a reduction of the rotational barrier. The greater the ability of the halogen to attract the bonding electrons towards it, the greater will be the opportunity for the contraction of geminal bond angles. This may be visualized as follows: The greater the electronegativity of the halogen, the further removed will the electron density be from the carbon atom of the C-halogen bond. The further removed are the electron densities of geminal orbitals, the smaller are their interactions with each other. The decreased interactions allow the geminal angles to contract compared to the situation where less bond polarization is the case. Dale cited the following bond angles to substantiate his argument: HCH in $CH_4=109.5^\circ$; FCF in $CH_2F_2=108^\circ$; HNH in $NH_3=107^\circ$; FNF in $NF_3=102^\circ$; HOH in $H_2O=104.5^\circ$; FOF in $F_2O=103^\circ$.

The observed rotational barriers for CH_3CH_2F (3.33 kcal/mole[8]), CH_3CHF_2 (3.18 kcal/mole[8]) and CH_3CF_3 (3.25 kcal/mole[8]) are all very similar. On the basis of steric effects, it would be expected that the greater the number of fluorine atoms in the series, the greater would be the barrier. To explain these results, Dale argued that as the number of fluorine atoms increase, the geminal bond angles tend to decrease. Thus an increased steric effect due to the substitution of additional fluorine atoms is counterbalanced by a decrease in the geminal bond angles, which leads to decreased interactions. It can then be claimed, following Dale's point of view, that the steric size of a fluorine atom is not only a function of its van der Waals radius, but also its electronegativity, which would determine its capacity to polarize bonds. Despite the fact that this qualitative reasoning should be mainly applied to the most electronegative halogen (fluorine), it does exemplify the importance of changes in bond angles on the magnitude of rotational barriers.

L. Radom and J. Stiles[11] have recently presented another argument to explain the observed barriers in monofluoro-, 1,1,-difluoro-, and 1,1,1-trifluoroethane. These authors carried out ab initio molecular orbital calculations on these compounds and were able to reproduce the experimentally observed barrier trends (see pg. 9). The theoretical results gave credence to the experimental results and convinced the authors that the effect of geminal fluoro substituents on rotational barriers was not additive. An explanation for the apparent decrease in the barrier height for di and trifluoroethane as compared to ethyl fluoride was proposed, which was based upon two contributing factors: (1) due to the phenomena of back-bonding as well as the ability of the fluorine substituent to accommodate a negative charge, the process shown in Fig. IV has importance. (2) It has been established both experimentally and theoretically[12] that a methyl group adjacent to a double bond prefers to have a C-H bond eclipse the double bond, as in Fig. V. The effect of the first factor on 1,1-difluoro- and 1,1,1-trifluoroethane is to impart double bond character to the C-F bonds which according to the second factor stabilizes the eclipsed conformations relative to the staggered forms, thus accounting for the observed barrier trends. This

Fig. IV

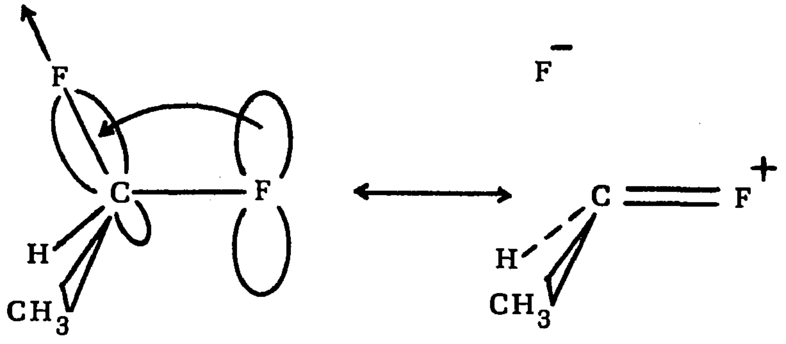
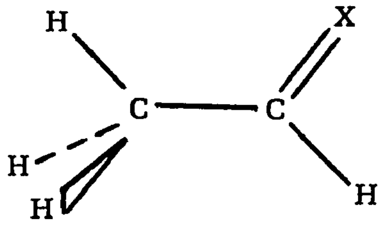


Fig. V



particular argument may also be extended to explain the similar reduction in barriers with an increased number of geminal chlorine atoms: CH_3CH_2Cl (3.68 kcal/mole[8]), CH_3CHCl_2 (3.49 kcal/mole[8]), and CH_3CCl_3(2.91 kcal/mole[8]).

J.E. Anderson and H. Pearson[13] studied the rotational barriers of pentamethylethane and the four pentamethylethyl halides. Their results are reported in Table III.

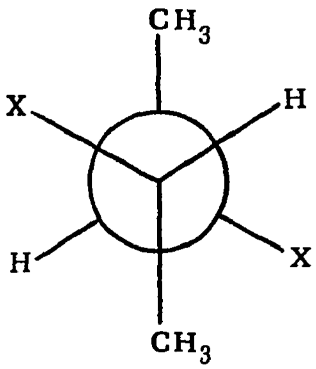
Table III. Rotational Barriers in $(CH_3)_3CC(CH_3)_2X$

X	Rotational Barriers (kcal/mole)
H	6.97
F	8.04
Cl	10.43
Br	10.73
I	11.14

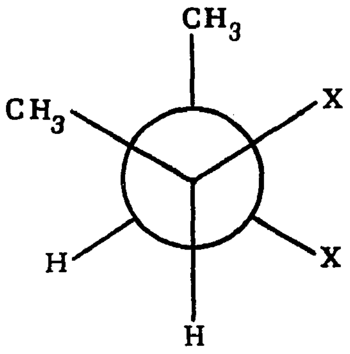
The relatively minor increase in rotational barriers in going from X=Cl, to X=Br, to X=I was attributed to the increased bond lengths and increased polarizabilities in the case of the latter two halogens, which counteract the effect of increased van der Waals radii.

Roberts and coworkers have suggested that the equality of the rotational barriers between the following pairs of ethanes, $CFBrClCBrCl_2$ (V) and $CFBrClCBr_2Cl$ (VI), and $CHFBrCClBr_2$ (VII) and $CHFClCBrCl_2$ (VIII) Table II, can be attributed to a cancellation of effects due to van der Waals radii and bond lengths. Bromine has a larger van der Waals radius than Cl; however, the C-Br bond length is longer than that of C-Cl and this will tend to decrease the non-bonded interaction of the bromine.

The theoretical calculations of barrier heights in several haloethanes by R.J. Abraham and K. Parry[14] emphasize the importance of the inclusion of electrostatic interactions. Both repulsive and attractive interactions had to be considered in order to obtain results in good agreement with experimentally observed barriers. In particular, their calculations of the difference in energy between the gauche and trans conformers of halogenated ethanes illustrates the influence of electrostatic factors on the total steric effect of the halogens. For example, the difference in energy between the trans and gauche conformers of meso 2,3-dihalobutane (IX and X) was shown experimentally to be 1.30 kcal/mole and 1.48 kcal/mole, with the trans form being favored in each case, when the halogens were chlorine and bromine, respectively.[15] The calculated energy differences between the trans and gauche rotamers of both dihalobutanes were in good agreement with the experimental values.

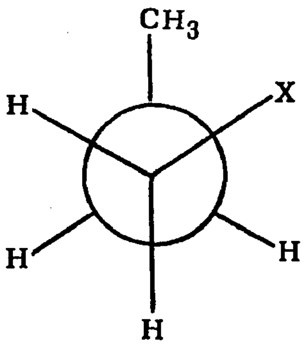


IX

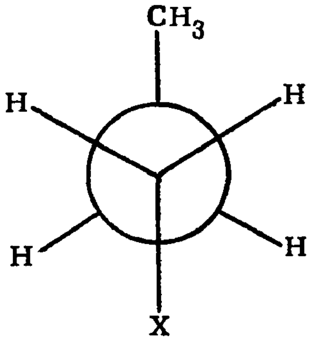


X

In each case the major contribution to the energy was calculated to be an attractive interaction between a methyl-H and a halogen, where this interaction was considerably greater than the calculated steric contribution to the energy. Such attractive forces had been alluded to previously by N. Sheppard[16] in an attempt to explain the very nearly equal stabilities of the gauche and trans conformers (XI, XII) of n-bromo and n-chloropropane. On the basis of just van der Waals repulsions alone, the trans conformers should be considerably more stable.



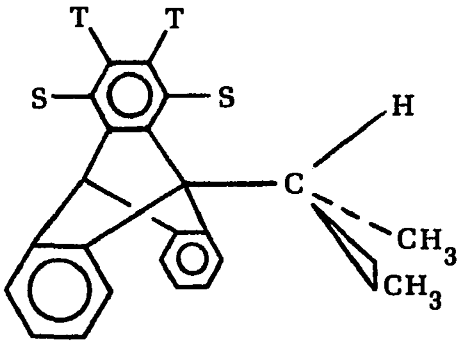
XI



XII

From the aforementioned investigations, one can see that the steric nature of the halogens is not clearly defined, and is still open to considerable debate. In order to successfully study the effect of just the van der Waals radii of the halogens on rotational barriers, a system must be chosen whereby the contribution to the overall barrier, due to the other previously mentioned factors will be greatly minimized. Such a situation can exist within systems where the van der Waals surfaces of the interacting groups are in very close proximity such that the resultant repulsion will be the dominant cause for the observed barriers. Compounds of structure I should exhibit such large degrees of van der Waals repulsions between opposing substituents.

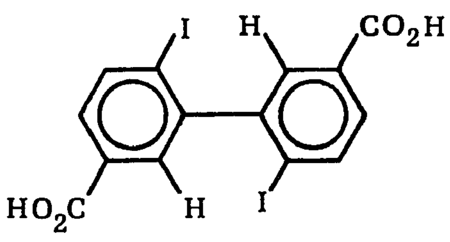
Initially we set out to synthesize compounds Ia-h.



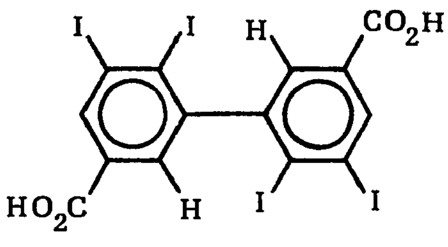
Ia, S=T=F
Ib, S=T=Cl
Ic, S=T=Br
Id, S=T=I

Ie, S=F, T=H
If, S=Cl, T=H
Ig, S=Br, T=H
Ih, S=I, T=H

It was felt that a comparison of the rotational barrier of Ie-h would provide information on the effects of van der Waals radii on rotational barriers. We hoped that such a study would give further insight into the relative steric sizes of the halogens. A comparison of compounds Ie-h with the correspoinding members of Ia-d was expected to provide information regarding buttressing effects. All examples to date of buttressing in the biphenyls, have led to increased rotational barriers. Westheimer[17] has pointed out a rather extreme example of the effect of buttressing in the biphenyls XIIIa and XIIIb. Here the relative

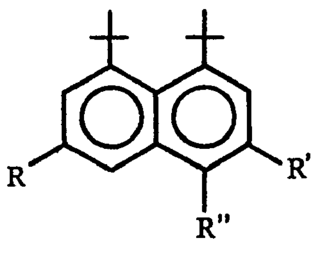


XIIIa



XIIIb

rates of racemization of XIIIa to XIIIb were found to be 30,000 to one. In our system (Ia-d) it is possible that the interaction of the halogens in the tetrahalotriptycenes is so severe that some of the halogens may be forced out of the plane of the aromatic ring, leading to perhaps lower rotational barriers compared to the corresponding members, Ie-h. Evidence exists in the literature of decreased barriers due to distortions caused by severe steric crowding. For example, it has been claimed by Anderson and Franck[18] that, as a result of the severe interactions between the peri substituents in naphthalenes XIVa-c, the t-butyl groups are forced to opposite sides of the plane of the naphthalene ring. This distortion reduces the steric hindrance to rotation about the t-butylnaphthalene bonds, and therefore, a very low barrier of only 6.5 kcal/mole is observed.



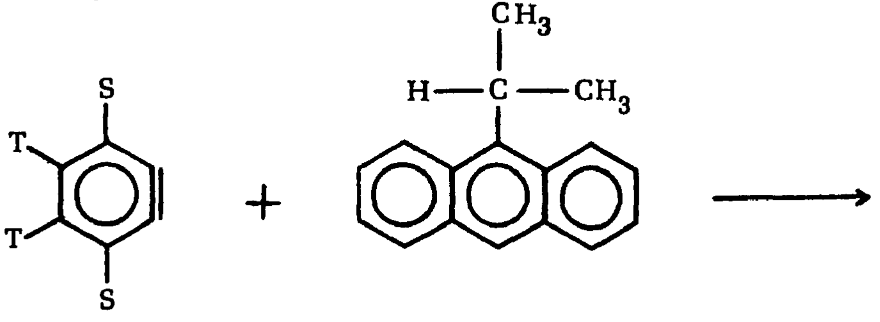
XIVa, R=R'=t-butyl, R"=H
XIVb, R=R"=H, R'=t-butyl
XIVc, R=t-butyl, R'=H, R"=$CH_2C_6H_5$

II Results and Discussion

(A) Discussion of Syntheses

(1) Syntheses of 9-Substituted Anthracenes

The syntheses of compounds Ia-h was accomplished by the addition of the appropriately substituted benzyne across the center ring of 9-isopropylanthracene (XV), as shown in equation 1.

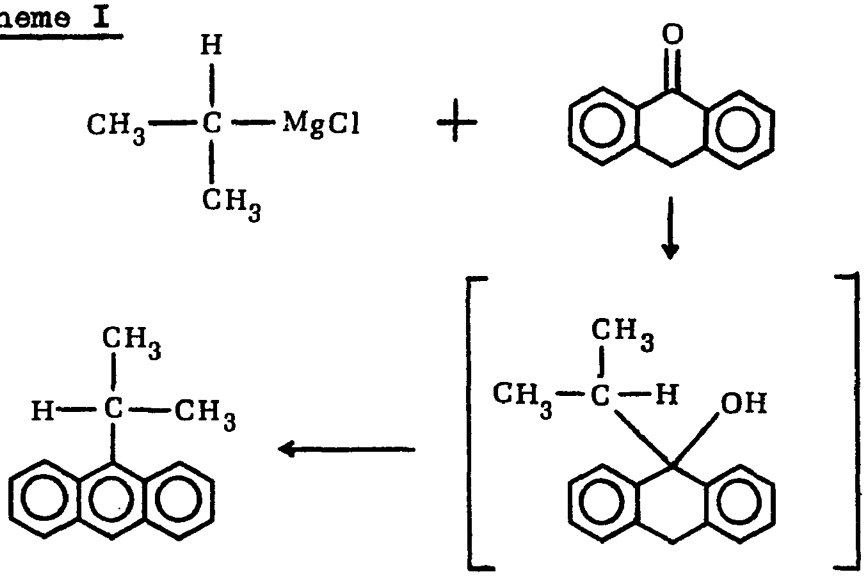


XV

I (1)

The preparation of 9-isopropylanthracene (XV) was achieved by the reaction of isopropyl magnesium chloride with a solution of anthrone in benzene (Scheme I).

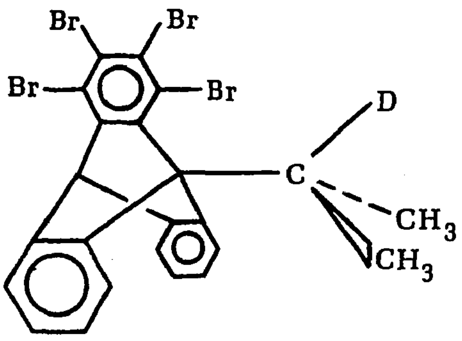
Scheme I



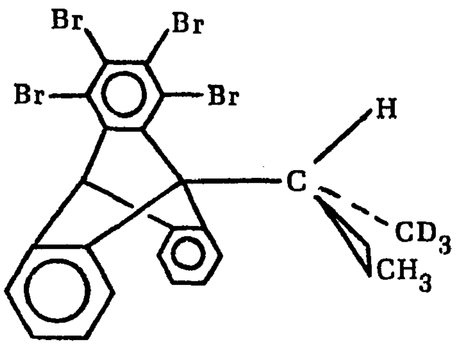
XV

The purification of the crude product required a careful chromatographic separation, since it appeared from the tlc's taken of various fractions that an unidentified material eluted from the column immediately after the desired product. A further complication arose in the recrystallization of XV from methanol. On some occasions, the first crop consisted of only a small amount of anthraquinone, according to nmr and ir analysis. In all probability the anthraquinone was not present in the crude product since it would not be expected to elute from the column simultaneously with the desired product. The presence of anthraquinone in the crude product could not be assessed by ir, nmr or tlc since small amounts are not distinguishable from the starting anthrone that was present. It appers, therefore, that 9-isopropylanthracene (XV) was being oxidized to anthraquinone during the recrystallization process. Consideralble difficulty was encountered in trying to obtain a second crop of product as explained in the Experimental Section (pg. 83).

One of the goals of this research was the preparation of compounds Ii and Ij, the aim being to develop a system which

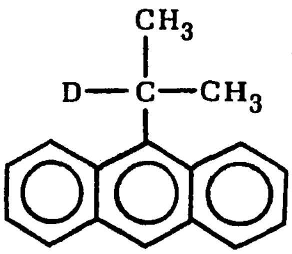


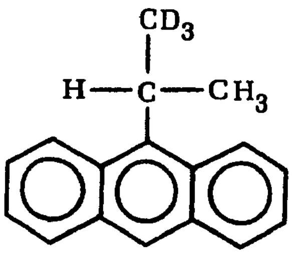
Ii



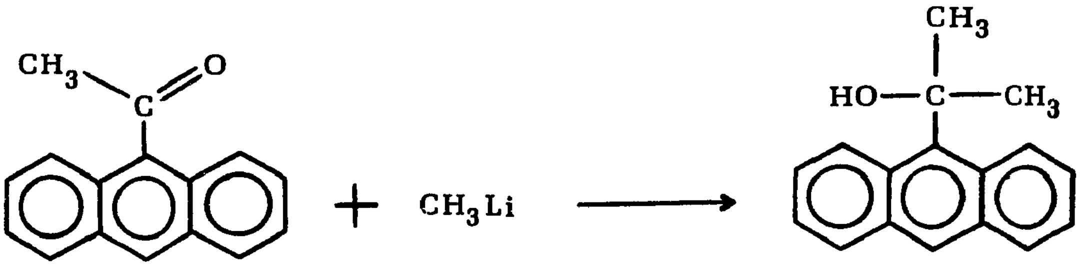
Ij

might exhibit a steric isotope effect on rotational barriers between sp^3 hybridized carbon atoms. It thus became necessary to prepare the deuterated 9-isopropylanthracenes XVI and XVII.


XVI

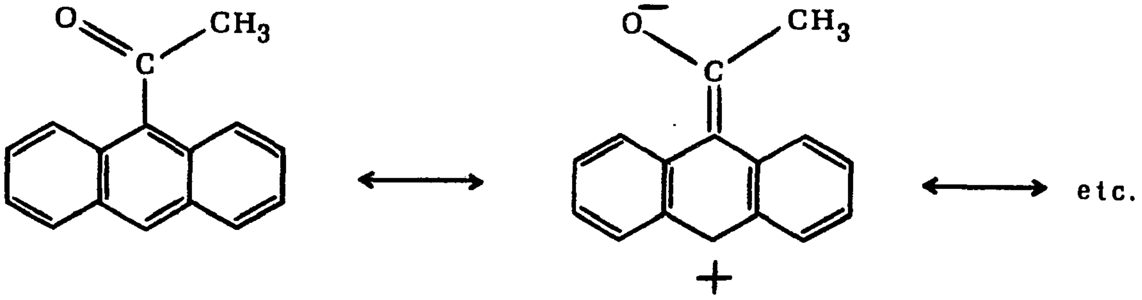

XVII

In order to synthesize XVII, we originally explored a route based on the reaction shown in equation 2. If this reaction


(2)

were successful then it could be repeated on the trideuteriomethyl analog (prepared by exchanging the α-methyl hydrogens of 9-acetylanthracene with deuterium) followed by the hydrogenolysis of the alcohol function to yield the desired 9-(1,1,1-trideuterio-2-propylanthracene (XVII). The reaction of equation (2) did not proceed at all, using various reaction times and either ether or benzene as the solvent. One can envision two explanations for the lack of reactivity of 9-acetylanthracene. (1) Due to steric hindrance, the acetyl group may not be conjugated with the aromatic rings, and therefore not coplanar with the anthracene nucleus. This non-coplanarity would result in appreciable steric hindrance towards the approach of a reagent to either face of the carbonyl group. (2) If the acetyl group were strongly conjugated with the aromatic rings such that resonance structures of the type shown in Fig. VI were important, then nucleophilic attack at the carbonyl would be considerably disfavored.

<u>Fig. VI</u>

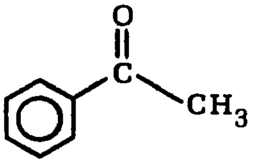
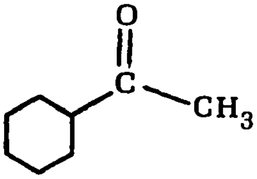
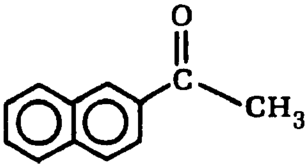
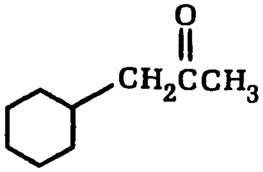
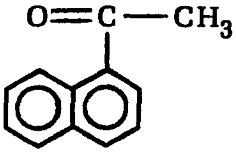
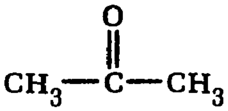


In principle, a possible means of distinguishing between explanations (1) and (2) would be to make use of uv and ir spectroscopy to estimate the degree of double bond character of the carbonyl group in 9-acetylanthracene.

It is known that the $n \longrightarrow \pi^*$ transition for aliphatic ketones is a rather weak absorption in the range of 275-300 nm ($\epsilon < 30$).[19] It has also been shown that due to conjugation with the benzene ring(s) the $n \longrightarrow \pi^*$ of aromatic ketones is shifted to higher wavelength. For example, the $n \longrightarrow \pi^*$ transitions of acetophenone and benzophenone appear at 319 and 325 nm respectively.[20] Therefore, if one would observe an $n \longrightarrow \pi^*$ transition in 9-acetylanthracene in the range of the latter two conjugated ketones, then this would be evidence in favor of explanation (2). Unfortunately, this approach could not be utilized since the $\pi \rightarrow \pi^*$ transition of the anthracene rings for the compound in question are very intense in the region of 347-382 nm[21] and therefore obscure the much weaker $n \rightarrow \pi^*$ transition.

The greater the double bond character of a carbonyl group, the stronger that bond is and therefore the higher its frequency of absorption in the ir region. Table IV compares the C=O stretching frequencies of a few aromatic and aliphatic ketones. The data given in Table IV indicates that the aromatic ketones exhibit stretching frequencies below the value

Table IV. Carbonyl Stretching Frequencies of Aromatic and Aliphatic Ketones[a]

Aromatic ketones	C=O[b]	Aliphatic ketones	C=O[b]
	1689		1709
	1681		1709
	1666	 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3$	1709

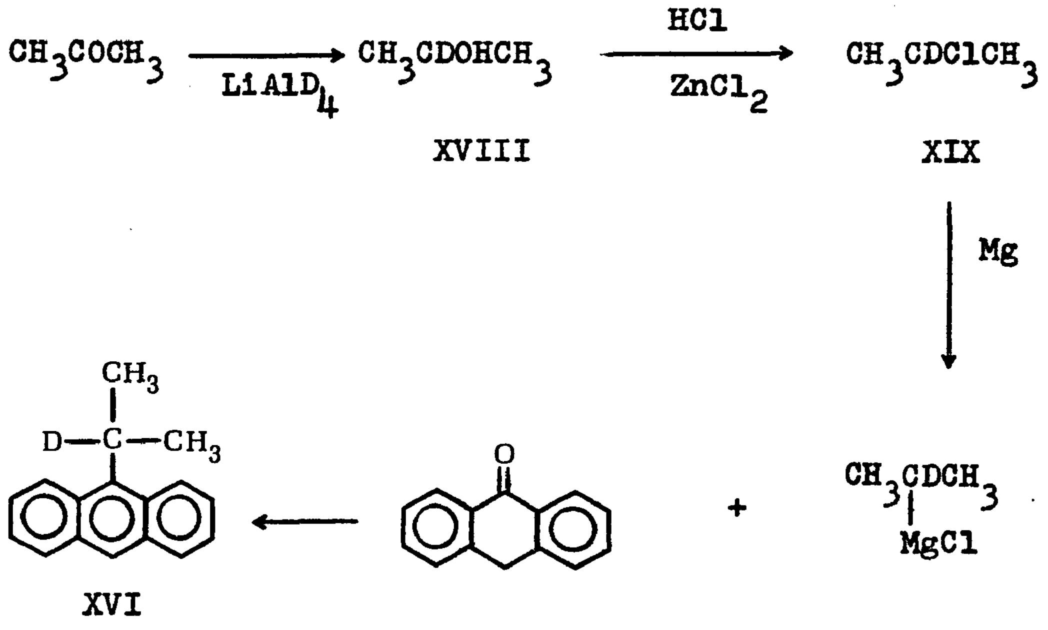
[a] data compiled from the Aldrich Library of Infrared Spectra by C. Pouchert and the Atlas of Spectral Data and Physical Constants for Organic Compounds by J.G. Grasselli.

[b] frequencies in cm.$^{-1}$

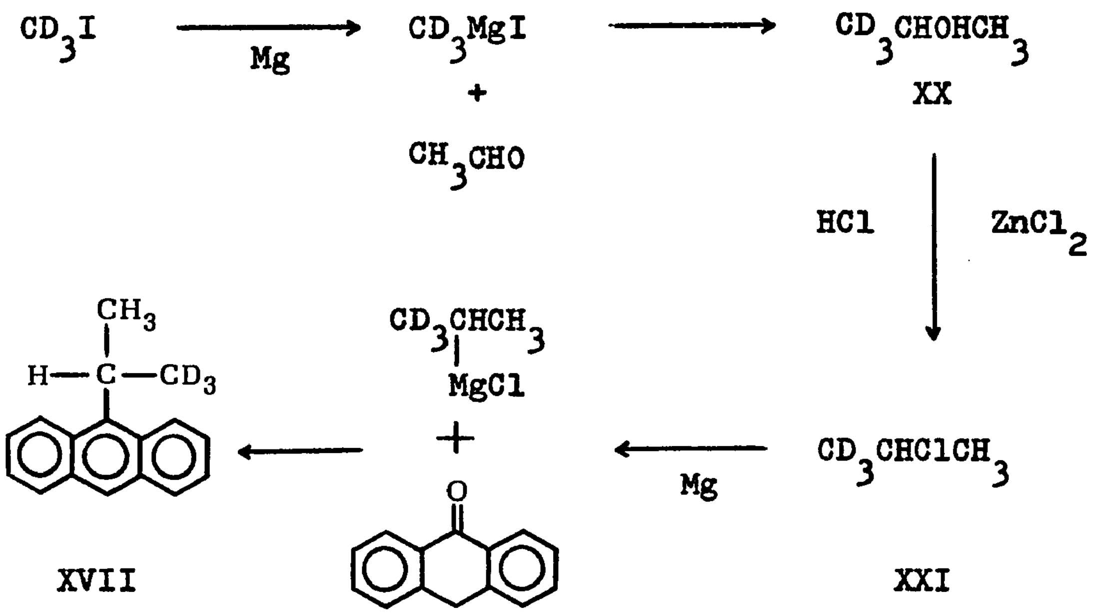
observed for the aliphatic ketones. One may attribute this shift to lower frequency to the conjugation of the carbonyl groups with the aromatic rings. The carbonyl stretching frequency of 9-acetylanthracene however, falls in between the values for the conjugated and non-conjugated ketones, suggesting that this system is not entirely planar and that there is some angle of twist between the plane of the carbonyl and the plane of the anthracene rings. Such a conclusion based upon the above ir data favors explanation (1) as to why no reaction occurred between CH_3Li and 9-acetylanthracene.

Schemes II and III illustrate the pathways ultimately

Scheme II



Scheme III

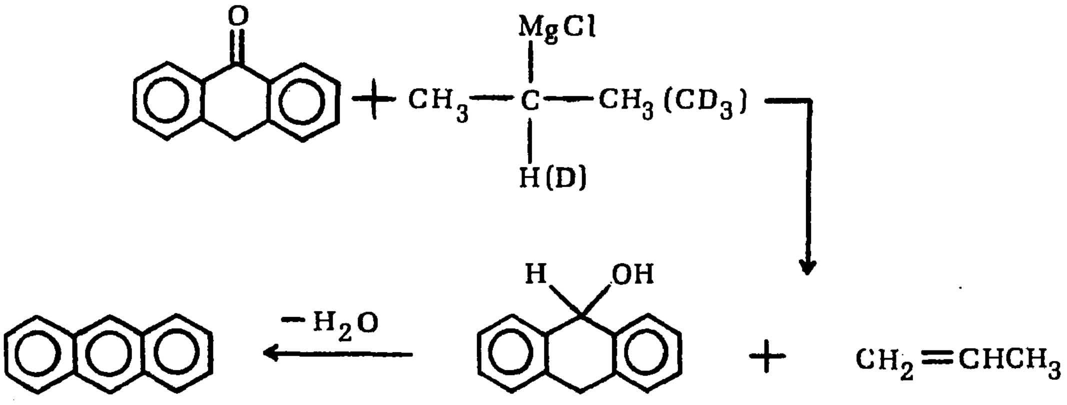


worked out for the synthesis of XVI and XVII, respectively.

These pathways differ only in the method of preparation of the appropriately deuterated isopropanols. The preparation of both alcohols, XVIII and XX were carried out using anhydrous ether as a solvent. We felt it necessary to completely remove the ether so that in the subsequent conversions to the chlorides, one would not form any ethyl chloride. We anticipated difficulties in separating the low-boiling ethyl and isopropyl chlorides from each other on the scale we had to work with. According to both pathways, any ethyl chloride present would be converted to a grignard species, which would likewise add to the carbonyl group of anthrone, ultimately forming 9-ethylanthracene. We also anticipated difficulties arising in separating the relatively large amounts of ether present from the deuterated alcohols (XVIII and XX) so that the following approach was taken. The ether was evaporated (first using aspirator vacuum, followed by a vacuum pump) before the hydrolyses (of the Al and Li salts from the $LiAlD_4$ reduction and the Mg salts from the CD_3MgI addition to acetaldehyde) were carried out. The dried salts were then hydrolysed and the product alcohols were distilled as an azeotropic mixture which contained approximately 13% H_2O by nmr analysis.

Substantial losses of material occurred during the purification of the deuterated 9-isopropylanthracenes (XVI and XVII). The nmr spectra of both crude products indicated the predominant presence of the desired products (XVI and XVII), however, approximately one half the original weight placed on the column could not be accounted for after chromatography. We believe that this loss is related to the fact that upon attempting to dissolve the crude deuterated 9-isopropylanthracenes in the chromatography eluent, benzene, an unidentified solid would not dissolve. This solid was filtered off and the filtrate evaporated to dryness. The residue was redissolved in benzene. Upon standing, within minutes, a solid began to precipitate from the solution. Thus the crude deuterated 9-isopropylanthracenes appear to have been contaminated with some benzene insoluble material whose presence could not be discerned by nmr spectroscopy. More of this solid could have precipitated out on the column and/or more of this solid may have formed on the column at the expense of the desired deuterated product. Due to its insolubility in benzene this solid would not be eluted from the column, thus accounting for the substantial loss in weight after chromatography. The final purification involved dissolution in hot methanol, which in the case of both deuterated 9-isopropylanthracenes resulted in small amounts of an insoluble material identified as anthracene by nmr and ir spectroscopy. After a hot filtration and cooling of the filtrate, more anthracene would deposit. The origin of anthracene in these preparations may arise via the reduction of anthrone to anthranol followed by dehydration as shown in Scheme IV.

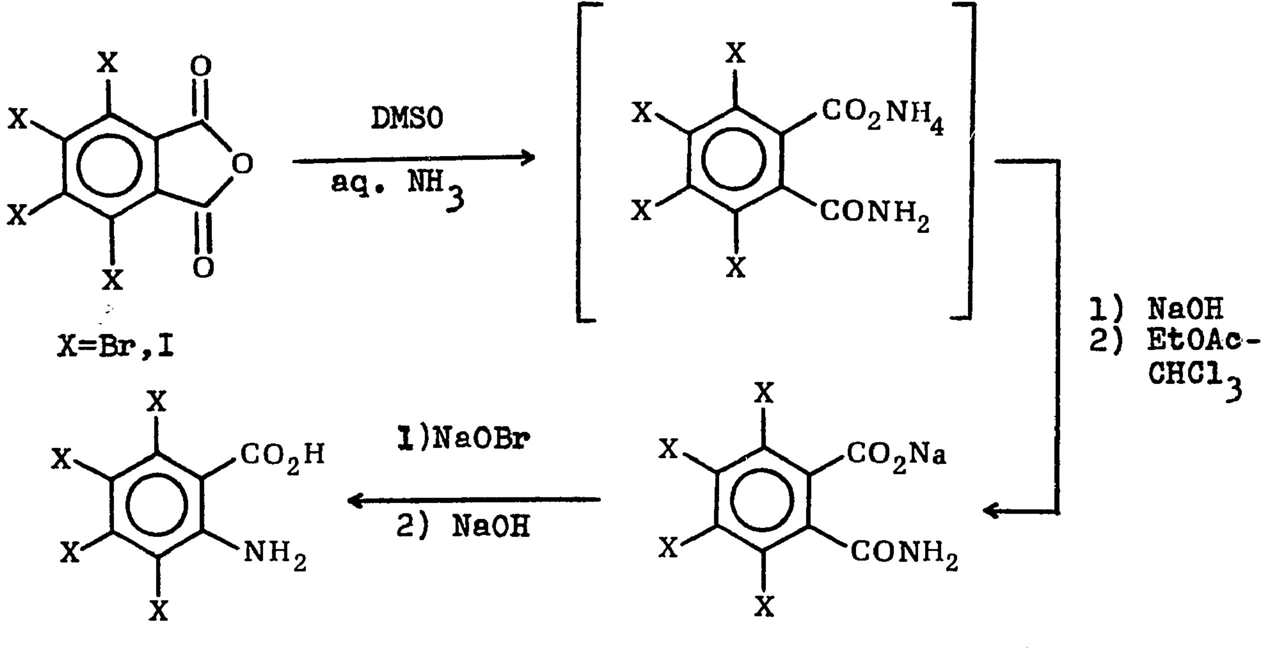
Scheme IV



(2) Syntheses of Anthranilic Acids

In most cases the appropriately substituted anthranilic acids were used as precursors for the desired benzynes. Following the procedure of L. Friedman and F.M. Logullo,[22] the benzynes were generated in situ via the diazotization of the corresponding anthranilic acids with isoamyl nitrite. The preparation of the anthranilic acids proved to be most tedious. Numerous attempts to reproduce preparations cited in the chemical literature for tetrahaloanthranilic acids, starting from the corresponding phthalic anhydrides or phthalimides (which had to be synthesized via the reaction of the corresponding anhydrides with concd. NH_4OH), failed. H. Heaney and coworkers[23] in 1971, claimed to have synthesized tetrabromoanthranilic acid (XXIII) in 78% yield and tetraiodoanthranilic acid (XXIV) in unspecified yield via the Hofmann reactions of the sodium salts of the corresponding tetrahalophthalamic acids (Scheme V).

Scheme V



XXIII, X=Br
XXIV, X=I

According to Heaney's procedure, the ammonium salt of the phthalamic acid is formed first but is not isolated. Addition of NaOH, followed by EtOAc and $CHCl_3$ results in the precipitation of the sodium phthalamate salt which is isolated. In our hands, several attempts to prepare tetrabromoanthranilic acid (XXIII) using varying concentrations of NaOH in the NaOBr solution resulted in mainly the formation of tetrabromophthalic acid.* We were finally successful after using approximately an 18-fold molar excess of NaOH compared to the starting anhydride. Our procedure involved a prolonged heating period for the Hofmann reaction, and is described in the experimental section (pg.90). Due to the rather vigorous reaction conditions necessary and the fact that the reproducibility is poor, we feel that this is not the method of choice for the synthesis of XXIII. (A better procedure will be discussed shortly.)

Initially, attempts were made to prepare tetrachloroanthranilic acid (XXV) via the Hofmann reaction of tetrachlorophthalamic acid, following a procedure described by W.R. Orndorff and E.H. Nichols.[24] This approach met with only occasional success in that with most attempts, it was found that the tetrachlorophthalamic acid was very readily hydrolysed to the corresponding diacid during its preparation as well as under the conditions of the Hofmann reaction. Our own procedure was eventually developed which yielded the tetrachloro (XXV), 3,6-dichloro (XXVI) and 3,6-dibromoanthranilic (XXVII) acids respectively in rather modest yields. This procedure involved the conversion of the halophthalic anhydrides into their ammonium phthalamate salts by bubbling gaseous NH_3 into a solution of the anhydride in dimethyl formamide. These salts, once isolated and thoroughly dried, were acidified to form the phthalamic acids, which were immediately subjected to the con-

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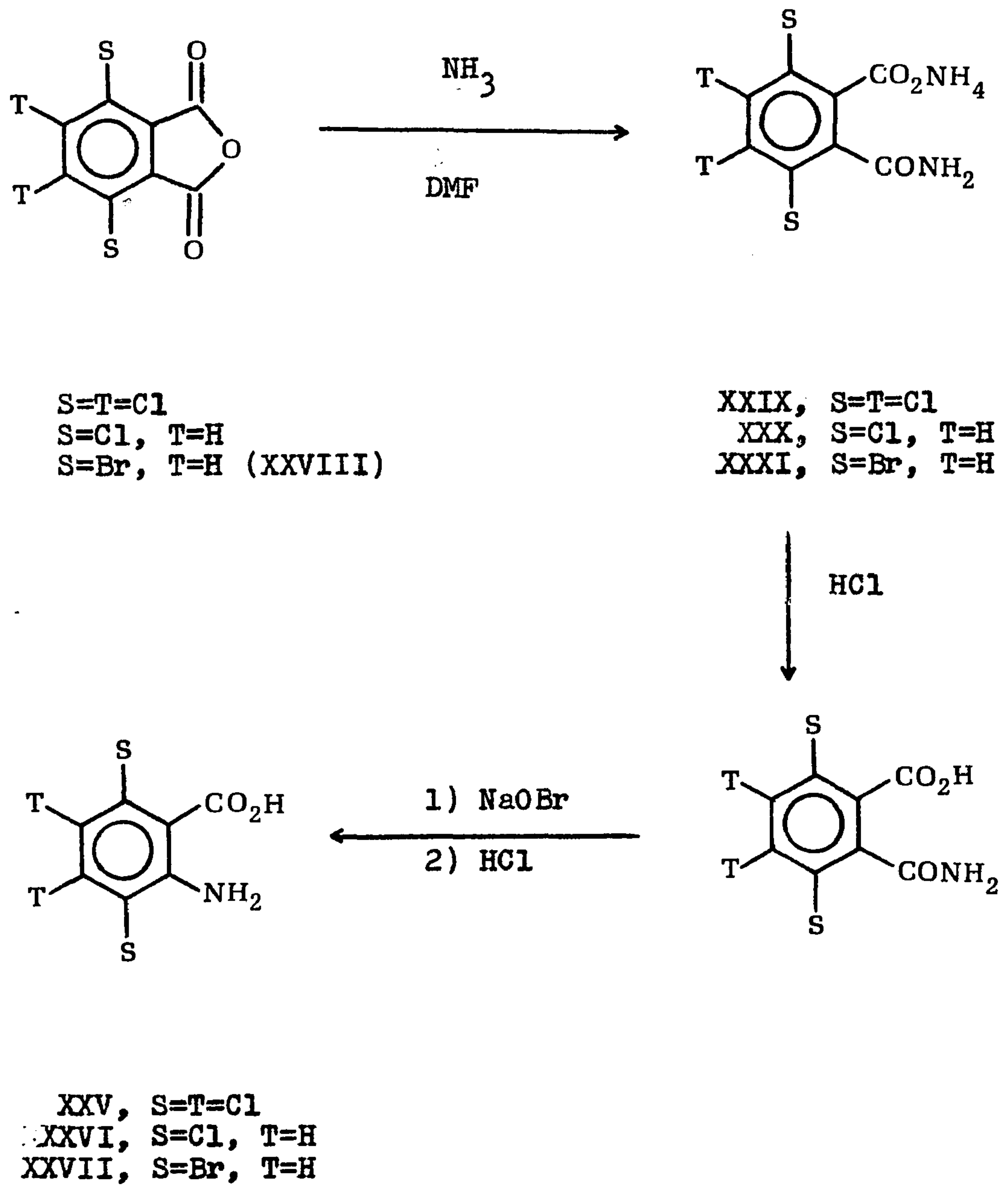
* A private communication from Dr. Heaney reported that the published procedure was not always reproducible.

ditions of the Hofmann reaction to yield the anthranilic acids. The sequence of reaction steps is indicated in Scheme VI. The importance of carrying out the conversion of the ammonium

Scheme VI



S=T=Cl
S=Cl, T=H
S=Br, T=H (XXVIII)

XXIX, S=T=Cl
XXX, S=Cl, T=H
XXXI, S=Br, T=H

XXV, S=T=Cl
XXVI, S=Cl, T=H
XXVII, S=Br, T=H

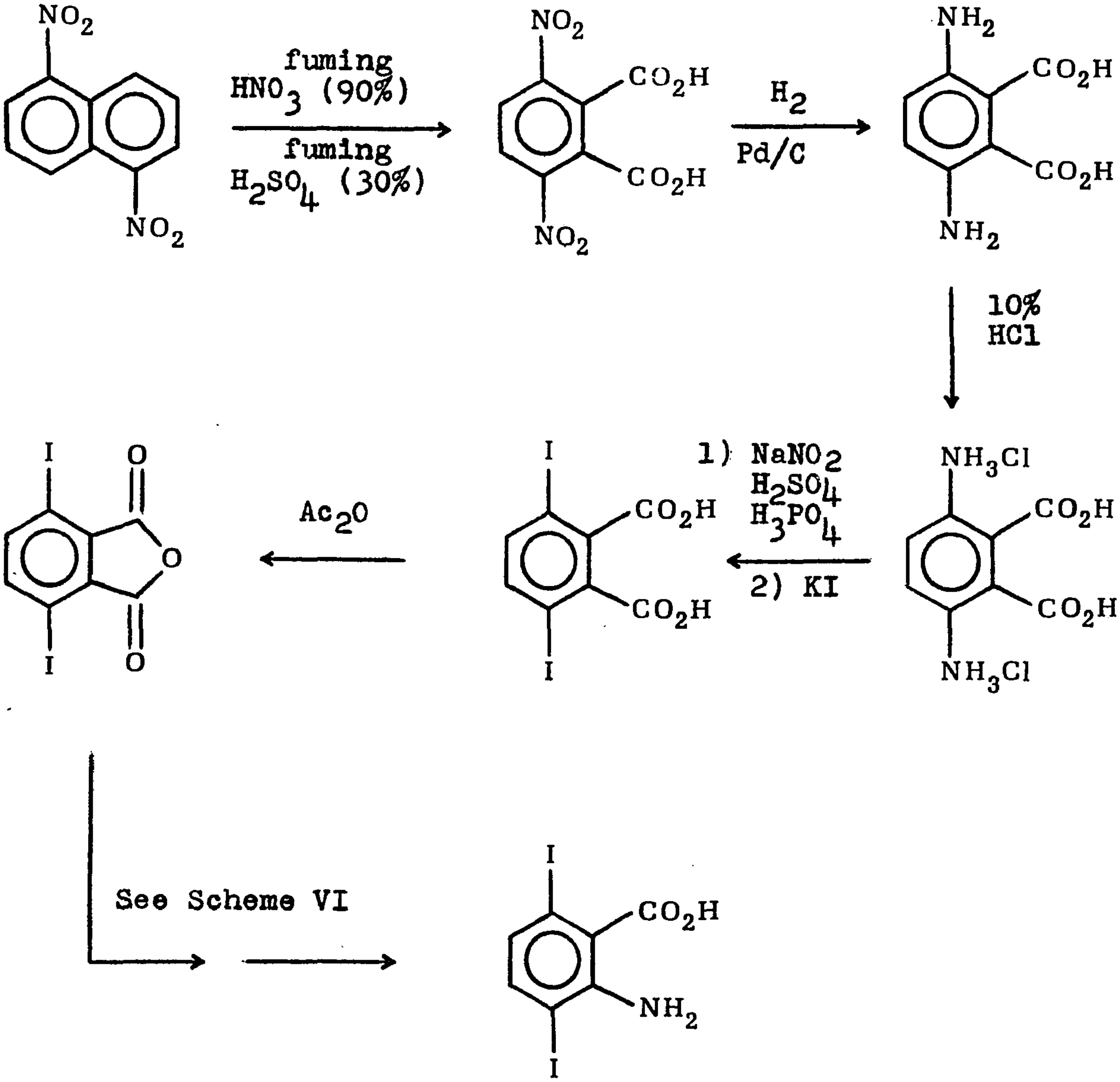
phthalamate salt to the final product, both rapidly and in the cold, cannot be overemphasized, in order to avoid hydrolysis of either the salt or the phthalamic acid. A small scale preparation of tetrabromoanthranilic acid (XXIII) via the route shown in Scheme VI was successful and therefore this approach is also recommended for the synthesis of XXIII.

Tetraiodoanthranilic acid (XXIV) was prepared by following a method described to us in a private communication by H. Heaney. This procedure differs mainly from Heaney's original method (Scheme V) in that (1) the anhydride is dissolved in dimethyl formamide and (2) the phthalamic acid, instead of its sodium salt, is isolated and treated with NaOBr solution.

We next attempted to synthesize 3,6-diiodoanthranilic acid (XXXII). Analogous to the preparation of the 3,6-dichloro (XXVI) and 3,6-dibromoanthranilic (XXVII) acids, the necessary precursor would be the 3,6-diiodophthalic anhydride. According to the chemical literature, this latter compound can be made by the iodination of phthalic anhydride in fuming H_2SO_4.[25] According to the authors, the crude product is a mixture of four iodine containing anhydrides, two of which can preferentially be converted into their diacids and then separated from the remaining two (including, supposedly, 3,6-diiodophthalic anhydride) by extraction with benzene. We were apparently successful (by ir) in reaching this stage of the synthesis. It was next claimed in the literature procedure that the two remaining anhydrides can be separated by dissolution in aqueous base followed by the careful adjustment of the pH of the solution. The experimental section of this paper however, was extremely vague and after several weeks of trial and error we were still unable to isolate any pure 3,6-diiodophthalic anhydride.

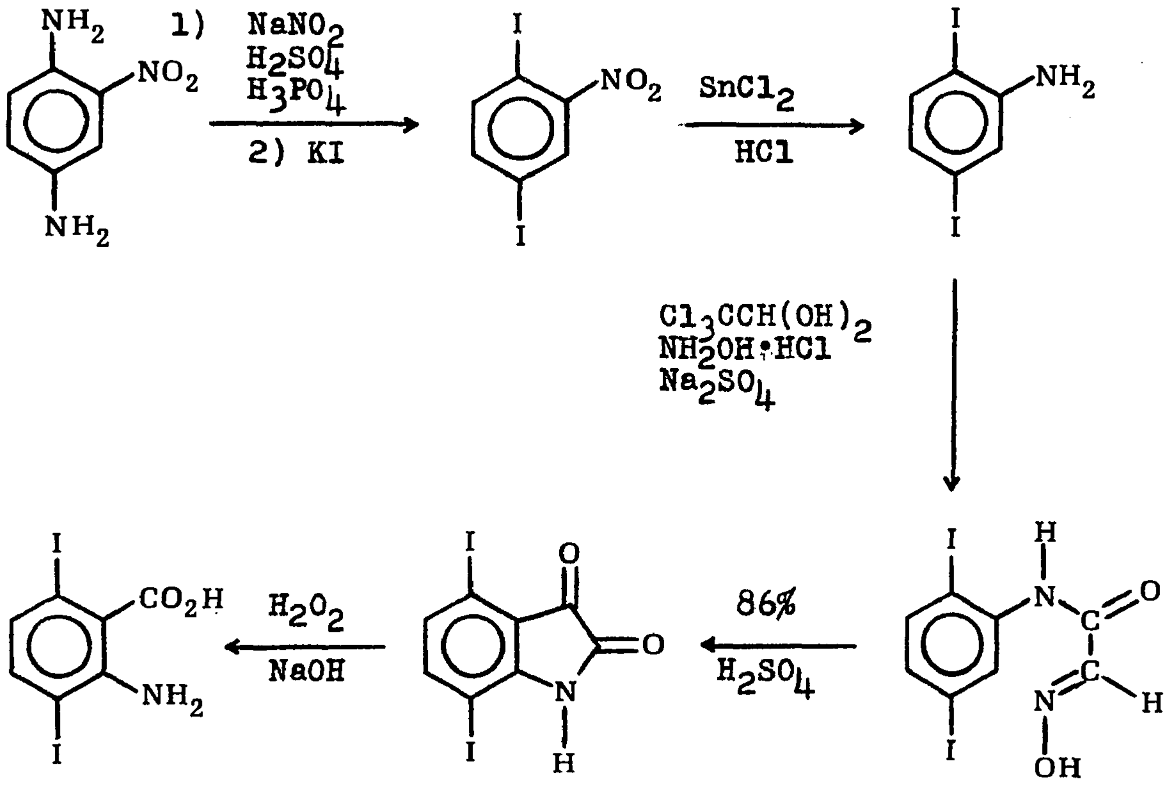
Two different routes were then explored in an effort to prepare 3,6-diiodoanthranilic acid (XXXII). Schemes VII and VIII outline these two approaches. Following Scheme VII, we

Scheme VII



XXXII

Scheme VIII



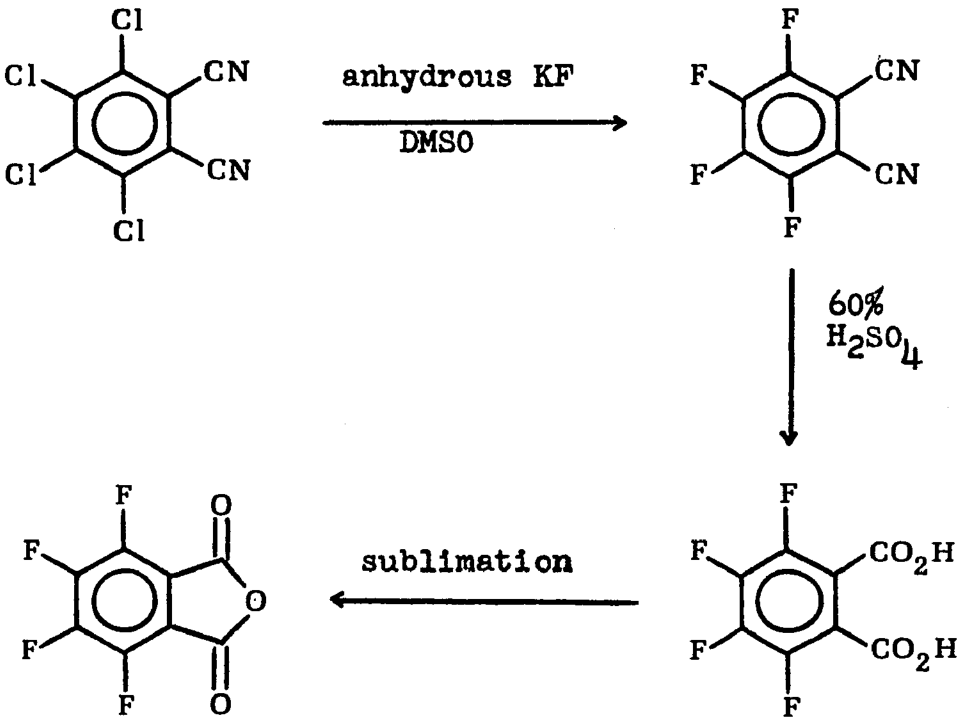
XXXII

were able to go as far as the bis-ammonium hydrochloride salt following literature preparations.[26,27] We did not attempt the next step in this scheme due to major difficulties encountered in trying to carry out a similar tetrazatization in the first conversion of Scheme VIII. This first step described in the chemical literature,[28] calls for the dropwise addition, with cooling in an ice-salt bath, of a solution of $NaNO_2$ in H_2SO_4 to a mixture of 2-nitro-p-phenylenediamine and H_3PO_4. After destruction of the excess nitrous acid with urea, a saturated solution of KI in H_2O was added to the reaction mixture. The KI addition was carried out with cooling in an ice-salt bath so that the supposedly formed bis-diazonium salt might selectively react with the iodide instead of H_2O to form phenols. To remove any phenols that might have formed, it was suggested that one add 2N KOH (amount not specified) to the crude product followed by steam distillation. In this manner, the potassium phenoxide salts would remain in the distillation pot, allowing for the separation of the volatile iodinated products. Sufficient amounts of 2N KOH were added to bring the mixture to pH eleven. During the distillation, it appeared as if the KOH was reacting, as evidenced by a decrease of the pH from eleven to eight. This decrease may have been due to the displacement of iodide by the base. At the same time, a good deal of iodine distilled over, suggesting that the iodinated products were decomposing. A pure product could not be isolated from the steam distillate. It was also thought that the yield of product may have been so poor due to a competing reaction which we initially attributed to the insolubility of the starting diamine in H_3PO_4. Due to this insolubility, much free diamine would be present at the time the nitrosylsulfuric acid ($NaNO_2$+H_2SO_4) was added. The nitrosylsulfuric acid, in contact with the H_3PO_4, was believed to release HONO,[28] which perhaps would diazotize one of the amino groups of the starting material. However, in the presence of a good deal of free diamine, instead of forming a bis-diazonium salt, the monodiazonium salt could couple with a molecule of free diamine to form an azo compound. We thus felt that it was important that the starting diamine be completely converted to the bis-ammonium salt, in order to avoid the possible dominance of this kind of side reaction. Along these lines, we followed a procedure by Schoutissen[29] for the diazotization of the weak base, 2,4-dinitroaniline. This preparation first required the dissolution of the amine in H_2SO_4 to which the nitrosylsulfuric acid was then added, follwed by the dropwise addition of H_3PO_4. The 2-nitro-p-phenylenediamine did appear to be considerably more soluble in the H_2SO_4, however, the subsequent steam distillation proceeded exactly as in the first attempt, and a pure product could not be obtained. Other variations in the experimental procedure for the tetrazatization were tried including the use of acetic acid in lieu of H_3PO_4, as suggested by Hodgson and Walker[30] in their synthesis of the bis-diazonium salt of o-phenylenediamine, with no success.

We next turned to the possibility that we might be able to obtain 3,6-diiodophthalic anhydride by a displacement reaction between NaI and 3,6-dichlorophthalic anhydride. The former anhydride would serve as the precursor to the desired 3,6-diiodoanthranilic acid (XXXII) via the reaction sequence of Scheme VI (see pg. 28). The procedure followed was fashioned after a report on the synthesis of 2,4-dinitroiodobenzene from a refluxing solution of 2,4-dinitrochlorobenzene in dimethyl formamide, containing NaI.[31] Repeated reactions under a variety of conditions, including changing the solvent to 2-butanone, were unsuccessful. This particular approach was finally abandoned.

Our efforts then turned towards the preparation of the tetrafluorobenzyne precursor, tetrafluoroanthranilic acid (XXXIII) in order to fulfill our goal of synthesizing triptycene Ia. Scheme IX illustrates the route followed to first

Scheme IX



prepare the tetrafluorophthalic anhydride.[32] This sequence of reactions presented considerable difficulties. The hydrolysis of the tetrafluorophthalonitrile posed the greatest problem in that the nitrile would readily sublime into the reflux condenser during the prolonged heating period (much longer than suggested in the literature preparation) necessary to cause the conversion to the diacid. Initial attempts, using the literature procedure, led to a mixture which appeared to contain some diamide due to partial hydrolysis.

As indicated in a paper by Tatlow in 1961,[33] tetrafluoroanthranilic acid (XXXIII) may be prepared from tetrafluorophthalimide by the Hofmann reaction. The conversion of tetrafluorophthalic anhydride into its imide initially was accomplished in very poor yield due to the sublimation from the reaction flask of the imide before the reaction temperature was hot enough to effect a complete conversion. (Tatlow suggested that the reaction mixture should be heated to 280° and allowed to remain at this temperature for one hour.) This problem of sublimation at temperatures below 200° was overcome by connecting a cold trap to the reaction flask. However, it appeared as if the crude imide was not very stable at the high reaction temperatures required and/or it was not very stable under the condition of a subsequent sublimation which was necessary in order to obtain pure product. Evidence for this was based upon the isolation of a purified product whose melting point was considerably higher than the literature value of 211°.[33] Despite efforts to avoid prolonged heating of the crude product at temperatures above 260°, and regardless of attempts to carry out the sublimation under milder conditions of temperature and pressure than previously employed, we were not able to isolate pure tetrafluorophthalimide in sufficient quantities to continue this approach.

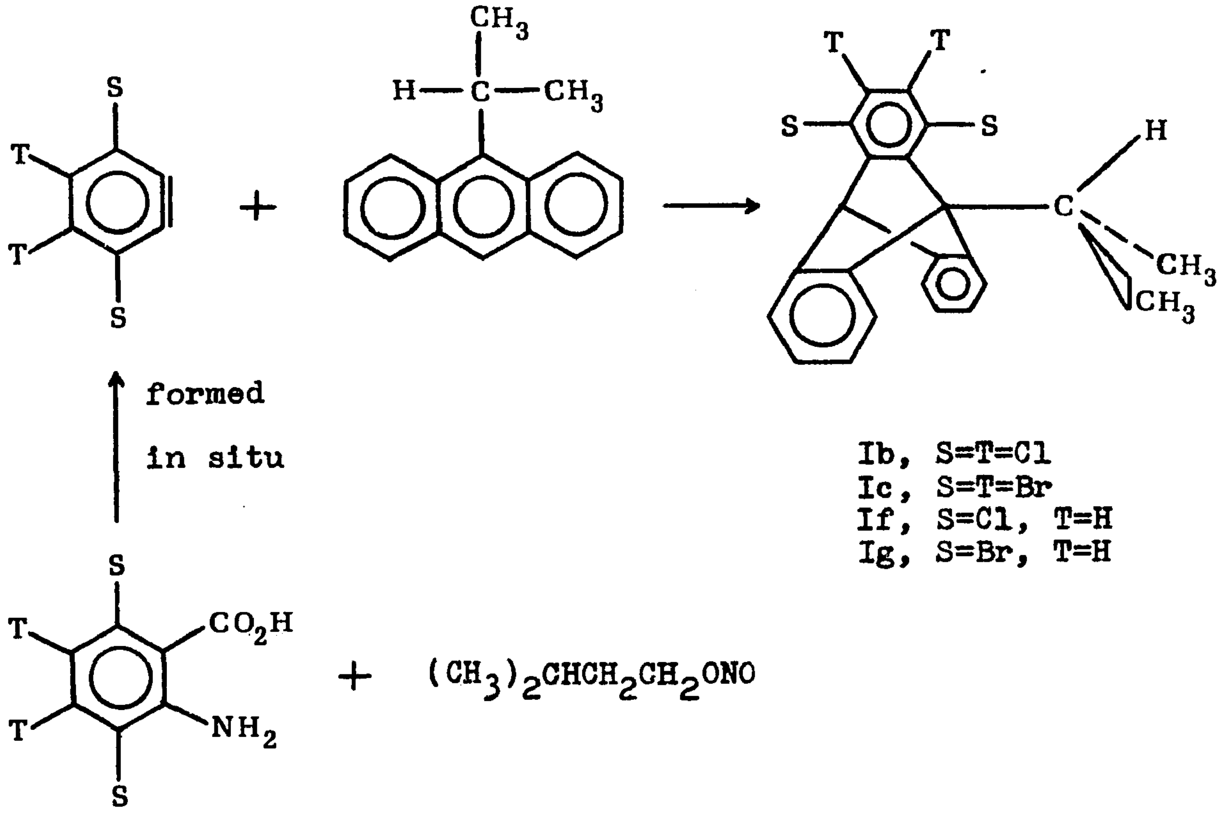
We then tried to prepare tetrafluoroanthranilic acid (XXXIII) directly from the corresponding anhydride via the ammonium tetrafluorophthalamate salt, following Scheme VI (see pg. 28). The product obtained from the reaction of gaseous NH_3 and tetrafluorophthalic anhydride was identified by ir spectroscopy as the diammonium carboxylate salt of tetrafluorophthalic acid. Apparently, the tendency for hydrolysis of either the starting anhydride or the ammonium phthalamate salt derived from it, under these reaction conditions is much greater than in the analogous reactions with the tetrabromo, tetrachloro, 3,6-dichloro and 3,6-dibromophthalic anhydrides. This is reasonable in view of the increased electrophilicity of the carbonyl carbon atoms in the tetrafluoro species. We finally abandoned the use of tetrafluoroanthranilic acid (XXXIII) as the precursor to tetrafluorobenzyne. We eventually generated tetrafluorobenzyne in the presence of 9-isopropylanthracene (XV) via the decomposition of lithium pentafluorobenzene (XXXIV).

(3) Syntheses of 9-Substituted Triptycenes

Compounds Ib, Ic, If and Ig were synthesized according to Scheme X using the appropriately substituted anthranilic acid as the benzyne precursor.

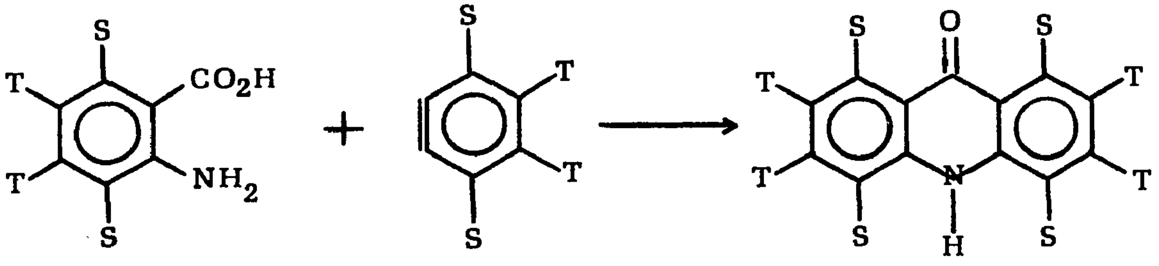
A solution of the anthranilic acid in diethyl carbitol ($(C_2H_5OCH_2CH_2)_2O$) was added, dropwise, to a refluxing solution of 9-isopropylanthracene (XV) and isoamyl nitrite in ethylene dichloride. The addition was rather slow in order to minimize the formation of acridones, which arise from the reaction between the benzyne and its precursor, the anthranilic acid, as shown in equation 3. In the syntheses of Ib, c and g acridones XXXV, XXXVI, and XXXVIII, respectively, were formed in relatively small amounts. These acridones precipitated from the reaction solution during the addition of the anthranilic acid and were therefore, readily removed by filtration. The exception was the tetrachloroacridone (XXXVII), which remained in solution and had to be separated from the desired product (If) by column chromatography.

Scheme X



Ib, S=T=Cl
Ic, S=T=Br
If, S=Cl, T=H
Ig, S=Br, T=H

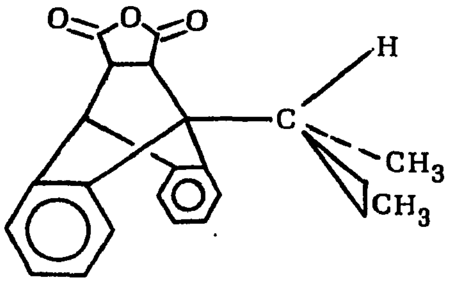
XXV, S=T=Cl
XXIII, S=T=Br
XXVI, S=Cl, T=H
XXVII, S=Br, T=H



(3)

XXXV, S=T=Cl
XXXVI, S=T=Br
XXXVII, S=Cl, T=H
XXXVIII, S=Br, T=H

Excess 9-isopropylanthracene (XV) was removed with maleic anhydride, at a temperature of approximately 215°, by conversion to compound XXXIX. This reaction mixture was allowed to

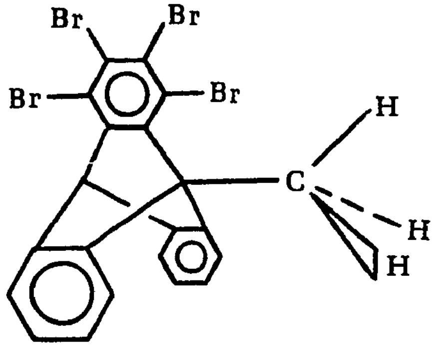


XXXIX

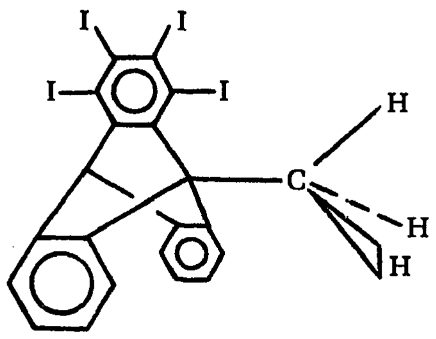
cool to 50°, and a solution of KOH in a 2:1 mixture of methanol and H_2O was added. This step served two purposes, (1) to convert the maleic anhydride adduct (XXXIX) into a dipotassium salt, which remained soluble in the aqueous media and (2) to precipitate the desired triptycene. Deuterated triptycenes Ii and Ij were prepared in the same manner via the reaction of tetrabromobenzyne with the appropriately deuterated 9-isopropylanthracenes (XVI and XVII).

In an effort to devise a system which might exhibit conformational stability of a methyl group, compounds Ik and Il were synthesized. These triptycenes were prepared by the addition of the appropriate tetrahalobenzyne to 9-methylanthracene. Precipitation of octabromo- (XXXVI) and octaiodoacridone (XL) respectively, occurred during the addition of the anthranilic acid solutions.

The triptycenes Ib, c, g, i, j, k, and l, were all purified



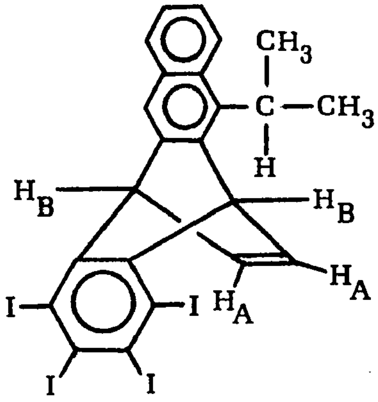
Ik



Il

by recrystallization to constant melting point, the exception being If, which had to be chromatographed before recrystallization.

Repeated attempts were made to synthesize compound Id via the addition of tetraiodobenzyne to 9-isopropylanthracene (XV) according to SchemeX (see pg. 37). No precipitation took place after the reaction mixture was allowed to stir overnight in the presence of the KOH solution, added to precipitate the triptycene product. The addition of H_2O to the diethyl carbitol layer, after removal of the basic layer, resulted in the formation of a black oil, the nmr spectrum of which was very complex. The isopropyl methyl region was largely obscured by the presence of diethyl carbitol, however, certain absorptions in the bridgehead-hydrogen and aromatic regions suggested the presence of the desired product. Two symmetrical multiplets were also found in the bridgehead-hydrogen region which may be attributed to the hydrogens labelled A and B in compound XLI, formed by the addition of the tetraiodobenzyne to the end ring of 9-isopropylanthracene (XV).

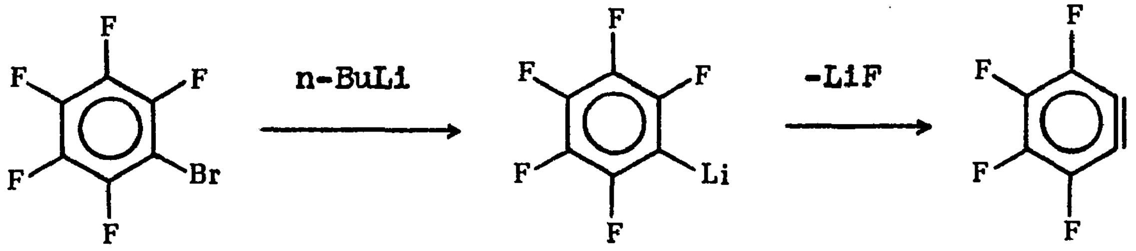


XLI

Tlc's were taken of the crude oil and despite the appearance of some five or six spots, it was encouraging to find that one of the spots had an R.F. value which corresponded to the R.F. values of pure samples of compounds Ib, c, f and g. Thus it was hoped that the product could be isolated by column chromatography, but this technique proved to be unfruitful. Each effort to synthesize Id resulted in the formation of octaiodoacridone (XL) as the major product. The fact that XL formed is evidence for the generation of tetraiodobenzyne. The difficulty in isolating any product (if indeed any was actually formed), coupled with the apparent formation of end-adduct (XLI), octaiodoacridone (XL) and after chromatography, fractions indicative of compounds derived from possibly isoamyl alcohol, all suggested that this particular benzyne was too hindered to add across the center ring of 9-isopropylanthracene (XV), thereby allowing other side reactions involving tetraiodobenzyne to predominate.

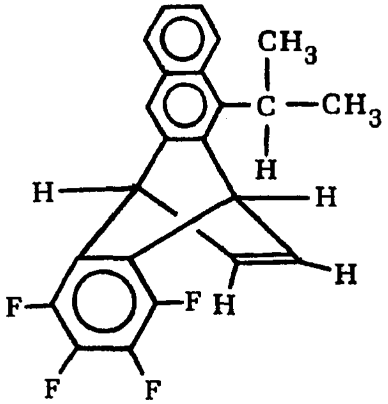
As mentioned in the previous section (Syntheses of Anthranilic Acids), due to our inability to synthesize tetrafluoroanthranilic acid (XXXIII), a different benzyne precursor was utilized, namely pentafluorobromobenzene (XXXIV). Scheme XI illustrates the formation of tetrafluorobenzyne from this species.

Scheme XI



XXXIV

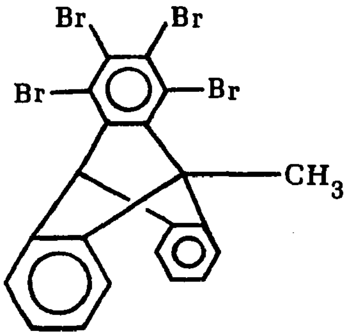
The reaction of the tetrafluorobenzyne with 9-isopropylanthracene (XV) yielded predominantly Ia and a considerable amount of 1,2,3,4-tetrafluoro-5,12-dihydro-5,12-ethenonaphthacene (XLII) (end adduct). Analogous addition products were not found in the syntheses of Ib, c, f and g, suggesting the decreased selectivity of tetrafluorobenzyne.



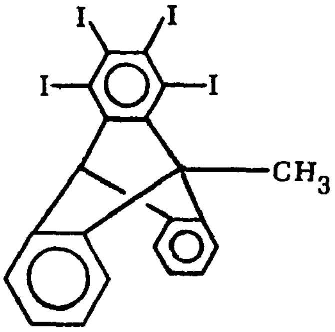
XLII

B Results and Discussion

In an effort to demonstrate conformational stability of a methyl group, compound Ik and Il were synthesized. In principle, the rotational barriers for these compounds can be calculated from the appearance of the methyl hydrogens, in their respective nmr spectra, as a function of temperature. At low enough temperatures, rotation about the C_9-C_{CH_3} single bond would be slow enough such that the methyl hydrogens would not all be equivalent. These hydrogens, under the condition of slow rotation, would be divided into two types, A and B, as illustrated in Fig. VII.

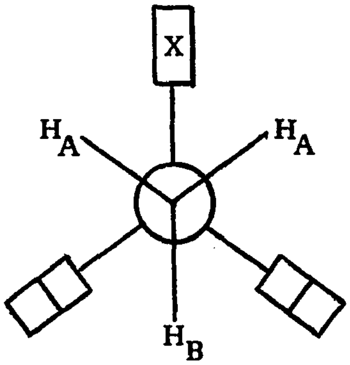


Ik



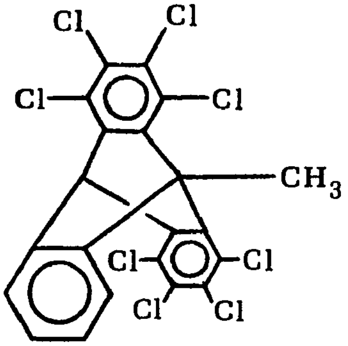
Il

Fig. VII



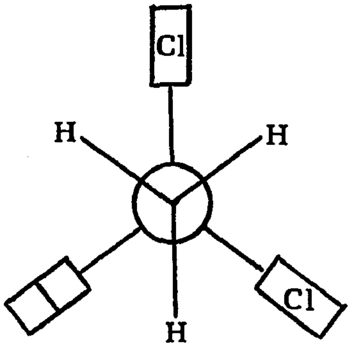
Ik, X=Br
Il, X=I

Some preliminary low temperature nmr work was done on compound Ik. However, before our nmr experiments were refined, Oki and Nakamura published a communication in which it was reported that compound XLIII exhibited restricted rotation of the methyl group at low temperature.[34] Upon lowering the temperature to -71.90°, the methyl signal of XLIII was observed to split into two multiplets, a triplet and a doublet, in a relative ratio of 1:2 respectively. This result may be understood from an inspection of the Newman projection of XLIII (Fig. VIII) which illustrate that two



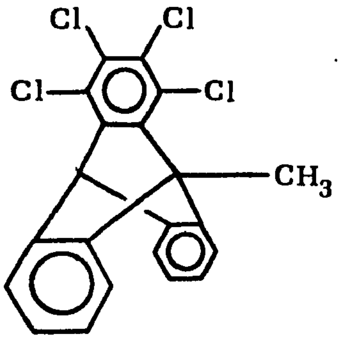
XLIII

Fig. VIII



types of hydrogens are present. The rotational energy barrier for XLIII, in terms of $\Delta G^{\ddagger}$, was found to be 10.6 ± 1.0 kcal/mole at 25°C. Following this communication, Oki, Nakamura, Nakanishi and Yamamoto published a paper on the barriers to rotation of methyl groups in a number of substituted 9-methyltriptycenes.[35] One such triptycene studied was exactly the compound we had synthesized, Ik. It was found that the low temperature nmr spectrum of this compound (temperature unspecified) exhibited splitting of the methyl signal into two broad signals with relative intensities of 2:1. The authors obtained a value for $\Delta G^{\ddagger}$ of 10.2 ± 1.0 kcal/mole at 25° for compound Ik. We attempted to repeat this work. A 3% solution of Ik in a 1:1 mixture of $CDCl_3$ and CS_2 was used. As the temperature was lowered past -10°, broadening of the methyl signal was observed; however, there was concurrent precipitation of solute. Finally, at approximately -52°, so much material had come out of solution that hardly any signal could be observed. Very similar results were obtained using varying mixtures of $CDCl_3$ and CS_2. We attribute the observed broadening to the precipitation of dissolved material. Thus, using the solvent system proposed by Oki and coworkers, we were not able to reproduce the reported experimental spectra.

Oki had also synthesized and measured the rotational barrier of 1,2,3,4-tetrachloro-9-methyltriptycene (Im) and found that this compound, at -95.5°, likewise gave rise to a methyl signal split into two broad bands in the expected 2:1 ratio. The value of $\Delta G^{\ddagger}$ for this chloro compound was found

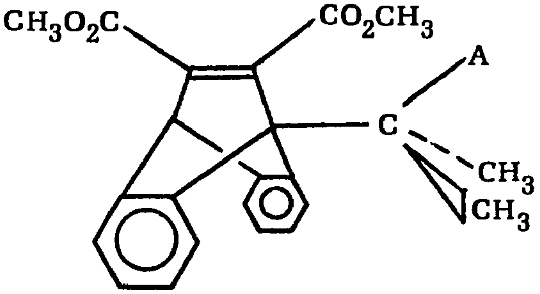


Im

to be equal within experimental error, to that found for the corresponding bromo compound (Ik). We attempted to obtain the low temperature nmr spectra of compound Il in order to determine if iodine, as the peri substituent, would lead to a larger $\Delta G^{\ddagger}$ value than that found for Ik and Im and possibly even a larger $\Delta G^{\ddagger}$ than that found for XLIII.

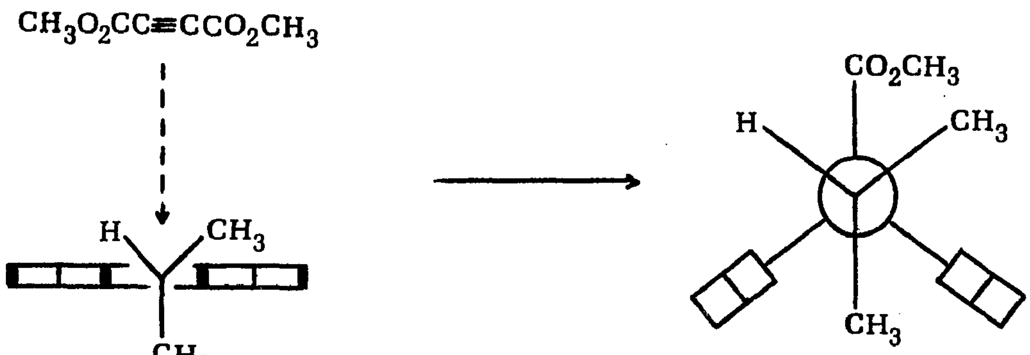
A dilute solution of Il was prepared in CS_2. (This compound appeared to be considerably more soluble in CS_2 than $CDCl_3$). Broadening of the methyl signal occurred as the temperature was reduced below +10° until at about -10°, the signal was barely visible due to precipitation of the compound. Other solvent combinations were tried such as varying proportions of $CFCl_3$ and CS_2; $CFCl_3$, CS_2 and CH_2Cl_2. However, Il proved to be insufficiently soluble in these solvent mixtures even at room temperature. A mixture of equal parts CH_2Cl_2 and CS_2 initially appeared promising. However, at a temperature of approximately -24°, the solute was almost entirely out of solution, such that the methyl signal could no longer be discerned.

Triptycenes Ib, Ic, If and Ig were synthesized and their rotational energy barriers measured by a conventional nmr line shape analysis. Based upon prior reports by Oki and coworkers,[3,4] we expected that the stereochemical course of the addition reaction between the various substituted benzynes and 9-isopropylanthracene (XV) would occur such that the dienophile would approach the anthracene π system from the side in between the two smallest groups, i.e., from the least hindered side. This expectation stemmed from the results of the synthesis of compounds IIIa and IIIc,[3,4] where despite the fact



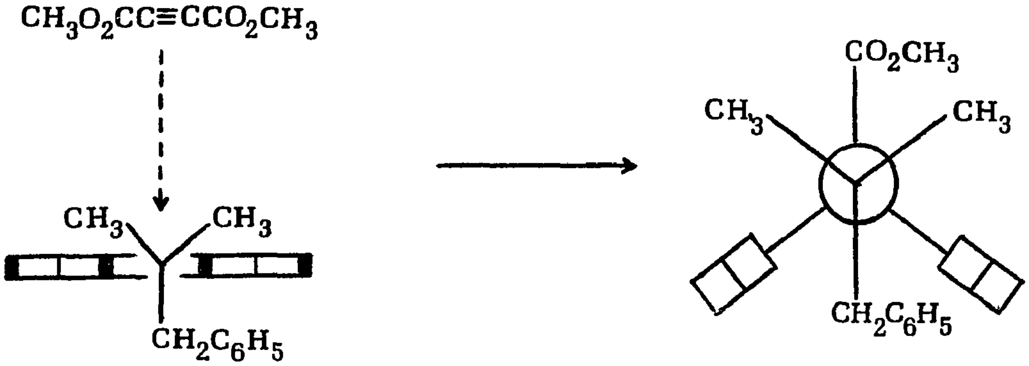
IIIa, A=H
IIIc, A=$CH_2C_6H_5$

that both of these compounds can exist in either an anti or a skew conformation, their preparation yielded only one conformer in each case. In the synthesis of IIIa, the authors found, by nmr analysis, that the skew conformer (IIIa') was formed exclusively. The nmr spectrum of IIIc indicated the sole formation of the anti conformer (IIIc''). It was argued that this stereospecificity was due to the preferential approach of the dienophile, dimethyl acetylenedicarboxylate, from in between the two smallest groups (equations 7 and 8). Inspection of conformer IIIa' (equation 7) indicates the presence of non-



(7)

IIIa'

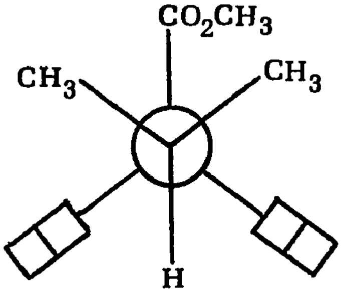


(8)

IIIc"

equivalent methyl groups. Thus, the observance of two doublets for these methyl groups was attributed to restricted rotation about the central carbon-carbon single bond. The fact that these doublets were of equal intensity served as evidence for the absence of the anti conformer, the reasoning for which follows: As can be seen from the Newman projection of the anti conformer (IIIa'') (Fig. IX), the equivalent methyl groups here, would have the same environment as that of the methyl group skew to the carbomethoxy and phenyl groups in conformer IIIa', and thus would be expected to have the same chemical shift. If the anti conformer (IIIa'') were present, one would

Fig. IX



IIIa"

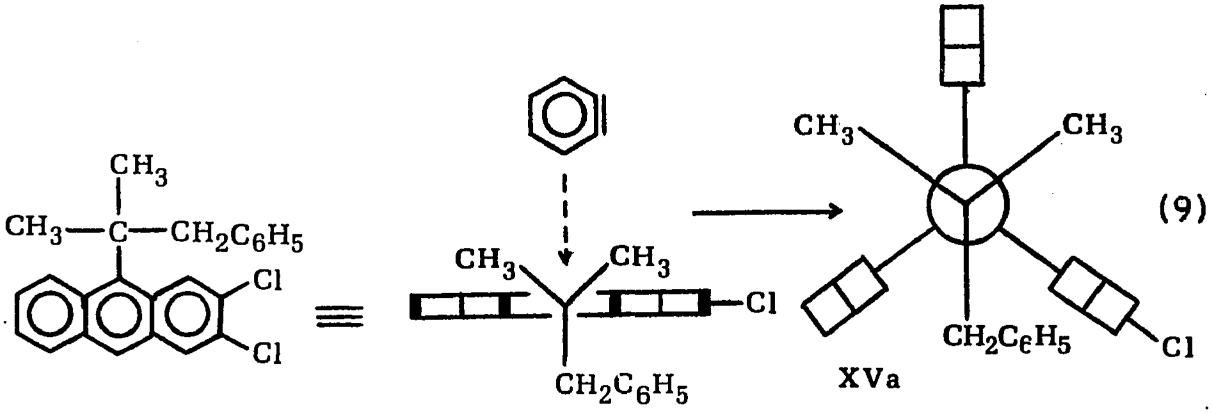
therefore expect an enhancement in the intensity of one of the two doublets for compound IIIa.

Only one doublet appeared for the methyl hydrogens in the nmr spectrum of IIIc, indicating that the stereochemical course of this reaction was as shown in equation 8.

More conclusive evidence supporting the proposed sterically controlled approach of the dienophile was presented by Oki and Yamamoto in a later paper on the stereospecific synthesis of non-interconverting rotational isomers.[36] Both the skew and the anti conformers of triptycene XLV were synthesized, independently of each other, using the reactions shown in equations 9 and 10.

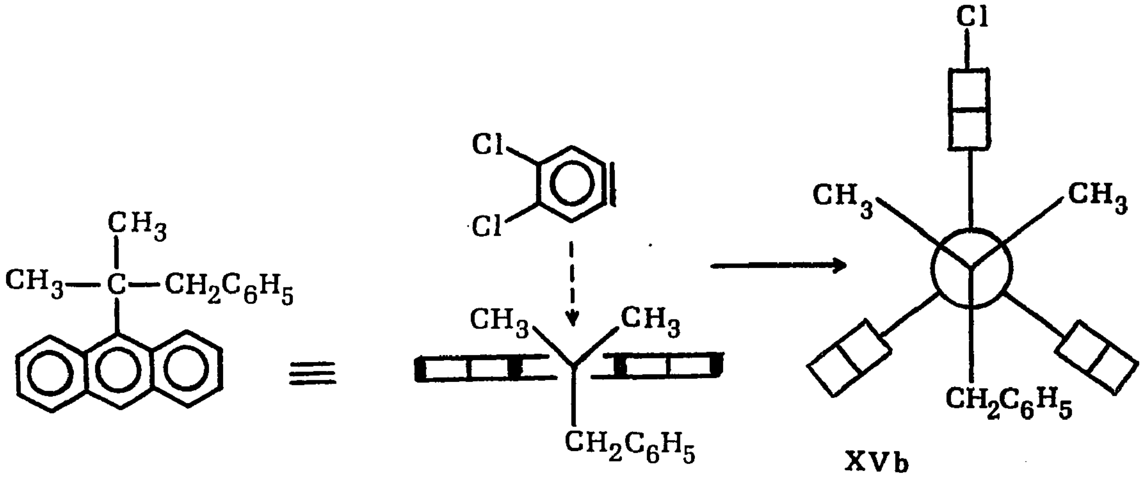
Such a high degree of stereospecificity strongly indicates that the approach of the dienophile is controlled by steric factors, where in this instance, entry from in between the two methyl groups is greatly preferred.

We expected that the syntheses of triptycenes Ib, c, f and g would lead in each case to only the respective skew conformers



XVa

(9)

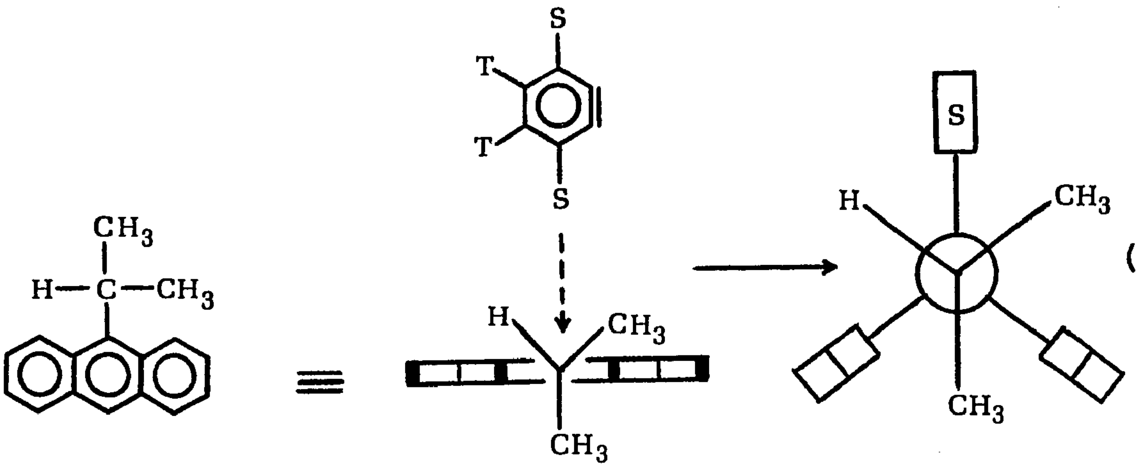


XVb

(10)

in which the isopropyl methyl groups would be non-equivalent, provided that the rotation about the C_9-C_{i-pr} bond was restricted at room temperature. The stereochemical result of the benzyne approaching from in between the methine hydrogen and a methyl group of the isopropyl moiety (sterically, the least hindered pathway) is illustrated in equation 11.

The nmr spectra of Ib, c, f, and g all showed two equal-intensity doublets for the methyl hydrogens at room temperature, indicating the presence of non-equivalent methyl groups. This non-equivalency is a result of restricted rotation about the C_9-C_{i-pr} bond. Two structural interpretations are possible: (1) Only the skew conformer (I') is present. This conformer contains two non-equivalent methyl groups, with different



(11)

XV

I'

chemical shifts, thus accounting for the two doublets. (2) Both anti (I'') and skew (I') conformers are present in equal quantities and each gives rise to a single doublet. In this case, one would have to postulate that the non-equivalent methyl groups of the skew conformer have the same chemical shift.

As the temperature was raised, the two doublets coalesced, and finally were transformed to a single doublet. Upon cooling back down to room temperature, the original spectra were again obtained. (Reproductions of both the experimental and calculated spectra are included in Section IV, pg. 114 .) These results strongly suggest that Ib, c, f, and g consist of only the skew conformers. If the anti conformers were present, (interpretation (2), preceeding paragraph), it would be highly fortuitous that on cooling back down to room temperature, equal amounts of the two conformers would reform, especially since the anti conformer would most likely be considerably less stable.

Additionally, interpretation (2) (preceding paragraph) can be argued against using a premise similar to the one employed by Oki (see pg. 47) to arrive at the claim that IIIa consisted of only the skew conformer (IIIa'); it would be expected that one of the methyl groups of the skew conformer (I') would have a very similar chemical shift to that of the methyl groups of the anti conformer, causing overlap of these signals. Thus, two equal intensity doublets would not be expected if any anti conformer (I'') were present.

The calculation of the energy barrier in terms of $\Delta G^{\ddagger}$ for Ib, c, f and g was accomplished by means of an nmr line shape analysis.[37] This analysis involved the use of a computer program (Saunders' SNMREX Program[38]), which provided for the generation of theoretical nmr spectra or line shapes corresponding to the region of the isopropyl methyl hydrogens. Each computer calculated spectrum has a rate constant for exchange associated with it. The calculated curves are then visually fitted to those of the experimentally determined nmr spectra taken at various known temperatures. Such a matching up of calculated vs experimental spectra allows for the assessment of a rate constant at a particular temperature. The temperature of a sample was measured by means of a technique which utilizes the known temperature dependence of the chemical shift difference between the two resonances of ethylene glycol. A.L. Van Geet, in 1968,[39] reported that the relationship between temperature and the chemical shift difference between the methylene and hydroxyl signals of ethylene glycol fit a straight line, given by equation 15. We determined the values of $\Delta \nu$ by

$$T = 466.0 - 1.694\,\Delta\nu \qquad (15)$$

$\Delta\nu$ = difference in chemical shift between CH_2 and OH signals

means of a frequency counter both before and after each scan. A run was rejected if $\Delta\nu$ before and after the scan showed a variance greater than one Hz. This corresponds to a maximum error in temperature of ± 1.7°C. Reproducibility within 0.5 Hz was usually observed.

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values (see Table V, below) were obtained

Table V. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ Values of Compounds Ib,c,f and g Derived from the Linear Plot of ln k/T vs 1/T

	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (EU)
Ib	32.25	18.73
Ic	25.89	5.16
If	29.78	14.91
Ig	29.89	17.20

from the linear plot of ln k/T vs 1/T. From the Eyring equation[40] (equation 16) the slope of this line is equal to $-\Delta H^{\ddagger}/R$ and the y intercept is equal to $\ln k_B/h + \Delta S^{\ddagger}/R$.

$$\ln k/T = -\Delta H^{\ddagger}/R(1/T) + \Delta S^{\ddagger}/R + \ln(k_B/h) \qquad (16)$$

From $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, using equation 17, $\Delta G^{\ddagger}$ can be evaluated at any temperature. The nature of this method is

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\ \Delta S^{\ddagger} \qquad (17)$$

such that factors leading to an error in $\Delta H^{\ddagger}$ in one direction will lead to an error in $\Delta S^{\ddagger}$ in the opposite direction, i.e., too large a slope ($\Delta H^{\ddagger}$) will lead to too small a value for the y intercept ($\Delta S^{\ddagger}$).[41] Thus, in applying equation 17, the errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ compensate and the actual error in $\Delta G^{\ddagger}$ is less than the errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. It is for this reason that most authors tend to compare $\Delta G^{\ddagger}$ values and do not compare, what might be thought to be more meaningful, $\Delta H^{\ddagger}$ values. $\Delta H^{\ddagger}$ values would be more meaningful in terms of assessing steric effects since entropy factors would not complicate the interpretation.

We chose to calculate $\Delta G^{\ddagger}$ at the temperature corresponding to the coalescence point of each of the four triptycenes (Ib,c,f and g), i.e., at the point where the minima between coalescing signals has just vanished.[42] For compound Ib, we did not have an experimental spectrum exactly at the coalescence temperature. We had one spectrum slightly below the coalescence point ($\Delta G^{\ddagger}$ was calculated at this temperature) and another just past the coalescence point. These two spectra differed in temperature by 8.8°. However, even if the calculation was carried out at a temperature some 4° away from actual coalescence, using equation 17, it can be shown for compound Ib that an error in temperature of as much as ± 20° would only introduce an error of ± 0.35 kcal/mole in $\Delta G^{\ddagger}$.

The values for $\Delta G^{\ddagger}$ (including error limits) and the temperature at which these values were calculated are given in Table VI. The error involved in each of these four barriers is approximately ± 0.2 kcal/mole. The error for each compound was obtained by assuming an error of ± 10% in the rate constants at coalescence (based upon an estimate of the accuracy

Table VI. $\Delta G^{\ddagger}$ Values for Compounds Ib,c,f and g at Coalescence

	$\Delta G^{\ddagger}$ (kcal/mole)	error (± kcal/mole)	°K Tc(coalescence temp.)
Ib	23.9	0.2	446
Ic	23.6	0.2	447
If	23.3	0.2	438
Ig	22.5	0.2	427

of matching calculated and computed spectra) and an error of ± 1° in temperature.

Because of the great structural similarity of the compounds under investigation, it may be argued that entropy effects in all of these species should be very similar. Thus, a comparison of $\Delta G^{\ddagger}$ values would be equivalent to a comparison of $\Delta H^{\ddagger}$ values such that conclusions concerning relative steric sizes could be drawn.

During the final stages of our work, Oki, F. Suzuki and H. Nakanishi reported the rotational barriers of Ib and Ic, which are in rather sharp contrast to our results. It was claimed that the methyl signals of Ib gradually coalesced with increasing temperature, with a $\Delta G^{\ddagger}$ value at 25° of 25.5 ± 2.3 kcal/mole. For the corresponding tetrabromo-9-isopropyltriptycene (Ic), the methyl signals "remained intact" up to a temperature of 200°, i.e., no coalescence of the signals was observed. Based upon this observation of the "temperature independence" of the methyl signals of compound Ic, as well as the chemical shift difference between the two methyl groups, the energy barrier in terms of $\Delta G^{\ddagger}$ was estimated to be in excess of 26 kcal/mole. The authors noted that the magnitude of the rotational barriers for Ib and Ic were in accordance with the van der Waals radii of the halogen atoms involved. As will be illustrated in Section IV, and as mentioned on page 50 , not only did we observe the coalescence of the four methyl signals of Ic at approximately 172°, but at approximately 182° a rather sharp doublet was also observed. One possible reason for this discrepancy * in the experimental variable temperature nmr spectra of Ic, is the fact that Oki et al. used hexachlorobutadiene as the high temperature solvent, while we used deuterionitrobenzene. However, initially we also recorded our high temperature spectra for Ib, c, f and g in hexachlorobutadiene, but we changed to deuterionitrobenzene because more concentrated solutions could be obtained, leading to improved spectra. We found that in hexachlorobutadiene compound Ic exhibited a single doublet at 173°.

The fact that we observed essentially equal rotational barriers for Ib, c, f and g can be explained qualitatively, in two ways. However, first a discussion of the rotational modes that probably take place is in order. Oki and Suda[3] have suggested, from a study of the rotational barriers of

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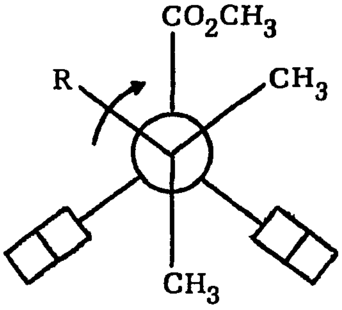
* Of possible relevancy are the facts that our m.p. for Ic was 312-314° while Oki et al. reported 290-292°, and we obtained a satisfactory analysis for our preparation, while Oki et al. did not.

IIIa' and IIIb, that the direction of rotation of the isopropyl group in IIIa' is as indicated by the arrow in Fig. X.

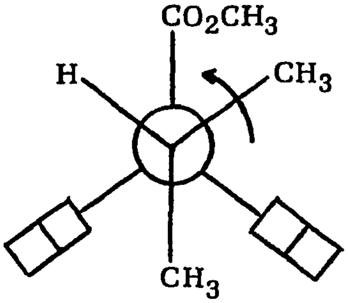
Fig. X



IIIa', R=H
IIIb , R=CH_3

The smallest group, hydrogen, rather than the larger methyl group, passes the group attached to the bicyclic skeleton which offers the greatest steric hindrance, i.e., the carbomethoxy group. This seems intuitively correct in terms of minimizing steric interactions in the transition state. Compound IIIa' exhibited a rotational barrier of $\Delta G^{\ddagger} = 17.7$ kcal/mole, while compound IIIb (Fig. X) exhibited a considerably higher barrier, in excess of 25 kcal/mole. It was argued that if the direction of rotation of the isopropyl group in IIIa' is as shown in Fig. XI, then IIIa' and IIIb would have very similar rotational barriers. In this case, the rotational processes for both IIIa' and IIIb would involve the two larger groups passing each other. Since these virtually identical interactions would mainly determine the magnitude of the respective rotational barriers, these barriers should be essentially the same. In our system (I'), a similar

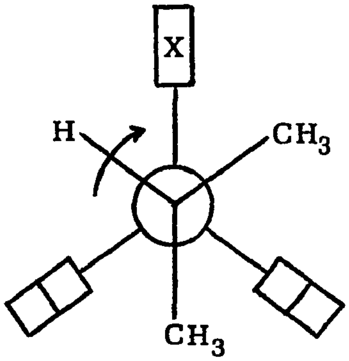
Fig. XI



IIIa'

direction of rotation (Fig. XII) seems most reasonable since

Fig. XII



I', X=Cl, Br

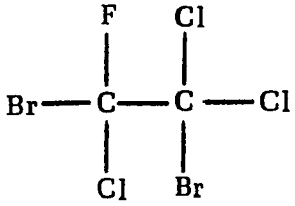
the two largest groups would not have to pass each other. Later (pg.67), when 1,2,3,4-tetrafluoro-9-isopropyltriptycene (Ia) is discussed, a further argument for this mode of rotation will be made.

We may now consider the following two possible explanations of the fact that Ib, c, f and g all show essentially equal rotational barriers.

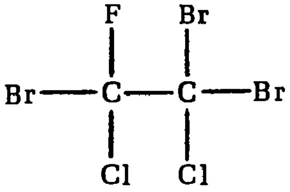
(1) A major purpose of studying compounds of series

I was to gain further insight into the relative steric size of the halogens. Such a study makes the assumption that the major interaction, which predominantly determines the magnitude of the overall barrier, occurs between the methine hydrogen of the isopropyl group and the halogenated phenyl ring. If this interaction were indeed the dominant cause for the restricted rotation, then our results of approximately equal rotational barriers for the four triptycenes initially studied suggest that van der Waals radii alone are not adequate gauges of steric effects. In this case, it could be argued that a compromise exists between the size of the halogens, as measured by their van der Waals radii, and their polarizabilities. Examples of rotational barriers in halogenated ethanes were cited in the Introduction Section, where it was pointed out that an uncertainty exists as to what factors are the major contributors to the overall steric size of the halogens. We attributed this uncertainty to the fact that for the low barriers being investigated, other secondary effects besides van der Waals radii might be playing a major role in determining the total steric requirement of the halogens. One explanation of our results is that even though we are dealing with substantially larger barriers, a consideration of van der Waals radii alone is still not sufficient to explain the relative steric size of the halogens, and polarizabilities must also be taken into account. A bromine atom, having a larger van der Waals radius than chlorine, would be expected to offer greater steric hindrance to rotation. However, bromine, being more polarizable than chlorine, can better distort itself so as to lessen steric interactions with an opposing substituent. A balance between the size of the bromine and chlorine atoms, as measured by their van der Waals radii, and their respective polarizabilities could then account for the observed equivalent barriers. This explanation appears to be more generally applicable than the one proposed by J.D. Roberts and coworkers,[9] in their attempt to account for the essentially equal barrier heights between compounds V and VI and between compounds VII and VII (Fig. XIII). These authors suggested that both chlorine and bromine have similar effects on rotational barriers as

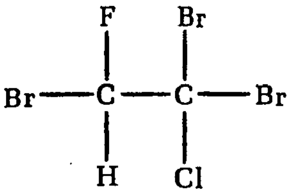
Fig. XIII



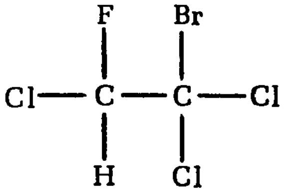
V



VI

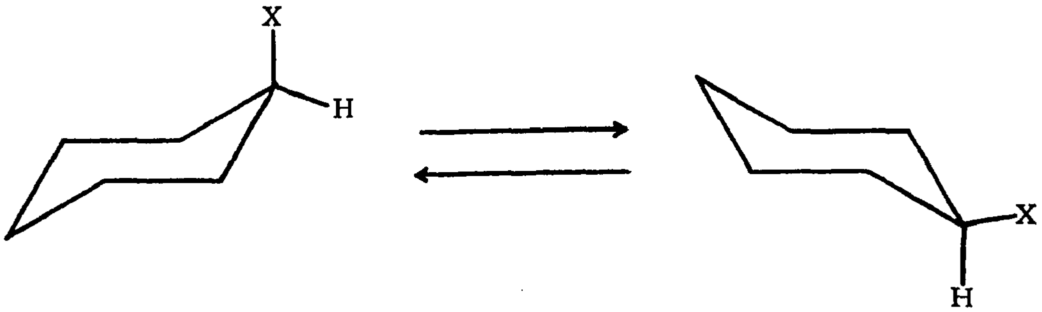


VII



VIII

a consequence of the fact that although bromine has a larger van der Waals radius, the carbon-bromine bond distance is greater than the carbon-chlorine bond distance. The greater C-Br bond length would tend to lessen the steric interaction between the bromine and an opposing group, thus compensating for its larger radius. Roberts' argument may be applicable to the system he studied, however, in the case of our hindered triptycenes, such an argument would not apply, since a longer C-Br bond length would bring the interfering bromine atom of Ic or Ig even closer to the isopropyl group, leading to a larger barrier than for the analogous chlorotriptycenes (Ib and If). The idea that radii and polarizabilities are both important in determining the steric effects of the halogens has previously been suggested by J. Berlin and F. R. Jensen[44] in their study of conformational preferences of the halocyclohexanes. To the extent that conformational preferences reflect the size of substituents, their results may be used as an argument that the halogen atoms with larger van der Waals radii tend to have more easily deformed electron clouds and hence are better able to minimize steric interactions. Such atoms, therefore tend to exhibit relatively small conformational preferences. These authors measured the position of equilibrium shown in equation 18 for X = F, Cl, Br and I. The data indicates how the contribution to the steric requirements of an atom due to increased size and increased polarizabilities work in opposite directions such that the larger Br and I atoms have somewhat lower conformational preferences for the equatorial position than a chlorine



(18)

X	ΔG (cal/mole)
F	250
Cl	513
Br	480
I	431

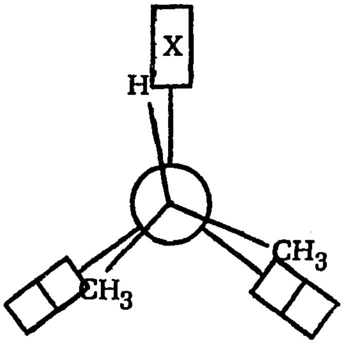
atom. The fluorine atom has considerably less conformational preference than the other halogens, and clearly possesses the smallest steric size of them all.

In our system, as long as the most severe interaction is one that involves the methine hydrogen and the halogenated phenyl ring, we would conclude that both chlorine and bromine have approximately the same steric requirement. These results would be consistent with the hypothesis that polarizabilities play an important role in determining the steric size of the halogens.

(2) A second explanation as to why the rotational barriers of Ib, c, f and g are essentially equal, in contrast to what was noted in Oki's paper[43] (see pg. 55) is based upon the premise that the major interaction responsible for the restricted rotation does not involve the halogen atom, but instead is due to the two CH_3--benzo interactions present in

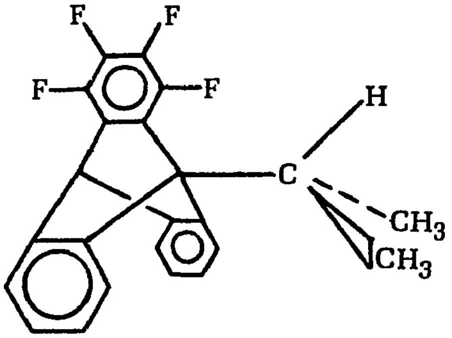
the transition state to rotation of I' (Fig. XIV). If this

Fig. XIV



interaction were the most severe, then any difference in steric size between the bromine and chlorine atoms would not be greatly reflected in the overall rotational barrier.

To distinguish between these two possibilities, we decided to study the rotational barrier of a fluoro substituted triptycene, i.e., Ia. If the steric size of the halogens are



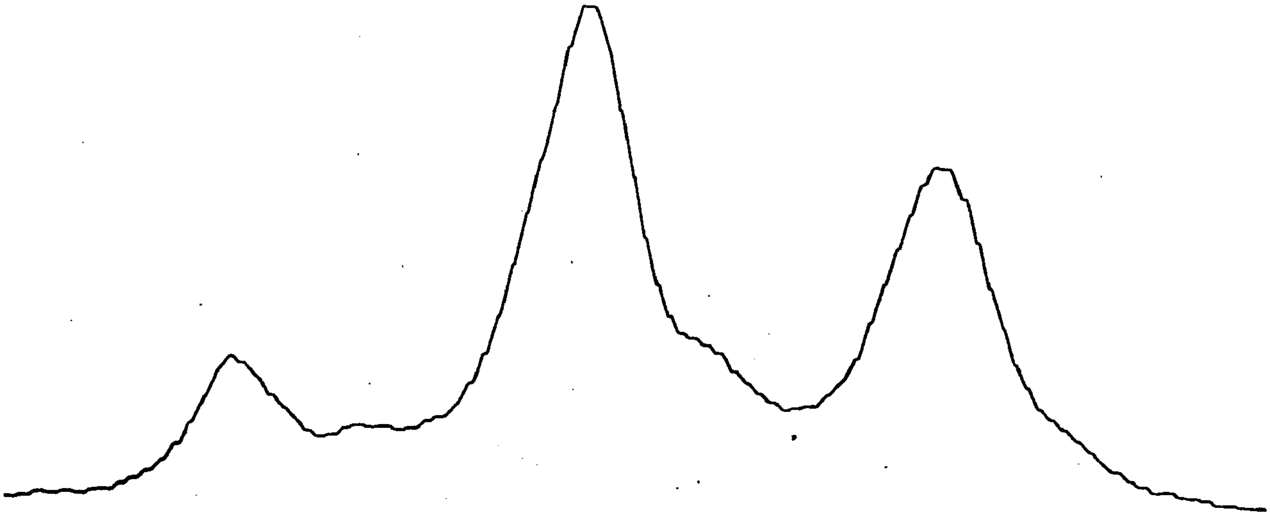
Ia

important in determining the rotational barrier (explanation 1, pg. 57), Ia would be expected to have a significantly lower barrier than Ib and Ic. We base this expectation on the significantly smaller van der Waals radius of fluorine compared to chlorine and bromine. (F, 1.35; Cl, 1.80; Br, 1.95) and on the results of Berlin and Jensen discussed on page 60.

If however, explanation (2) is correct, the rotational barriers of Ia, b, and c should not differ significantly from each other since the halogen would not be involved in the major interaction which determines the overall barrier.

The room temperature nmr spectrum of Ia was quite different compared to the other four triptycenes already studied. The isopropyl methyl hydrogens did not appear as two symmetrical doublets, but instead as essentially an unsymmetrical triplet (Fig. XV). The presence of such a triplet suggested

Fig. XV Methyl Isopropyl Region of the NMR Spectrum of 1,2,3,4-Tetrafluoro-9-isopropyltriptycene (Ia) at Room Temperature (60 MHz)



restricted rotation about the C_9-$C_{i\text{-}pr}$ bond where the methyl hydrogens of the skew conformer (Ia') are non-equivalent. In this instance, compared to Ib, c, f and g, the methyl hydrogens are closer in chemical shift causing an overlap of the individual doublets as shown schematically in Fig. XVI. If only the skew conformer (Ia') were formed, as was the case with triptycenes Ib, c, f and g, then the triplet arising from the overlap depicted in Fig. XVI would be symmetrical. In order to account for the appearance of an unsymmetrical triplet, it is postulated that in this particular synthesis the anti conformer (Ia'') is formed as well. If the chemical shift of the equivalent methyl groups of conformer Ia'' coincided with that of one of the methyl groups of the skew conformer (Ia') (See pg. 47 for a discussion of which methyl group of Ia' would most likely have a chemical shift in common with the methyl groups of Ia''), then an unsymmetrical triplet would result (Fig. XVII). From Fig. XVII we see that approximately equal amounts of anti and skew conformers would have to be present to give rise to the experimental nmr pattern.

Fig. XVI

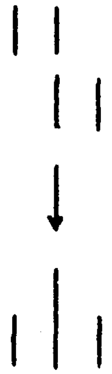
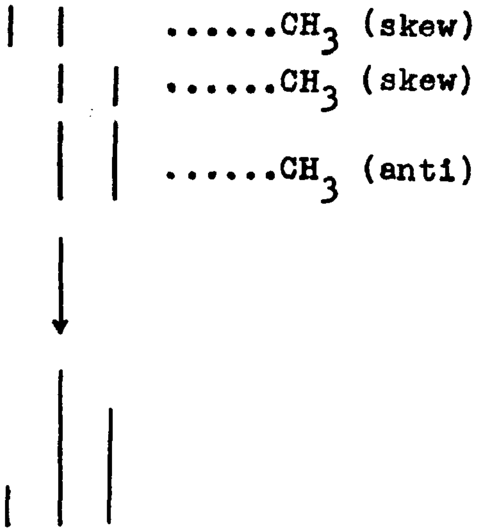
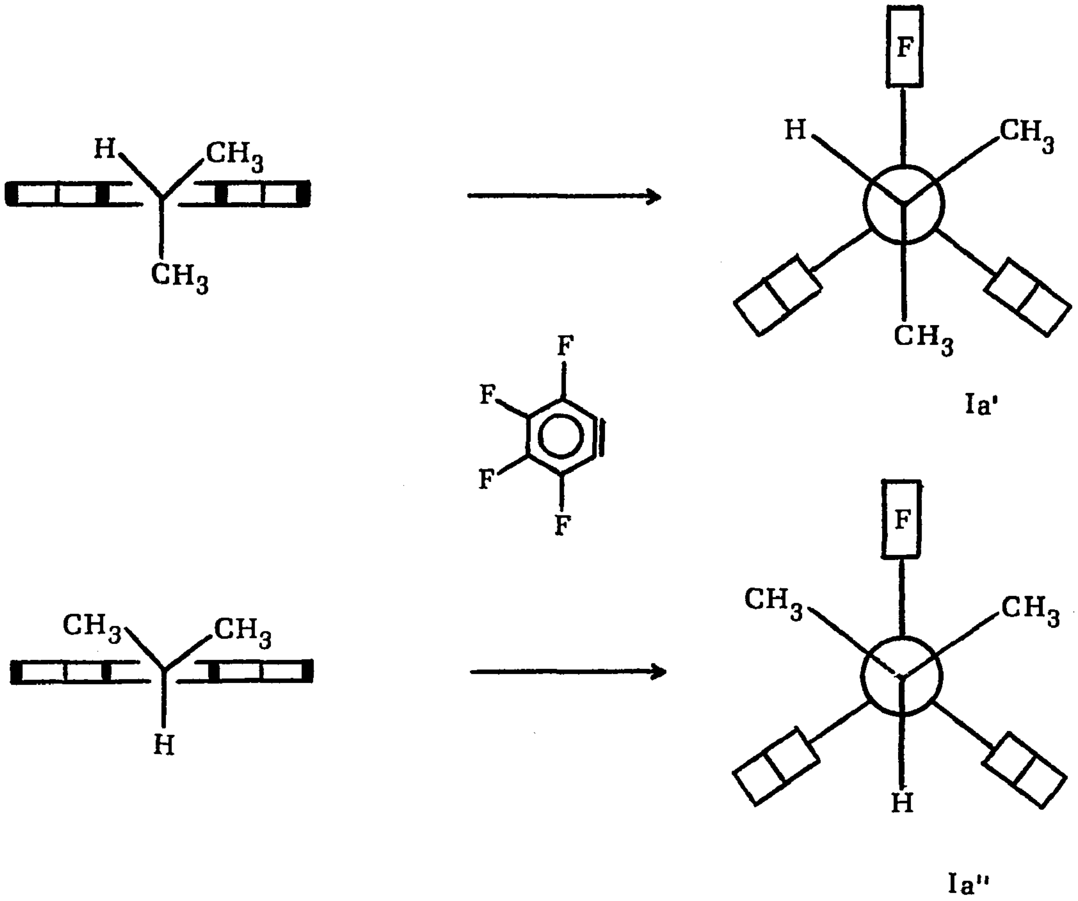


Fig. XVII



The formation of both the anti and skew conformers in this case is plausible if one considers the steric requirement of the tetrafluorobenzyne to be considerably less than that of the tetrachloro and tetrabromobenzynes. The smaller fluorobenzyne could approach the two possible 9-isopropylanthracene (XV) conformers with much less steric selectivity (equation 19), thus giving rise to both Ia' and Ia''.

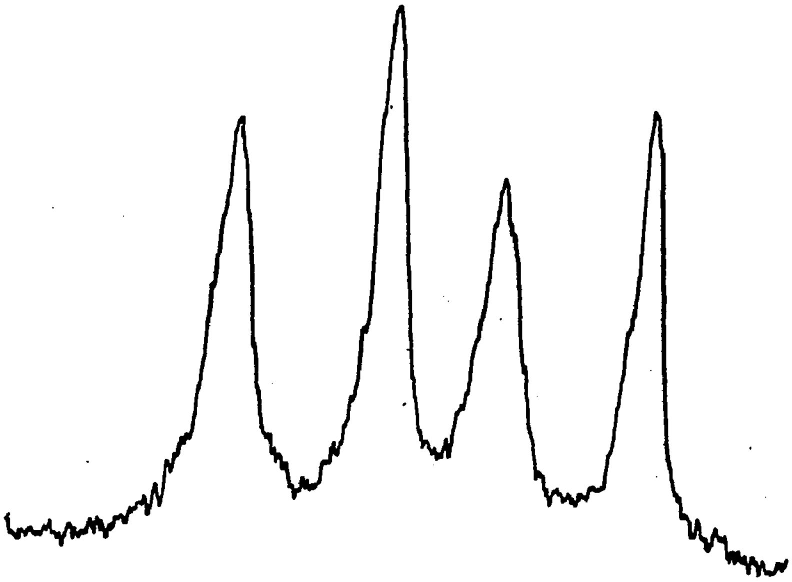
Upon raising the temperature (Reproductions of the experimental variable temperature spectra of Ia (100 MHz) are given in Section IV.), one doublet was always present whose appearance was independent of temperature, while a second doublet gradually grew with increasing temperature. At a temperature of 166° C, two doublets were evident (pg.117). Using a 60 MHz instrument, at a temperature of 183.5° the two doublets were approximately of equal intensity (Fig. XVIII). We interpret this high temperature spectrum as representing an approximately equal mixture of rapidly interconverting skew



(19)

conformers and the anti conformer, which does not change as a function of temperature. In the event that the anti and skew conformers were likewise exchanging rapidly, only a single doublet would have been observed at elevated temperatures. Thus, a barrier to rotation still exists between the anti and skew conformers at the maximum obtainable temperature of the nmr instrument. Upon returning to room temperature, the original nmr pattern was reproduced. This would not be expected if the anti and skew conformers were interconverting at the elevated temperature, unless fortuitously, the original ratio of conformers formed at room temperature was exactly the

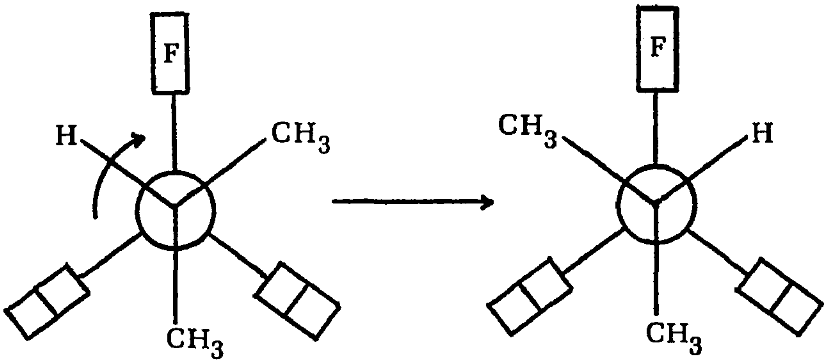
Fig. XVIII Methyl Isopropyl Region of the NMR Spectrum of 1,2,3,4-Tetrafluoro-9-isopropyltriptycene (Ia) at 183.5° (60 MHz)



same as the equilibrium composition established at high temperature. The fact that the chemical shift difference between the peaks that we assign to be the anti and skew conformers remained the same in both the high and room temperature scans lends further strength to our interpretation of the nmr spectrum of Ia.

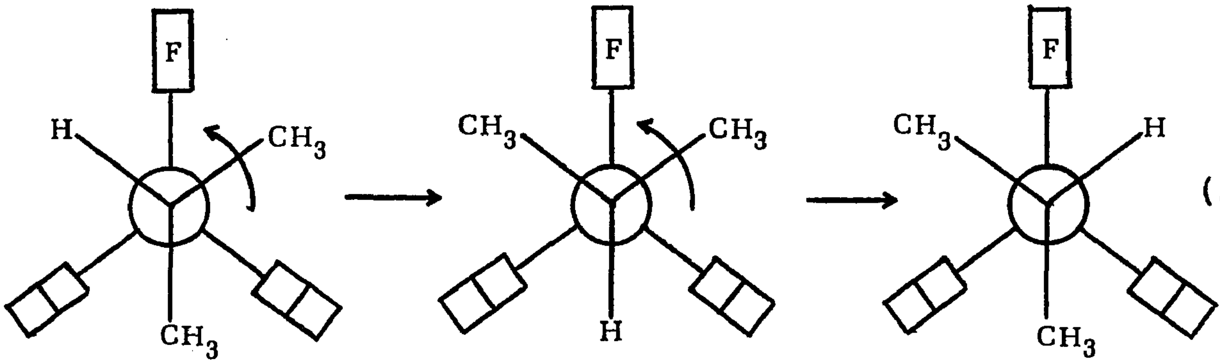
The variable temperature nmr spectra of compound Ia also give further insight into the direction of rotation of the isopropyl group for all of the isopropyl triptycenes investigated. The fact that we still observed restricted rotation between the skew and anti conformers of Ia at the high temperature limit, as well as the fact that the original spectrum was reproduced upon cooling back down to room temperature, indicates that no conversion between the skew and the anti forms occur during heating.

Theoretically, the skew conformers may interconvert with each other via two rotational modes, one involving the methine hydrogen passing the fluorinated ring (equation 20), and the



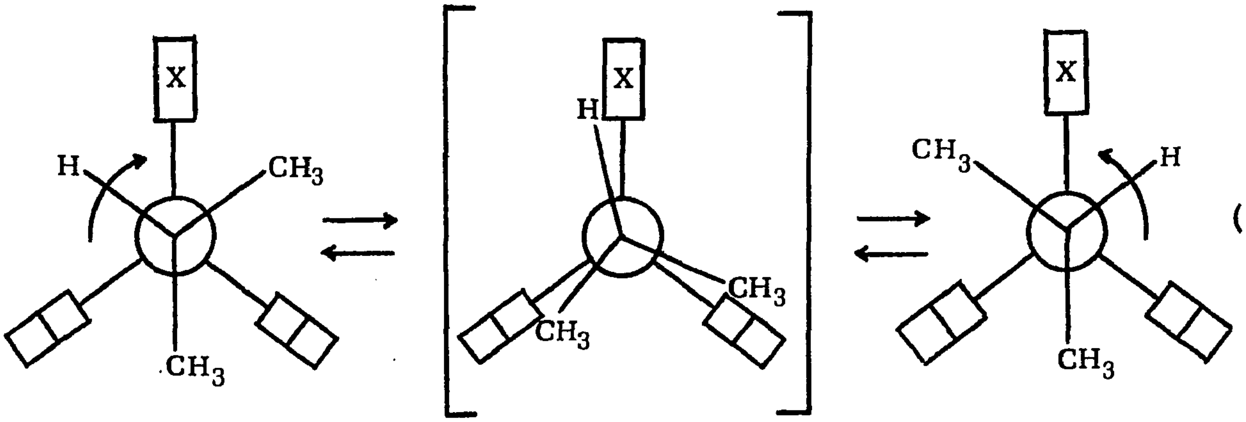
(20)

other involving a 240° rotation in the opposite direction, where the methyl group passes the fluorinated ring (equation 21). However, this latter mode of rotation may now be eliminated since it initially involves the same rotation as necessary for the interconversion of the skew and anti conformers, a rotation which can be ruled out on the basis of the variable temperature nmr spectra of Ia.



(21)

If there is no rotation of the methyl group past the fluorine in compound Ia, then the analogous rotation for the corresponding chloro and bromotriptycenes would likewise not occur since chloro--methyl and bromo--methyl interactions would certainly involve greater steric hindrance than a fluoro--methyl interaction. In view of the nmr data for compound Ia, a more general statement can be made: the isopropyl groups of all the halogenated triptycenes studied rotate with a to and fro motion (equation 22) which alone leads to the direct interconversion of the skew conformers.



(22)

We were not able to obtain the $\Delta G^{\ddagger}$ for compound Ia by means of a complete line shape analysis. Difficulty was encountered in attempting to generate matching theoretical line shapes. In contrast to compounds Ib, c, f and g, where the isopropyl methyl hydrogens very clearly changed from two distinct doublets to a triplet, then to a broad hump indicative of coalescence, and finally to a single doublet, the changes in Ia were much more nondescript. It was thus impossible to match the calculated and experimental spectra with any degree of accuracy. The overlapping doublet of the anti conformer also contributed significantly to our difficulties in attempting to match spectra. We therefore had to apply an alternate method for the calculation of $\Delta G^{\ddagger}$ for compound Ia. The same method was likewise applied to compounds Ib, c, f and g in order to be able to reliably compare the rotational barriers of all five triptycenes under investigation. The procedure of choice was to make use of an approximation equation (coalescence equation) (equation 23) developed by H. S. Gutowsky and C. H. Holm[45] for the determination of the rate constant (k_c) at the coalescence point.

$$k_c = \frac{\pi \Delta \nu}{2^{\frac{1}{2}}} \tag{23}$$

The $\Delta \nu$ of equation 23 represents the difference in chemical shift between the exchanging sites at slow exchange. This parameter can be obtained for all five triptycenes (Ia, b, c, f and g) from their respective room temperature nmr spectra. From the k_c value, $\Delta G^{\ddagger}$ can be calculated at the coalescence temperature, using the Eyring equation in the following form (equation 24): The approximation equation has been utilized

$$\Delta G^{\ddagger} = -RT\ 2.303 \log \left[\frac{h\ k_c}{k_B Tc} \right] \tag{24}$$

$h = 6.626 \times 10^{-27}$ erg sec (Planck's constant)
$k_B = 1.380 \times 10^{-16}$ erg deg^{-1} (Boltzmann's constant)

for the calculation of $\Delta G^{\ddagger}$ for the coalescence of singlets associated with uncoupled diastereotopic atoms or groups.[46] M. Raban, D. Kost and E. Carlson[42] have shown that this equation is likewise applicable to systems containing an equally intense pair of doublets coalescing into a single doublet, which is the case for our series of compounds. These authors attempted to determine the general validity of the approximation equation by carrying out a systematic comparison of rate constants obtained by the coalescence equation (equation 23) with those obtained from line shape analyses. They found that the values of k_c obtained by the approximation equation for both equally intense coalescing singlets or doublets were within 20% of the rate constants obtained from complete line shape analyses. The authors also pointed out that an error of 25% in k_c translates into an error in $\Delta G^{\ddagger}$ of only 0.1 kcal/mole at approximately 300°K. Such an error is considered quite tolerable, and therefore, the use of the approximation equation around 300°K is perfectly acceptable. Since we are dealing with considerably higher coalescence temperatures (>400°K), it was necessary to test the reliability of the coalescence equation for the calculation of $\Delta G^{\ddagger}$ for compounds Ib, c, f and g. The $\Delta G^{\ddagger}$ values obtained by the coalescence equation were compared with the previously determined values based upon a line shape analysis (Table VII). The agreement between the $\Delta G^{\ddagger}$ values calculated by both methods appears to be quite good, thus giving credibility to the approximation method for these four triptycenes. A sample calculation of $\Delta G^{\ddagger}$ using the coalescence equation is given in

Table VII. Comparison of $\Delta G^{\ddagger}$ Values for Compounds Ib,c,f and g, Calculated by a Line Shape Analysis and by the Coalescence Equation

	$\Delta G^{\ddagger}$ from line shape analysis (kcal/mole)	$\Delta G^{\ddagger}$ from coalescence eq. (kcal/mole)
Ib	23.9	23.2
Ic	23.6	23.3
If	23.3	22.7
Ig	22.5	22.1

Fig. XIX for compound Ic.

Fig. XIX Sample Calculation of $\Delta G^{\ddagger}$ via the Coalescence Equation for Compound Ic

$Tc = 446.5^{\circ}K$ (coalescence temperature)

$$\Delta \nu = 9.55 \text{ Hz}$$

$$k_c = \frac{\pi \Delta \nu}{2^{\frac{1}{2}}} = \frac{\pi (9.55)}{2^{\frac{1}{2}}} = 21.216$$

$$\Delta G^{\ddagger} = -RT\ 2.303 \log \left[\frac{h\ k_c}{k_B Tc} \right]$$

$$\Delta G^{\ddagger} = -8.134 \times 10^{7}\ (446.5)\ 2.303 \log \left[\frac{6.626 \times 10^{-27} \times 21.216}{1.380 \times 10^{-16} \times 446.5} \right]$$

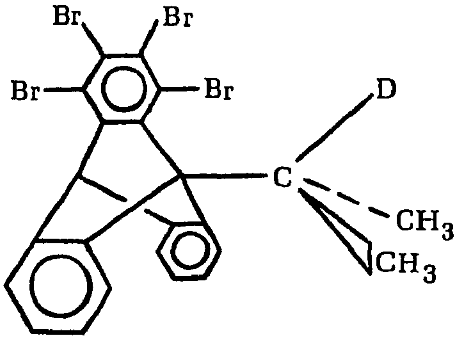
$$\Delta G^{\ddagger} = 97{,}373 \times 10^{7} \times \text{cal}/4.184 \text{ erg} = 23.3 \text{ kcal/mole}$$

Such a check was not possible for compound Ia, since we were not able to calculate $\Delta G^{\ddagger}$ by a line shape analysis. However, an estimate of the error involved in the $\Delta G^{\ddagger}$ of Ia calculated by the approximation equation could be obtained by taking into account (1) the ± 20% error in k_c reported by

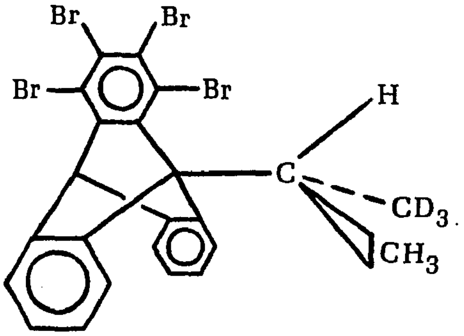
Raban and coworkers and (2) a ± 10° error in the determination of the coalescence temperature. An energy barrier of 22.8 kcal/mole was found for compound Ia following the mathematical format of Fig. XIX. The recalculation of $\Delta G^{\ddagger}$ while assuming a ± 20% error in k_c, resulted in an error of ± 0.15 kcal/mole at the coalescence temperature of Ia. It was more difficult, compared to compounds Ib, c, f and g, to ascertain which experimental high temperature spectrum of Ia corresponded to coalescence. In this case, the resonances for the non-equivalent methyl hydrogens over a 20° temperature range were quite broad until one was obviously past the coalescence point, as evidenced by the appearance of a new doublet for the rapidly exchanging skew conformers. As a result, an error of as much as ± 10° in the coalescence temperature was used, for which an error in $\Delta G^{\ddagger}$ of ± 0.55 kcal/mole was computed. The total error in $\Delta G^{\ddagger}$ from the ± 20% error in k_c and the ± 10° error in the coalescence temperature was thus ± 0.70 kcal/mole.

A similar error analysis of the $\Delta G^{\ddagger}$ values of Ib, c, f and g, based upon the coalescence equation, assuming a ± 20% error in k_c and a ± 1° error in temperature (This temperature error is due only to the ability to measure the temperature of the nmr sample since the assessment of the coalescence point for compounds Ib, c, f and g was far less ambiguous than for compound Ia.) indicated that the total error for Ib, c, f and g, respectively was: ± 0.20, ± 0.25, ± 0.20, ± 0.20 kcal/mole. Therefore, the value of 22.8 ± 0.70 kcal/mole for compound Ia, is equal within experimental error, to those of the $\Delta G^{\ddagger}$ values for Ib, c, f and g. This result of essentially equal rotational barriers for the fluoro, chloro, and bromotriptycenes suggests that the major interaction responsible for the overall barrier is <u>not</u> the one involving the isopropyl methine hydrogen and the halogenated phenyl ring, but instead is the one that involves the two isopropyl methyl groups and an unhalogenated ring (see pgs. 61-62).

Finally, we have measured the rotational barriers of compounds Ii and Ij. The purpose of investigating these compounds,



Ii



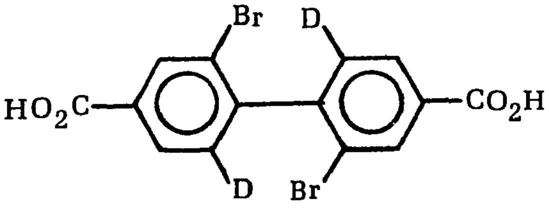
Ij

in light of our initial experimental results, was two-fold: (1) due to the rather large barriers found for compounds Ib, c, f and g, we felt that Ii and Ij would be ideal for studying steric isotope effects. Specifically, we wished to demonstrate the existence of a steric isotope effect on rotational barriers between two sp^3 hybridized carbon atoms. (2) a comparison of the rotational barriers of Ii and Ij with those of the corresponding undeuterated compound (Ic) might help to assess which interaction in the rotational transition state of these triptycenes is of the highest energy and therefore contributes the most to the overall rotational barrier.

L. S. Bartell[47] proposed in 1961 that secondary isotope effects may be manifestations of the steric difference between a hydrogen and a deuterium atom. The principle behind this difference in size lies in the fact that the amplitudes of vibration of a bonded hydrogen atom are larger than the vibrational amplitude of a heavier deuterium atom. The anharmonicity of these vibrations results in a longer C-H bond length compared to the C-D bond. As a consequence of the longer C-H bond, the degree of non-bonded interactions is expected to be greater for a hydrogen atom than a deuterium atom. Thus, for a transition state which is rather severely crowded compared to the ground state situation, the origin of an observed secondary isotope effect could be steric in nature. Such a steric isotope effect is expected to be an inverse one, i.e., $k_H/k_D < 1$.

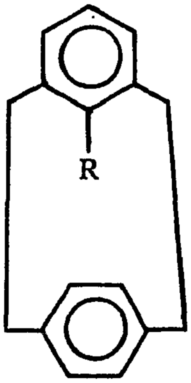
The rate of racemization of optically active biphenyl derivatives have been used to demonstrate the effect of differences in size between hydrogen and deuterium, since the rate of such a process is predominantly determined by steric factors. As an example of the observance of a steric isotope effect within the biphenyl system, L. Melander and R. Carter[48] measured the rate of racemization of compound XLVII and its undeuterated analog. The isotope effect, k_H/k_D, was found to be 0.84.

Recently, V. Boekelheide, S. A. Sherrod, R. L. da Costa and A. Barnes[49] demonstrated the existence of a steric isotope



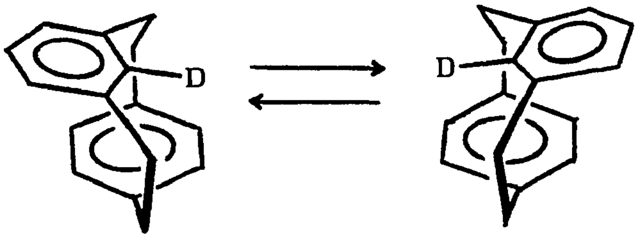
XLVII

effect on the rate of conformational ring flipping in a (2.2)-metaparacyclophane (XLVIII). This ring flipping is illustrated



XLVIIIa, R=H
XLVIIIb, R=D

in equation 25, where the R group (H or D) impinges on the π

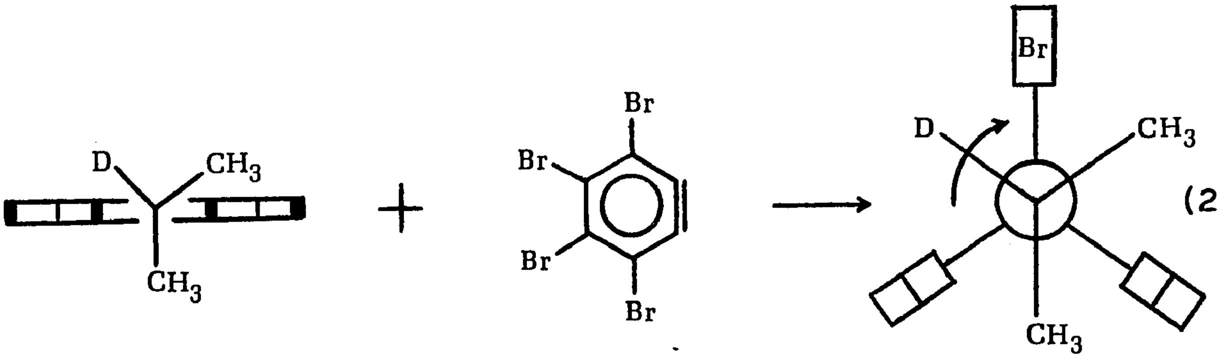


(25)

cloud of the para-bridged ring. The authors felt that the severe crowding for R=H in the transition state for ring flipping, as evidenced by a barrier of approximately 20 kcal/mole,[50] should result in the observance of a steric isotope effect upon replacing the hydrogen with deuterium. An inverse isotope effect ($k_H/k_D = 0.83$) was found, indicative of its steric origin.

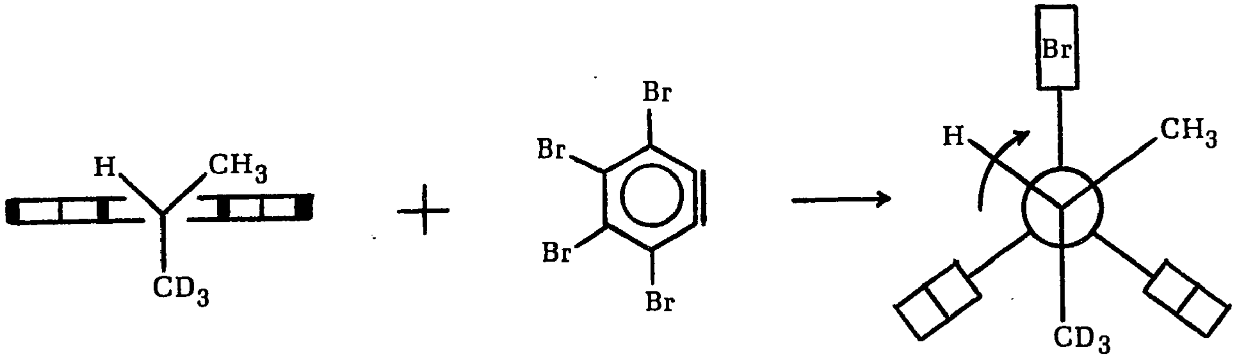
In order to understand how the rotational barriers of Ii and Ij, in relation to Ic, may aid in determining which is the most severe interaction in the rotational transition state, we refer to equations 26 and 27. The conformations shown, Ii', Ij' and Ij'', are those expected on the basis of the same steric control of the entering benzyne as in the synthesis of the corresponding undeuterated triptycene, Ic. The curved arrows indicate the direction of rotation (See pgs. 67-69 for a discussion of the rotational mode of the isopropyl group.) of the deuterated isopropyl group. It can be seen that for compound Ii, the rotational transition state will involve a deuterium passing the brominated phenyl ring, and in both possible conformations of Ij, the transition state will involve a CD_3 group passing a phenyl ring. Therefore, a comparison of the magnitude of the steric isotope effect for Ii and Ij should indicate whether the H--Br interaction or a CH_3--benzo interaction is larger. For example, if compound Ii would exhibit an isotope effect while Ij would not, this would serve as evidence that the H--Br interaction is larger than the CH_3--benzo interaction.

The room temperature nmr spectra of Ii and Ij in the


D
CH$_3$
CH$_3$
Br
Br
Br
Br
Br
D
CH$_3$
CH$_3$

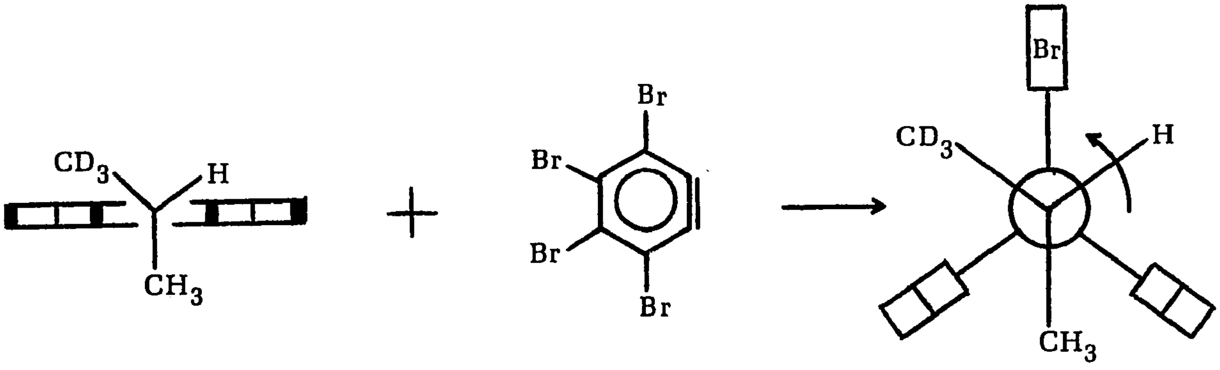
Ii'

(26)


H
CH$_3$
CD$_3$
Br
Br
Br
Br
Br
H
CH$_3$
CD$_3$

Ij'

(27)


CD$_3$
H
CH$_3$
Br
Br
Br
Br
Br
CD$_3$
H
CH$_3$

Ij''

region of the deuterated isopropyl groups was, as one might predict based upon the products shown in equations 26 and 27 and assuming restricted rotation, a doublet and two equal intensity doublets, respectively. The energy barriers for compounds Ii and Ij were obtained by an nmr line shape analysis where the $\Delta G^{\ddagger}$ values were calculated at the coalescence temperature. Table VIII presents these values. (The error analysis here was carried out in the same manner as described for compounds Ib, c, f and g on pages 53-54). These values are within experimental error of the $\Delta G^{\ddagger}$ obtained for compound Ic. The method of nmr line shape analysis is therefore not sensitive enough to make the kind of subtle distinctions necessary for the detection of a steric isotope effect on rotational energy barriers.

Table VIII. $\Delta G^{\ddagger}$ Values from Line Shape Analysis of Ic, Ii and Ij

	$\Delta G^{\ddagger}$ (kcal/mole)	Tc °K (coalescence temp.)
Ic	23.3 ± 0.70	446.5
Ii	22.9 ± 0.75	445.4
Ij	23.4 ± 0.85	444.8

A more precise method for obtaining rates of exchange may be applicable, namely the use of a double irradiation nmr technique developed by S. Försen and R. A. Hoffman.[51] This method was employed by V. Boekelheide and coworkers in their steric isotope study of the metaparacyclophanes XLVIa and XLVIb, after an analysis based upon the coalescence of the

AA'XX' pattern for the protons of the para-bridged ring showed no distinction in the rate of ring flipping between the deuterated and undeuterated analog.[49] The technique as applied to compounds Ii and Ij would require recording a spectrum in the isopropyl methyl region of one of the exchanging sites while double-irradiating the other exchanging site and vice versa. Obviously, such a method can only apply to uncoupled, non-overlapping signals. Its success in our case would depend upon the ability to selectively double-irradiate one methyl group apart from the other. The difference in chemical shifts between the exchanging methyl groups of compounds Ii and Ij are 9.8 Hz and 9.5 Hz, respectively. In contrast, the difference in chemical shifts in Boekelheide's work was 100 Hz. The applicability of this method to Ii and Ij should be investigated in the future.

From our results on the deuterated triptycenes (Ii and Ij) we cannot make any conclusions regarding the magnitude of the H--Br and CH_3--benzo interactions. However, based upon the equality of the rotational barriers within series I (Table VII, pg. 72; pg. 73), we conclude that the CH_3--benzo interaction is the predominant one.

III Experimental

All room temperature nmr spectra (except where noted) were recorded on a JEOL JNM-MH-100 spectrometer and all variable temperature nmr spectra (except where noted) were recorded on a JEOL C-60 HL spectrometer. An nmr spectrum of 1,2,3,4-tetrafluoro-5,12-dihydro-5,12-ethenonaphthacene (XLII) was recorded on a Varian HR-220 MHz instrument at Rockefeller Institute, New York, N.Y. Infrared spectra were recorded on a Beckman IR-20A spectrophotometer. Mass spectra were determined on a Varian CH5 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.

Triptycenes Ia, b, c, f and g all appeared as a single spot in the following tlc systems: alumina, benzene; silica gel, benzene; alumina, 1:1 benzene/hexane; and silica gel, 1:1 benzene/hexane.

Boiling points are uncorrected and melting points are corrected.

(A) Preparation of 9-Substituted Anthracenes

(1) Preparation of 9-Isopropylanthracene (XV)

Into a 500-ml. three-necked flask fitted with a condenser containing a drying tube, a pressure-equalizing addition funnel, and a magnetic stirrer, was placed 100 ml. of 3.1 M isopropyl magnesium chloride in ether. A solution of 19.4 g. (0.10 mole) of anthrone in 235 ml. of warm benzene was added dropwise over a period of 30 min. The reaction mixture was allowed to reflux overnight, after which it was carefully poured into a mixture of 200 ml. of concd. HCl and 600 ml. of ice. The aqueous layer was extracted once with 100 ml. of ether. The organic layers were combined and washed twice with 600-ml. portions of H_2O, dried over $MgSO_4$, and evaporated under reduced pressure to yield 18.21 g. of crude product. Nmr analysis indicated the presence of approximately 28% anthrone. The 9-isopropylanthracene (XV) was separated from most of the anthrone by washing the crude product with 75 ml. of ether, and cooling the wash liquid to approximately -10° in order to precipitate some of the anthrone that had dissolved. The anthrone was filtered off and the filtrate was evaporated under reduced pressure to yield a crude product containing approximately 11% anthrone (by nmr analysis). Further purification was achieved by column chromatography on 800 g. of alumina using benzene as the eluent. Recrystallization from methanol yielded 5.85 g. (27%) of white fluffy crystals (XV); m.p. 72.5-74° (lit.[52] m.p. 75-76°); nmr ($CDCl_3$) δ 1.75 (d, J 8 Hz, 6H, CH_3) 4.62 (septet J 8 Hz, 1H, methine-H), 7.26-8.63 (complex pattern, 9H, aryl-H); ir (KBr) 1380, 1360 cm.$^{-1}$ (CH_3).

There was considerable difficulty in trying to obtain a second crop in that, upon reheating the mother liquor, a small amount of an insoluble material would remain which could not be readily identified by nmr spectroscopy. The mixture was filtered hot and allowed to cool. This resulted in an oiling-out of material rather than crystallization. Attempts to re-dissolve the oil in additional hot solvent resulted in the formation of more insoluble material. This sequence of events kept repeating itself. Finally a second crop was forced out of the hot solution by rapid cooling. It weighed 1.05 g.; m.p. 70-71°.

(2) Preparation of 9-(2-d-2-propyl)anthracene (XVI)

(a) Preparation of Isopropanol-2-d (XVIII)

Into a 250-ml. one-necked flask containing a magnetic stirrer, fitted with a three-way adapter which was equipped with two condensers in series (cooled by circulating ethanol at 0°) topped by a drying tube, and a pressure-equalizing addition funnel, was placed 50 ml. of anhydrous ether, to which 4.2 g. (0.10 mole) of $LiAlD_4$ was added in small portions while the flask was cooled in an ice bath. A solution of 11.6 g. (0.20 mole) of acetone in 15 ml. of anhydrous ether was added dropwise over a period of 3 hr. and 40 min. The addition was carried out at room temp. at such a rate that refluxing was maintained throughout. After the addition was complete, the reaction mixture was allowed to stir at room temp. for an additional 15 min., followed by a reflux period of 1 hr. The contents of the flask were evaporated to dryness, first under reduced pressure using a water aspirator (a drying tube was interposed between the aspirator and the flask) and finally at 9 mm. using a vacuum pump.

The hydrolysis of the solid residue was carried out under a N_2 atmosphere in an ice-salt bath, by the slow dropwise addition of 50 ml. of H_2O followed by 40 ml. of concd. HCl. The hydrolysed reaction mixture was distilled through a vigreux column, whereupon the product (XVIII), containing 13% by weight of H_2O (by nmr analysis), was collected; b.p. 79.5-80°. Correcting for the presence of H_2O, the weight of product was 9.6 g. (83%).

(b) Preparation of Isopropyl Chloride-2-d (XIX)

Anhydrous $ZnCl_2$ (108 g., 0.080 mole) and 48 ml. (0.575 mole) of concd. HCl were placed in a 250-ml. one-necked flask containing a magnetic stirrer. The flask was immersed in an ice-H_2O bath and stirred until almost all the $ZnCl_2$ had dissolved, at which time 11.0 g. of isopropanol-2-d (XVIII), containing 13% H_2O (0.157 mole of XVIII), was added, and the flask was fitted for simple distillation. The flask was immersed in an oil bath at a temp. of 78° whereupon the reaction mixture became cloudy. Shortly after, distillation began. The product (XIX) was collected in a dry-ice acetone cooled receiver, as a single fraction b.p. 32-35°, over a period of 45 min. During this time the oil bath temp. was gradually raised to 98°. The distillate was washed once with an equal volume of cold H_2O and dried over K_2CO_3 for approximately 30 min. in the freezer. The clear colorless liquid was pipeted away from the drying agent to yield 9.61 g. (78%) of XIX; mass spec., m/e (rel. intensity using linear mass scan) 79, 81 (16.8, 5.5), 64, 66 (21.8, 7.5), 44 (100). A comparison of the P-1 to P peaks of C_3H_6DCl with the P-1 to P peaks of C_3H_7Cl yielded the following respective ratios: 78/79 = 0.0244, 77/78 = 0.0252, which allowed us to conclude that there was no detectable amount of C_3H_7Cl in C_3H_6DCl, within experimental error.

(c) Preparation of 9-(2-d-2-propyl)anthracene (XVI)

The following reaction was conducted under a N_2 atmosphere. Into a 500-ml. three-necked flask fitted with a pressure-equalizing addition funnel, two condensers connected in series (cooled by circulating ethanol at 0°) and a magnetic stirrer were placed 2.83 g. (0.118 mole) of Mg and 30 ml. of anhydrous ether. A small crystal of iodine was added to the flask. The resulting brown solution was decolorized in approximately 10 min., after which one ml. of a solution of 9.34 g. (0.118 mole) of isopropyl chloride-2-d (XIX) in 15 ml. of anhydrous ether was added. After 5 min. another 1-ml. portion of the isopropyl chloride solution was added. The reaction mixture began to reflux gently. The remainder of the isopropyl chloride solution was added dropwise over a period of 1 hr. and 10 min. The rate of addition was such that refluxing was maintained throughout, without external heating. The reaction mixture was refluxed for an additional 1 hr., after which a solution of 5.82 g. (0.0265 mole) of anthrone in 175 ml. of benzene was added dropwise, at room temp. over a period of 7 hr. The reaction mixture was allowed to reflux overnight, after which it was carefully poured into a mixture of 60 ml. of concd. HCl and 300 ml. of ice. The aqueous layer was extracted with 200 ml. of ether. The combined organic layers were washed with 200 ml. of H_2O, dried over $MgSO_4$, and evaporated under reduced pressure to yield 6.47 g. of crude product. Purification was achieved by column chromatography on 600 g. of alumina using benzene as the eluent, to yield 3.76 g. of a lemon-colored solid. This solid was dissolved in 75 ml. of hot methanol and filtered to remove a small amount of insoluble material. Upon cooling the filtrate, a small amount of an off-white solid deposited which was identified by nmr and ir spectroscopy as anthracene. During the suction filtration of the anthracene, some white fluffy crystals precipitated from the filtrate. This material corresponded to 1.42 g. of product (XVI); m.p. 70-71°. The mother liquor was evaporated to dryness to obtain an additional 1.42 g. of XVI; m.p. 68-71°. Both solids had identical nmr spectra and were combined. Total yield 43%; nmr ($CDCl_3$) δ 1.74 (s, CH_3), 7.18-8.54 (complex pattern, aryl-H); mass spec., m/e (rel. intensity using linear mass scan)221 (59.5), 206 (100). It was found by a comparison of the P-1 to P ratios in XVI and XV (the undeuterated 9-isopropylanthracene) that the product consisted of 99% d_1 and 1% of the d_0 species.

(3) Preparation of 9-(1,1,1-trideuterio-2-propyl)-anthracene (XVII)

(a) Preparation of 1,1,1-Trideuterio-2-propanol (XX)

The following reaction was conducted under a N_2 atmosphere. Into a 1-l. one-necked flask containing a magnetic stirrer and fitted with a three-way adapter which was equipped with a pressure-equalizing addition funnel and two condensers connected in series (cooled by circulating ethanol at 0°) were placed 8.3 g. (0.35 mole) of Mg and 100 ml. of anhydrous ether. A solution of 33.0 g. (0.227 mole) of CD_3I (Norell Chem. Co., Inc., Landisville, N.J., 90% CD_3I, 10% CD_2HI by mass spec.) in 30 ml. of anhydrous ether was added over a period of 4 hr. and 36 min. Throughout the addition, refluxing was maintained without any external heating. The reaction mixture was refluxed in a hot H_2O bath for an additional 1 hr. after which the flask was immersed in ice, and a solution of 10.4 g. (0.227 mole) of acetaldehyde in 40 ml. of anhydrous ether was added dropwise over a period of 2 hr. The reaction mixture was stirred at room temp. for 10 min., followed by 2 hr. at reflux and evaporated to dryness, first under reduced pressure using a water aspirator (a drying tube was interposed between the aspirator and the flask) and finally at approximately 9 mm. using a vacuum pump for 13 hr. The solid residue was hydrolysed by the dropwise addition of 50 ml. of H_2O followed by 45 ml. of concd. HCl with cooling in an ice bath. The pH of the solution was adjusted to 7 by the addition, in small portions, of solid $NaHCO_3$, after which the flask was fitted for distillation through a vigreux column. The product (XX), was collected at a constant boiling temp. of 80° and contained approximately 13% by weight of H_2O accordin to nmr analysis. Correcting for the presence of H_2O, the weight of product was 9.26 g. (67%).

(b) Preparation of 1,1,1-Trideuterio-2-chloropropane (XXII)

The same apparatus and experimental procedure as that described in the preparation of isopropyl chloride-2-d (XIX) were used. A mixture of 10.64 g. of 1,1,1-trideuterio-2-propanol (XX) containing 13% H_2O (0.147 mole of XX) 101 g. (0.750 mole) of anhydrous $ZnCl_2$ and 45 ml. (0.536 mole) of concd. HCl was distilled over a boiling point range of 31.5-34.5°. After washing once with cold H_2O and drying over K_2CO_3, the yield of product (XXII) was 8.24 g. (68%). Due to faulty instrumental operation, the sample of XXII set aside for mass spectral analysis was lost.

(c) Preparation of 9-(1,1,1-Trideuterio-2-propyl)anthracene (XVII)

The same apparatus and experimental procedure as that described in the preparation of 9-(2-d-2-propyl)anthracene (XVI) were used. A solution of 8.20 g. (0.101 mole) of 1,1,1-trideuterio-2-chloropropane (XXII) in 15 ml. of anhydrous ether was added dropwise over a period of 1 hr. and 10 min. to a mixture of 2.42 g. (0.101 g.-atom) of Mg in 25 ml. of anhydrous ether. A solution of 4.93 g. (0.0254 mole) of anthrone in 100 ml. of benzene was added dropwise to the grignard reagent over a period of 4 hr. and 35 min. After hydrolysis, the yield of crude product was 5.42 g. Purification by column chromatography on approximately 330 g. of alumina, using benzene as the eluent, yielded 3.12 g. of a lemon-colored solid. This solid was dissolved in 25 ml. of hot methanol and filtered to remove a small amount of insoluble material which was identified by nmr spectroscopy as predominantly anthracene and a small amount of the desired deuterated 9-isopropylanthracene (XVII). Upon allowing the filtrate to cool, a small amount of solid deposited which was identified as anthracene by ir spectroscopy. (Not enough material was present for an nmr spectrum). During the suction filtration to remove this anthracene, white fluffy crystals precipitated from the filtrate. This material corresponded to 803 mg. of product (XVII); m.p. 69-70°; nmr ($CDCl_3$) δ 1.75 (d, J 6 Hz, CH_3), 4.57 (septet, J 6 Hz, methine-H), 7.22-8.58 (complex pattern, aryl-H); mass spec., m/e (rel. intensity using linear mass scan) 223 (89.8), 208 (80), 205 (100). It was found by a comparison of the P-1 to P ratios in XVII and XV (the undeuterated 9-isopropylanthracene) that the product consisted of 86% d_3 and 14% of the d_2 species. The mother liquor was reheated and filtered while hot, to remove some turbidity. Upon cooling in ice, a second crop of white crystals was obtained weighing 334 mg; m.p. 70.5-71°. The first and second crops were combined for a total yield of 21%.

(B) Preparation of Anthranilic Acids

(1) Preparation of Tetrabromoanthranilic Acid (XXIII)

A mixture of 178 g. (0.380 mole) of tetrabromophthalic anhydride and 500 ml. of dimethyl sulfoxide was placed in a beaker containing a magnetic stirrer and was stirred for 10 min. at room temp. A white slurry resulted which became a clear solution upon the addition of 81 ml. of concd. NH_4OH solution. The reaction mixture was stirred for 10 min. and a solution of 15.38 g. (0.385 mole) of NaOH in 20 ml. of H_2O was added. Stirring was continued for an additional 30 min. whereupon a solution of 800 ml. of $CHCl_3$ and 360 ml. of 95% ethanol was slowly poured into the reaction beaker. A white solid precipitated which was filtered off, washed with 116 ml. of the filtrate and air dried. The solid was partially dissolved in 500 ml. of H_2O in a 5-l. flask containing a magnetic stirrer. A solution containing 50.0 g. (1.25 moles) of NaOH, 67 g. (0.83 mole) of bromine and 550 ml. of H_2O was added in small portions, with cooling in an ice bath. An additional 140 g. (3.50 moles) of NaOH in 1-l. of H_2O was added and the reaction mixture was heated in an oil bath at a temp. of 120° for 24 hr., resulting in a bright orange solution. Upon cooling to room temp. a tan solid deposited which was filtered off and washed with concd. NaOH solution. This solid was identified by ir spectroscopy as the Na salt of tetrabromoanthranilic acid (XLIX); ir (KBr) 3440, 3340 (NH_2), 1550 $cm.^{-1}$ (COO^-). The salt was dissolved in 750 ml. of hot H_2O and the resulting solution was acidified with 300 ml. of 20% HCl, whereupon an off-white solid precipitated. The solid was filtered off, washed with 5 l. of H_2O and dried under vacuum to yield 50.5 g. of crude product. Recrystallization from 1.2:1 H_2O-ethanol yielded 46.16 g. (27%) (Additional material may be obtained from the mother liquor.) of product (XXIII); m.p. 208-210° (lit.[53] m.p. 205°); ir (KBr) 3460, 3350 (NH_2), 1670 (COOH) 1585 $cm.^{-1}$ (NH_2).

(2) Preparation of Tetraiodoanthranilic Acid (XXIV)

Tetraiodophthalic anhydride (16.29 g., 0.025 mole) was dissolved in 100 ml. of dimethyl formamide at room temp., and the resulting solution was cooled to 5° in an ice bath. Concd. NH_4OH solution (5.2 ml., 0.081 mole) was added dropwise over a period of 2 min. resulting in a temp. rise from 5 to 13°. A solution of 6.5 ml. H_2SO_4 (0.12 mole) in 200 ml. of H_2O was then added causing the temp. of the reaction mixture to reach 30°. Within minutes a pale yellow solid precipitated which was filtered off, and without delay, was partially dissolved in a solution of 1.1 g. (0.0275 mole) of NaOH in 100 ml. of H_2O. A NaOBr solution (prepared in advance and kept in ice to be used cold) consisting of 5.6 g. (0.035 mole) of bromine, 3.3 g. (0.0825 mole) of NaOH and 100 ml. of H_2O was added, rapidly, with cooling in an ice bath. An additional 100 ml. of H_2O was added and the slightly turbid reaction mixture was stirred at room temp. for 75 min. Within 15 minutes a considerable amount of yellow solid had precipitated. The reaction mixture was stirred for an additional 75 min. at an oil bath temp. of approximately 80°, after which the yellow solid was filtered off, washed with H_2O, and air dried to yield 13.70 g. of the Na salt of the desired anthranilic acid (L); ir (KBr) 3320 (NH_2), 1550 $cm.^{-1}$ (COO^-).

The salt was dispersed in 700 ml. of H_2O, and the resulting fine suspension was acidified to pH 1 with 10 ml. of concd. HCl, whereupon a yellow solid precipitated. The solid was filtered off, washed with H_2O and dried under vacuum to yield 11.5 g. of crude product. Recrystallization from 350 ml. of 95% ethanol yielded 10.9 g. (68%) of yellow crystals (XXIV); m.p. 206-208° (lit.[54] 211°, dec.); ir (KBr) 3450, 3350, (NH_2), 1685 (COOH), 1605 $cm.^{-1}$ (NH_2).

(3) Preparation of 3,6-Dibromoanthranilic Acid (XXVII)

(a) Preparation of 3,6-Dibromophthalic Anhydride (XXVIII)

A mixture of 200 g. (1.36 mole) of phthalic anydride and 611 g. of 60% fuming H_2SO_4 was placed in a 2-l. three-necked flask fitted with a mechanical stirrer (glass paddle), a pressure-equalizing addition funnel containing a drying tube, and a thermometer. The 60% fuming H_2SO_4 was prepared by the dropwise addition of 900 g. (1.12 moles)of Sulfan (B & A, Morristown, N.J.) to 1,500 g. (1.52 moles) of H_2SO_4 over a period of two hr. The mixture was heated to 55°. During this heating period, 1.0 g. (0.0039 mole) of iodine was added. Once the desired temp. was reached, 260 g. (1.62 moles) of bromine was added dropwise. Throughout the addition of the bromine, the temp. inside the flask was maintained at 55° by the use of a thermowatch (I^2R, Cheltenham, Penn.). The addition was complete in 1 hr. and 46 min., after which the reaction mixture was allowed to reflux until it appeared as if there were very little bromine left in the flask (as evidenced by the cessation of reflux). This required approximately three days. The temp. inside the flask was then gradually raised to 200° over a period of 36 hr. and kept at this temp. for 3 hr. The final reaction mixture was a dark red liquid which upon cooling overnight solidified into a tan paste. The paste was transferred in small portions into a large bucket containing 6 l. of ice. A white solid resulted which was filtered off, washed with 26 l. of H_2O and dried under vacuum to yield 63.23 g. of crude product.

Two recrystallizations from acetic acid yielded long white crystals which were dried in a vacuum dessicator over NaOH pellets for 24 hr. The yield of this first crop was 22.18 g. (XXVIII); m.p. 210-213° (lit.[55] m.p. 208-210°). Second crops from both recrystallizations were obtained and combined to yield an additional 8.10 g. of product; m.p. 207-209°. The total combined yield was 7.3%; nmr (acetone) δ 8.15 (s, aryl-H); ir (KBr) 1845, 1750, $cm.^{-1}$ (anhydride).

(b) Preparation of Ammonium 3,6-Dibromophthalamate (XXXI)

Gaseous NH_3 was slowly bubbled through a saturated solution of 11.52 g. (0.0378 mole) of 3,6-dibromophthalic anhydride (XXVIII) in 60 ml. of dimethyl formamide, contained in a 250-ml. three-necked flask fitted with a thermometer, a KOH drying tube, a sintered glass gas inlet tube, and a magnetic stirrer. Upon bubbling the NH_3 into the flask, there was an initial temp. rise from 28 to 46° within approximately 5 min. Shortly after, a white precipitate formed. The NH_3 was bubbled through for a total of 2 hr. The final reaction mixture, which only contained a small amount of solid, was poured into 300 ml. of benzene. Additional white solid precipitated. The solid was filtered off, washed with two 50-ml. portions of benzene, and dried under vacuum to yield 8.37 g. of product (XXXI); m.p. $275-277^{\circ}$. Various repetitions of essentially this same procedure resulted in yields as low as 65% and as high as 100%; ir (KBr) 3080 (broad, N-H), 1600 ($CONH_2$), 1425, 1380, 1340 $cm.^{-1}$ (NH_4^+, COO^-).

(c) Preparation of 3,6-Dibromoanthranilic Acid (XXVII)

The following solutions were prepared in advance and kept in ice to be used cold: (1) 3.1 g. (0.077 mole) of NaOH in 420 ml. of H_2O; (2) NaOBr solution, containing 11.2 g. (0.070 mole) of bromine and 8.4 g. (0.21 mole) of NaOH in 280 ml. of H_2O. All of the operations to be described were carried out with cooling in an ice bath.

A saturated solution of 23.8 g. (0.070 mole) of ammonium 3,6-dibromophthalamate (XXXI) in 80 ml. of H_2O was prepared in a beaker. A few pieces of ice were added followed by 14 ml. (0.70 mole) of concd. HCl. A white paste formed immediately leaving only a small amount of liquid which was decanted off. The paste was washed three times with 21-ml. portions of H_2O. Immediately after these washings, the paste was dissolved in the NaOH solution mentioned above with vigorous manual stirring. The NaOBr solution was quickly added, in small portions, until the reaction mixture became slightly yellow and gave a positive test towards starch-iodide paper. Approximately 150 ml. of NaOBr solution, out of a total of 290 ml., was required to reach this end-point. The reaction mixture was heated for 1 hr., during which time the oil bath temp. rose from 51 to 84°. The flask was cooled to room temp., and the solution was brought to pH 1 by the addition of 10 ml. of concd. HCl. A light beige, fluffy solid precipitated, which was filtered off, washed with one 100-ml. portion of H_2O, followed by two 50-ml. portions of H_2O, and dried under vacuum to yield 3.95 g. of crude product. The filtrate from the crude product was extracted three times with 200-ml. portions of ether and the combined ether extracts were washed once with 200 ml. of H_2O. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure to yield 2.50 g. of a light beige solid. Based upon identical ir spectra, the two solids were combined and recrystallized from 91 ml. of 4:1 benzene-heptane to yield 4.57 g. of light beige whisker-like crystals (XXVII); m.p. 148-149° (lit.[56] m.p. 146°).

In an attempt to improve this yield, we wished to re-extract the filtrate of the crude product. However, before doing so the pH was checked, and it had increased to approximately six upon standing a few hr. The solution was acidified to pH 3 by the dropwise addition of concd. HCl, and was then extracted with ether as mentioned above. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure to yield 1.88 g. of a light brown solid. Recrystallization from 4:1 benzene-heptane yielded 1.53 g. (total yield 30%; additional material may be obtained from the mother liquors) of pure product (XXVII); m.p. 148-150° ($CDCl_3$) δ 6.37 (broad s, 2 H, NH_2), 7.01 (d, J 10 Hz, 1 H, aryl-H), 7.49 (d, J 10 Hz, 1 H, aryl-H); ir (KBr) 3450, 3340 (NH_2), 1650 cm.$^{-1}$ (COOH), 1580 cm.$^{-1}$ (NH_2).

(4) Preparation of 3,6-Dichloroanthranilic Acid (XXVI)

(a) Preparation of Ammonium 3,6-Dichlorophthalamate (XXX)

The same apparatus and essentially the same experimental procedure as that described for the preparation of ammonium 3,6-dibromophthalamate (XXXI) were used. 3,6-Dichlorophthalic anhydride (10.08 g., 0.047 mole) was dissolved in 35 ml. of dimethyl formamide. The gaseous NH_3 was bubbled in quite vigorously such that after 8 min. the temp. inside the flask rose from 28 to 50°. The final reaction mixture contained a white precipitate, which was filtered off, washed with benzene, and dried under vacuum to yield 11.12 g. (94%) of product

(XXX); m.p. 246-248°; ir (KBr) 3090 (broad, N-H), 1655 ($CONH_2$), 1575 (COO^-), 1425, 1375, 1340 cm.$^{-1}$ (NH_4^+, COO^-).

(b) Preparation of 3,6-Dichloroanthranilic Acid (XXVI)

The following solutions were prepared in advance and kept in ice to be used cold: (1) 1.76 g. (0.0440 mole) of NaOH in 240 ml. of H_2O; (2) NaOBr solution containing 6.4 g. (0.040 mole) of bromine and 4.8 g. (0.12 mole) of NaOH in 180 ml. of H_2O. All of the operations to be described were carried out with cooling in an ice-salt bath.

A mixture of 22 ml. H_2O and 8 ml. (0.096 mole) concd. HCl was placed in a beaker containing a magnetic stirrer. Powdered ammonium 3,6-dichlorophthalamate (XXX) (10.04 g., 0.040 mole) was added over a period of four min. A very thick white paste resulted which was washed twice with 8-ml. portions of H_2O. The washings were decanted off and the white paste was dissolved in the cold NaOH solution mentioned above. The NaOBr solution was immediately added in small portions until the reaction mixture gave a positive test towards starch-iodide paper. Approximately 100 ml. of NaOBr solution, out of a total of 180 ml., was required to reach this end-point. The reaction mixture was stirred for an additional 10 min., after which the solution still gave a positive test towards starch-iodide paper. The reaction mixture was heated for 1 hr. at an oil bath temp. of 65°. The flask was cooled to room temp., and the solution was carefully acidifed to pH 3 by the dropwise addition of concd.

HCl. At this pH, there was no precipitate present. The solution was extracted twice with 200-ml. portions of ether. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure to yield 1.00 g. of a tan solid. The aqueous layer was brought to pH 1 whereupon a solid precipitated. The solid was filtered off, washed twice with H_2O, and taken up into ether. The ether solution was dried over $MgSO_4$ and evaporated under reduced pressure to yield 1.26 g. of a mustard yellow solid. The two solids obtained were combined and recrystallized from 55 ml. of 2:1 benzene-heptane to yield 1.68 g. (28%) (Additional material may be obtained from the mother liquor.) of tan whisker-like crystals (XXVI); m.p. 154-156° (lit.[57] m.p. 148-150°); nmr $CDCl_3$ δ 6.64 (broad s, 2 H, NH_2), 6.76 (d, J 9 Hz, 1 H, aryl-H), 7.32 (d, J 9 Hz, 1 H, aryl-H); ir (KBr) 3490, 3380, (NH_2), 1665 (1680 shoulder) (COOH), 1595 cm.$^{-1}$ (NH_2).

(5) Preparation of Tetrachloroanthranilic Acid (XXV)

(a) Preparation of Ammonium Tetrachlorophthalamate (XXIX)

The same apparatus, except for a 500-ml. three-necked flask, and essentially the same experimental procedure as that described for the preparation of ammonium 3,6-dibromophthalamate (XXXI) were used. The tetrachlorophthalic anhydride (21.9 g., 0.0765 mole) was dissolved to 400 ml. of dimethyl formamide. The gaseous NH_3 was bubbled in quite vigorously such that after 10 min. the temp. inside the flask rose from 26 to 41°. The

NH_3 was bubbled through for 1 hr. The final reaction mixture contained a white precipitate, which was filtered off, washed with benzene and dried under vacuum to yield 24.0 g. (98%) of product (XXIX); m.p. 339-341°; ir (KBr) 3150 (broad, N-H), 1665 ($CONH_2$), 1600 (COO^-), 1395, 1325 $cm.^{-1}$ (NH_4^+, COO^-).

(b) Preparation of Tetrachloroanthranilic Acid (XXV)

The following solutions were prepared in advance and kept in ice to be used cold: (1) 200 ml. of 5% H_2SO_4; (2) 2.2 g. (0.055 mole) of NaOH in 300 ml. of H_2O; (3) NaOBr solution, containing 11.2 g. (0.070 mole) of bromine and 6.6 g. (0.165 mole) of NaOH in 375 ml. of H_2O. All of the operations to be described were carried out with cooling in an ice bath.

Ammonium tetrachlorophthalamate (XXIX) (16.0 g., 0.050 mole) was dissolved in 400 ml. of H_2O. To this solution was added the dilute H_2SO_4 solution mentioned above, which resulted in the formation of a white precipitate. The solid was quickly filtered off, washed twice with H_2O, and allowed to air dry for only 1-2 min. in order to minimize hydrolysis. This solid was then immediately dissolved in the cold NaOH solution mentioned above, quickly followed by the addition, in small portions, of the NaOBr solution until the reaction mixture turned pale yellow and gave a positive test towards starch-iodide paper. Approximately 250 ml. of NaOBr solution, out of a total of 400 ml., was required to reach this end-point. The reaction mixture was stirred with cooling for 70 min., after which it was heated at an oil bath temp. of 65° for 30 min. Upon cooling, a precipitate formed which was removed by filtration. Acidification of the filtrate with concd. HCl caused an off-white solid to precipitate. This slurry was extracted three times with 250-ml. portions of ether. The ether extracts were combined, washed with 400 ml. of H_2O, dried over $MgSO_4$, and evaporated under reduced pressure to yield 7.9 g. of crude product. Recrystallization from 100 ml. of benzene yielded 2.3 g. (17%) of off-white fluffy crystals (XXV); m.p. 183.5-184.5° (lit.[24] 182-183°); ir (KBr) 3500, 3390, (NH_2), 1680 (broad, COOH), 1595 $cm.^{-1}$ (NH_2).

(C) Preparation of 9-Substituted Triptycenes

(1) Preparation of 1,2,3,4-Tetrabromo-9-isopropyltriptycene (Ic)

A mixture of 1.00 g. (0.00454 mole) of 9-isopropylanthracene and 16 ml. of ethylene dichloride was placed in a 100-ml. three-necked flask containing a magnetic stirrer and fitted with a condenser containing a drying tube and a pressure-equalizing addition funnel which was kept above the level of the condenser's cooling surface by means of a glass extension. The mixture was brought to reflux, at which point 1.19 g. (0.0102 mole) of isoamyl nitrite was added. Once the reaction mixture was again at reflux, a solution of 4.08 g. (0.0090 mole) of tetrabromoanthranilic acid (XXIII) in 65 ml. of diethyl carbitol (purified by treatment with excess $LiAlH_4$ at room temp., followed by distillation from the hydride; b.p. 72° (12 mm.)) was added dropwise over a period of 2.5 hr. During the addition, a small amount of a yellow solid formed which was identified as octabromoacridone (XXXV); m.p. 350-351° (lit.[59] m.p. 350°); ir (KBr) 3340 (N-H), 1660 cm.$^{-1}$ (C=0). After the addition, the reaction mixture was refluxed for 1 hr., filtered with suction while still warm, and the ethylene dichloride removed by simple distillation. The distillation was stopped upon reaching a head temp. of approximately 140-145°. The temp. of the oil bath was raised to 215°, at which point 1.0 g. (0.010 mole) of maleic anhydride was added. The reaction mixture was allowed to stir for an additional 15 min. at this temp. The flask was removed from the bath and when the temp. of its contents was at approximately 50°, a solution of 4.25 g. (0.0788 mole) of KOH in 19 ml. of H_2O and 28 ml. of methanol was added. Within several min., a small amount of precipitate was evident. The reaction mixture was stirred overnight at room temp. The solid was filtered off, washed with 80% aqueous methanol, and dried under vacuum to yield 17 mg. of crude product. Two recrystallizations from toluene (to constant m.p.) yielded 246 mg. (10%) of white crystals (Ic) m.p. 312-314° (lit.[43] m.p. 290-292°). A second crop of very pale yellow crystals weighing 104 mg. was obtained which had the identical nmr spectrum as that of the first crop; m.p. 307-311°; nmr ($CDCl_3$) δ 1.76 (d, J 6 Hz, CH_3) 1.88 (d, J 6 Hz, CH_3), 4.63 (septet, J 6 Hz, methine-H); ir (KBr) 1390, 1370 cm.$^{-1}$ (CH_3); mass spec., m/e (rel. intensity using linear mass scan) 608, 610, 612, 614, 616 (5.5, 20.8, 29, 19.5, 5.5), 565, 567, 569, 571, 573, (7.8, 29, 40.5, 28, 7.5), 529, 531, 533, 535 (6.5, 17, 17.6), 487, 489, 491, 493, (22, 67, 74, 32), 450, 452, 454 (15, 28.5, 15), 407, 409, 411 (545, 100, 54).

Anal. calcd. for $C_{23}H_{16}Br_4$: C, 45.14; H, 2.63; Br, 52.23. Found: C, 45.34; H, 2.51; Br, 52.08.

(2) Preparation of 1,2,3,4-Tetrachloro-9-isopropyltriptycene (Ib)

The same apparatus and experimental procedure, as well as the molar quantities of reagents, as described in the preparation of 1,2,3,4-tetrabromo-9-isopropyltriptycene (Ic) were used except that the tetrachloroanthranilic acid (XXV) (2.47 g., 0.0090 mole) was dissolved in 45 ml. of diethyl carbitol and was added over a period of 2 hr. and 45 min. to the refluxing solution of 9-isopropylanthracene (XV) and isoamyl nitrite. During the addition, a small amount of octachloroacridone (XXXV) was formed; m.p. 380-381°; ir (KBr) 3370 (N-H), 1665 cm.$^{-1}$ (C=O). Five minutes after the addition of the KOH solution, the crude product began to precipitate out. The reaction mixture was stirred overnight, and the resulting pale yellow solid was filtered off, washed with 25 ml. of 80% aqueous methanol, and dried under vacuum to yield 460 mg. of crude product. Recrystallization from 6 ml. of toluene yielded 161 mg. (8.2%) (Additional material may be obtained from the mother liquor.) of white crystals (Ib); m.p. 284-286° lit.[43] m.p. 267-269°); nmr ($CDCl_3$) δ 1.76 (d, J 6 Hz, CH_3), 1.89 (d, J 6 Hz, CH_3), 4.37 (septet, J 6 Hz, methine-H), 5.91 (s, bridgehead-H), 6.87-7.91 (complex pattern, aryl-H); ir (KBr) 1390, 1370 cm.$^{-1}$ (CH_3);

mass spec., m/e (rel. intensity using linear mass scan) 430, 432, 434, 436 (26, 35, 18, 5.5), 387, 389, 391, 393 (76, 95.5, 49.5, 13), 352, 354, 356, 358 (100, 98, 33, 12.5), 317, 319, 321 (65, 43, 12).

Anal. calcd. for $C_{23}H_{16}Cl_4$: C, 63.62; H, 3.71; Cl, 32.66. Found: C, 63.40; H, 3.58; Cl, 32.72.

(3) Preparation of 1,4-Dibromo-9-isopropyltriptycene (Ig)

The same apparatus and experimental procedure, as well as the molar quantities of reagents, as described in the preparation of 1,2,3,4-tetrabromo-9-isopropyltriptycene (Ic) were used except that the 3,6-dibromoanthranilic acid (XXVII) (2.65 g., 0.0090 mole) was dissolved in 17 ml. of diethyl carbitol and was added over a period of 1 hr. to the refluxing solution of 9-isopropylanthracene (XV) and isoamyl nitrite. During the addition a small amount of 1,4,5,8-tetrabromoacridone (XXXVIII) was formed; m.p. 309-310°; ir (KBr) 3350 (N-H), 1640 $cm.^{-1}$ (C=O); nmr ($CDCl_3$) δ 7.47 (d, J 8.5 Hz, aryl-H), 7.71 (d, J 8.5 Hz, aryl-H). There was no evidence of a precipitate several minutes after the addition of the KOH solution. Upon stirring overnight, a tan solid did form which was filtered off, washed with 18 ml. of 80% aqueous methanol, and dried under vacuum to yield 1.39 g. of crude product. Three recrystallizations from toluene (to constant m.p.) yielded 555 mg. (27%) of large shiny white crystals (Ig); m.p. 303.5-304°. More material was obtained from the mother liquors; second crop - first recrystallization (Ig'), 111 mg., m.p. 296-299°; second crop - second recrystallization (Ig''), 70 mg., m.p. 300-301°; nmr ($CDCl_3$) δ 1.79 (d, J 7 Hz, CH_3), 1.92 (d, J 7 Hz, CH_3), 4.48 (septet, J 7 Hz, methine-H), 5.94 (s, bridgehead-H), 6.92-8.04 (complex pattern, aryl-H); ir (KBr) 1395, 1375 $cm.^{-1}$ (CH_3); mass spec., m/e (rel. intensity using linear mass scan) 452, 454, 456 (19, 37, 20), 437, 439, 441 (2, 4, 2), 409, 411, 413 (29, 57, 30), 373, 375 (14, 14) 330, 332 (100, 100).

Anal. calcd. for $C_{23}H_{18}Br_2$: C, 60.82; H, 3.99; Br, 35.19. Found: C, 61.08; H, 4.06; Br, 34.91.

(4) Preparation of 1,4-Dichloro-9-isopropyltriptycene (If)

The same apparatus and experimental procedure, as well as the molar quantities of reagents, as described in the preparation of 1,2,3,4-tetrabromo-9-isopropyltriptycene (Ic) were used except that the 3,6-dichloroanthranilic acid (XXVI) (1.95 g., 0.0090 mole) was dissolved in 25 ml. of diethyl carbitol and was added over a period of 45 min. to the refluxing solution of 9-isopropylanthracene (XV) and isoamyl nitrite. At the end of the addition there was no evidence of acridone formation. Immediately after the addition of the KOH solution, a precipitate formed. After stirring overnight, the solid was filtered off, washed with 25 ml. of 80% aqueous methanol, and dried under vacuum to yield 1.147 g. of crude product. The infrared spectrum contained bands at 1670 and 3380 $cm.^{-1}$, indicating the presence of an acridone.

The crude product was chromatographed on 125 g. of acidic alumina (Woelm, activity 1) using benzene as the eluent. The first material eluted from the column was 0.987 g. of a white solid whose ir spectrum no longer contained the above-mentioned absorption bands. Two recryallizations from toluene (to constsnt m.p.) yielded 399 mg. (24%) (Additional material may be obtained from the mother liquors.) of large white crystals (If); m.p. 273.5-275°; nmr ($CDCl_3$) δ 1.80 (d, J 7 Hz, CH_3), 1.93 (d, J 7 Hz, CH_3), 4.35 (septet, J 7 Hz, methine-H) 5.92 (s, bridgehead-H), 6.80-8.04 (complex pattern, aryl-H); ir (KBr) 1390, 1370 cm.$^{-1}$ (CH_3); mass spec., m/e (rel. intensity using linear mass scan) 364, 366, 368 (20, 13, 2.5), 349, 351, 353 (3, 2, 0.5), 329, 331 (17.5, 6), 321, 323, 325 (71, 47, 8.5), 286, 288 (100, 46).

Anal. calcd. for $C_{23}H_{18}Cl_2$: C, 75.62; H, 4.97; Cl, 19.41. Found: C, 75.67; H, 5.06; Cl, 19.39.

Once the product (If) was removed from the column, the eluent was changed to $CHCl_3$, whereupon a light brown solid was collected which was identified as an acridone, probably 1,4,5,8-tetrachloroacridone (XXXVII).

(5) Preparation of 1,2,3,4-Tetrafluoro-9-isopropyltriptycene (Ia)

The following reaction was conducted under a N_2 atmosphere. A mixture of 3.00 g. (0.0136 mole) of 9-isopropylanthracene (XV), 5.55 g. (0.0225 mole) of pentafluorobromobenzene and 250 ml. of hexane was placed in a 500 ml. three-necked flask containing a magnetic stirrer and fitted with a thermometer, a pressure-equalizing addition funnel and a condenser. A 2.3 M solution of n-BuLi in hexane (32 ml., 0.0736 mole) was added dropwise over a period of 2 hr. and 45 min. with periodic cooling in an ice-H_2O bath to maintain the temp. inside the flask between 21 and 23°. The reaction mixture was allowed to stir an additional 1 hr. at room temp. after which it was cooled, and 120 ml. of H_2O was added dropwise. The resulting two layers were separated, and the organic layer was washed four times with 200-ml. portions of H_2O, dried over $MgSO_4$ and evaporated under reduced pressure to yield 5.18 g. of a viscous orange oil.

The residue was dissolved in 12 ml. of hexane, and the resulting solution was cooled to approximately 0°, whereupon the preferential precipitation of 1,2,3,4-tetrafluoro-5,12-dihydro-5,12-ethenonaphthacene (XLII) (end-adduct) occurred. This solid was removed by filtration, and the filtrate was evaporated to dryness under reduced pressure. Repetition of this procedure two times with 5-ml. and 1-ml. portions of hexane, respectively, resulted in the precipitation of additional end-adduct. The combined solids were recrystallized from $CHCl_3$ to yield 23 mg. of XLII; m.p. 217-220°; nmr ($CDCl_3$) δ 1.59, 1.61 (d*, J 7 Hz, CH_3), 4.07 (septet, J 7 Hz,

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* The methyl hydrogens actually appear as two doublets, separated by 2 Hz (100 MHz). This separation is not due to coupling with any other proton in the compound as evidenced by proton decoupling experiments. The separation is also not due to long range coupling with F as evidenced by the fact (cont'd. bottom next page)

methine-H), 5.51, 6.14 (two symmetrical multiplets, vinyl-H's and bridgehead-H's), 6.89-8.21 (complex pattern, aryl-H); mass spec., m/e (rel. intensity using linear mass scan) 368 (44), 353 (19), 325 (100).

Anal. calcd. for $C_{23}H_{16}F_4$: C, 74.99; H, 4.38; F, 20.63. Found: C, 74.96; H, 4.35; F, 20.90.

A second crop yielded an additional 17 mg.; m.p. 217-218°.

Evaporation under reduced pressure of the final hexane filtrate yielded 5.158 g. of a viscous oil, which was purified further by column chromatography on 700 g. of acidic alumina (Woelm, activity 1) using hexane as the eluent. The first material eluted from the column consisted of 225 mg. of a pale yellow solid, which by nmr analysis corresponded to the desired product (Ia). This solid turned white upon washing with hexane (these washings were saved), after which it was recrystallized from 3 ml. of hexane to yield 21 mg. of white crystals (Ia); m.p. 187-187.5°; nmr ($CDCl_3$) δ 1.75, 1.81, 1.87 (unsymmetrical triplet, CH_3), 3.69 (septet, methine-H), 5.61 (slightly split due to F coupling, bridgehead-H), 6.83-7.76 (complex pattern, aryl-H); ir (KBr) 1385, 1370 cm.$^{-1}$ (CH_3); mass spec., m/e (rel. intensity using linear mass scan.) 368 (31), 353 (4), 337 (6), 325 (100),

that the spacing increased from 1.0 ± 0.2 Hz at 60 MHz to 2.0 ± 0.2 Hz at 100 MHz to 3.6 ± 0.1 Hz at 220 MHz. We attribute the presence of two doublets to the chirality of the molecule, whereby the methyl groups are diasteriotopic and have slightly different chemical shifts.

306 (10).

Anal. calcd. for $C_{23}H_{16}F_4$: C, 74.99; H, 4.38; F, 20.63. Found: C, 74.81; H, 4.51; F, 20.64.

A whitish solid which crystallized out of the above hexane washings was filtered off, washed with hexane (again, the washings were saved) and recrystallized from 1.1 ml. of hexane to yield an additional 22 mg. of white crystals (Ia); m.p. 188-189°. More of the desired product may be obtained from the mother liquors as well as the latter hexane wash.

Immediately after elution of the product, another material was obtained weighing a total of 0.984 g., which by nmr analysis was mainly the desired tetrafluorotriptycene (Ia). However, an extra singlet was present at δ 5.74. All attempts to purify this material by recrystallization from various solvents failed, and finally after rechromatography on 140 g. of acidic alumina, with hexane as the eluent, an additional 50 mg. of pure product (by nmr) was obtained. This material was recrystallized from hexane to yield 16 mg. of white crystals (Ia); m.p. 192.5-193.5°. A second crop afforded an additional 19 mg.;m.p. 191-192°.

(6) Preparation of 1,2,3,4-Tetrabromo-9-methyltriptycene (Ik)

The same apparatus (except for a 250-ml. three-necked flask), and experimental procedure as described in the preparation of 1,2,3,4-tetrabromo-9-isopropyltriptycene (Ic) were used. A solution of 9.4 g. (0.021 mole) of tetrabromoanthranilic acid (XXIII) dissolved in 95 ml. of diethyl carbitol was added dropwise over a period of 1 hr. and 15 min. to a refluxing solution of 2.00 g. (0.0104 mole) of 9-methylanthracene and 2.6 g. (0.022 mole) of isoamyl nitrite in 32 ml. of ethylene dichloride. During the addition a small amount of octobromoacridone (XXXV) was formed; m.p. 350-351° (lit.[59] m.p. 350°); ir (KBr) 3340 (N-H), 1660 cm.$^{-1}$ (C=O). Within minutes after the addition of the KOH solution a tan precipitate was evident. The reaction mixture was stirred overnight, after which the solid was filtered off, washed with 40 ml. of 80% aqueous methanol, and dried under vacuum to yield 3.046 g. of crude product. Three recrystallizations from xylene (to constant m.p.) yielded 837 mg. (10%) of large white crystals (Ik); m.p. 308-309.5° (lit.[35] m.p. 302°); nmr ($CDCl_3$) δ 2.88 (s, CH_3), 6.36 (s, bridgehead-H), 7.22-7.82 (symmetrical pattern, aryl-H); ir (KBr) 1375 cm.$^{-1}$ (CH_3); mass spec., m/e (rel. intensity using linear mass scan) 580, 582, 584, 586, 588 (10, 40, 61, 40, 10), 569 (4), 501, 503, 505, 507 (22, 60, 59, 21), 486, 488, 490, 492 (20, 56, 55, 20), 422 (52), 424 (100), 426 (52).

Anal. calcd. for $C_{21}H_{12}Br_4$: C, 43.19; H, 2.07; Br, 54.74. Found: C, 43.24; H, 2.06; Br, 54.71.

A second crop of crystals from the combined mother liquors of the three recrystallizations afforded an additional 82 mg.; m.p. 308-310°.

(7) Preparation of 1,2,3,4-Tetraiodo-9-methyltriptycene (Il)

The same apparatus and experimental procedure as described in the preparation of 1,2,3,4-tetrabromo-9-methyltriptycene (Ik) were used. A solution of 6.7 g. (0.0105 mole) of tetraiodoanthranilic acid (XXIV) dissolved in 60 ml. of diethyl carbitol was added dropwise over a period of 1 hr. to a refluxing solution of 1.00 g. (0.00523 mole) of 9-methylanthracene and 1.38 g. (0.0118 mole) of isoamyl nitrite in 16 ml. of ethylene dichloride. During the addition a considerable amount (1.58 g.) of octaiodoacridone (XL) was formed; m.p. slow continuous dec.; ir (KBr) 3420 (N-H), 1640 cm.$^{-1}$ (C=O). After stirring overnight in the presence of the KOH solution, the reaction mixture consisted of two layers, but no precipitation of product had occurred. The layers were separated, and within 45 min. after the addition of 40 ml. of H_2O to the organic layer, a solid precipitated. This solid was filtered off, washed with 20 ml. of H_2O, and dried under vacuum to yield 712 mg. of crude product. Additional crude product (216 mg.) which had slowly precipitated in the filtrate was isolated 48 hr. later and combined with the original solid. Two recrystallizations from dimethyl formamide yielded 75 mg. of mustard-colored crystals (Il); m.p. 280.5-281° dec.; nmr (CS_2) δ 2.63 (s, CH_3), 6.10 (s, bridgehead-H), 6.92-7.60 (symmetrical pattern, aryl-H); ir (KBr) 1375 cm.$^{-1}$ (CH_3); mass spec., m/e (rel. intensity using linear mass scan) 772 (39.2), 645 (18.7), 630 (30), 518 (28.6), 517 (100), 503 (11.3).

Anal. calcd. for $C_{21}H_{12}I_4$: C, 32.68; H, 1.57; I, 65.76. Found: C, 32.40; H, 1.60; I, 65.49.

A second crop from the second recrystallization afforded an additional 59 mg.; m.p. 285-286° dec. Additional material could not be obtained from the mother liquor of the first recrystallization due to the inadvertent evaporation of too much solvent, resulting in the decomposition of the residue.

(8) Preparation of 1,2,3,4-Tetrabromo-9-(2-d-2-propyl)-triptycene (Ii)

The same apparatus and experimental procedure as described in the preparation of the 1,2,3,4-tetrabromo-9-isopropyltriptycene (Ic) were used except that the number of moles of reagents were half as much. The tetrabromoanthranilic acid (XXIII) was dissolved in 55 ml. of diethyl carbitol and added over a period of 2 hr. and 25 min. to the refluxing solution of 9-(2-d-2-propyl)anthracene (XVI) and isoamyl nitrite in 8 ml. of ethylene dichloride. During the addition a small amount of octabromoacridone (XXXVI) was formed; m.p. 350-351° (lit.[59] m.p. 350°); ir (KBr) 3340 (N-H), 1660 cm.$^{-1}$ (C=O). Within 15 min. after the addition of the KOH solution a tan precipitate was evident. The reaction mixture was stirred overnight, after which the solid was filtered off, washed with 22 ml. of 80% aqueous methanol, and dried under vacuum to yield 317 mg. of crude product. Recrystallization from 8 ml. of toluene yielded 171 mg. of white crystals (Ii); m.p. 313-316°; nmr ($CDCl_3$) δ 1.70 (s, CH_3), 1.84 (s, CH_3), 6.00 (s, bridgehead-H), 6.86-7.94 (complex pattern, aryl-H); mass spec., m/e (rel. intensity using linear mass scan) 609, 611, 613, 615, 617 (7, 25, 36.8, 23, 7), 565, 567, 569, 571, 573 (8, 27, 41, 27, 8), 530, 532, 534, 536 (8, 19, 17, 7), 486, 488, 490, 492 (19, 52, 56, 25), 451, 453, 455 (17, 31.5, 17), 407, 409, 411 (51.5, 100, 64.5). It was found by a comparison of the P-1 to P ratios in Ii and Ic (the undeuterated analog), that the product consisted of 98.7% d_1 and of 1.3% d_0 species.

A second crop afforded an additional 36 mg.; m.p. 313-315°. The total yield from the first and second crops combined was 15%.

(9) Preparation of 1,2,3,4-Tetrabromo-9-(1,1,1--trideuterio-2-propyl)triptycene (Ij)

The same apparatus and experimental procedure, as well as the molar quantities of reagents, as that described in the preparation of 1,2,3,4-tetrabromo-9-isopropyltriptycene (Ic) were used except that the tetrabromoanthranilic acid (XXIII), dissolved in 55 ml. of diethyl carbitol, was added over a period of 4 hr. to the refluxing solution of 9-(1,1,1-trideuterio-2-propyl)anthracene (XVII) and isoamyl nitrite. During the addition, a small amount of octabromoacridone (XXXVI) formed; m.p. 350-351° (lit.[59] m.p. 350°); ir (KBr) 3340 (N-H), 1660 cm.$^{-1}$ (C=O). Upon stirring overnight in the presence of the KOH solution, a tan solid precipitated. This solid was filtered off, washed with 20 ml. of 80% aqueous methanol, and dried under vacuum to yield 808 mg. of crude product. Recrystallization from 19 ml. of toluene yielded 438 mg. of white crystals (Ij); m.p. 313-316°; nmr ($CDCl_3$) δ 1.72 (d, J 7 Hz, CH_3), 1.85 (d, J 7 Hz, CH_3), 4.55 (septet, J 7 Hz, methine-H), 5.98 (s, bridgehead-H), 6.86-7.94 (complex pattern, aryl-H); mass spec., m/e (rel. intensity using linear mass scan) 611, 613, 615, 617, 619 (8, 28, 40, 27, 7), 565, 567, 569, 571, 573 (14, 56, 85, 56, 16), 532, 534, 536, 538 (12, 32, 31, 10), 486, 488, 490, 492 (34, 98.3, 100, 39.5), 453, 455, 457 (32, 60.5, 31). It was found by a comparison of the P-1 to P ratios for both Ij and Ic (undeuterated analog), that the product consisted of 86.1% d_3 and of 13.9% d_2 species.

A second crop afforded an additional 25 mg.; m.p. 312-315°. The total yield from the first and second crops combined was 17%.

IV Variable Temperature NMR Spectra

NMR Parameters at Slow Exchange for the Isopropyl Methyl Region of Compounds Ia,b,c,f,g,i and j in Deuterionitrobenzene

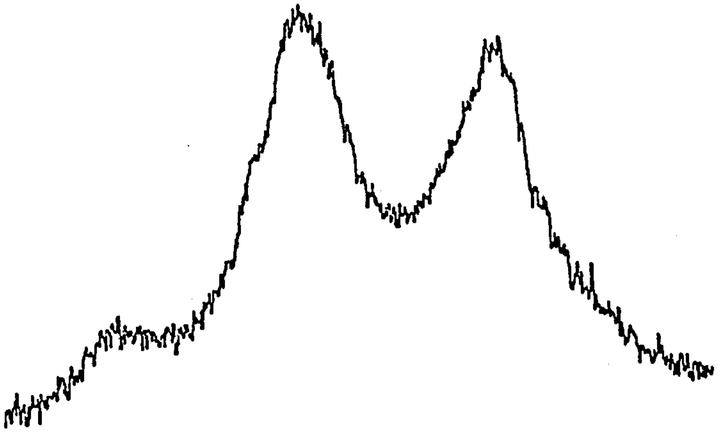
	$\Delta\nu$ (Hz)	J^c (Hz)	J^d (Hz)
Ia	4.5[a]	ca. 7.5	ca. 7.5
Ia	7.5[b]	ca. 7.5	ca. 7.5
Ib	10.40[a]	7.5	7.3
Ic	9.55[a]	7.6	7.1
If	10.40[a]	7.8	7.4
Ig	10.50[a]	7.2	7.4
Ii	9.8[a]		
Ij	9.5[a]	7.0	6.0

[a] Values obtained from a 60 MHz instrument
[b] Values obtained from a 100 MHz instrument
[c] Low frequency doublet
[d] High frequency doublet

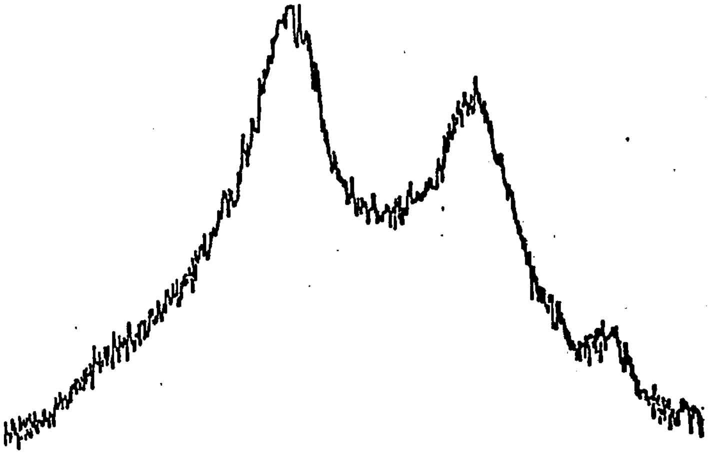
Experimental Variable Temperature Spectra for Ia

T in ^{o}K; Tc = coalescence temperature

T = 413

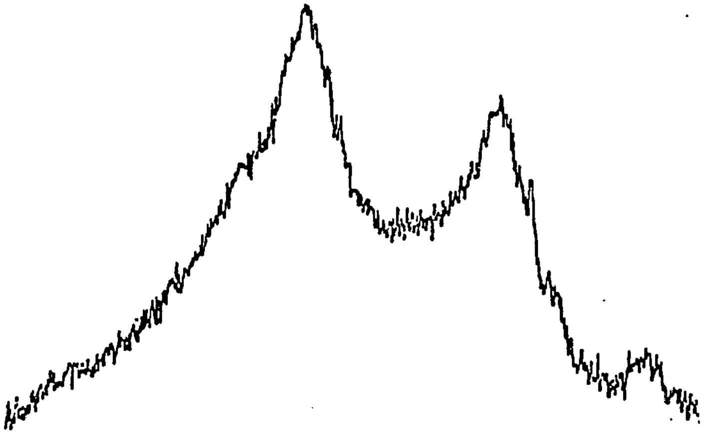


T = 424

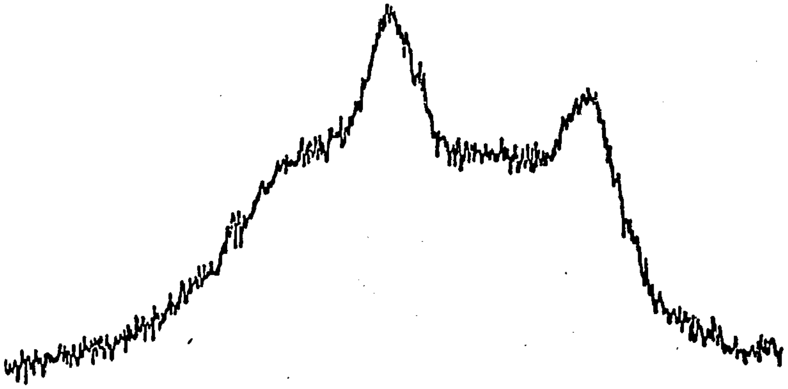


Cont'd. for Compound Ia

Tc = 425.4

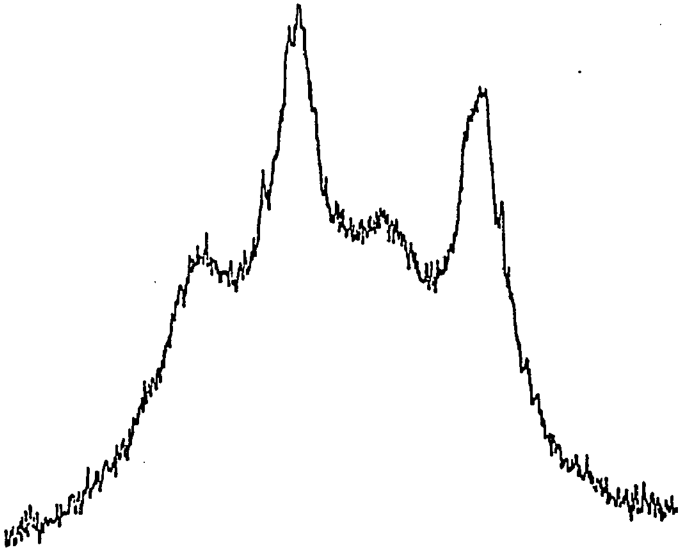


T = 431



Cont'd. for Compound Ia

T = 434



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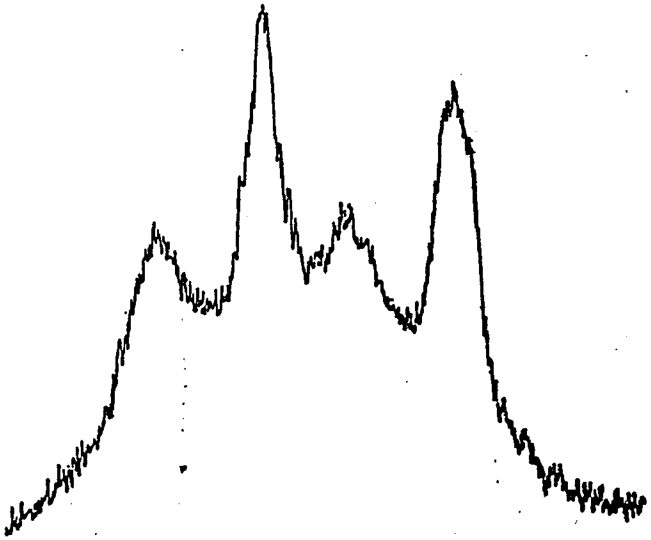
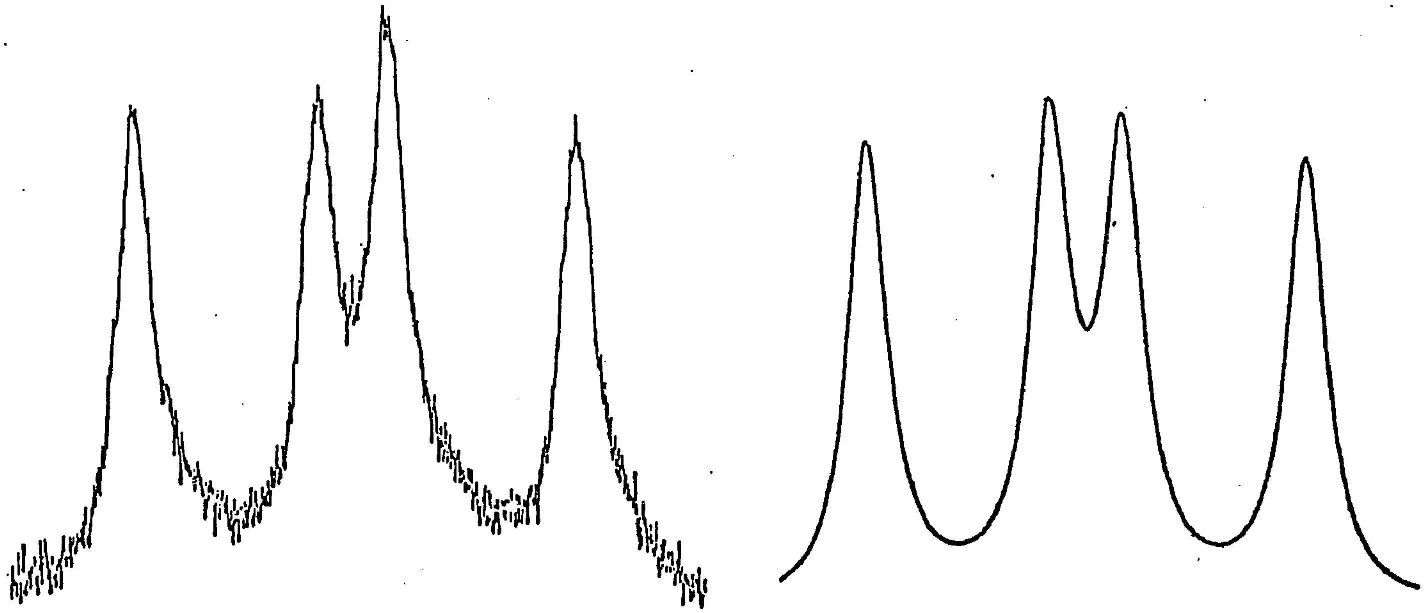


Comparison of Experimental and Calculated Variable Temperature Spectra for Ib

Rate constants in $\sec^{-1}$, T in °K; Tc = coalescence temperature



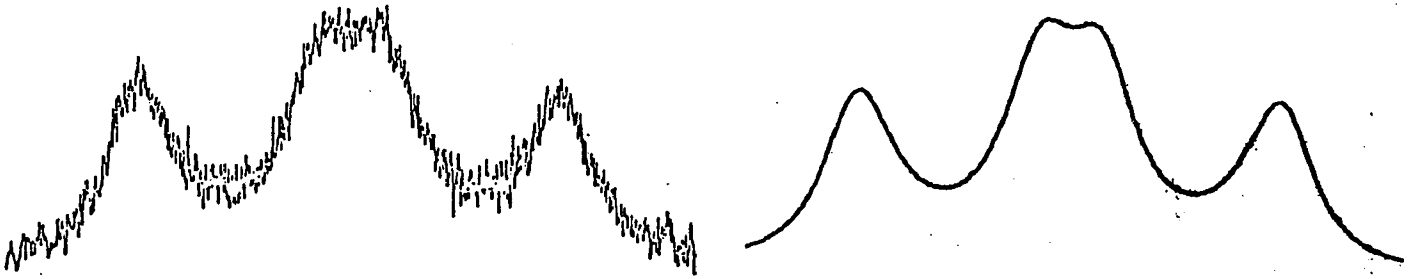
Experimental

Calculated

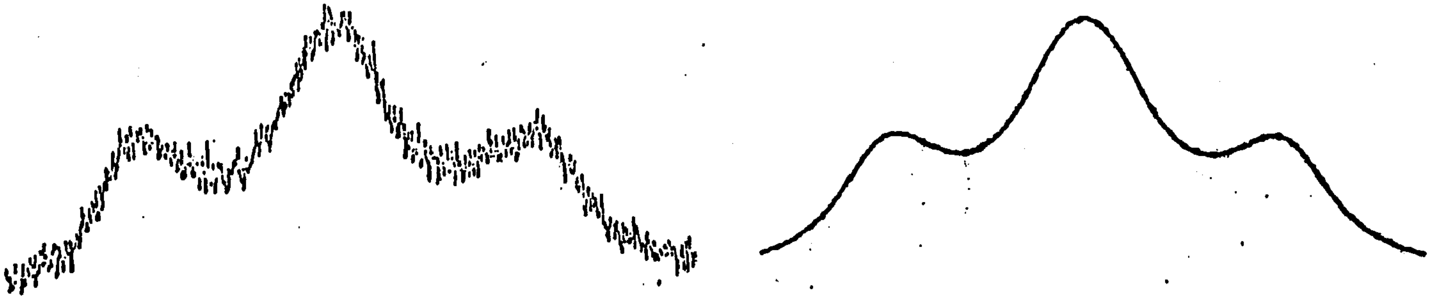
k = 1
T = 406.2

Cont'd. for Compound Ib

Experimental Calculated



k = 6
T = 424.3

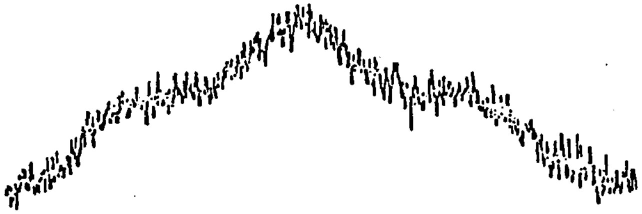


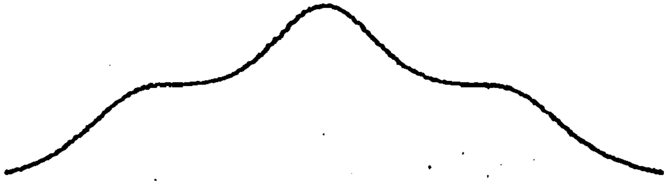
k = 12
T = 438.4

Cont'd. for Compound Ib

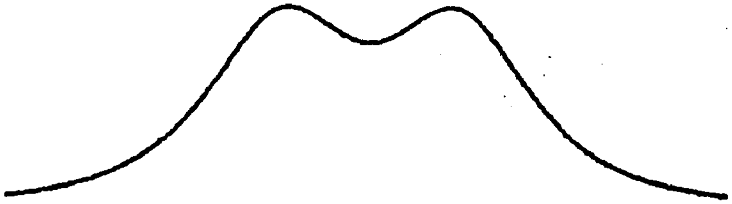
Experimental

Calculated





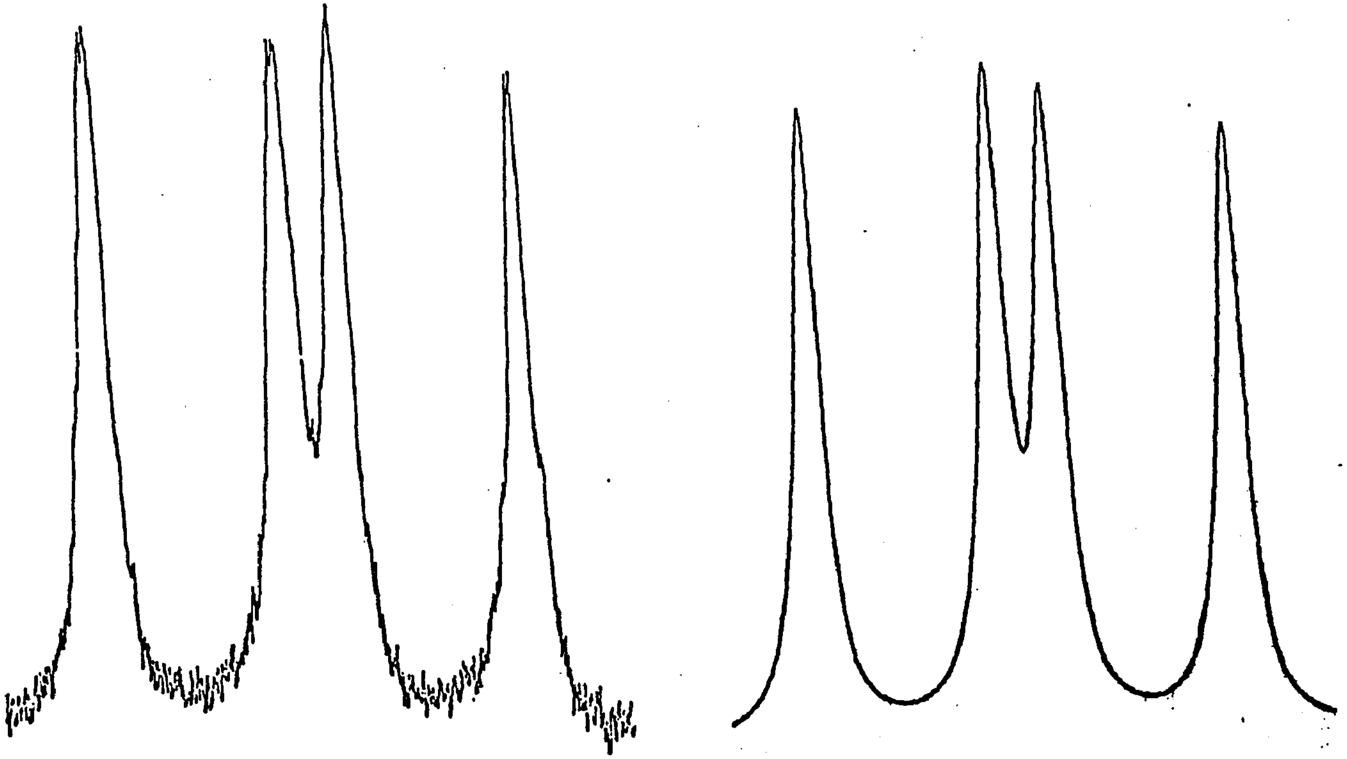
k = 16
Tc = 445.7



k = 35
T = 454.5

Comparison of Experimental and Calculated Variable Temperature Spectra for Ic

Rate constants in sec^{-1}, T in °K; Tc = coalescence temperature



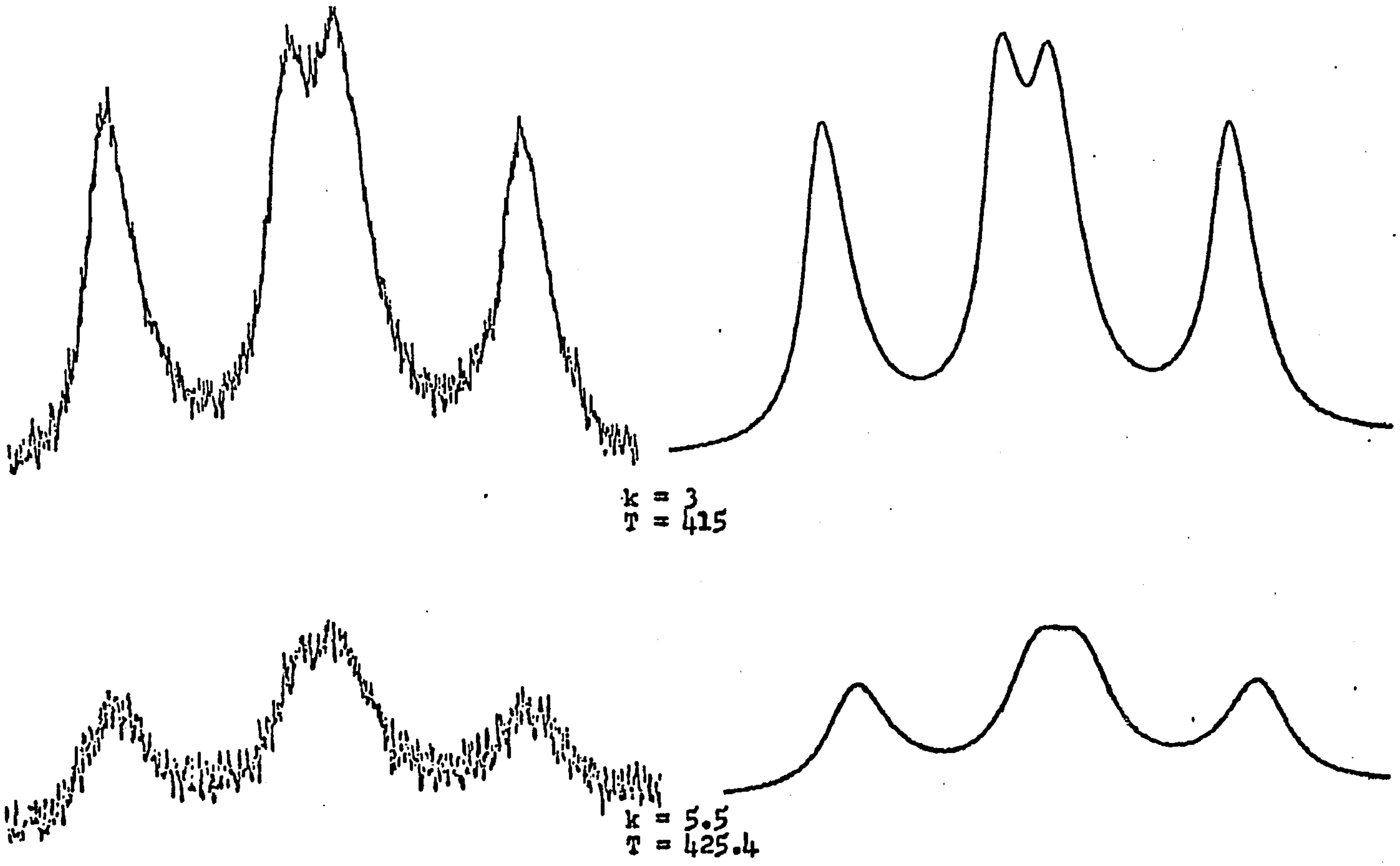
Experimental

Calculated

k = 0
T = 385.9

Cont'd. for Compound Ic

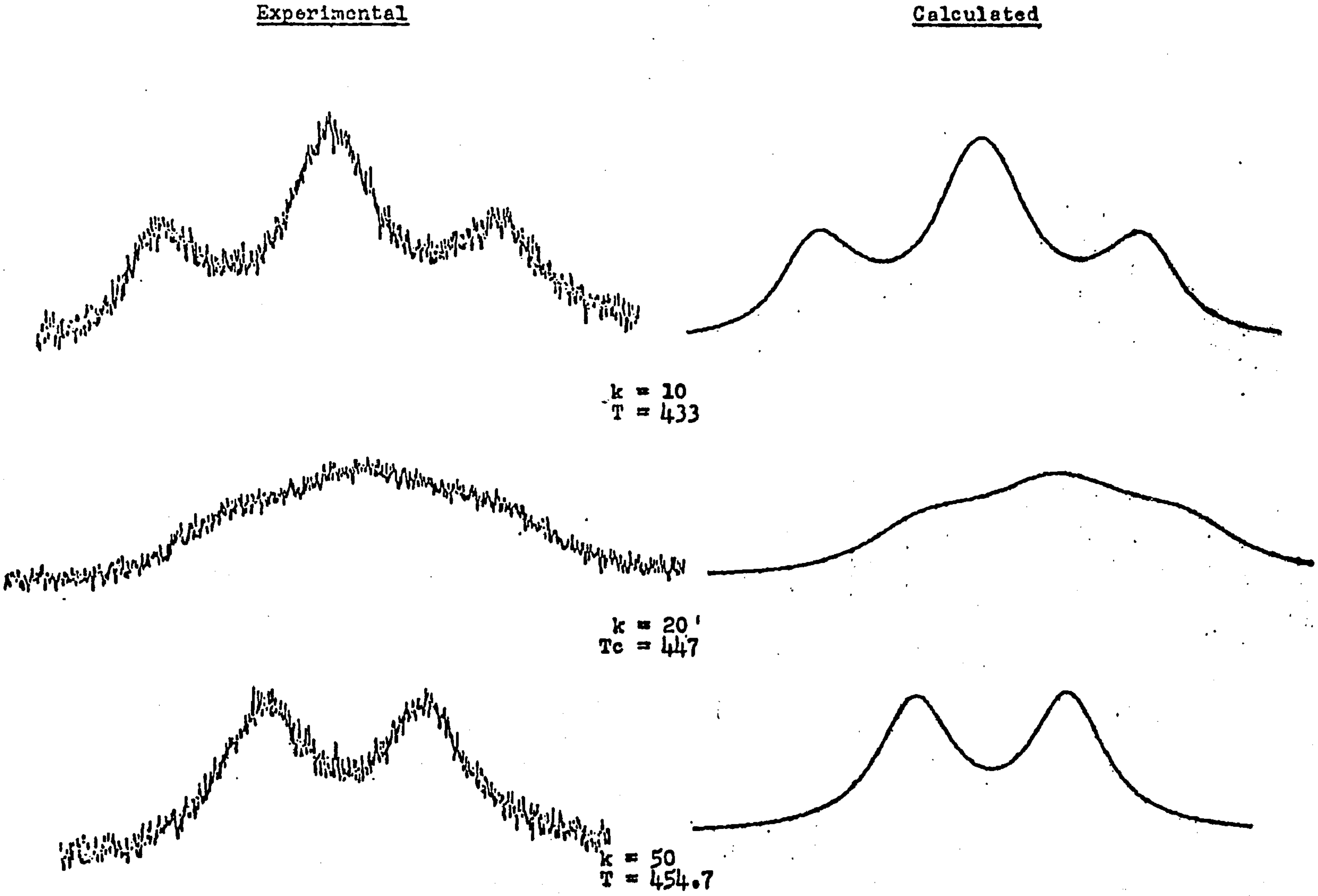
Experimental **Calculated**



k = 3
T = 415

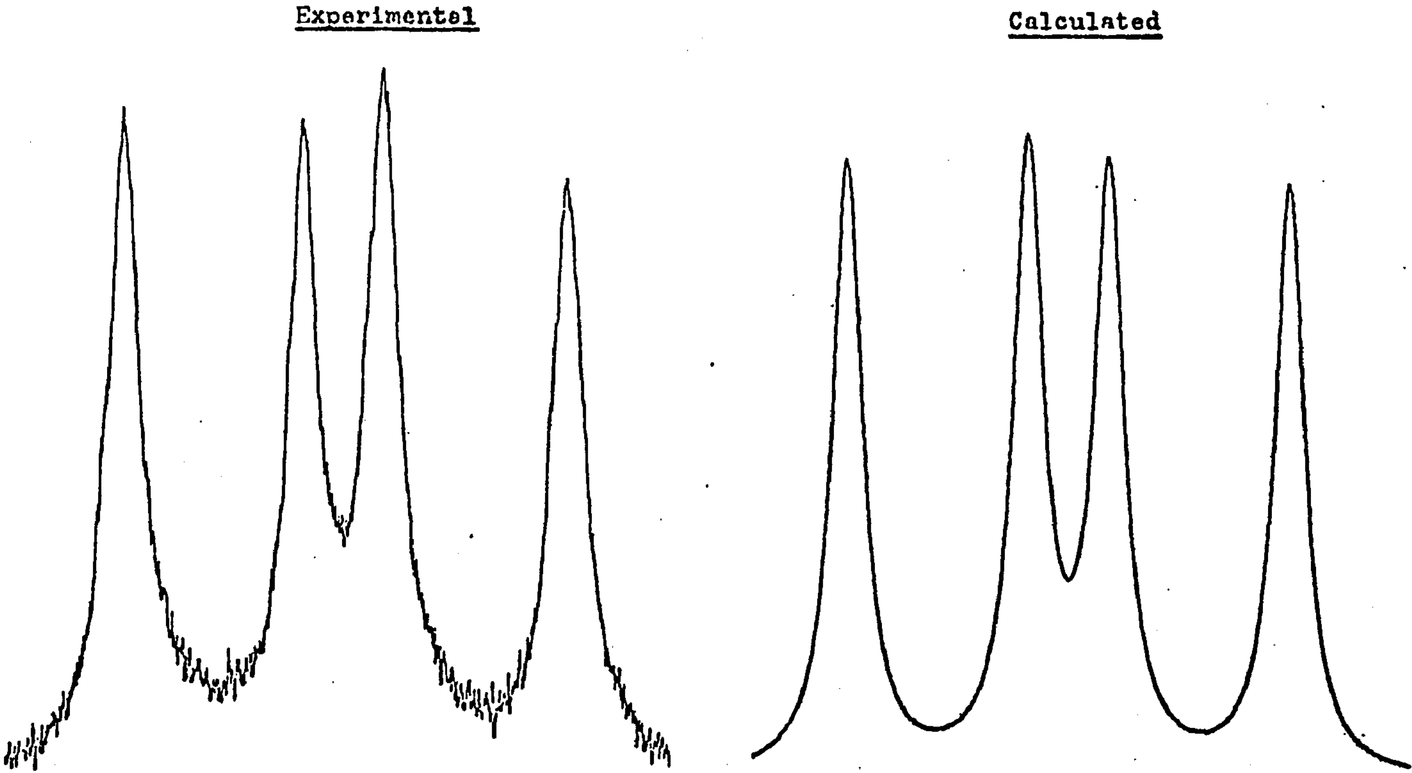
k = 5.5
T = 425.4

Cont'd. for Compound Ic



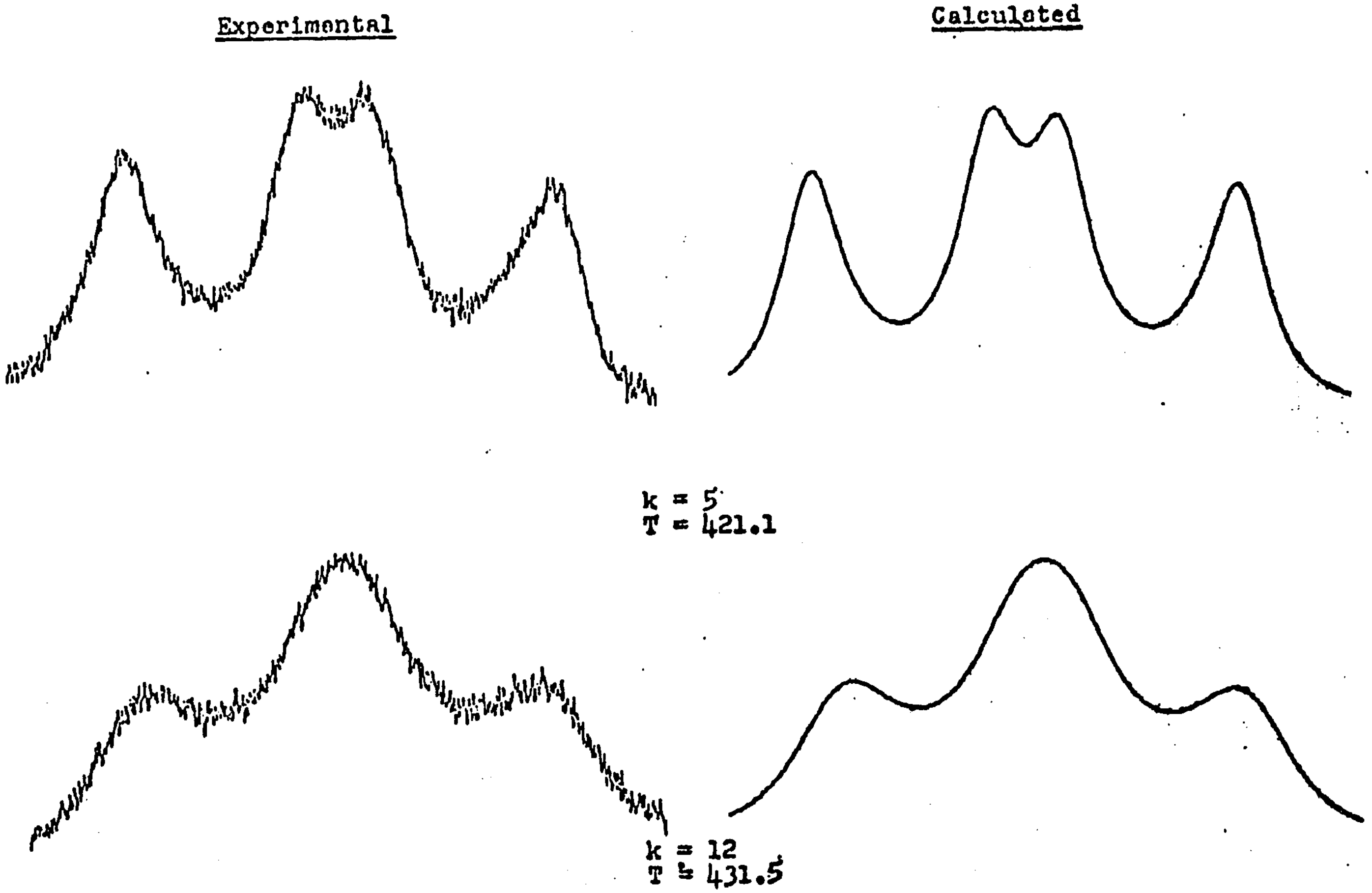
Comparison of Experimental and Calculated Variable Temperature Spectra for If

Rate constants in sec^{-1}, T in ^{o}K; To = coalescence temperature

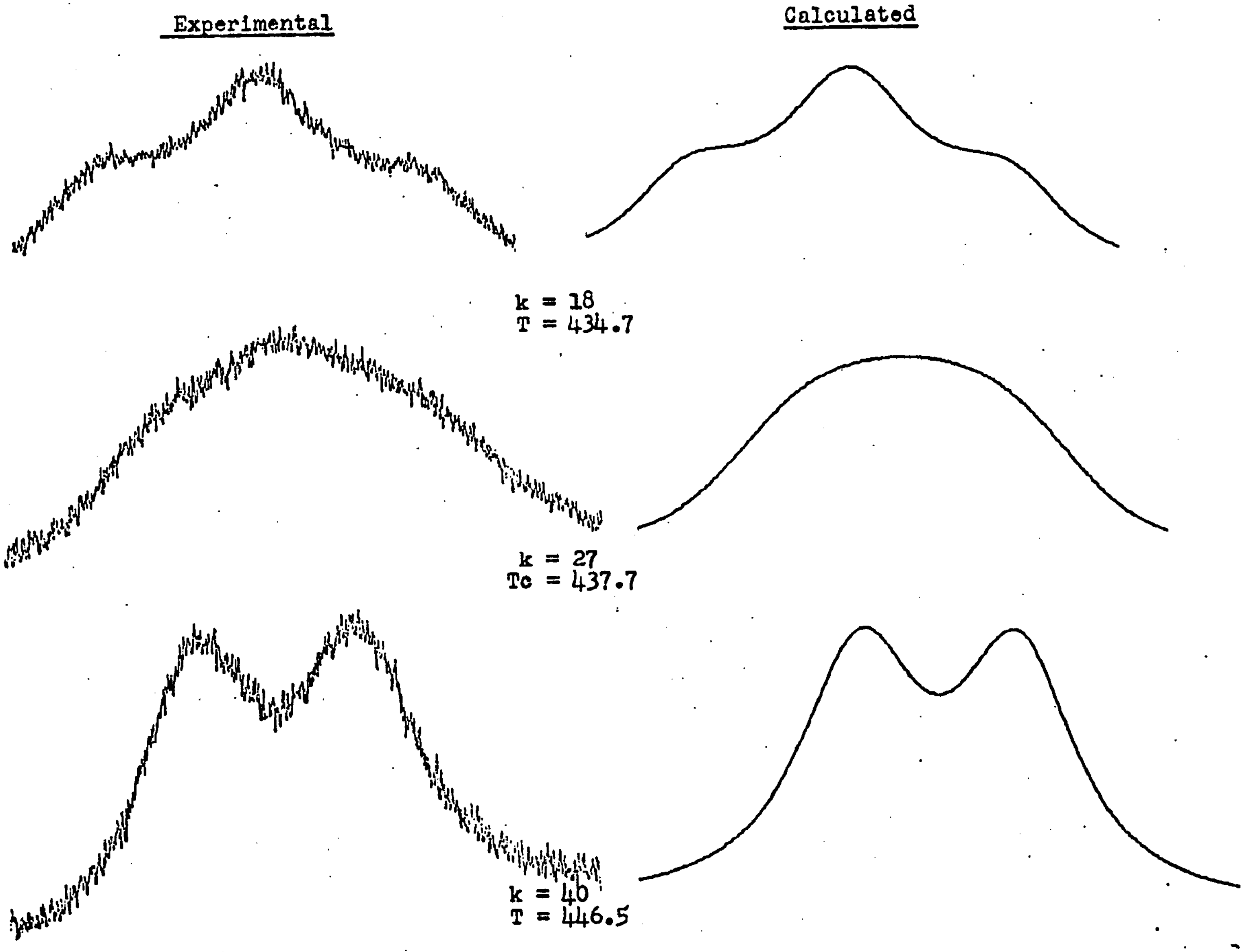


k = 0
T = 385.9

Cont'd. for Compound If

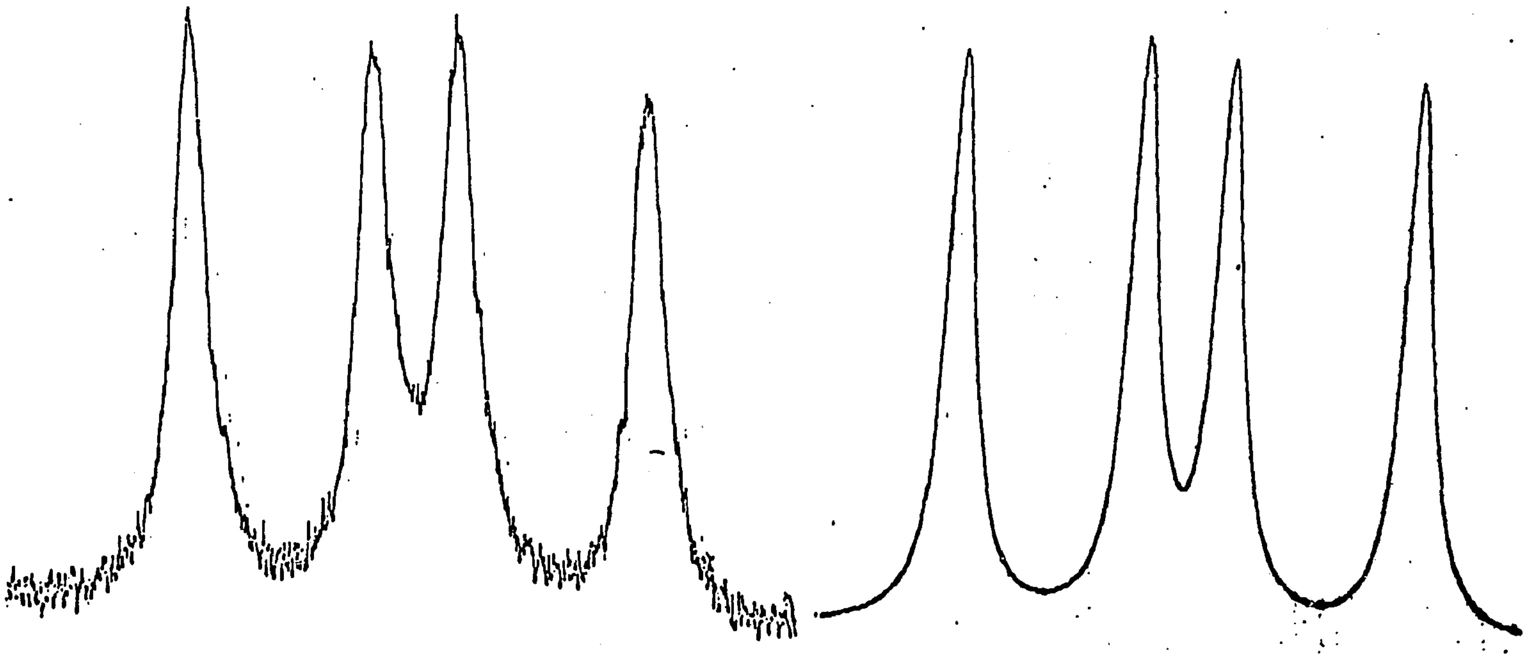


Cont'd. for Compound If



Comparison of Experimental and Calculated Variable Temperature Spectra for Ig

Rate constants in sec^{-1}, T in ^{o}K; Tc = coalescence temperature



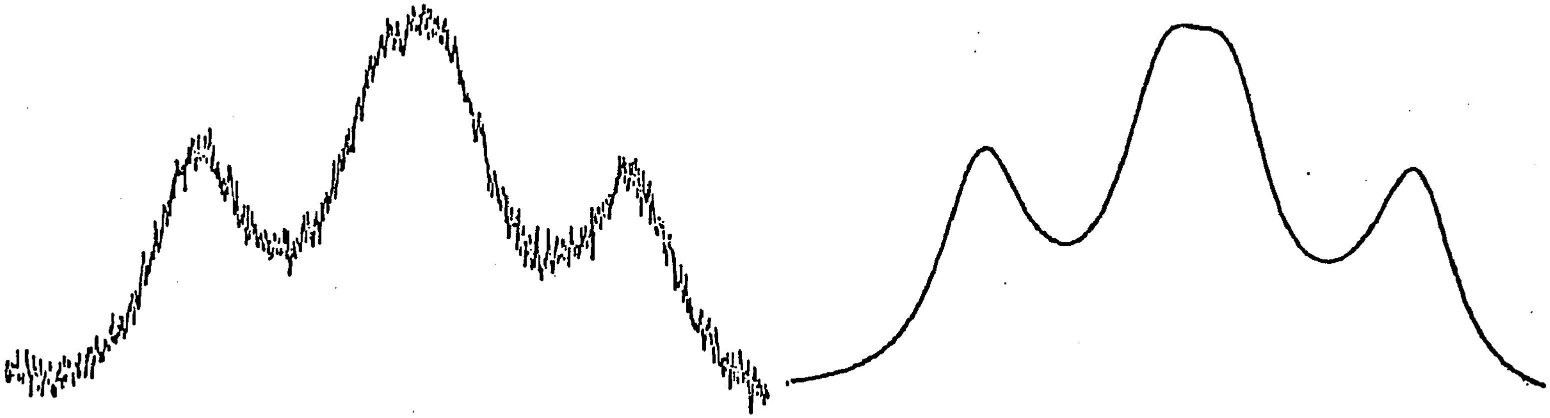
Experimental

Calculated

k = 0
T = 385.9

Cont'd. for Compound Ig

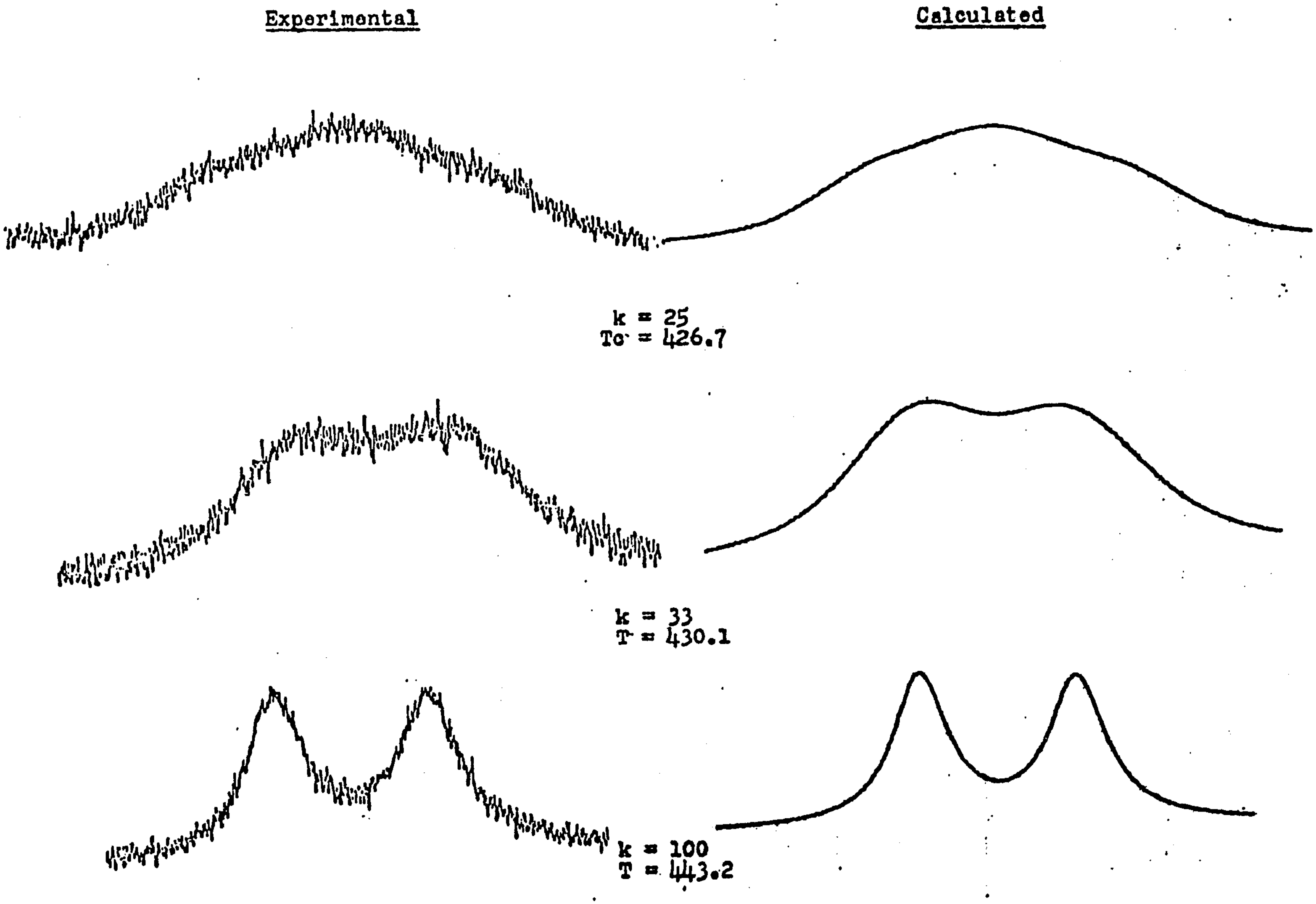
Experimental **Calculated**



k = 9
T = 415

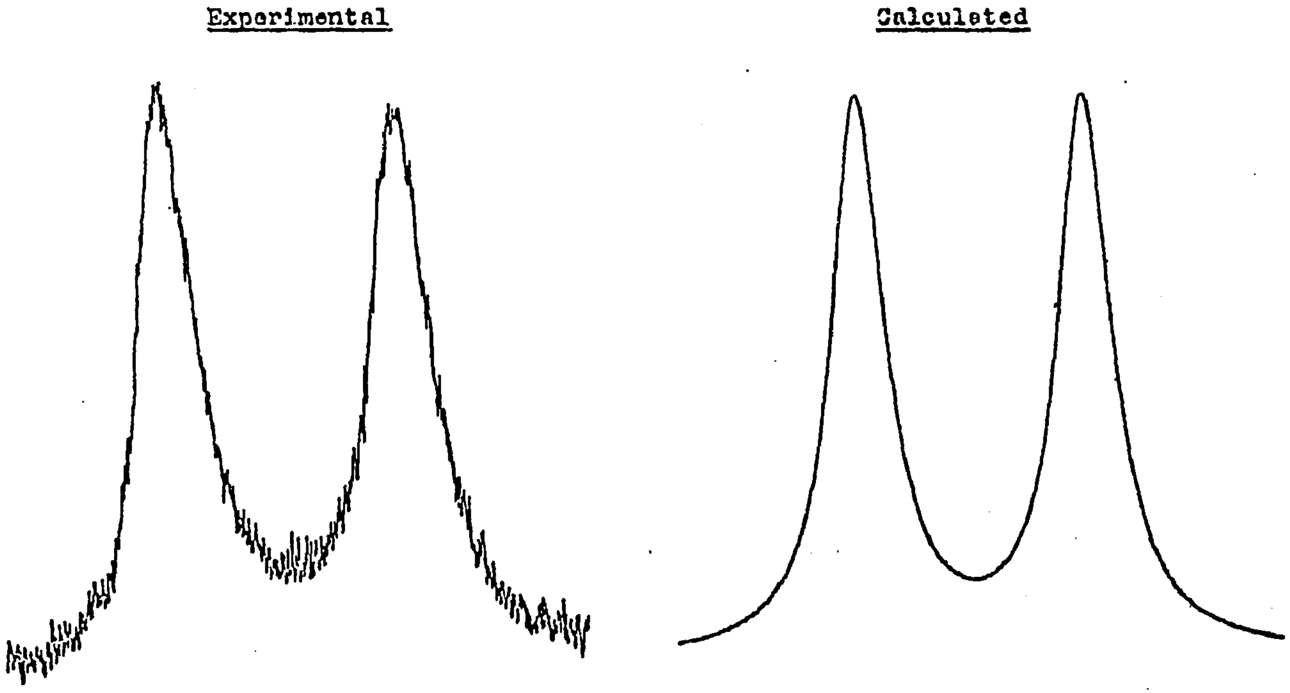
k = 12
T = 417.6

Cont'd. for Compound Ig



Comparison of Experimental and Calculated Variable Temperature Spectra for I1

Rate constants in $\sec^{-1}$, T in °K; Tc = coalescence temperature



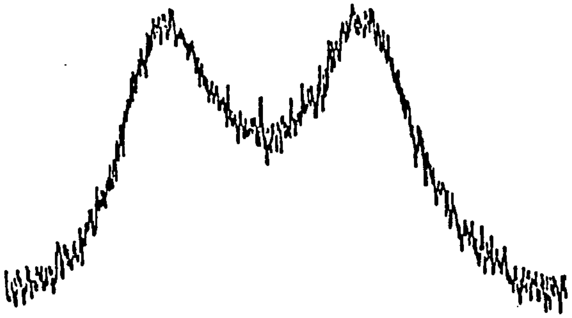
Experimental

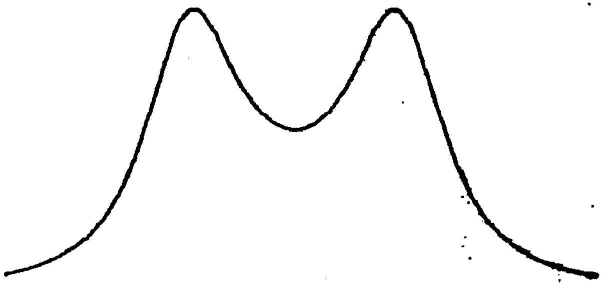
Calculated

k = 0
T = 385.9

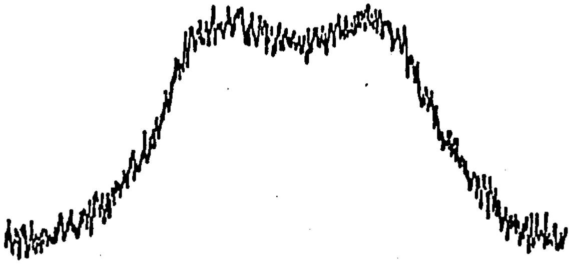
Cont'd. for Compound II

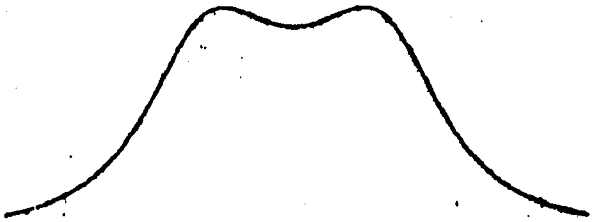
Experimental **Calculated**





k = 7
T = 427.7

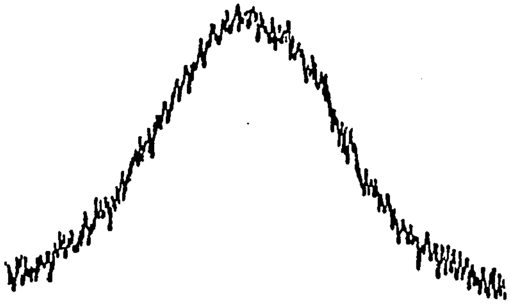




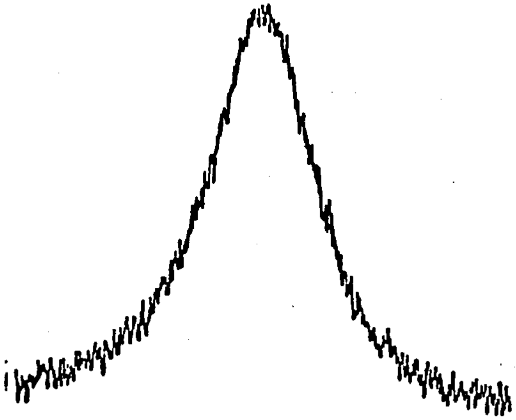
k = 13
T = 437.1

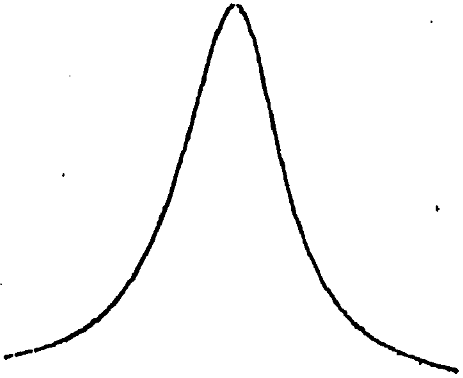
Cont'd. for Compound II

Experimental **Calculated**



k = 26
Tc = 444.8

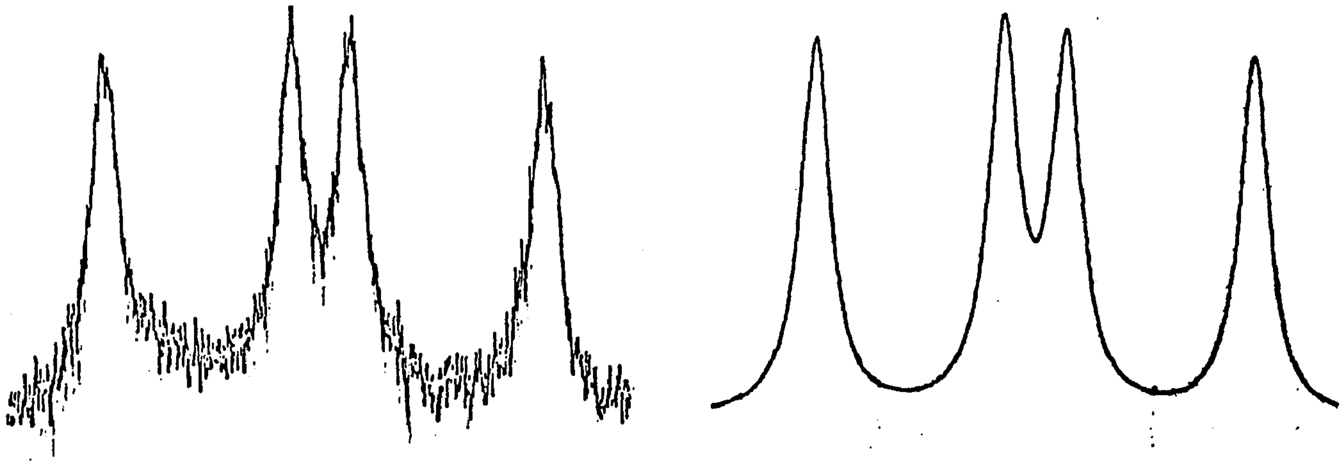




k = 60
T = 451.5

Comparison of Experimental and Calculated Variable Temperature Spectra for II

Rate constants in sec^{-1}, T in ^{o}K; Tc = coalescence temperature



Experimental

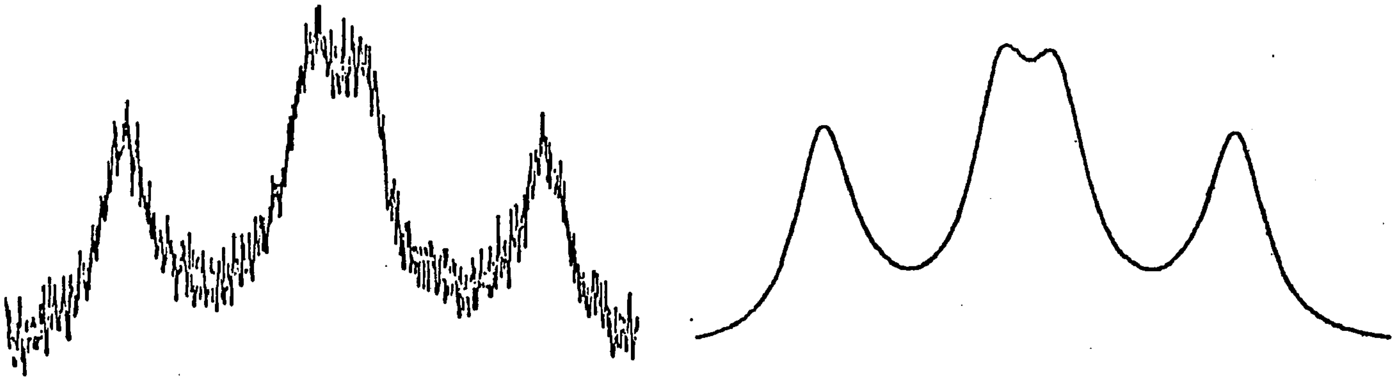
Calculated

k = 0
T = 389.5

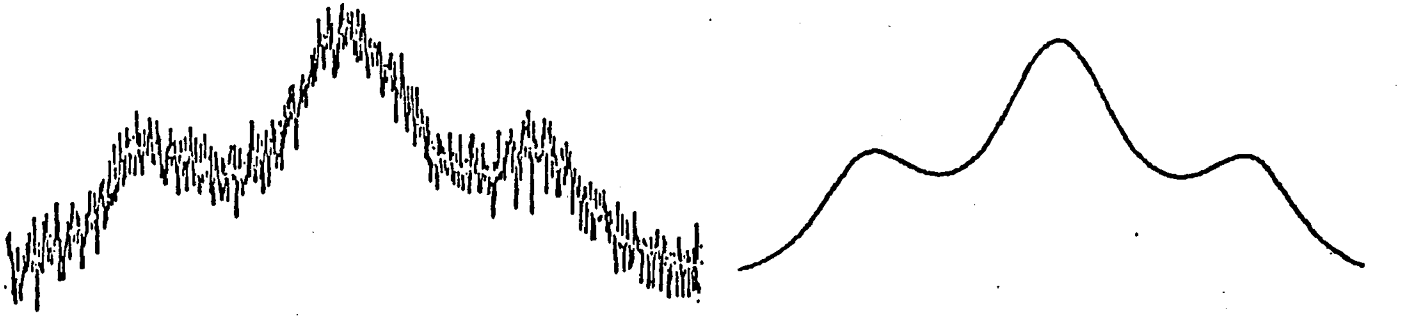
Cont'd. for Compound Ij

Experimental

Calculated



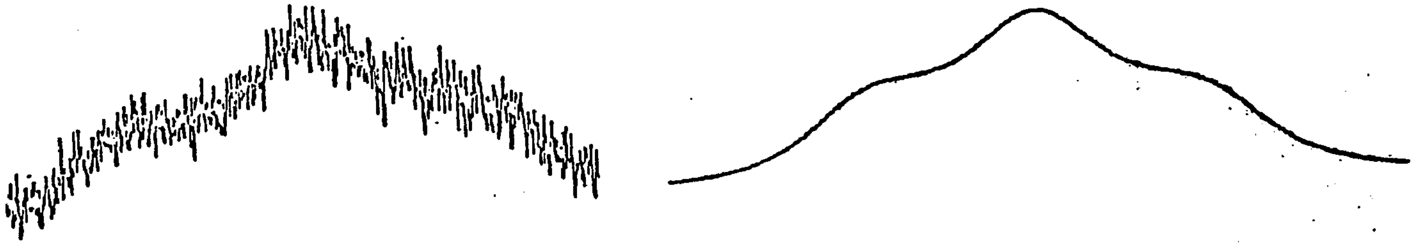
k = 9
T = 421.3



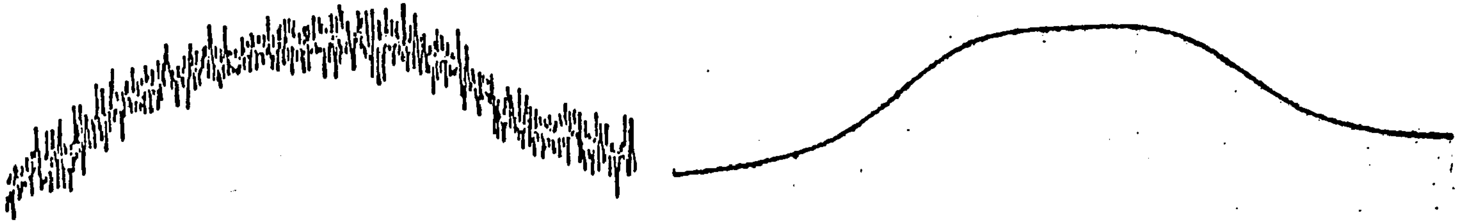
k = 22
T = 430.4

Cont'd. for Compound Ii

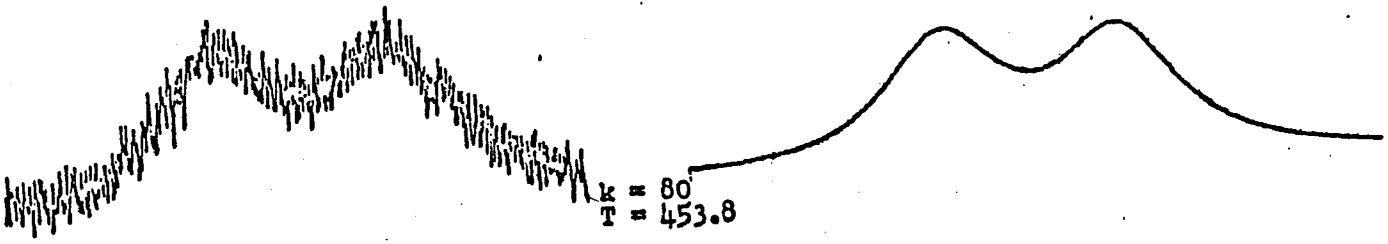
Experimental **Calculated**



k = 35
T = 436.5



k = 50
Tc = 445.4



k = 80
T = 453.8

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