The University of Manitoba

A PROTON MAGNETIC RESONANCE INVESTIGATION OF THE BARRIERS TO INTERNAL ROTATION AND THE STABLE CONFORMERS OF SOME BENZYLIC AND BENZALIC COMPOUNDS

by

Werner Danchura

A Thesis

Submitted to

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ABSTRACT

A new NMR method, called the J method, for the investigation of barriers to internal rotation and ground state rotational conformations of benzyl and benzal compounds in solution is described. The method relies on the dependence of the long-range six-bond side-chain proton to *para* ring proton coupling constant on the angle of internal rotation. The method is applied to 3,5-dibromoisopropylbenzene, for which the rotational barrier is found to be 2.0 ± 0.2 kcal/mole and the low energy conformation is found to have the C_α-H bond oriented in the plane of the benzene ring. The rotational barriers in benzal halides are also investigated. The effect of α-substituent electronegativity on the six-bond coupling is estimated and used in the determination of the barriers of benzal chloride and bromide, which are 2.2 ± 0.3 and 3.5_5 ± 0.6 kcal/mole, respectively. The rotational barriers in 3,5-dichlorophenylcyclohexane, 2-(3,5-dichlorophenyl)-1,3-dithiane, -1,3-dioxane, and -1,3-dioxolane are found to be 2.1 ± 0.3, 2.3_5 ± 0.4, 0.5 ± 0.2, and 0.8_5 ± 0.3 kcal/mole, respectively. In all these benzal compounds the minimum energy conformation has the C_α-H bond oriented in the aromatic ring plane.

A similar linear dependence of the long-range six-bond coupling on the α-substituent electronegativity in benzyl compounds is used to determine the barriers in 3,5-dichlorobenzyl alcohol and selenol, which are found to be 0.3 ± 0.2 and 3.6 ± 1.0 kcal/mole,

respectively. The barriers in 3,5-dichlorobenzylamine, -benzyldimethylamine, and -benzyldimethylarsine are found to be 0.3 $\pm$ 0.3, 0.8 $\pm$ 0.3, and 3.0 $\pm$ 0.7 kcal/mole, respectively. All these compounds have a minimum energy conformation in which the C_{α}-X bond, where X is a substituent, is oriented perpendicular to the aromatic ring plane, except for the benzyl alcohol where the C_{α}-X bond prefers the plane of the phenyl ring.

The long-range six-bond coupling between the side-chain proton(s) and a para ring fluorine in a variety of p-fluorobenzyl- and -benzal compounds is studied in order to determine whether this coupling can also be used to find the barrier and the ground state rotational conformation. The barriers from the proton-fluorine coupling are generally higher than the barriers from the proton-proton coupling but the same minimum energy conformations are predicted by both couplings. The rotational barrier in 3,5-dichlorobenzyl cyanide was found to be 0.3 $\pm$ 0.2 kcal/mole in this investigation, and the low energy conformation had the C-CN bond oriented perpendicular to the ring plane. The long-range proton-proton coupling constant is assumed to give the more reliable barrier.

The rotational barriers and minimum energy conformations of diphenylmethane derivatives are found from both the long-range proton-proton and proton-fluorine couplings. The barrier is 1.1 $\pm$ 0.2 kcal/mole in 3,5-dibromodiphenylmethane and 1.5 $\pm$ 0.2

kcal/mole in 4,4'-difluorodiphenylmethane, the latter value determined from the temperature dependence of the proton-fluorine coupling. In both compounds the minimum energy conformation is the gable conformation, in which the $C_{\alpha}-\phi$ bond is perpendicular to the aromatic ring plane for both rings.

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A Note on Units

The rotational barriers in this work are all reported in energy units of cal/mole or kcal/mole rather than in the contemporary SI units of J/mole or kJ/mole. This occurs for the following reasons. Most of the barriers from the references had units of kcal/mole. The computer program EXPECT, which calculates $\langle \sin^2\theta \rangle$ versus V_2 curves was written to input and output barrier values in kcal/mole. Finally, the publications which resulted from this work reported the rotational barriers in kcal/mole.

The conversion factor between kcal/mole and kJ/mole is

$$1 \text{ kcal/mole} = 4.184 \text{ kJ/mole}$$

INTRODUCTION

One of the dynamic motions which can occur in polyatomic molecules is the rotation of one part of the molecule relative to another part about a single bond which joins the two parts. The part which is larger, or consists of more atoms, is usually designated the frame while the part which is smaller and has fewer atoms is usually designated the top. In discussions of internal rotation the top is assumed to rotate relative to the stationary frame.

As the internal rotation proceeds an infinite number of rotational conformations are formed and then reformed as the rotation repeats itself. If the internal rotation is free, that is, there are no interactions between the two parts of the molecule hindering their rotation, then any and all of the rotational conformations are equally likely to occur. Most often, however, a hindering potential is present which causes a certain number of conformations to become stable, that is, to have a lower potential energy than the other conformations. These low energy or minimum energy conformation might all have the same energy, in which case the hindering potential is symmetric. On the other hand, the stable conformations may have local minimum energies which are not equal and the hindering potential is then asymmetric.

A molecule having a symmetric potential hindering internal rotation has stable conformations of the same minimum potential energy, and transitonal conformations of the same maximum potential energy. During internal rotation, the molecule interconverts from one minimum energy conformation to another by passing through the maximum energy, transitional, conformation. The difference in energy between the stable and the transitional conformations is known as the barrier to internal rotation. Investigations of internal rotations in molecules are concerned with the determination of the geometry of the stable conformations, the fraction of molecules in local stable conformations of different energies, and the determination of the energy differences between local stable conformations or between stable and transitional conformations.

A nuclear magnetic resonance technique for determining barriers to internal rotation and the low energy conformations of benzyl and benzal compounds has been developed in this laboratory and named the J method. In this method the observed six-bond spin-spin coupling constant between the benzyl protons (ϕ-CH_2X; ϕ = phenyl) or benzal proton (ϕ-CHX_2) and the _para_ ring proton is used to calculate an average value of $\sin^2\theta$, which describes the orientation of the benzyl or benzal top relative to the phenyl ring. This $\sin^2\theta$ value is a function of the rotational barrier and the functional relationship can be calculated using quantum and statistical mechanics. From this relationship, barriers to rotation in the range 0 to 4 kcal/mole can be estimated and the minimum energy conformation, in some cases, unequivocally deduced.

Nuclear magnetic resonance has been one of the more powerful physical methods used in the investigation of internal rotation in molecules. A particular technique called dynamic nuclear magnetic resonance (1,2) or DNMR was, and is, widely used to determine barriers to rotation in the range 4 to 30 kcal/mole, and, thus, is a complement to the J method. In the DNMR method the resonance signal of an exchanging proton is measured as a function of the temperature and the lineshape of the signal is calculated and plotted by computer. A parameter in the calculation is the rate constant for the transfer of magnetization between the different sites, and exact simulation of the experimental lineshape yields this rate constant. The temperature dependence of the rate constant is used to determine the thermodynamic activation parameters, $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$, the free energy, enthalpy, and entropy of activation, respectively. $\Delta H^{\ddagger}$ is related to E_0, the activation energy at absolute zero, which, in turn, is related to V, the energy difference between the transition state and the initial state. This last term can be thought of as the barrier to internal rotation, in the case where this motion is the exchange process. Hence, although $\Delta H^{\ddagger}$ and V are not equal, there being a small difference between them, $\Delta H^{\ddagger}$ is often taken as the barrier.

Another NMR technique which has been used to estimate rotational barriers relies on the measurement of spin-lattice relaxation times (3). If the internal rotational motion contributes to the relaxation and can be separated as a component in the relaxation mechanism expression, the potential barrier can be calculated from an Arrhenius-like equation.

Results determined by the J method are compared, whenever possible, with barriers and stable conformations predicted by other methods such as electron diffraction, microwave and far-IR spectroscopy, and ESR spectroscopy (4). Both electron diffraction and microwave spectroscopy require the molecules in the gas phase but allow highly accurate determination of the conformational structures of the molecule, especially the latter technique. Whereas in some cases microwave spectroscopy can determine fairly accurate rotational barriers, electron diffraction usually only yields rough estimates of the barrier. Because the complexity of the experimental data increases greatly with the size of the molecule, both methods are limited to fairly small molecules.

Far-infrared spectroscopy can directly measure the absorption frequency of the torsional motion associated with the internal rotation of a molecule in the gas, liquid, or solid state. A particular model is postulated to describe the molecular dynamics, which includes the internal rotation, and the correct barrier is the one which gives the best fit to the experimental data.

The ESR method for determining barriers is completely analogous to the J method with the difference that it is the hyperfine coupling constant which is used in the determination of the barrier rather than the nuclear spin-spin coupling constant (5), and that the barrier is determined for a radical rather than a neutral electron-paired molecule.

Besides comparing barriers and conformations determined by the J method to those determined by other physical methods, they can also be compared to barriers and conformations predicted by theoretical calculations (6). With the advent of large and fast computers and available programs, semi-empirical and *ab initio* molecular orbital calculations are easily performed. However, although the calculation of the energy for a particular molecular geometry is relatively fast, the determination of a rotational barrier requires the calculation of the energy of various rotational conformations of a molecule in order to find the ground and transition state. Then, geometry optimizations of these conformations must be performed to minimize the energies, the difference between which is taken to be the barrier. These procedures are time consuming and costly, and often only partial geometry optimization can be afforded.

The reliability of the calculated barriers increases from the semi-empirical methods to the *ab initio* methods. The calculation of energies by the latter method is quite accurate but the cost of the geometry optimization necessary for accurate values of the barrier is often prohibitive. Thus, molecular orbital calculations of barriers are often used as a check of the consistency of the magnitude of an experimentally determined barrier and the predicted ground and transition state.

In the present work the determination of the stable conformations and barriers to rotation of some benzyl and benzal compounds is discussed. A description of the theoretical aspects and experimental requirements of the J method is given. Then, the J method is applied to the benzyl and benzal compounds loosely grouped according to the type of side-chain substituent of the parent toluene molecule.

The benzal compounds are considered first, with the first compound investigated being isopropylbenzene. The rotational barrier of some derivatives of isopropylbenzene have been determined by other experimental methods and these barriers are compared to that found for isopropylbenzene by the J method.

The benzal halides are considered next and the effect of side-chain substituent electronegativity on the barrier determination is discussed. This factor is thought to be quite important when the electronegativity of the substituent has a value greater than that of hydrogen.

The final group of benzal compounds to be investigated are those in which the α carbon of toluene is incorporated into an alicyclic ring. The minimum energy conformations and barriers to rotation of derivatives of phenylcyclohexane, 2-phenyl-1,3-dithiane, 2-phenyl-1,3-dioxane, and 2-phenyl-1,3-dioxolane are determined by the J method.

The benzyl compounds, for which the barriers and stable conformations are determined, are grouped according to the group of the periodic table to which the side-chain substituents belong. Thus, one set of compounds investigated is benzyl alcohol and selenol, while another set is benzylamine, benzyldimethylamine, and benzyldimethylarsine. As with the benzal compounds, the α-substituent electronegativity is an important consideration in the determination of the barriers in the benzyl compounds.

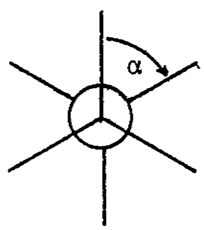
The J method requires the experimentally determined six-bond side-chain proton - ring proton coupling constant of the benzyl or benzal compound under investigation in order to determine the rotational barrier. A series of para-fluoro substituted benzyl and benzal compounds are studied to discover whether the six-bond coupling between the side-chain proton and the para ring fluorine nucleus is also suitable for use in the J method.

Finally, the J method is used to investigate the barrier and stable conformations of derivatives of diphenylmethane. Both the proton-proton and the proton-fluorine coupling, as mentioned above are used.

THEORETICAL AND EXPERIMENTAL CONSIDERATIONS

1. The Hindered Rotor Potential

A simple example of internal rotation is the ethane molecule, in which the two methyl groups rotate relative to each other about the carbon-carbon single bond. The internal rotation is best illustrated by Newman projections of the ethane molecule where the view is down the axis of rotation. Much experimental and theoretical information demonstrates that the ethane molecule prefers



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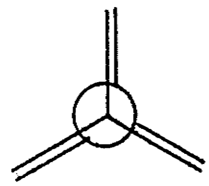

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a minimum energy conformation in which the C-H bonds are staggered, 1, and has a maximum energy conformation when the C-H bonds are eclipsed, 2.

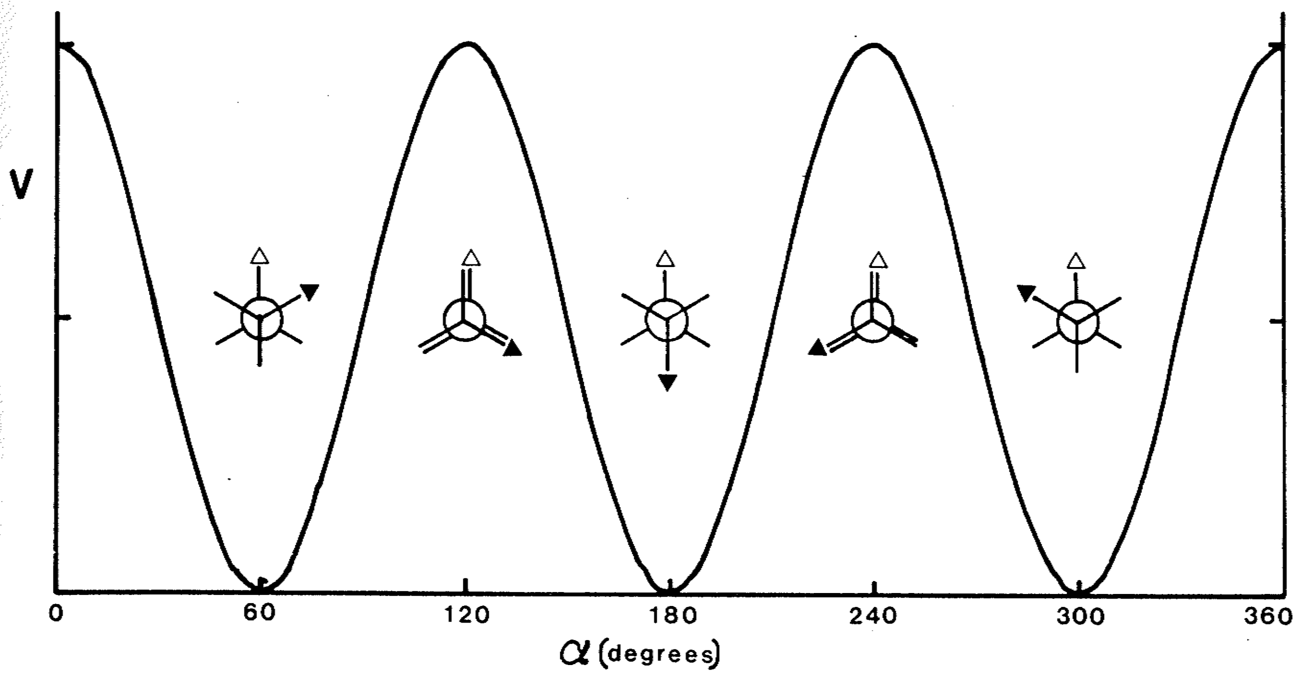
The properties of the potential energy hindering internal rotation can be inferred by rotating one methyl group about the other by a full revolution. If the eclipsed conformation is used to define a 0° orientation, then the rotation can be described by the dihedral angle α, as shown in 1. The energy is a maximum again at 120°, and so on for the full revolution. Thus the potential energy profile has three maxima and three minima of the same energies, and is shown in figure 1a.

The diagram shows that the potential function repeats itself

Figure 1. a) The potential energy of an ethane molecule is plotted against the angle of internal rotation, α. The potential energy profile is three-fold symmetric.

b) A two-fold symmetric potential is plotted against the angle of internal rotation, α. The potential is described by equation [4].

a



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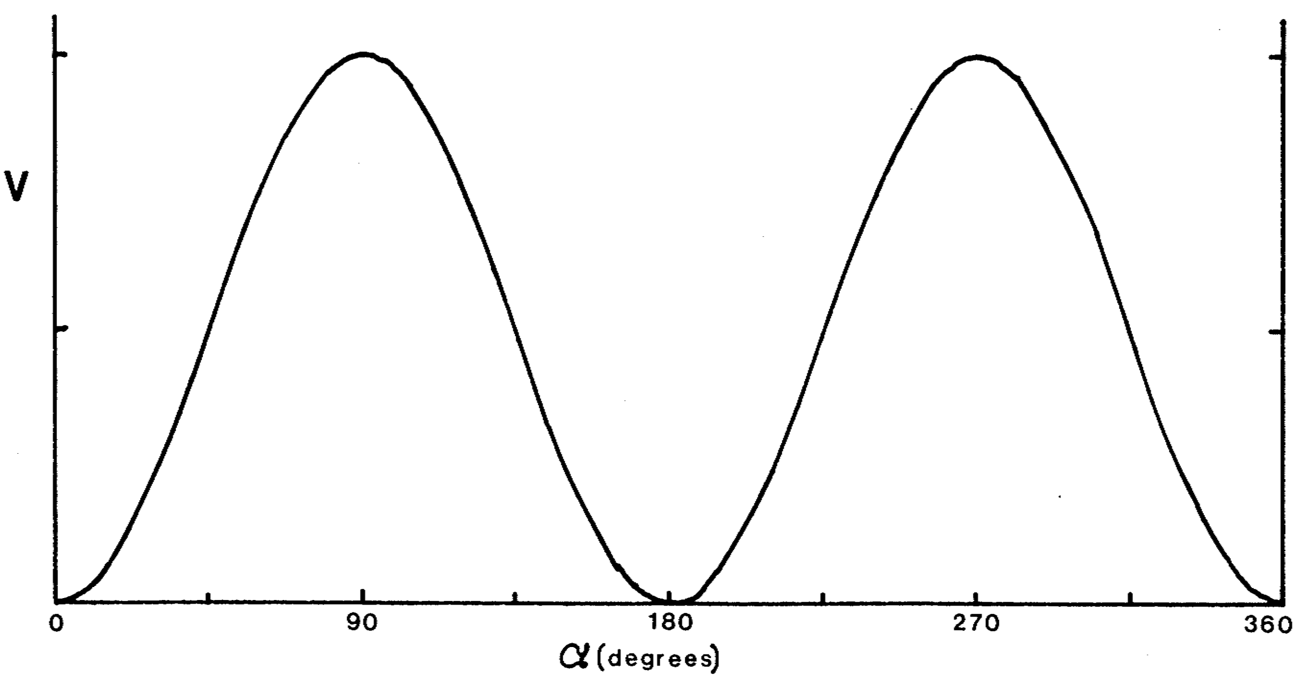
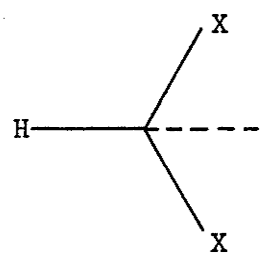


three times within the 360° revolution and, hence, has a period of 120°. Because of the three repetitions it is called a 3-fold symmetric potential and this designation applies to other periodic functions. Thus, there can be 2-, 6-, or n-fold symmetric potentials. In the majority of molecules, however, the period of the potential function is 360° and the potential is described as asymmetric.

The potential energy function describing the internal rotation in benzal and benzyl compounds is assumed to be 2-fold symmetric. This is easily seen by inspecting the projection of the molecule along the axis of rotation, illustrated in 3 to 5. The dashed



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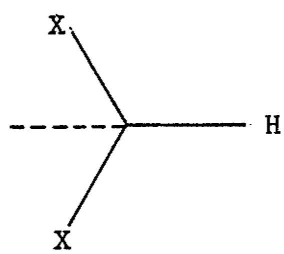

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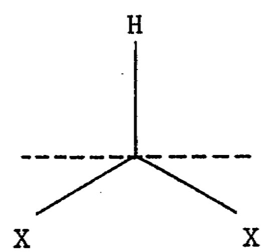

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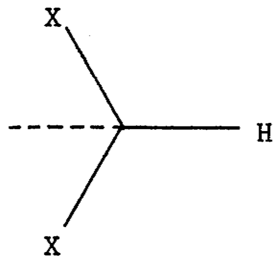
line represents the phenyl ring plane and the solid triangular-shaped lines represent the projection of the benzal top. Replacing one X substituent with a hydrogen, H, transforms the benzal top into a benzyl top. The rotational conformations, 3 to 5, are considered possible minimum energy conformations, and a rotation of the top by 180° in any one of these produces an identical conformation to the original as shown in 6 to 8. The potential energy profile of



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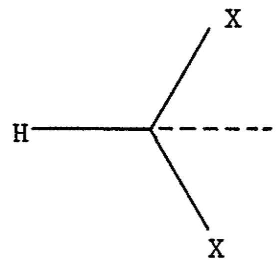

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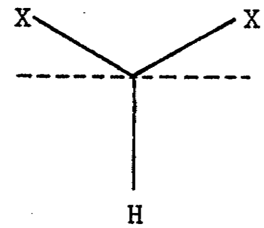

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the rotation appears as in figure 1b with two energy minima and a period of 180°, and, thus, the potential energy function is 2-fold symmetric.

A mathematical description of the potential hindering internal rotation begins with the observation that all such functions are periodic. They can then be represented by a Fourier series,

$$F(\alpha) = \sum_{n=0}^{\infty} b_n \cos(n\alpha) + \sum_{n=0}^{\infty} a_n \sin(n\alpha) \qquad [1]$$

where α is the angle describing the orientation of the top relative to the frame about the axis of internal rotation. The potential is an even function of α and, hence, can be represented by the cosine Fourier series,

$$F(\alpha) = \sum_{n=0}^{\infty} b_n \cos(n\alpha). \qquad [2]$$

This equation is manipulated so that the function is zero when α is zero and the function and coefficient labels are changed to V to yield the expression most used to describe the potential,

$$V(\alpha) = \sum_{n=0}^{\infty} \frac{V_n}{2} [1-\cos(n\alpha)]. \qquad [3]$$

The coefficients, V_n, are determined experimentally.

The characteristics of the coefficients depend on the symmetry of the potential. For an n-fold symmetric potential only the coefficients which are integer multiples of n are non-zero. For example, if the potential is 3-fold symmetric the coefficients, V_3, V_6, V_9,... are non-zero. Experimental values of the coefficients of symmetric potentials show that the preceding term is almost always much greater than the following term in the series, or, in algebraic symbolism for the example above, $V_3 >> V_6 >> V_9 ...$. In most experimental investigations of potentials which are symmetric, only the first term is determined and designated the barrier to rotation. Thus, for benzyl and benzal compounds, the potential function describing the internal rotation is taken to be

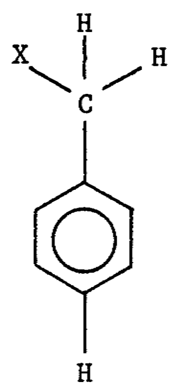
$$V(\alpha) = \frac{V_2}{2} [1-\cos(2\alpha)]. \qquad [4]$$

An asymmetric potential in general has all coefficients non-zero and predictions as to the relative magnitudes of the values are impossible. In most cases of molecules with asymmetric potentials, more than one coefficient must necessarily be determined, and the more coefficients which are determined, the better the description of the potential.

2. <u>The J Method</u>

i) <u>the stereospecific six-bond coupling constant, $^{6}J_{p}^{H,CH_n}$</u>

The J method for determining rotational barriers is specifically applicable to benzyl and benzal compounds, 9 and 10, in which the six-bond coupling between the side-chain proton, H_α, and the para ring proton, H_4, is transmitted



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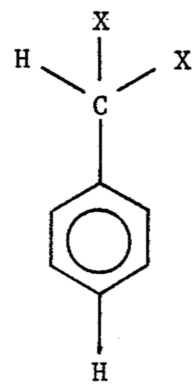

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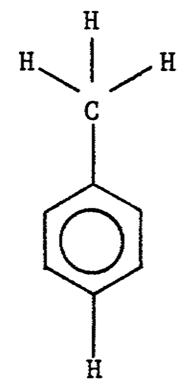


11

by the π electrons via a σ-π mechanism (7,8). This statement is supported by both experimental and theoretical evidence. In toluene, 11, the six-bond coupling between the methyl protons and the *para* proton, $^{6}J_{p}^{H,CH_3}$, has a value of -0.62 Hz (9). In *para*-xylene, the seven-bond coupling between the protons on the two methyl groups, $^{7}J_{p}^{CH_3,CH_3}$, has the same magnitude but opposite sign to the analogous coupling in toluene, namely +0.62 Hz (10). This fact is predicted for a σ-π coupling mechanism (11,12).

INDO MO FPT calculations of the six-bond coupling in toluene (13) give the exact experimental value while CNDO/2 calculations predict a zero value. Since the INDO calculations include π interactions in the formalism while CNDO/2 calculations do not

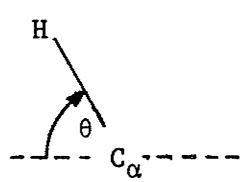
(14), the inferrence is that the coupling is transmitted solely by the π electrons.

By analogy to the Heller-McConnell relation for the hyperfine coupling in radicals (8), the transmission of the six-bond coupling, ${}^6J_p^{H,CH_n}$, by a σ-π mechanism implies that the coupling has a stereospecific dependence on the angle θ given by the expression

$$ {}^6J_p^{H,CH_n} = {}^6J_0^{H,CH_n} + {}^6J_{90}^{H,CH_n} \langle\sin^2\theta\rangle \ . \qquad [5]$$

The angle θ is defined as the angle of rotation of two planes, one containing the C_1-C_α-H fragment and the other containing the aromatic ring. The intersection of the two planes is the C_1-C_α bond axis which is also the axis of rotation of the two planes. The projection of the two planes perpendicular to the rotation axis is shown in 12 where the dashed line is the benzene ring plane. ${}^6J_p^{H,CH_n}$ is the experimentally observed coupling, ${}^6J_0^{H,CH_n}$ is the contribution to the coupling from a non-σ-π mechanism, ${}^6J_{90}^{H,CH_n}$ is the coupling through the π electrons which is a maximum at θ equal to 90°, and $\langle\sin^2\theta\rangle$ is the ensemble average of $\sin^2\theta$ over the hindered rotor states.

If the six-bond coupling, ${}^6J_p^{H,CH_n}$, arises solely from a σ-π mechanism then the term ${}^6J_0^{H,CH_n}$ should be negligible. This is observed in 2,6-dichlorobenzal bromide, 13, where the minimum



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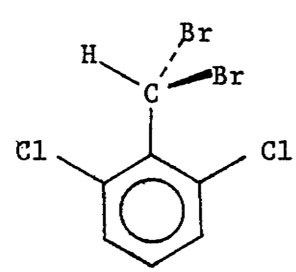

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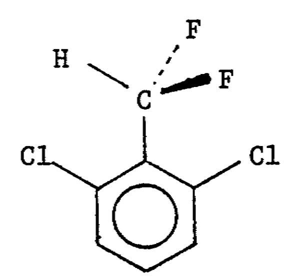


14

energy conformation is as indicated, with the proton in the plane of the benzene ring, and a rotational barrier of 18 kcal/mole (15). The high barrier implies that the proton is held rather rigidly in the plane of the ring. The six-bond coupling, ${}^{6}J_{p}^{H,CH}$, is unobservable or is at least less than 0.03 Hz. ${}^{6}J_{p}^{H,CH}$ is also unobservable in 2,6-dichlorobenzal fluoride, 14, which has the same minimum energy configuration as 12, but a barrier of no more than 8 kcal/mole (16), implying a larger torsional motion than in 11. INDO MO FPT calculations yield a negligibly small six-bond coupling in toluene when θ is zero (13). From these results it is justifiable to rewrite equation [5] as

$$ {}^{6}J_{p}^{H,CH_n} = {}^{6}J_{90}^{H,CH_n} \langle \sin^2\theta \rangle \qquad [6] $$

Equation [6] is the working equation of the J method. ${}^{6}J_{p}^{H,CH_n}$ is the experimentally determined coupling constant in benzyl and benzal compounds. ${}^{6}J_{90}^{H,CH_n}$ is initially determined for toluene, from experimental data, and then used for the different benzyl and benzal compounds. In some cases the toluene value must be modified as discussed later when the individual compound is considered. From the experimental coupling constant, ${}^{6}J_{p}^{H,CH_n}$, and an estimate of ${}^{6}J_{90}^{H,CH_n}$, the value of $\langle \sin^2\theta \rangle$ is calculated. The $\langle \sin^2\theta \rangle$ values can also be calculated as a function of the barrier to rotation, V_2, and a comparison of the value determined from the coupling constant with values corresponding to a series of potential barriers allows an estimate of the rotational barrier in the molecule.

ii) <u>analytical determination of $<\sin^2\theta>$</u>

As previously mentioned, $<\sin^2\theta>$ is the ensemble average of $\sin^2\theta$ over the hindered rotor states and is calculated by the procedure of Ayscough et al. (5). The states and their energies are found by solving the Schrödinger equation where $\hat{H}$ is the

$$\hat{H}\,\psi_m = E_m\,\psi_m$$

hamiltonian operator which is itself a sum of the kinetic and potential energy operators, $\hat{T}$ and $\hat{V}$, respectively. E_m is the energy of the mth state and ψ_m is the wave function describing the mth state. The model which is used to describe the internal rotation is that of the top, the benzyl or benzal rotor, rotating about the axis of rotation, the C_1-C_α bond, relative to the stationary frame, the benzene ring. The orientation of the top relative to the frame is given by the angle defining internal rotation, α. The only motion of the molecule is assumed to be the internal rotation and, hence, the kinetic energy is dependent on only one parameter, the angle α. The kinetic energy operator is then

$$\hat{T} = -\frac{\hbar^2}{2I_r}\frac{d^2}{d\alpha^2} \qquad [7]$$

where $\hbar$ is Planck's constant divided by 2π and I_r is the reduced moment of inertia of the molecule. The potential energy operator is just the 2-fold symmetric potential function, equation [4],

$$\hat{V} = \frac{V_2}{2}\,[1-\cos(2\alpha)]. \qquad [4]$$

The hamiltonian is $\hat{T} + \hat{V}$ so that the Schrödinger equation for the system is

$$\left\{\frac{-\hbar^2}{2I_r}\frac{d^2}{d\alpha^2} + \frac{V_2}{2}\left[1-\cos(2\alpha)\right]\right\}\psi_m = E_m\,\psi_m \qquad [8]$$

The solutions of this equation, ψ_m, can be expanded as odd (o) and even (e) Fourier series, where $a_{m\lambda}$ and $b_{m\lambda}$ are the coefficients

$$\psi_m^o = \sum_{\lambda=1}^{\infty} a_{m\lambda}\pi^{-1/2}\sin(2\lambda\alpha) \qquad [9]$$

$$\psi_m^e = b_{m0}(2\pi)^{-1/2} + \sum_{\lambda=1}^{\infty} b_{m\lambda}\pi^{-1/2}\cos(2\lambda\alpha) \qquad [10]$$

of the expansion terms. The energy levels of each state m, and the expansion coefficients, $a_{m\lambda}$ and $b_{m\lambda}$, are determined by diagonalization of the odd and even hamiltonian matrices. The elements of the matrices are

$$\langle\psi_0^e \mid \hat{H} \mid \psi_0^e\rangle = \frac{V_2}{2} \qquad [11]$$

$$\langle\psi_0^e \mid \hat{H} \mid \psi_1^e\rangle = \langle\psi_1^e \mid \hat{H} \mid \psi_0^e\rangle = \frac{-V_2}{2^{3/2}} \qquad [12]$$

$$\langle\psi_m^e \mid \hat{H} \mid \psi_m^e\rangle = \langle\psi_m^o \mid \hat{H} \mid \psi_m^o\rangle = \frac{2\hbar^2 m^2}{I_r} + \frac{V_2}{2} \quad m = 1,2,\ldots n \qquad [13]$$

$$\langle\psi_m^e \mid \hat{H} \mid \psi_{m\pm1}^e\rangle = \langle\psi_m^o \mid \hat{H} \mid \psi_{m\pm1}^o\rangle = \frac{-V_2}{4} \quad m = 1,2,\ldots n \qquad [14]$$

All the other matrix elements are zero. The series expansion is truncated at the nth term.

In order to determine the ensemble average $\langle\sin^2\theta\rangle$, the expectation values of $\sin^2\alpha$, $\langle\psi_m^{o(e)}|\sin^2\alpha|\psi_m^{o(e)}\rangle$, for each level must be determined. An analytical expression for the expectation value can be derived in terms of the energy and expansion coefficients of each state. Thus, the hamiltonian matrix can be written as

$$\langle\psi_m^{o(e)} \mid \hat{H} \mid \psi_m^{o(e)}\rangle = \langle\psi_m^{o(e)} \mid \hat{T} + \hat{V} \mid\psi_m^{o(e)}\rangle$$

$$= \langle\psi_m^{o(e)} \mid \hat{T} \mid\psi_m^{o(e)}\rangle + \langle\psi_m^{o(e)} \mid \hat{V} \mid\psi_m^{o(e)}\rangle .$$

Rearrangement of the terms yields

$$\langle\psi_m^{o(e)} \mid \hat{V} \mid \psi_m^{o(e)}\rangle = \langle\psi_m^{o(e)} \mid \hat{H} \mid \psi_m^{o(e)}\rangle - \langle\psi_m^{o(e)} \mid \hat{T} \mid \psi_m^{o(e)}\rangle . \quad [15]$$

Now, the potential energy operator, equation [4] can be rewritten as

$$\hat{V} = V_2 \sin^2\alpha \ . \quad [16]$$

The first term on the right hand side of equation [15] is the energy of the mth hindered rotor state, $E_m^{o(e)}$. Then, if equation [16] is substituted for $\hat{V}$, $E_m^{o(e)}$ for the hamiltonian matrix expression, and equation [7] for $\hat{T}$, equation [15] becomes

$$\langle\psi_m^{o(e)}|V_2 \sin^2\alpha|\psi_m^{o(e)}\rangle = E_m^{o(e)} - \langle\psi_m^{o(e)}|\frac{-\hbar^2}{2I_r}\frac{d^2}{d\alpha^2}|\psi_m^{o(e)}\rangle \quad [17]$$

The kinetic energy matrix elements can be easily determined. The expectation values of $\sin^2\alpha$ for the odd and even state functions are given by

$$<\psi_m^o \; |\sin^2\alpha| \; \psi_m^o> = \frac{E_m^o}{V_2} - \frac{2\hbar^2}{I_r V_2} \sum_{\lambda=1}^{\infty} \lambda^2 |a_{m\lambda}|^2 \qquad [18]$$

$$<\psi_m^e \; |\sin^2\alpha| \; \psi_m^e> = \frac{E_m^e}{V_2} - \frac{2\hbar^2}{I_r V_2} \sum_{\lambda=0}^{\infty} \lambda^2 |b_{m\lambda}|^2 \qquad [19]$$

The energies and expansion coefficients have already been determined by the diagonalization of the hamiltonian matrix and, thus, the sums in equations [18] and [19] are truncated at the nth term.

The quantum statistical average of the $\sin^2\alpha$, denoted by $<\sin^2\alpha>$, is

$$<\sin^2\alpha> = \sum_{p=0}^{\infty} <\psi_p \; |\sin^2\alpha| \; \psi_p> \frac{\exp(-E_p/kT)}{\sum_{p=0}^{\infty} \exp(-E_p/kT)} \qquad [20]$$

where the sums are over both the odd and even states, k is the Boltzmann constant and T is the absolute temperature.

The angle α is defined to be zero for the minimum energy conformation of the molecule. The angle θ is the angle between the ring plane and the C_α-H bond as defined previously, and is zero when the bond is in the plane of the ring. Thus, α and θ are the same parameter although they may differ by a constant angular term. For certain minimum energy conformations α and θ are equivalent. For other conformations where α and θ are not the same the relationship between the two angles must be deduced from a trigonometric identity and substituted in the left hand side of equations [18] and [19] to yield the expectation values of $\sin^2\theta$, which are then used to calculate the ensemble average. The J method requires $<\sin^2\theta>$ rather than $<\sin^2\alpha>$.

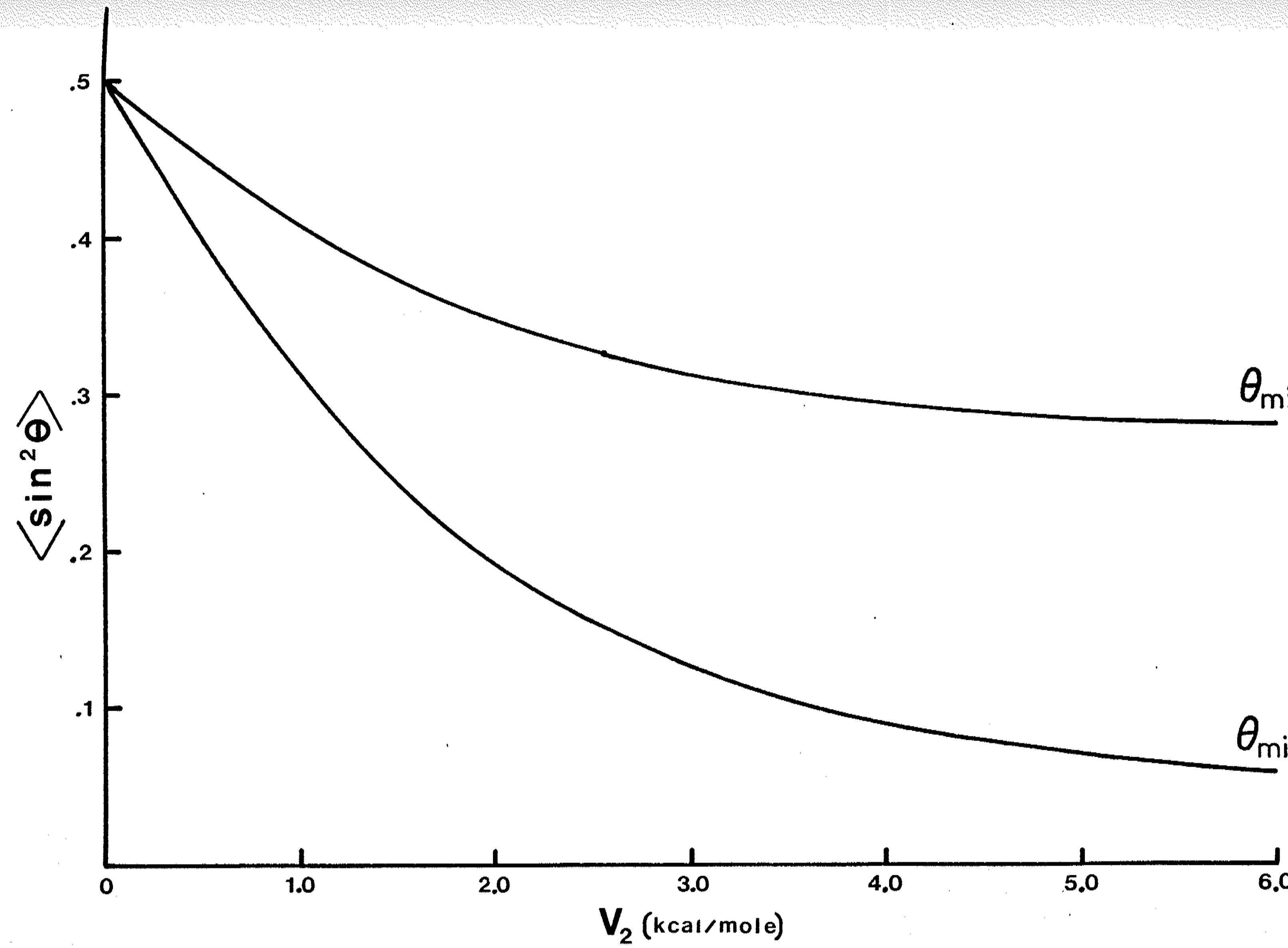
The important result of the calculation is that $<\sin^2\theta>$ is a function of the barrier to rotation, V_2. Thus, the barrier can be found from the experimental value of $<\sin^2\theta>$ determined by NMR and a table or graph of $<\sin^2\theta>$ versus V_2.

iii) <u>numerical calculation of $<\sin^2\theta>$</u>

A computer program was written to calculate $<\sin^2\theta>$ as a function of the barrier, V_2, the reduced moment of inertia, I_r, and the absolute temperature, T. Thus, for a constant temperature and reduced moment, a series of points corresponding to the variation of $<\sin^2\theta>$ with V_2 could be calculated, listed, and plotted. Moreover, $<\sin^2\theta>$ versus V_2 curves could be calculated for minimum energy conformations in which θ was 0° or 30°. Examples of both curves are shown in figure 2.

The reduced moment of inertia, I_r, was calculated with another computer program which used the procedure and equations described by Pitzer et al. (17a,b,c). The co-ordinates of the molecule were required and were calculated from the standard geometries proposed by Pople et al. (14). Because the symmetry of the rotation about the C_1-C_α bond is less than three-fold, the reduced moment of inertia varies with the angle of rotation, α. However, $<\sin^2\theta>$ is very insensitive to I_r and the small variation during the rotation is considered negligible. This can be seen in the data of $<\sin^2\theta>$ as a function of I_r in table 1. The value of I_r used in the calculation of the $<\sin^2\theta>$ versus V_2 curves is that calculated for the assumed low energy conformer.

Figure 2. The calculated values of <$\sin^2\theta$> are plotted against the two-fold symmetric barrier to internal rotation, V_2, for a reduced moment of inertia of 1.0×10^{-38} g cm^2, a temperature of 305 K, and two possible minimum energy conformations denoted by $\theta_{min} = 0°$ and $\theta_{min} = 30°$. The θ_{min} values are the angles of internal rotation the C_α-H bond assumes relative to the benzene ring plane in the presence of an infinite barrier.



.5
.4
.3
.2
.1
⟨sin²θ⟩
θmin = 30°
θmin = 0°
0
1.0
2.0
3.0
4.0
5.0
6.0
V2 (kcal/mole)

Another parameter which affects the calculation is the number of terms used in the expansion of the wave functions. The default values in the program are 10 and 11 terms for the odd and even matrices, respectively. There are then 21 states and energy levels which are used in the final summation for $<\sin^2\theta>$. The truncation of the series after 10 terms was considered adequate for the accuracy of the experiment, although the number of terms in the expansion could have been set to a maximum of 50. Values of $<\sin^2\theta>$ for a series of increasing basis functions are tabulated in table 1.

The temperature used in the calculations of $<\sin^2\theta>$ was in most cases 305 K, the ambient temperature of the NMR probe and, thus, of the sample. However, in the investigation of diphenylmethane derivatives, a temperature study of the stereospecific six-bond fluorine, proton coupling was performed. The change in $<\sin^2\theta>$ with a relatively large change in temperature is small as shown in table 1.

The data in table 1 show the variation of $<\sin^2\theta>$ with each of the parameters: barrier to rotation, reduced moment of inertia, number of basis functions, and temperature. All parameters, except the one investigated, were held at arbitrary constant values.

iv) $\underline{{}^6J_{90}^{H,CH_n}}$

${}^6J_{90}^{H,CH_n}$ is required to calculate $<\sin^2\theta>$ from the experimentally determined coupling constant, ${}^6J_p^{H,CH_n}$. ${}^6J_{90}^{H,CH_n}$ can be found for toluene by assuming that there is free rotation of table 1

Variation of $\langle \sin^2\theta \rangle$ with some parameters.

V_2 = 1.0 kcal/mole

V_2 kcal/mole	$\langle \sin^2\theta \rangle$, θ = 0°	$\langle \sin^2\theta \rangle$, θ = 30°
0.0	0.500	0.500
0.5	0.402	0.451
1.0	0.312	0.408
1.5	0.245	0.373
2.0	0.192	0.346
2.5	0.154	0.327
3.0	0.126	0.313
3.5	0.107	0.303
4.0	0.092	0.296
4.5	0.081	0.290

$I_r = 1.0 \times 10^{-38}$ g cm^2

I_r g cm^2	$\langle \sin^2\theta \rangle$, θ = 0°	$\langle \sin^2\theta \rangle$, θ = 30°
10.0×10^{-38}	0.318	0.409
5.0	0.317	0.409
1.0	0.315	0.408
0.8	0.315	0.408
0.6	0.314	0.407
0.4	0.313	0.407
0.2	0.311	0.406
0.1	0.311	0.406
0.05	0.313	0.406
0.01	0.324	0.412

T = 305 K

T °K	$\langle \sin^2\theta \rangle$, θ = 0°	$\langle \sin^2\theta \rangle$, θ = 30°
260	0.289	0.394
270	0.295	0.398
280	0.301	0.401
290	0.307	0.404
300	0.313	0.406
310	0.318	0.409
320	0.323	0.412
330	0.328	0.414
340	0.332	0.416
350	0.337	0.418

#E.T. = 10

#ET	$\langle \sin^2\theta \rangle$, θ = 0°	$\langle \sin^2\theta \rangle$, θ = 30°
10	0.315	0.408
15	0.312	0.406
20	0.311	0.405
25	0.310	0.405
30	0.310	0.405
35	0.310	0.405
40	0.310	0.405
45	0.310	0.405
50	0.310	0.405

V_2, barrier to rotation

I_r, reduced moment of inertia

T, temperature

#E.T., number of expansion terms; n for the odd hamiltonian matrix, n+1 for the even hamiltonian matrix

As $\langle \sin^2\theta \rangle$ is varied with one parameter, the other parameters are set to the values noted above the table.

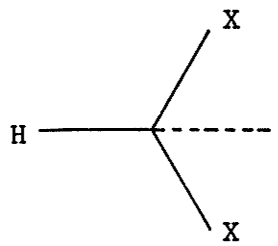
the methyl top, which follows from the very small magnitude of the rotational barrier, 0.014 kcal/mole (18). Now, $<\sin^2\theta>$ is 0.5 for a zero barrier, and with ${}^6J_p^{H,CH_3}$ = -0.62 Hz in toluene (9), equation [6] is solved to give a ${}^6J_{90}^{H,CH_3}$ value of -1.24 Hz.

This value depends on the σ-π overlap of the C_α-H σ bonds of the methyl group with the π orbitals of the benzene ring. This overlap can be affected by substituents on the methyl group or the ring, which can change the C_1-C_α-H bond angle or the electron density of the C_α-H bond. These considerations are specific to the substituents and will be discussed in the sections on the individual compounds.

Ring substituents which are assumed to have no effect on ${}^6J_{90}^{H,CH_n}$ are chlorine and bromine atoms in the 3 and 5 ring positions. Many of the compounds had the 3,5-dihalo substituents in order to facilitate the analysis of their spectra. The assumption is supported by experimental data of some ring-substituted toluene derivatives (19,20), which show negligible perturbations of the long range side-chain protons to the ring proton couplings and especially the ${}^6J_p^{H,CH_3}$ value in 3,5-dichlorotoluene (21) which is -0.60 ± 0.02 Hz, equal to the value in toluene within experimental error.

v) $<\sin^2\theta>$ and the minimum energy conformation

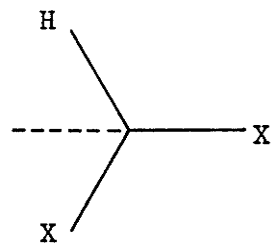
Figure 2 shows two $<\sin^2\theta>$ versus V_2 curves, one for a minimum energy conformation in which θ_{min} = 0° and one for which θ_{min} = 30°. The set of possible minimum energy conformations for benzal compounds is shown in <u>15</u> to <u>17</u> with the corresponding



$\theta_{min} = 0°$

$0.5 \geq \langle \sin^2\theta \rangle \geq 0.0$

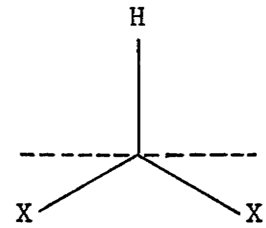
<u>15</u>



$\theta_{min} = 60°$

$0.5 \leq \langle \sin^2\theta \rangle \leq 0.75$

<u>16</u>

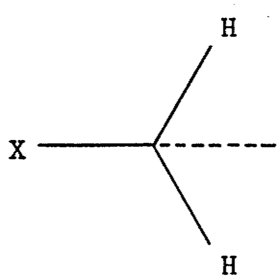


$\theta_{min} = 90°$

$0.5 \leq \langle \sin^2\theta \rangle \leq 1.0$

<u>17</u>

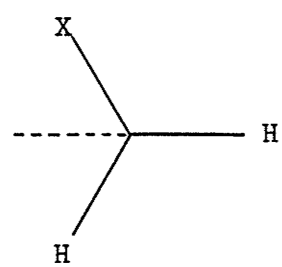
θ_{min} value. The set for benzyl compounds is shown in <u>18</u> to <u>20</u>. Since the benzyl compounds have two coupling protons in the top there are two θ values which give the orientations of the C_α-H



$\theta_{min} = (60°,60°)$

$0.5 \leq \langle \sin^2\theta \rangle \leq 0.75$

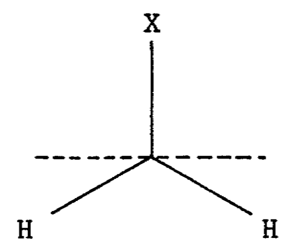
<u>18</u>



$\theta_{min} = (0°,60°)$

$0.5 \geq \langle \sin^2\theta \rangle \geq 0.375$

<u>19</u>



$\theta_{min} = (30°,30°)$

$0.5 \geq \langle \sin^2\theta \rangle \geq 0.25$

<u>20</u>

bonds relative to the phenyl ring plane. θ is always defined with respect to the coupling nuclei and if two coupling species are present in the top, say hydrogen and fluorine, then θ_{min} may have different values for the same preferred conformation.

The θ_{min} values allow the determination of the limits of $\langle\sin^2\theta\rangle$ as the barrier becomes very large or infinite. In this case the configuration of the molecule is locked into that of the minimum energy conformer and $\langle\sin^2\theta\rangle$ is just $\sin^2\theta$ where θ is the value in the rigid minimum energy conformer. Where there are two θ_{min} values the resultant $\sin^2\theta$ is the average of $\sin^2\theta$ for the two angles, viz., $\sin^2\theta$ for 19 is $(\sin^2 0° + \sin^2 60°)/2$. Since free rotation yields a $\langle\sin^2\theta\rangle$ value of 0.5, the limits of $\langle\sin^2\theta\rangle$ for the various conformations 15 to 20 are known, and given below the respective θ_{min} values in the diagrams.

The ranges of $\langle\sin^2\theta\rangle$ for the particular minimum energy conformers are in some cases mutually exclusive. Thus, for 15 the range is from 0.0 to 0.5 whereas for 17 the range is from 0.5 to 1.0. Any experimental value of $\langle\sin^2\theta\rangle$ will indicate the minimum energy conformation if only these two conformations are considered as possible. Thus, in some cases the J method can be used to determine the geometry of the preferred conformation.

EXPERIMENTAL METHODS

1. Materials and Synthesis

i) 3,5-dibromoisopropylbenzene

3,5-dibromoisopropylbenzene (3,5-dibromocumene) was prepared from p-isopropylaniline (p-cumidine) (Aldrich Chemical Co.). The synthesis followed exactly the procedure of Benkeser et al. (22) in which the cumidine is first brominated and then diazotized to yield the final desired product.

ii) benzal chloride and benzal bromide

The benzal chloride and benzal bromide were purchased from the Aldrich Chemical Co.

iii) 4-methylbenzal fluoride

4-Methylbenzal fluoride was prepared by fluorination of 4-methylbenzaldehyde (Aldrich) with sulfur tetrafluoride. The procedure followed exactly that of Rowbotham et al. (16).

iv) 3,5-dichlorobenzal chloride

3,5-dichlorobenzal chloride was prepared by the free radical chlorination of 3,5-dichlorotoluene (Aldrich). The method was exactly as described in the article by Fuhr et al. (23).

v) 3,5-dichlorophenylcyclohexane

The 3,5-dichlorophenylcyclohexane was prepared by a Grignard reaction of 3,5-dichlorophenylmagnesium bromide and cyclohexanone to a tertiary alcohol. Hydrogenation with a palladium charcoal catalyst produced the desired compound. The steps in this synthesis were outlined by Eidenschink et al. (24).

The preparation and reaction of the Grignard reagent follows. The procedure was the same for all subsequent syntheses which required a Grignard reagent and reaction, and will be referred to as these syntheses are described.

In a 100 ml 3-necked flask, fitted with a dropping funnel, reflux condenser and gas inlet tube, were placed 10 ml of anhydrous ether, 0.55 g of magnesium turnings and a crystal of iodine. In the dropping funnel was placed a solution of 5 g of 1-bromo-3,5-dichlorobenzene (Pfalz and Bauer) in 15 ml of anhydrous ether. The system was flushed with nitrogen and the 1-bromo-3,5-dichlorobenzene solution added dropwise with stirring. Reflux was initiated and maintained by gentle heating with a water bath. After addition was completed the solution was refluxed for an additional one half hour. Then a solution of 22 g of cyclohexanone in 15 ml of anhydrous ether was added dropwise from the dropping funnel. The solution was refluxed again for one half hour after which 25 ml of a 30% sulphuric acid solution were added and the final solution vigorously mixed. After 15 minutes the aqueous and ethereal layers were separated and the former solution washed with two 15 ml portions of ether. The combined ether solutions were then dried over magnesium sulphate.

The ether solution, after filtration, was rotary evaporated to yield the alcohol which was redissolved in anhydrous ethyl alcohol.

Reduction by catalytic hydrogenation was effected over palladium activated charcoal (10% Pd). The ethyl alcohol solvent was removed by rotary evaporation under reduced pressure to yield the product which was used at this stage to make up the NMR sample. That the product was actually 3,5-dichlorophenylcyclohexane was verified by a mass spectrum and the NMR spectrum which were unequivocal.

vi) <u>2-(3,5-dichlorophenyl)-1,3-dithiane</u>

The synthesis of this compound involved bubbling anhydrous hydrogen chloride (Matheson) through a solution of 1,3-propane-dithiol (Aldrich Chemical Co.) and 3,5-dichlorobenzaldehyde (Aldrich Chemical Co.). The procedure followed exactly that described by Seebach et al. (25) with the exception that 3,5-dichlorobenzaldehyde was used instead of benzaldehyde. The prepared compound was verified by a mass spectrum and the NMR spectrum.

vii) <u>2-(3,5-dichlorophenyl)-1,3-dioxane</u>

A solution of 1.4 g of 1,3-propanediol (Aldrich) in 40 ml of benzene was prepared. To the solution was added 2.0 g of 3,5-dichlorobenzaldehyde (Aldrich) and a small amount of p-toluenesulfonic acid. The mixture was then placed in a Stark & Smyth apparatus and refluxed overnight. The next day the solution was washed with two 40 ml portions of water, three 40 ml portions of sodium bicarbonate solution, and again with two 40 ml portions of water. The benzene layer was dried over anhydrous magnesium sulfate and then evaporated on a rotary evaporator. The product, 2-(3,5-dichlorophenyl)-1,3-dioxane, was used to prepare the NMR sample.

viii) 2-(3,5-dichlorophenyl)-1,3-dioxolane

The procedure to prepare the dioxolane derivative is exactly the same as to prepare the dioxane derivative described immediately above. To a solution of 1.0 g ethylene glycol (Aldrich) in 40 ml of benzene was added 2.0 g of 3,5-dichlorobenzaldehyde. This final solution was placed in a Stark & Smyth apparatus and refluxed overnight. The solution was then washed with two 40 ml portions of water, three 40 ml portions of a sodium bicarbonate solution, and again with two 40 ml portions of water. The benzene layer was dried over anhydrous magnesium sulfate and then evaporated in a rotary evaporator. The product of 2-(3,5-dichlorophenyl)-1,3-dioxolane was used to prepare the sample.

ix) 3,5-dichlorobenzyl alcohol

The formation of 3,5-dichlorobenzyl alcohol followed from the reduction of 3,5-dichlorobenzoic acid by lithium aluminum hydride. The apparatus consisted of a three-necked 250 ml round bottom flask with a stopper, dropping funnel, and reflux condenser attached. Into the flask was placed 50 ml of dry ether followed by 2.0 g of lithium aluminum hydride. Any hydride adhering to the neck or sides of the flask was washed down with a further 25 ml of ether. In the dropping funnel was placed a solution of 10 g of 3,5-dichlorobenzoic acid in 75 ml of dry ether. The ether-hydride solution was magnetically stirred for about ten minutes and then the dichlorobenzoic acid solution was added dropwise so as to produce a gentle reflux. The solution was stirred approximately ten minutes past the addition of the last drop of the dichlorobenzoic acid solution, and then water was carefully added dropwise to decompose the lithium aluminum hydride. When no reaction was observed with further addition of water, the solution was filtered and the ether layer was separated and dried over anhydrous magnesium sulphate. The ether was then removed on the rotary evaporator and the product remaining, the 3,5-dichlorobenzyl alcohol was used to make the NMR sample.

x) <u>3,5-dichlorobenzyl selenol</u>

The 3,5-dichlorobenzyl selenol was prepared by the reaction of 3,5-dichlorobenzyl magnesium bromide with selenium powder. In order to produce the Grignard reagent, 3,5-dichlorobenzyl alcohol (the preparation of which is described immediately above) was reacted with PBr_3 to yield the bromide which was then used to prepare the magnesium bromide.

The sample of 3,5-dichlorobenzyl alcohol prepared above, less a small amount used for preparation of the NMR sample, was redissolved in 75 ml of anhydrous ether and placed in a three-necked flask with stopper, dropping funnel and reflux condenser attached. With stirring, 10 ml of PBr_3 was added dropwise from the dropping funnel. Stirring was continued for two hours. The solution was then neutralized by the addition of 75 ml of sodium bicarbonate. The ether layer was separated and washed with three 50 ml portions of water, and then dried over anhydrous magnesium sulphate. The filtered solution was used to prepare the Grignard reagent by exactly the same procedure as described in the dichlorophenylcyclohexane synthesis, v).

The benzyl selenol was now prepared by the procedure of Foster (26) for the preparation of phenylselenol. To the Grignard reagent contained in a three-necked flask fitted with a reflux condenser, a glass stopper replacing the dropping funnel, and a glass inlet tube, was slowly added 4.0 g of dry powdered selenium. During the addition the solution was magnetically stirred and heated to a gentle reflux which was continued for a half hour after the last addition of selenium. The solution was then poured over 100 g of cracked ice to which was added 10 ml of concentrated hydrochloric acid and the mixture hand stirred. The ether and aqueous layers were separated and the aqueous layer was washed with small portions of ether. The combined ether extracts were dried over anhydrous calcium chloride. The solution was then filtered and the ether removed on a rotary evaporator to yield the product, 3,5-dichlorobenzyl selenol, which was used to prepared the NMR sample.

xi) <u>3,5-dichlorobenzylamine</u>

The compound was purchased from the Aldrich Chemical Company.

xii) <u>3,5-dichlorobenzyldimethylamine</u>

3,5-dichlorobenzyldimethylamine was prepared by the reaction of 3,5-dichlorobenzyl bromide with dimethylamine. The 3,5-dichlorobenzyl bromide was prepared by reducing 3,5-dichlorobenzoic acid to 3,5-dichlorobenzyl alcohol with lithium aluminum hydride, as described in section ix), and subsequent conversion of the benzyl alcohol to the benzyl bromide by reaction with PBr_3 as described in section x).

2.0 g of 3,5-dichlorobenzyl bromide were dissolved in 50 ml of benzene and gaseous dimethylamine (Matheson) was bubbled through the solution for approximately fifteen minutes. The 3,5-dichlorobenzyldimethylamine precipitated in the solution and was filtered off. The solid was washed with several portions of benzene and let dry before it was used in preparation of the NMR sample.

xiii) <u>3,5-dichlorobenzyldimethylarsine</u>

3,5-dichlorobenzyldimethylarsine was prepared by a Grignard reaction of 3,5-dichlorobenzylmagnesium bromide with dimethyliodoarsine. The procedure exactly followed that of Schmidt et al. (27) with the exception that 3,5-dichlorobenzyl bromide was used rather than benzyl bromide. The benzyl bromide derivative was prepared from the 3,5-dichlorobenzoic acid as described in sections ix) and x).

The dimethyliodoarsine was synthesized from methyldiiodoarsine. The reagents involved in the synthesis of methyldiiodoarsine were arsenic (III) oxide (Alfa Ventron), sodium hydroxide (Fisher), methyl iodide (Fisher), sulfur dioxide (Matheson) and sodium iodide (Fisher). The procedure followed exactly that described by Millar et al. (28a).

The dimethyliodoarsine followed from the methyldiiodoarsine and the synthesis required the same reagents listed for the synthesis of the methyl diiodoarsine and followed the procedure again described by Millar et al. (28b).

The Grignard reaction was carried out in a three-necked flask fitted with a dropping funnel, reflux condenser and gas inlet tube. In the flask were placed 0.50 g of magnesium, 15 ml of anhydrous ether, and a crystal of iodine. In the dropping funnel were placed 5 g of the dried prepared 3,5-dichlorobenzylbromide in 35 ml of anhydrous ether. The system was flushed with nitrogen and magnetic stirring of the solution in the flask was begun. The bromide was then slowly added so as to maintain a reflux. At the end of the addition, the solution was heated with a water bath and refluxed for a further half hour. The solution was then filtered into a clean dry dropping funnel which was then fitted onto a three-necked flask with a reflux condenser and gas inlet tube attached. In the flask were placed 3.6 g of dimethyliodoarsine in 25 ml of anhydrous ether. The system was flushed with nitrogen and the Grignard reagent was slowly added with stirring. Reflux was effected during addition by a heated water bath and maintained for a further half hour. The solution was then poured over 50 g of crushed ice to which was added 10 ml of 30% sulphuric acid. The mixture was hand stirred. The ether and aqueous layers were separated and the aqueous layer washed with several small portions of ether. The combined ether layers were dried over anhydrous magnesium sulphate. The filtered solution was rotary evaporated to yield the product, 3,5-dichlorobenzyldimethylarsine which was used to prepare the NMR sample.

xiv) <u>p-fluorotoluene derivatives</u>

The following compounds were purchased commercially: p-fluorotoluene, p-fluorobenzyl chloride, p-fluorobenzyl bromide, p-fluorobenzal chloride and p-fluoroisopropylbenzene, from the Aldrich Chemical Co. and p-fluorobenzyl cyanide, from the Parish Chemical Co.

xv) <u>3,5-dichlorobenzyl cyanide</u>

3,5-dichlorobenzyl cyanide was produced by reacting 3,5-dichlorobenzyl bromide, the preparation of which is described in sections xi) and x) above, with KCN (Baker). A 100 ml three-necked flask was fitted with a reflux condenser, a dropping funnel and a stopper. In the flask were placed 1.7 g of KCN in 25 ml of reagent grade acetone, and in the dropping funnel were placed 5 g of 3,5-dichlorobenzyl bromide in 25 ml of acetone. The KCN solution was first heated with a water bath and stirred to dissolve the KCN. Then the benzyl bromide solution was added slowly while the solution in the flask was refluxed. After the final addition of the bromide the solution was refluxed for a further four hours. The solution was then filtered and rotary evaporated to yield the product, 3,5-dichlorobenzyl cyanide which was used to prepare the sample.

xvi) <u>diphenylmethane derivatives</u>

The following compounds were purchased commercially: 4-amino diphenylmethane, from K and K chemicals, and 4,4'-difluorodiphenylmethane from the Aldrich Chemical Company.

The 3,5-dibromodiphenylmethane was prepared from the 4-aminodiphenylmethane by bromination of the amino compound followed by diazotization and deamination of the 3,5-dibromo-4-aminodiphenylmethane. The procedures were standard and are described in the text by Vogel (29).

2. Sample Preparation

The samples were prepared by weighing into glass vials the compound solute and the solvent to give the correct concentration in mole per cent. In the cases where the samples were prepared as volume per cent, the solute and the solvent were introduced directly into the NMR sample with Pasteur pipettes and the concentrations were estimated by measuring the relative heights of the solute and solvent in the tube. The tubes were precision-bore 5 mm OD type. In both cases small amounts of tetramethylsilane (TMS) were added as a lock and reference compound. The samples were degassed by the freeze-pump-thaw technique and at least five cycles were performed before the tube was sealed with a torch.

3. Spectroscopic Method

The proton magnetic resonance spectra were recorded in the frequency sweep mode on a Varian HA-100-D spectrometer at an ambient probe temperature of 305 ± 1 K. Sections of the spectrum containing any resolvable peaks were recorded at least four times at a spectral dispersion of 1 Hz/cm and sweep rates of 0.02 or 0.01 Hz/s. Marker lines were placed at approximately 5 Hz intervals. The frequency of a line was the difference between the sweep and manual oscillator frequencies read from a frequency counter. The positions of the markers and the peaks between the markers were measured along a straight edge ruler by a vertical line on a triangle with a vernier attached. From the measured positions and the frequencies of the markers, the frequencies of the peaks were linearly interpolated, and averaged over the number of times the particular sets of peaks were recorded. A standard deviation was calculated for each peak frequency determined and was always less than 0.02 Hz.

In order to simplify some spectra and determine the relative signs of coupling constants, full and partial decoupling (30) or tickling experiments (31) were performed. The centre frequency of a peak or region to be irradiated was set on a Hewlett-Packard HP 4204 A oscillator and the strength of the irradiating field was adjusted manually to give the desired effect.

The fluorine magnetic resonance spectra of 4,4'-difluorodiphenylmethane were recorded in the FT mode on a Bruker WH-90 spectrometer at a frequency of 84.69 MHz. The ring protons of the compound were selectively decoupled with a decoupler system which was part of the spectrometer. The spectra were recorded at different temperatures and the temperatures were measured by a thermocouple supplied with the instrument.

The parameters used to obtain the spectra were a pulse width of 2.8 μs corresponding to a tip angle of approximately 40°, a spectral width of 500 Hz, an acquisition time of about 32 s, and a data storage area in the computer of 32 K words.

The use of the FT spectrometer for recording the fluorine spectrum of the 4,4'-difluorodiphenylmethane raises the question of whether the spectral parameters determined from the FT spectrum would be the same as those determined from a cw spectrum, that is, whether there are any systematic errors inherent in the two types of spectra. An analysis of the spectra of p-flourobenzylthiol recorded under similar conditions on each of the spectrometers mentioned above (32) showed that any differences in the spectral parameters not due to small concentration and solvent effects were completely negligible. As an example, $^{6}J_{p}^{F,CH_2}$ was determined to be 0.719(3) Hz from the cw spectrum and 0.717(3) Hz from the FT spectrum, where the number in parentheses is the standard deviation in the last significant figure.

4. Computations

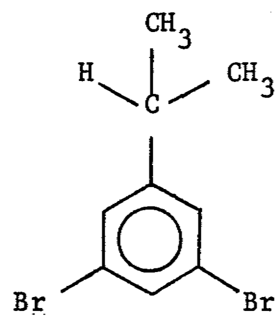
Almost all of the spectral analyses and simulations were done by the computer program LAME (33,34). Initial guesses of the spectral parameters are entered into the program which then produces a plot of the theoretical spectrum. When the theoretical and experimental spectra are quite similar in appearance, the peak frequencies of the experimental spectrum are matched with the frequencies calculated by the program. The program is then allowed to iterate and determine the values of the parameters which yield a minimum in the root mean square deviation. A standard deviation is calculated for each of the spectral parameters, that is, the chemical shifts and coupling constants. The experimental deviation is assumed to be two or three times the calculated standard deviation and is almost always taken to be ± 0.02 Hz.

The methyl decoupled spectrum of p-methylbenzal fluoride was first analyzed by means of the program LAME. The spectral parameters found in this way were used in the computer program NUMARIT (54,55) to determine the long-range methyl couplings. The program was used in the non-iterative mode and the final spectral parameters, that is, the methyl couplings, were those values which produced the best visual fit between the simulated and experimentally observed spectra.

Molecular orbital calculations were performed at the semi-empirical level by an INDO program (14,35) and at the *ab initio* level by a GAUSSIAN 70 program (36,37). Standard geometries (14,38) were used in all cases in the determination of the atom coordinates of the considered molecules.

RESULTS AND DISCUSSION

1. 3,5-Dibromoisopropylbenzene



In order to test the J method, model benzyl and benzal compounds were required. It was necessary that the preferred or low energy conformation and the barrier to internal rotation of these compounds be known, so that they could be compared to those predicted by the J method.

From an investigation of benzylfluoride (39), the six-bond coupling of an α-proton to the _para_-proton was found to be dependent on the electronegativity difference between the α-substituent and the α-proton. Hence, the model compounds were also required to have α-substituents with electronegativities equal or almost equal to hydrogen. Suitable compounds were then ethylbenzene as a model benzyl compound and isopropylbenzene as a model benzal compound, because the methyl group has an electronegativity similar to that of hydrogen. For both compounds, the NMR spectrum at 100 MHz was too complex to analyze. However, the spectra of the 3,5-dibromo derivatives of the two compounds were amenable to analysis. Whereas the preparation, analysis, and results for

3,5-dibromoisopropylbenzene are described herein, 3,5-dibromoethylbenzene was described previously (40).

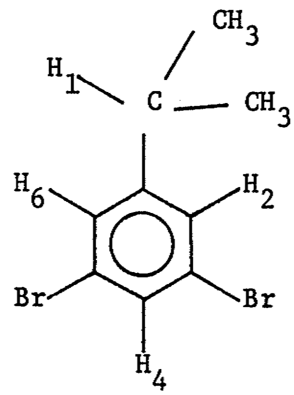
i) spectral analysis

The NMR sample was prepared as a 10 mol % solution of the compound in CS_2 with a small amount of TMS added. The NMR spectrum was recorded at 305 K on a Varian HA-100 spectrometer and was only consistent for a 3,5-disubstituted isopropylbenzene compound. No coupling of the methyl protons to the ring protons was observed except for a slight broadening of the peaks of the protons ortho to the isopropyl group.

The spectrum was analyzed with the computer program LAME (33, 34). Although resonances for the isopropyl and methine protons were observed, individual peaks could not be resolved or identified. Hence, only the peaks for the ring proton resonances were assigned frequencies in the analysis. The resultant spectral parameters are tabulated in table 2.

ii) the preferred rotational conformation and the barrier to internal rotation

From table 2 the experimental value of ${}^{6}J_{p}^{H,CH}$ is -0.25 ± 0.02 Hz. If ${}^{6}J_{90}^{H,CH}$ is deduced, then $\langle \sin^2\theta \rangle$ can be calculated from equation [6]. In toluene, ${}^{6}J_{90}^{H,CH_3}$ is -1.24 Hz. As mentioned in the Introduction, ring substitution of halogens, in this case bromine, should have a negligible effect on the magnitude of ${}^{6}J_{90}^{H,CH_n}$. That substitution of a methyl group for a proton on the methyl top also has a negligible effect on this table 2. The ^{1}H spectral parameters of 3,5-dibromoisopropylbenzene.



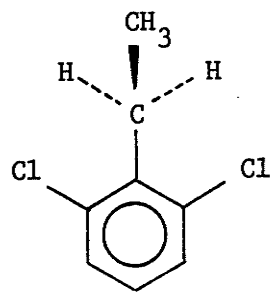
Parameter	Value
ν_1	280.0[a]
$\nu_2 = \nu_6$	721.230(3)[b]
ν_4	738.088(2)
ν_{CH_3}	121.0
$J_{12} = J_{16}$	-0.568(7)
J_{14}	-0.253(5)
J_{1,CH_3}	7.0
$J_{24} = J_{46}$	1.769(3)[c]

[a]All values are in Hz.

[b]The numbers in brackets show the standard deviation of the last decimal place.

[c]The RMS deviation between observed and calculated transition frequencies was 0.005 Hz.

coupling is indicated by the observed six-bond coupling in 2,6-dichloroethylbenzene, 21 (19).



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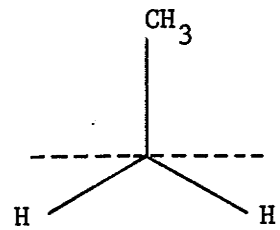
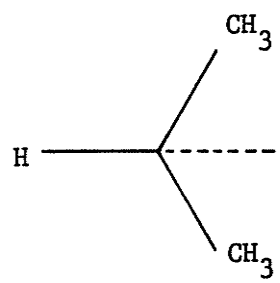


22

In this compound, 22 is the minimum energy conformation and the barrier to rotation is at least 3 kcal/mol, implying that the rotor is held fairly rigidly in this conformation. A recent study of 2,6-difluoroethylbenzene (53) found a barrier to rotation of 6.0 $\pm$ 2.0 kcal/mole. It is reasonable to assume that the barrier would be even greater in 2,6-dichloroethylbenzene. Hence, a quite rigid rotational conformation of the latter compound is confirmed. Then $\langle \sin^2\theta \rangle$ for the rigid conformation is 0.25 and, for ${}^6J_{90}^{H,CH_2} = -1.24$ Hz, the toluene value, ${}^6J_p^{H,CH_2}$ is predicted to be $-1.24 \times 0.25 = -0.31$ Hz. The observed coupling is -0.29 ± 0.02 Hz, in a benzene solution. Thus, the methyl substituent has no noticeable effect on ${}^6J_{90}^{H,CH_2}$. It is assumed that substitution of a second methyl group on the rotor similarly has no effect on ${}^6J_{90}^{H,CH}$. The *ortho* ring chlorines in 21 also have no effect on ${}^6J_{90}^{H,CH_2}$ although they do influence the barrier and minimum energy conformation of the benzyl top, which suggests *meta* ring chlorines should have a similar negligible intrinsic effect on the coupling.

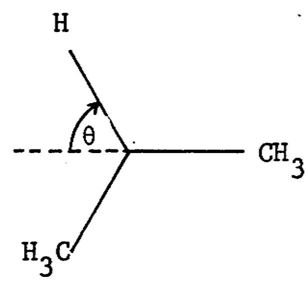
If $^6J_{90}^{H,CH}$ is taken to be -1.24 Hz in 3,5-dibromoisopropylbenzene, then $\langle \sin^2\theta \rangle = -0.25/-1.24 = 0.20$. This value allows the prediction of the minimum energy conformation. The possible minimum energy orientations of the isopropyl moiety with respect to the benzene ring plane are shown in 23 to 25. The angle θ is the dihedral angle between



$\theta_{min} = 0°$

$0.0 \leq \langle \sin^2\theta \rangle \leq 0.50$

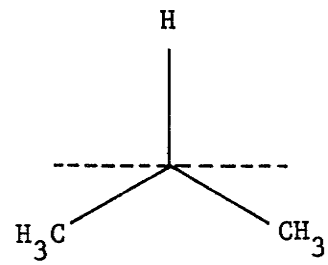
23



$\theta_{min} = 60°$

$0.5 \leq \langle \sin^2\theta \rangle \leq 0.75$

24



$\theta_{min} = 90°$

$0.5 \leq \langle \sin^2\theta \rangle \leq 1.0$

25

the C_α-H bond and a ring carbon *ortho* to the isopropyl substitution position, while θ_{min} is the dihedral angle in the minimum energy conformer. Also shown are the limits of $\langle \sin^2\theta \rangle$ when there is a zero barrier (the top rotates freely) and an infinite barrier (the top is locked in the minimum energy orientation). The experimentally determined value of $\langle \sin^2\theta \rangle$, 0.20, is not within the limits for conformations 24 and 25 but is within the limits for 23; hence, this must be the minimum energy conformation among the three for 3,5-dibromoisopropylbenzene.

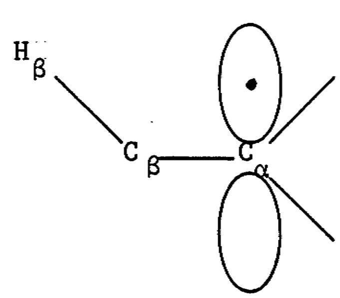
A plot of $\langle \sin^2\theta \rangle$ versus V_2 was prepared by specifying the low energy conformer as 23, the reduced moment of inertia as 1.1×10^{-38} gcm^2, the temperature as 305 K, and the number of terms in the trigonometric expansion series as 10 (odd) and 11 (even). From this plot the barrier to internal rotation was interpolated as 2.0 ± 0.2 kcal/mole. The error is based solely on the experimental error in the determination of ${}^{6}J_{p}^{H,CH}$, ± 0.02 Hz.

iii) comparison with other data

Several methods have been used to determine the barrier to rotation and the preferred conformation of the isopropyl rotor relative to the benzene ring in p-isopropylbenzene derivatives. Most determinations have used an electron paramagnetic resonance method very similar to the J method (41). In a spin-radical the hyperfine coupling between the unpaired spin density in a π orbital and a β-hydrogen atom is given by the expression

$$a_{\beta} = (B_0 + B_2 \langle\cos^2\phi\rangle)\rho_C^{\pi} \qquad [21]$$

where a_{β} is the hyperfine splitting constant, B_0 and B_2 are constants, ρ_C^{π} is the spin density in the adjacent carbon p_z orbital, and ϕ is the dihedral angle about the $C_{\beta} - C_{\alpha}$ bond, between the $C_{\beta}- H_{\beta}$ bond and the axis of the p_z orbital. The various terms are illustrated below in 26 and 27.



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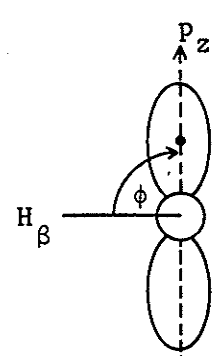

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Note should be taken of the change in notation of ring substituents. Previously the isopropyl carbon bonded to the ring and the proton bonded to this carbon were denoted as the α carbon and the α proton, whereas in the discussion following, the carbon and proton are denoted as the β carbon and β proton.

For the case of isopropylbenzene ϕ is defined in the same manner as θ in the J method except that ϕ is 0 when the $C_\beta - H_\beta$ bond is perpendicular to the benzene ring plane and θ is 0 when the $C_\beta - H_\beta$ bond is in the ring plane. Thus, $\langle\sin^2\theta\rangle$ and $\langle\cos^2\phi\rangle$ have the same meaning in the two methods.

$B_0\rho_C^\pi$ can be considered as a measure of the spin transmission through the σ system and $B_2\rho_C^\pi$ as a measure of the spin transmission by a hyperconjugative interaction. The similarity between equations [5] and [21] shows that $B_0\rho_C^\pi$ is analogous to ${}^6J_0^{H,CH_n}$. $B_0\rho_C^\pi$, unlike ${}^6J_0^{H,CH_n}$, is usually non-zero but much smaller than $B_2\rho_C^\pi$ and this fact is often used to approximate equation [21] as

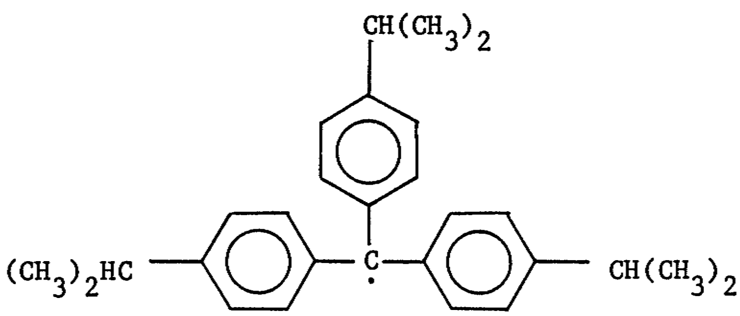
$$a_\beta = B_2 \langle\cos^2\phi\rangle\rho_C^\pi \qquad [22]$$

The method of determining the rotational barrier in simple alkylbenzene radicals from the β hyperfine splitting is to find the ratio of the splitting in an alkyl derivative a_β^R, where R represents a particular alkyl top, and in the derivative where the alkyl top is replaced by a methyl top, $a_\beta^{CH_3}$. Since a methyl top can be considered a free rotor $\langle\cos^2\phi\rangle = 0.5$ and, following equation [21], the ratio can be written as

$$\frac{a_\beta^R}{a_\beta^{CH_3}} = \frac{B_0^R/B_2^R + \langle\cos^2\phi\rangle}{B_0^{CH_3}/B_2^{CH_3} + 0.5} \qquad [23]$$

where the equality of B_2^R and $B_2^{CH_3}$, and B_0^R and $B_0^{CH_3}$ is assumed for simple unstrained alkyl groups (42). If the hyperfine splittings are determined as a function of the temperature and $\langle\cos^2\phi\rangle$ is calculated for each temperature as a function of the rotational barrier, then the best fit to the experimental data yields the barrier and the B_0/B_2 terms. If the B_0/B_2 terms are known then a determination of the hyperfine splitting ratio at one temperature is sufficient to yield the rotational barrier, as in the J method.

Bauld, Hudson and Hyde (43) used the temperature dependence of the β hyperfine splitting in the neutral p,p',p"-triisopropyl-trityl radical 28 in toluene solution to determine a barrier to



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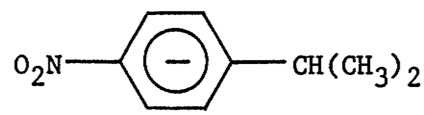
rotation of the isopropyl top of 2.13 kcal/mole. The $\langle\cos^2\phi\rangle$ values were calculated in a similar manner as the $\langle\sin^2\theta\rangle$ values for the J method with the exception that the former procedure solved the explicit Mathieu equation for the torsional wavefunctions and energies (41). The calculated values for $\langle\cos^2\phi\rangle$ and $\langle\sin^2\theta\rangle$

should, nevertheless, be equal for the two procedures.

The ratio B_0^R/B_2^R, where R now refers to the isopropyl top, was also determined to be 0.119 (43). This value was assumed equal to $B_0^{CH_3}/B_2^{CH_3}$. Furthermore, this ratio was also assumed the same for radicals with simple unstrained alkyl substituents (42).

An earlier determination, by McKinney and Geske (44), of the hyperfine splitting in the anion radical of p-nitroisopropylbenzene 29 in an acetonitrile solution



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resulted in a barrier of 1.0 kcal/mol and predicted a minimum energy conformation, for the same reasons as described previously, in which $\phi = 90°$ or $\theta = 0°$. The barrier can be considered unreliable as the authors used a short form of equation [23],

$$\frac{a_\beta^R}{a_\beta^{CH_3}} = 2 \langle\cos^2\phi\rangle \qquad [24]$$

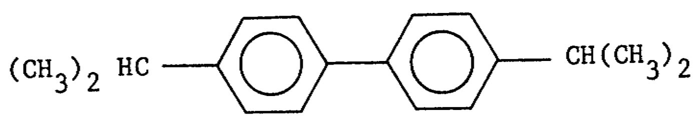
which follows if equation [22] is used in the derivation of the ratio. The reason for the use of equation [22] is that $B_0 << B_2$ in most cases. However, B_0 need not be very much less than $B_2\langle\cos^2\phi\rangle$, especially if $\langle\cos^2\phi\rangle$ is small. This is the case for the isopropylbenzene derivatives.

The authors also did not use the quantum statistical method described previously to find $\langle\cos^2\phi\rangle$ as a function of the barrier, V_2, but one in which harmonic oscillator energies and wave functions were used as approximations to the torsional energies and wavefunctions below the barrier, and rigid rotor ones above the barrier (45).

Stock and Young (46) re-examined the data of McKinney and Geske (44) on the p-isopropylnitrobenzene radical. They also used the approximate equation [24] to determine the value of $<\cos^2\phi>$ but did calculate the functional dependence of $<\cos^2\phi>$ on V_2 by the method of Bauld et al. (41), described previously, in which the Schrödinger equation for the torsional motion of the isopropyl top, transformed to the Mathieu equation, is solved numerically. The barrier predicted by this method was 1.7 kcal/mole.

The data of McKinney and Geske was also re-examined in this laboratory. The β proton hyperfine splittings at 233 K were 1.672 $\pm$0.015 and 3.965 $\pm$ 0.011 G for the p-isopropyl and p-methylnitrobenzene, respectively, for a ratio, $a_\beta^{ipr}/a_\beta^{CH_3} = 0.421$. If the B_0/B_2 ratios in equation [23] are assumed the same and equal to 0.119, the value found by Bauld et al. (43) for the p,p',p"-isopropyltrityl radical, then $<\cos^2\phi> = 0.142$. From a plot of $<\cos^2\phi>$ (or $<\sin^2\theta>$) as a function of the barrier V_2 at 233 K and for a reduced moment of 1.1 x 10^{-38} gcm^2, the barrier is found to be 2.0 kcal/mol. The β proton hyperfine splittings were also determined at 263, 283, and 333 K and had values of 1.712, 1.757 and 1.793 G in the p-isopropyl radical. For a $a_\beta^{CH_3}$ value of 3.965 G (this splitting is constant over the temperature range within the experimental errors) the $<\cos^2\phi>$ values are 0.148, 0.155, and 0.161. From plots of $<\cos^2\phi>$ vs V_2 at the three temperatures the barriers are 2.1, 2.2 and 2.5 kcal/mole, respectively. Although there is an increase of the barrier with temperature the first three values are the same, within the experimental error, as the barrier determined for 3,5-dibromoisopropylbenzene by the J method.

Another isopropylbenzene derivative investigated by the ESR technique was the anion radical of p,p'-diisopropylbiphenyl 30 (47).



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Again, $<\cos^2\phi>$ was determined from the β proton hyperfine splitting by equation [24]. However, the internal rotation potential, used in the Schrödinger equation was not the usual two-fold symmetric potential (equation [4]), but a four-term cosine series.

$$V(\alpha) = V_0 \sum_{i=0}^{3} a_i \cos 2i\alpha \qquad [25]$$

with

$$a_0 = \frac{1}{18}\left(\frac{9\,V_m}{V_0} + 4\right), \qquad [26a]$$

$$a_1 = \frac{4}{9}, \qquad [26b]$$

$$a_2 = \frac{2}{9}, \qquad [26c]$$

and

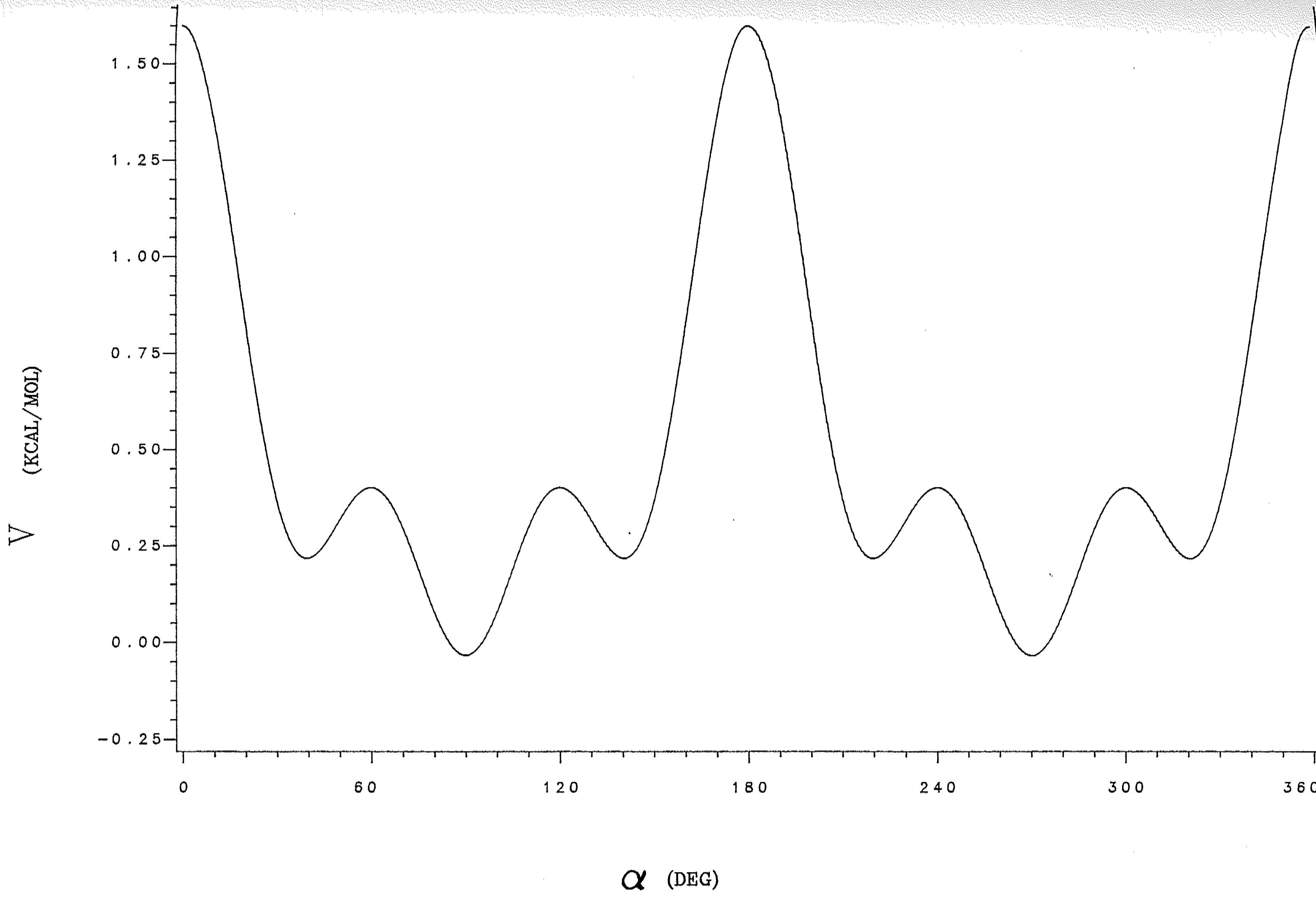
$$a_3 = \frac{1}{18}\left(8 - \frac{9V_m}{V_0}\right). \qquad [26d]$$

The potential energy profile for this function is illustrated in figure 3 for V_0 = 1.2 kcal/mole and V_m = 0.5 kcal/mole. With the energies and torsional wave functions obtained from the Schrödinger equation, plots of $\langle \cos^2 \phi \rangle$ versus temperature for different values of V_0 and V_m were produced and compared with the experimental temperature dependence of $\langle \cos^2 \phi \rangle$ as determined from the hyperfine splittings. The best fit occurred for V_0 = 1.2 kcal/mole and V_m = 0.5 kcal/mole.

In order to support the use of the double minimum potential, as opposed to the two-fold symmetric potential, the non-bonded interaction energies, described by the Lennard-Jones 6-12 potential function between the groups of the isopropyl top and the ortho ring protons, were calculated as a function of the internal rotation angle. The interaction energy profile had a double minimum shape as in figure 3.

Previous calculations of non-bonding interaction energies of a benzal rotor and aromatic ortho substituents also showed a double minimum potential, (48). In both calculations the bond lengths and angles used were those common to analogous groups (14, 49). The bonds were even allowed to bend away from each other (48), although by the same amount for each bond, but the double minimum in the energy profile still remained. However, in calculations where the bond lengths and bond angles were adjusted independently of each other (50), the non-bonding interaction energy did yield a two-fold symmetric potential. In fact, Mannschreck and Ernst (51) found that the calculated double

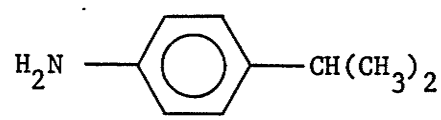
Figure 3. A plot of the double minimum potential hindering the internal rotation of the isopropyl top in p,p'-diisopropylbiphenyl as proposed by Nemoto et al. (47). Equations [25] and [26a-d] were used in the calculation of the potential energy profile with V_0 = 1.2 kcal/mole and V_m = 0.5 kcal/mole.


V (KCAL/MOL)
1.50
1.25
1.00
0.75
0.50
0.25
0.00
-0.25
0
60
120
180
240
300
360
α (DEG)

minimum potential for an isopropyl rotor on an aromatic ring becomes a two-fold potential if the full bond angles and bond lengths are optimized at each increment of the rotational angle.

In the above ESR experiment the ratio $a_{\beta}^{ipr}/a_{\beta}^{CH_3}$ was determined to be 0.417 for the p,p'-diisopropylbiphenyl anion radical at 188 K, which, upon substitution into equation [23], gives a value of 0.143 for $\langle\cos^2\phi\rangle$. B_0/B_2 is again assumed to be 0.119. From a plot of $\langle\cos^2\phi\rangle$ versus V_2 at 188 K the barrier is found to be 1.6 kcal/mole.

An investigation by Chachaty et al. (52) of alkylaniline compounds included p-isopropylaniline, 31. The NMR spectra of a series



31

of alkylaniline nickel (II) acetylacetonate complexes in deuterated chloroform solutions were recorded and the contact shifts of the hydrogen and carbon nuclei determined. These were then used to calculate the hyperfine splitting of the various nuclei. In the case of the β protons and γ carbons (designated β carbons in this article), the hyperfine splittings allowed the determination of $\langle\cos^2\phi\rangle$. For the p-isopropylaniline $\langle\cos^2\phi\rangle$ was 0.63 for C_γ and 0.23 for H_β. From the functional dependence of $\langle\cos^2\phi\rangle$ on V_2, the barrier was determined to be 1.5 kcal/mole.

A second determination of the barrier in p-isopropylaniline in chloroform solution from spin-lattice relaxation (T_1) data, was performed by Chachaty et al. The temperature dependence of the relaxation time of the β carbon was determined and used to calculate the barrier, V_2, from an Arrhenius relation. The barrier was predicted to be 2.8 $\pm$ 0.1 kcal/mol. This type of procedure requires a careful separation of the overall and internal motional contributions to the relaxation time. An unsuccessful separation may explain the rather large barrier.

Chachaty et al. also performed INDO molecular orbital calculations on p-isopropyl aniline in order to determine a theoretical barrier to rotation of the isopropyl group about the $C_\alpha - C_\beta$ bond. The energy of the molecule was calculated as a function of the angle of internal rotation and was found to be a minimum when θ was 0° ($C_\beta - H_\beta$ in the aromatic ring plane) and a maximum when θ was 90° ($C_\beta - H_\beta$ perpendicular to the ring plane). The shape of the potential between 0° and 90° was not a perfect sine curve, but a two-fold symmetric potential was indicated and deviation from a sine curve might be minimized by geometry optimization of the bond lengths and angles for each rotational conformation. The difference between the energy maximum and minimum was calculated to be 3.5 kcal/mole. Because no geometry optimization was performed, and because of the semi-empirical character of the calculations, this value cannot be taken as an accurate value of the barrier or a confirmation of either of the two values of the barrier determined experimentally in the same work.

iv) summary

The barriers to rotation and the minimum energy conformation of some derivatives of isopropylbenzene are listed in table 3. In all investigations the rotational conformation in which the of the isopropyl moiety is in the plane of the benzene ring was deduced to have the minimum energy. In all but one investigation the hindering potential was assumed to be two-fold symmetric with the maximum energy conformation having the C_α-H bond perpendicular to the benzene ring plane. A double minimum potential was predicted in one case, and verified by calculations of non-bonding interactions. However, the calculations can be adjusted to remove the double minimum and to predict a two-fold symmetric potential. This latter potential is also predicted by semi-empirical molecular orbital calculations.

Of the barriers listed in table 3, the value of 2.13 kcal/mol for the barrier in the p,p',p"-triisopropyltrityl radical was the closest to the J method value. It was determined from the temperature dependence of the β proton hyperfine splitting, a_β, and the angular dependence of this splitting given by the expression

$$a_\beta = (B_0 + B_2 \langle\cos^2\phi\rangle)\rho_C^\pi \qquad [21]$$

and described previously. The ratio B_0/B_2 was also determined. Similar procedures for finding the barrier neglected the B_0/B_2 term and can be assumed to be in some error as B_0/B_2 is not negligible with $\langle\cos^2\phi\rangle$ for the small values of the latter parameter found in isopropylbenzene derivatives. The corresponding term, table 3. Rotational barriers of some isopropylbenzene derivatives.

Derivative	Solvent	Minimum Energy Conformation[a]	Barrier (kcal/mole)	Method	Reference
3,5-dibromoisopropylbenzene	CS_2	A	2.0	NMR(^6J_p)	this work
p,p',p"-triisopropyltrityl	toluene	A	2.13	ESR(a_β)	43
p-isopropylnitrobenzene	acetonitrile	A	1.0	ESR(a_β)	44
			1.7[b]	ESR(a_β)	46
			2.0,2.1,2.2,2.5[b]	ESR(a_β)	this work
p,p'-diisopropylbiphenyl	dimethoxymethane	A	V_0=1.2, V_m=0.5[c]	ESR(a_β)	47
		A	1.6[d]	ESR(a_β)	this work
p-isopropylaniline nickel(II) acetylacetonate	$CDCl_3$	A	1.5	NMR(contact shift, a_β)	52
p-isopropylaniline	$CDCl_3$	A	2.8	NMR(T_1)	52

[a]The possible minimum energy conformations are labelled so that A, θ_{min} = 0°; B, θ_{min} = 60°; C, θ_{min} = 90°, where θ is the dihedral angle between the C_α-H bond and a ring carbon <u>ortho</u> to the isopropyl substituent.

[b]The barriers were calculated from the hyperfine splitting data of reference 44.

[c]The barriers refer to a double minimum potential where A is the absolute minimum, B in the maximum and C is the local minimum.

[d]The barrier was calculated from the hyperfine splitting data of reference 47.

${}^{6}J_{o}^{H,CH_n}$, in the expression describing the six-bond side-chain to ring coupling, equation [5], was found to be zero within experimental error (15,16) (see Theoretical and Experimental Considerations above).

If the proton hyperfine splitting values in the p-isopropylnitrobenzene and the p,p'-diisopropylbiphenyl radicals are used with the B_0/B_2 ratio for the p,p',p"-triisopropyltrityl radical, barriers of 2.0, 2.1, 2.2 and 2.5 kcal/mole are found for four different temperatures for the former compound, and 1.7 kcal/mole for the latter. The deviations of some of these values from the predicted value of 2.0 kcal/mol could indicate that the B_0/B_2 ratio is not the same for all isopropyl derivatives.

The barrier of 1.5 kcal/mole for the p-isopropylaniline Ni(II) acetylacetonate was determined from the γ carbon hyperfine splittings calculated from experimentally determined contact shifts. The procedure which was followed to find $\langle \cos^2\phi \rangle$ was lengthy and could have been subject to accumulations of small errors. The barrier of 2.8 kcal/mole for the uncomplexed p-isopropylaniline was determined in the same work from T_1 data which yielded the barrier as an activation energy from an Arrhenius relation. That the activation energy found in this way is actually the barrier to rotation is moot.

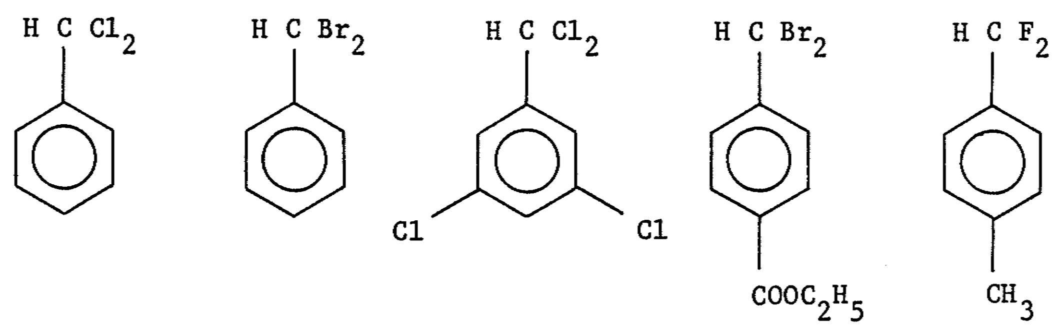
As can be seen, the rotational barrier determined for 3,5-dibromoisopropylbenzene is comparable to barriers determined for other isopropylbenzene derivatives by other methods, and is even the same within experimental error in one case. Thus the J method is a suitable method for determining barriers of compounds to wich it can be applied.

2. Benzal Halides

The J method, when applied to 3,5-dibromoisopropylbenzene, yielded a rotational barrier comparable in magnitude to barriers of other isopropylbenzene derivatives determined by other physical methods. It was then considered a suitable technique for investigating the rotational barriers of other benzal compounds and, thus, is applied now to the benzal halides. Because the hydrogens of the methyl top are replaced by atoms of greater electronegativity, the effect of α-substituent electronegativity on the six-bond coupling, ${}^{6}J_{90}^{H,CH}$, is considered. As well, the possibility of using the six-bond proton – fluorine coupling, ${}^{6}J_{p}^{H,CF_2}$, to determine a barrier in benzal fluoride is investigated.

i) spectral analysis

NMR samples of the following compounds were prepared: benzal chloride, 10 volume % in CS_2, 32; benzal bromide, 10 volume % in CS_2, 33; 3,5-dichlorobenzal chloride, 10 volume % in CCl_4, 34; 4-$COOC_2H_5$-benzal chloride, 10 mole % in CS_2, 35; 4-methylbenzal fluoride, 20 mole % in C_6D_6, 36, with a small amount of TMS added



32 33 34 35 36

as an internal lock and reference. The spectrum of each was recorded on a Varian HA-100D spectrometer at 305 K. In the case of the 4-methylbenzal fluoride, the methyl decoupled spectrum, as well as the fully coupled spectrum, was recorded. Partial decoupling experiments on this compound indicated the sign of the seven-bond coupling, ${}^{7}J_{p}^{CH_3,F}$ to be the same as the two bond coupling, ${}^{2}J^{H,F}$, namely positive. The spectra of all the compounds, except for the fully coupled one of 4-methylbenzal fluoride, were analyzed with the use of the computer program LAME (33,34). An example of the spectral simulation from the analysis is shown for benzal chloride in figure 4. Only the decoupled spectrum of 4-methylbenzal fluoride was analyzed by LAME. The fully coupled spectrum was analyzed with the computer program NUMARIT (54,55) in a non-iterative mode. The parameters used in this analysis were those from the LAME analysis, except for those of the methyl group. Thus, the NUMARIT analysis produced the methyl group chemical shift and coupling constants. The NMR parameters of all the compounds but the 4-methylbenzal fluoride are given in table 4. Those of the 4-methylbenzal fluoride are given in table 5.

ii) substituent dependence of ${}^{6}J_{90}^{H,CH}$

The observed six-bond coupling in benzyl and benzal systems is given by the expression

$$ {}^{6}J_{p}^{H,CH_n} = {}^{6}J_{90}^{H,CH_n} \langle \sin^2\theta \rangle . \qquad [6] $$

The coupling is transmitted solely by a σ-π mechanism and any angle

Figure 4. The observed and calculated proton magnetic resonance spectra at 100 MHz of a 10 volume % solution of benzal chloride in CS_2. The spectral parameters used for the simulation are given in table 4.

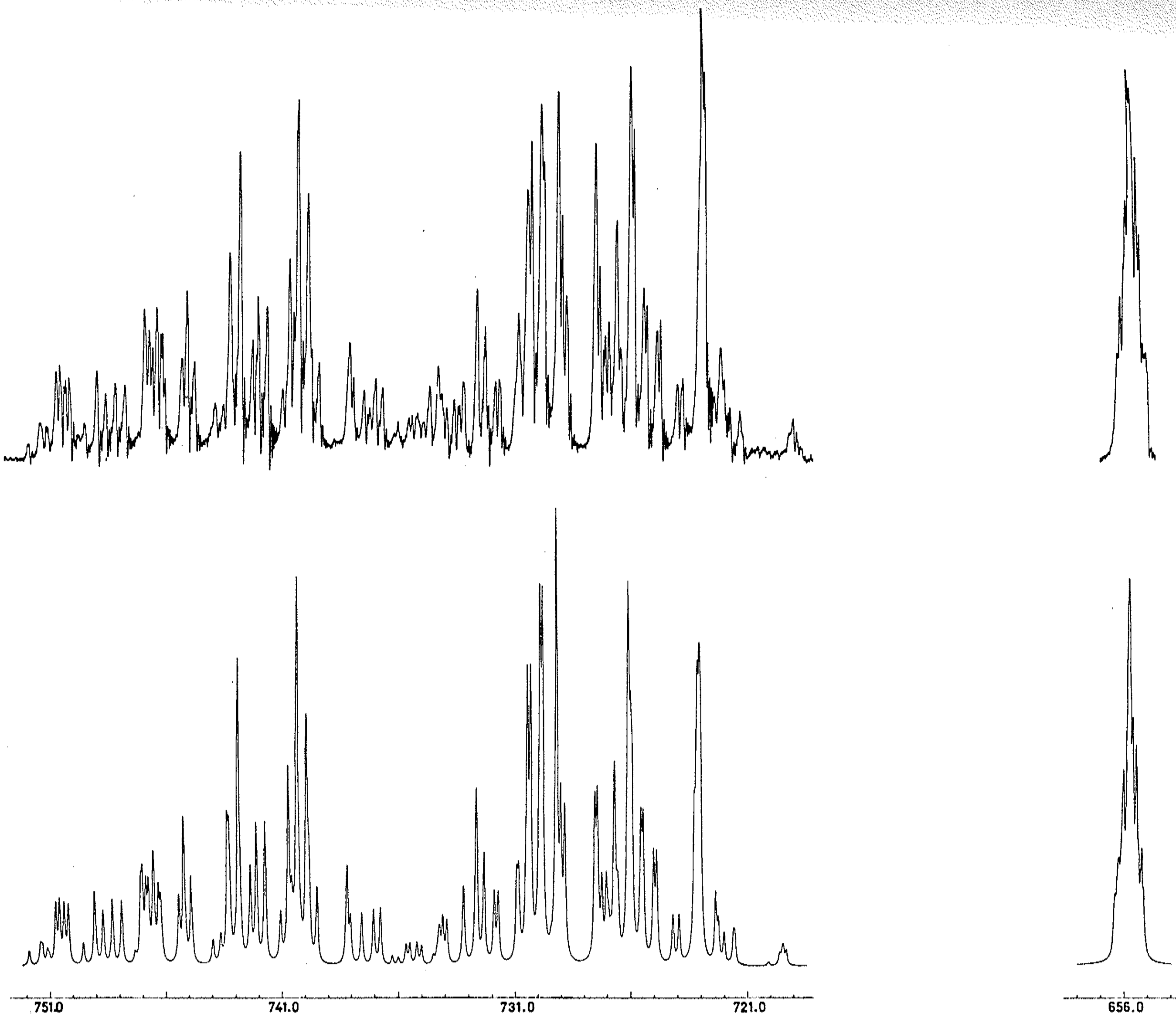
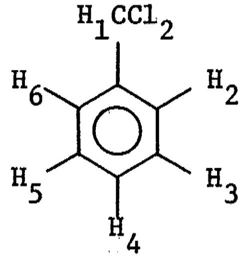
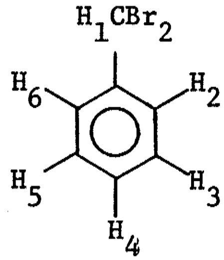
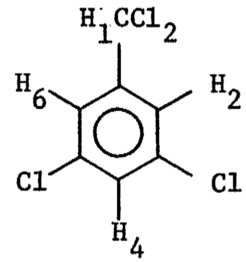
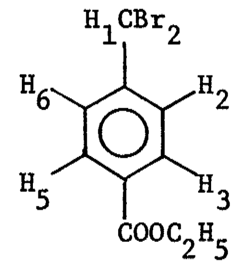

751.0
741.0
731.0
721.0
656.0

table 4. Chemical shifts and coupling constants of some benzal halide derivatives

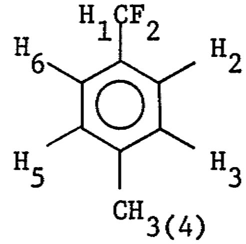
				
ν_1 [a]	655.784(5) [b]	652.282(7)	652.612(6)	659.836(5)
$\nu_2 = \nu_6$	744.291(4)	744.620(4)	739.285(7)	754.258(4)
$\nu_3 = \nu_5$	727.871(5)	725.137(5)		795.047(4)
ν_4	725.798(7)	720.303(6)	728.583(7)	
$J_{12} = J_{16}$ [c]	-0.426(7)	-0.382(6)	-0.446(7)	-0.378(6)
$J_{13} = J_{15}$	0.260(7)	0.285(7)		0.296(6)
J_{14}	-0.212(11)	-0.120(10)	-0.178(9)	
$J_{23} = J_{56}$	7.880(8)	7.888(7)		8.215(6)
$J_{24} = J_{46}$	1.230(7)	1.174(7)	1.880(7)	
$J_{25} = J_{36}$	0.575(7)	0.554(6)		0.537(6)
J_{26}	2.080(7)	2.143(5)		1.798(7)
$J_{34} = J_{45}$	7.475(5)	7.474(5)		
J_{35}	1.384(7)	1.386(6)		2.085(7)
RMS error	0.028	0.0157	0.0216	0.0174

[a]Chemical shift in Hz to low field of internal TMS.

[b]The number in parentheses is the standard deviation in the last one or two decimal places.

[c]Coupling constant in Hz.

table 5. Chemical shifts and coupling constants in p-methylbenzal fluoride.



LAME ANALYSIS	
ν_1 [a]	626.828(2) [b]
$\nu_2 = \nu_6$	716.286(2)
$\nu_3 = \nu_5$	696.883(2)
$J_{12} = J_{16}$ [c]	-0.462(3)
$J_{13} = J_{15}$	0.247(3)
J_{1F}	56.622(3)
$J_{23} = J_{56}$	7.920(4)
$J_{25} = J_{36}$	0.588(3)
$J_{26} =$	1.866(4)
$J_{2F} = J_{6F}$	-1.169(3)
J_{35}	1.975(4)
$J_{3F} = J_{5F}$	0.891(3)
RMS Error	0.0178
NUMARIT ANALYSIS	
ν_{14}	207.7
J_{14}	0.23(2) [d]
$J_{24} = J_{46}$	0.33(2)
$J_{34} = J_{45}$	-0.72(2)
$J_{4F} =$	1.46(2)

[a] Chemical shift in Hz to low field of internal TMS.

[b] The number in parentheses is the standard deviation in the last decimal place.

[c] Coupling constant in Hz.

[d] The number in parenthesis is an error estimated from the standard deviations of the other NMR parameters above.

independent term, ${}^{6}J_{0}^{H,CH}$, is considered negligible. Again, θ is the dihedral angle between the C_{α}-H bond and a C_1-$C_{\underline{ortho}}$ ring bond. When θ is constrained to 0^{o} as in 2,6-dichlorobenzal bromide (15) the ${}^{6}J_{p}^{H,CH}$ coupling is unobservable. When θ is 90^{o} the observed coupling should be equal to ${}^{6}J_{90}^{H,CH}$, the maximum value transmitted by the σ-π mechanism.

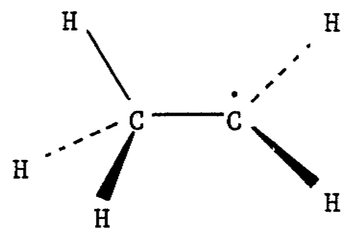
A substituent on the ring should have no effect on the coupling through the π system. However, substituents which replace hydrogens on the methyl top of toluene (α-substituents) could affect the coupling by changing the hyperconjugative interaction of the C_{α}-H bond with the π orbitals of the ring. If α-substituents have a greater electronegativity than the replaced hydrogens, they would tend to polarize the C_{α}-H bond and decrease the overlap with the ring π orbitals and, hence, decrease the magnitude of ${}^{6}J_{90}^{H,CH}$.

For substituents with electronegativities comparable to hydrogen, such as the methyl group in isopropylbenzene, the ethyl group in ethylbenzene (40), and the SH group in benzyl mercaptan (56), the ${}^{6}J_{90}^{H,CH}$ coupling shows no definite indication of being reduced from its value of -1.24 Hz in toluene.

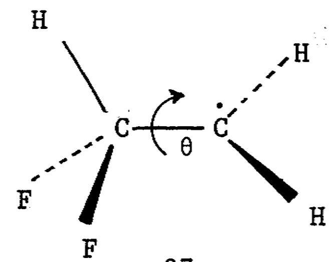
That α-substituents with electronegativities greater than that of hydrogen decrease the magnitude of ${}^{6}J_{90}^{H,CH}$ is shown by theoretical calculations. INDO molecular orbital calculations of the six-bond coupling, ${}^{6}J_{p}^{H,CH}$, in toluene, as a function of θ (13) give ${}^{6}J_{90}^{H,CH}$ = -1.24 Hz. This is exactly the same value as predicted from the observed coupling, ${}^{6}J_{p}^{H,CH}$ = -0.62 Hz, and

$<\sin^2\theta> = 0.5$ which results from the almost free rotation of the methyl group. An INDO calculation of $^6J_{90}^{H,CH}$ in benzal fluoride (16) gives a value -0.87 Hz, a clear reduction from -1.24 Hz.

The reduction of $^6J_{90}^{H,CH}$ in going from a methyl top to a difluoromethyl top (CHF_2) is supported by experimental and theoretical data for some fluoroalkyl radicals (57), specifically the ethyl radical 36, and the β,β-difluoroethyl radical, 37. The β



36



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proton hyperfine splittings in the two radicals are dependent on the dihedral angle, θ, between a C_β-H_β bond and the axis of the p_z orbital containing the unpaired electron. (Note the difference in notation for radicals where C_α is the carbon on which the unpaired electron is said to be localized, and for electron-paired phenyl compounds where C_α is a substituent carbon directly bonded to the ring.) The angle dependence of the hyperfine splitting is given by the expression where a_β^H is the β proton hyperfine split-

$$a_\beta^H = A_H + B_H <\cos^2(\theta + \theta_0)> \qquad [27]$$

ting and A_H, B_H, and θ_0 are empirical constants. The form of this equation is the same as that of equation [5],

$$^6J_p^{H,CH} = {}^6J_o^{H,CH_n} + {}^6J_{90}^{H,CH_n}<\sin^2\theta>. \qquad [5]$$

The term A_H can be taken as a measure of the hyperfine interaction transmitted through the σ system and the coefficient B_H as a measure of the hyperfine interaction transmitted via a hyperconjugative or σ-π mechanism. Thus, B_H is analogous to ${}^6J_{90}^{H,CH}$. The constants, A_H, B_H and θ_0 were fitted to INDO calculated data and these values were consistent with the experimental data (57). The B_H value was found to decrease from 51 G in the ethyl radical to 41 G in the β,β-difluoroethyl radical. The fractional decrease of B_H is 0.80 and is comparable to 0.70 for the INDO calculated ${}^6J_{90}^{H,CH}$.

iii) <u>barriers to rotation in the benzal halides</u>

The observed six-bond coupling, ${}^6J_p^{H,CH}$, is -0.26, -0.19$_5$, and -0.12 Hz in the benzal fluoride, chloride, and bromide respectively. The value of -0.26 is the average of two analyses of the spectral data of two samples, while -0.19$_5$ is the average of the values for the coupling in benzal chloride and 3,5-dichlorobenzal chloride. In order to use equation [6] to determine the rotational barriers, ${}^6J_{90}^{H,CH}$ must be known. The range of possible values for ${}^6J_{90}^{H,CH}$ can be estimated from the following considerations.

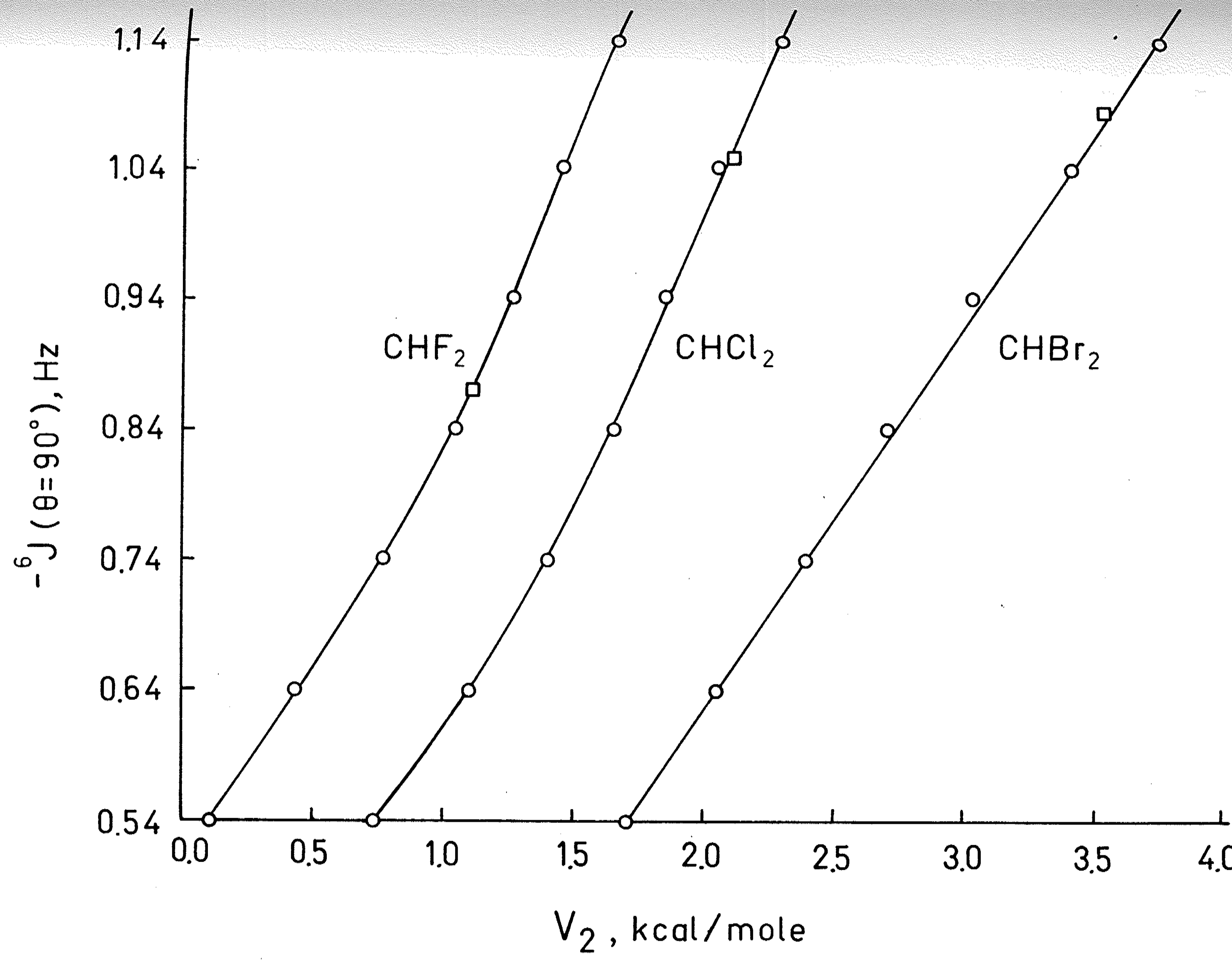
The value of ${}^6J_{90}^{H,CH_3}$ in toluene, -1.24 Hz, is decreased in magnitude by α-substituents having electronegativities greater than that of hydrogen. Thus, 1.24 Hz is an upper limit for the magnitude of ${}^6J_{90}^{H,CH}$ in the benzal halides.

When determining the lower limit of ${}^6J_{90}^{H,CH}$, the possible minimum energy conformations must be considered. The three most probable conformations are for $\theta_{min} = 0^o$, $\theta_{min} = 60^o$, and $\theta_{min} = 90^o$, where θ has been defined previously. In the case of benzal fluoride, ${}^{6}J_{90}^{H,CH}$ = -0.52 Hz for free rotation, i.e., $\langle \sin^2\theta \rangle$ = 0.5. If a barrier is present the magnitude of ${}^{6}J_{90}^{H,CH}$ will increase for the $\theta_{min} = 0^{o}$ conformation and decrease for the $\theta_{min} = 60^{o}, 90^{o}$ conformations. Because it is highly unlikely that ${}^{6}J_{90}^{H,CH}$ is less than -0.52 Hz in magnitude, the $\theta_{min} = 0^{o}$ conformation is assumed to be the actual minimum energy conformation of the molecule, and -0.52 Hz is the lower limit of ${}^{6}J_{90}^{H,CH}$. This value can also be taken as the lower limit for the benzal chloride and bromide.

Because the electronegativities of chlorine and bromine are less than that of fluorine, ${}^{6}J_{90}^{H,CH}$ must be intermediate between -1.24 Hz and -0.52 Hz. This is only the case if the minimum energy conformation has $\theta_{min} = 0^{o}$. For the other conformations ${}^{6}J_{90}^{H,CH}$ could only have values less than -0.52 Hz in magnitude.

For each compound a range of barriers can be obtained from the range of ${}^{6}J_{90}^{H,CH}$ and the observed six-bond coupling, ${}^{6}J_{p}^{H,CH}$. The ratio of the couplings yields a value of $\langle \sin^2\theta \rangle$ which is used to interpolate a rotational barrier from a plot of $\langle \sin^2\theta \rangle$ versus V_2. A series of these plots were prepared for reduced moments of intertia of 0.4, 1.02, and 1.27 x 10^{-38} g cm^2 which were those of the benzal fluoride, chloride, and bromide, respectively, and a temperature of 305 K. Plots of the absolute value of the six-bond coupling, $|{}^{6}J_{90}^{H,CH}|$, against the barrier, V_2, are shown in figure 5. The plots show that the actual rotational barriers of the compounds lie between the limits of 0.0 to 1.8 kcal/mol for benzal fluoride, 0.7 to 2.4 kcal/mol for benzal chloride, and 1.7 to 3.8

Figure 5. A plot of the possible values of $|{}^6J_{90}^{H,CH}|$ and the respective barriers to rotation in benzal fluoride, chloride, and bromide. The open squares indicate a barrier corresponding to a value of $|{}^6J_{90}^{H,CH}|$ predicted from INDO MO FPT calculations of benzal fluoride and inferred for benzal chloride and bromide from a linear relationship between the coupling and halide electronegativity, as shown in figure 6.



1.14
1.04
0.94
0.84
0.74
0.64
0.54
$-^6J(\theta=90°)$, Hz
CHF_2
$CHCl_2$
$CHBr_2$
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
V_2, kcal/mole

kcal/mol for benzal bromide.

Estimates of the barriers in the benzal halides can be made in the following way. If ${}^6J_{90}^{H,CH}$ in benzal fluoride is taken as -0.87 Hz, the value given by INDO MO FPT calculations, then $<\sin^2\theta>$ = -0.26/-0.87 = 0.30 which corresponds to a barrier of 1.1 $\pm$ 0.2 kcal/mole. The error in the barrier corresponds to an error of $\pm$ 0.02 Hz in the experimental coupling constant.

The barriers for the benzal chloride and bromide follow from the assumption that ${}^6J_{90}^{H,CH}$ in the benzal halides is a linear function of the α-substituent electronegativities, E_α. The functional dependency can be determined from the two points: E_F = 3.98, ${}^6J_{90}^{H,CH}$ = -0.87 Hz and E_H = 2.2, ${}^6J_{90}^{H,CH}$ = -1.24 Hz, which yields ${}^6J_{90}^{H,CH}$ = -1.04 Hz for E_{Cl} = 3.16 and ${}^6J_{90}^{H,CH}$ = -1.08 Hz for E_{Br} = 2.96. From these values and the experimental six-bond coupling constants the barriers are calculated to be 2.2 $\pm$ 0.3 kcal/mole for benzal chloride and $3.5_5 \pm 0.6$ kcal/mole for benzal bromide. The points corresponding to the ${}^6J_p^{H,CH}$ and V_2 values are shown in figure 5.

Because $<\sin^2\theta>$ decreases non-linearly as V_2 increases, the same error in ${}^6J_p^{H,CH}$, and, thus, in $<\sin^2\theta>$, produces larger deviations in V_2 when V_2 is large. Hence the J method becomes rather insensitive for barriers greater than 3 kcal/mole.

A barrier for benzal fluoride has been determined to be 0.18 kcal/mol by an *ab initio* molecular orbital calculation at the STO-3G level (36). This value corresponds to $<\sin^2\theta>$ = 0.463, and with ${}^6J_p^{H,CH}$ = -0.26 Hz, predicts ${}^6J_{90}^{H,CH}$ to be -0.56 Hz. If this new value is used instead of -0.87 Hz for ${}^{6}J_{90}^{H,CH}$ in benzal fluoride in the above procedure for estimating the barriers in the benzal halides, then ${}^{6}J_{90}^{H,CH}$ is predicted to be -0.87 Hz for benzal chloride and -0.95 Hz for benzal bromide. The rotational barriers are, then, 1.6 and 2.9 kcal/mole, respectively. The numbers involved in these procedures are listed in table 6 and are plotted in figure 6.

The long-range couplings between the ring protons and the side-chain benzal proton in the benzal halides and some derivatives are tabulated and listed in table 7 for comparison and show that ring substitution has very little effect on these couplings. All the same couplings in the parent and derivative compounds are equal within the experimental error of ± 0.02 Hz, although there is certainly some slight deviation in the six-bond coupling, ${}^{6}J_{p}^{H,CH}$, which is used to determine the barriers. It is not known whether this deviation results from experimental error, some solvent effect, because the compounds compared were not dissolved in the same solvent, or a slight change in the rotational barrier on ring substitution. However, these slight deviations in the couplings are negligible when considered against the large uncertainty in ${}^{6}J_{90}^{H,CH}$.

iv) <u>the long-range coupling to ${}^{19}F$ in benzal fluoride</u>

Benzal fluoride is unique among the benzal halides in that it has another observable six-bond coupling, from the <u>para</u> proton to the two fluorine atoms on the benzal top, and denoted by ${}^{6}J_{p}^{H,CF_2}$. This coupling can be used to determine barriers to internal rotation, just as the six-bond proton-proton coupling, if the intrinsic substituent dependence is known, and if the coupling is solely

Figure 6. A plot of the linear relationship between $|{}^6J_{90}{}^{H,CH}|$ and E_X, the α-substituent electronegativity. The solid circles indicate $|{}^6J_{90}{}^{H,CH}|$ for toluene and two estimates of this coupling of this coupling in benzal fluoride, from INDO MO FPT and ab initio STO-3G calculations. The open circles show the interpolations of $|{}^6J_{90}{}^{H,CH}|$ for benzal chloride and bromide from the respective electronegativities of chlorine and bromine

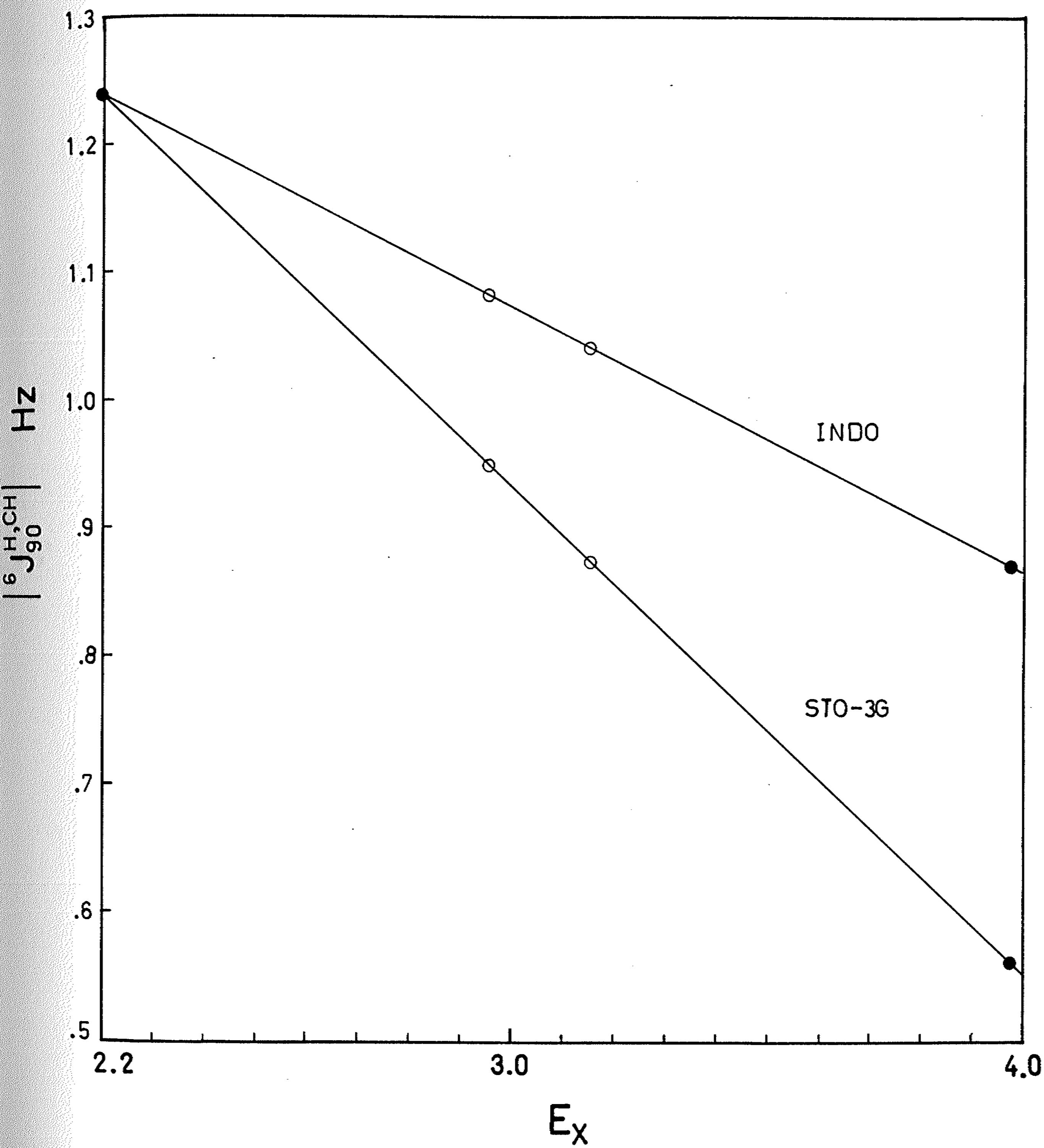

1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
$|{}^6J_{90}^{H,CH}|$ Hz
INDO
STO-3G
2.2
3.0
4.0
E_X

table 6. Substituent electronegativities and $^{6}J_{90}^{H,CH}$

	Atom	E_x[a]	$^{6}J_{90}^{H,CH}$	$^{6}J_{p}^{H,CH}$	$\langle \sin^2\theta \rangle$	V_2
I[b]	F	3.98	-0.87 Hz	-0.26 Hz	0.30	1.1 kcal/mole
	Cl	3.16	-1.04	-0.19_5	0.19	2.2
	Br	2.96	-1.08	-0.12	0.11	3.5_5
	H	2.2	-1.24			
II[c]	F	3.98	-0.56	-0.26	0.46	0.18
	Cl	3.16	-0.87	-0.19_5	0.22	1.6
	Br	2.96	-0.95	-0.12	0.13	2.9
	H	2.2	-1.24			

[a]The electronegativities are from Inorganic Chemistry, 2nd Ed., James E. Huheey, Harper and Row, New York, N.Y. 1978.

[b]$^{6}J_{90}^{H,CH}$ determined from INDO calculation.

[c]$^{6}J_{90}^{H,CH}$ determined from STO-3G calculation.

table 7. Long-range side-chain to ring proton coupling constants in some benzal compounds.

	$^{4}J_{o}^{H,CH}$	$^{5}J_{m}^{H,CH}$	$^{6}J_{p}^{H,CH}$
benzal fluoride[a] (C_6D_6)[b]	-0.46[c]		-0.25
3,5-dichlorobenzal fluoride[a] (CS_2)	-0.49		-0.28
benzal chloride (CS_2)	-0.43		-0.21
3,5-dichlorobenzal chloride (CCl_4)	-0.45		-0.18
benzal bromide (CS_2)	-0.38	0.28_5	
4-$COOC_2H_5$-benzal bromide (acetone)	-0.38	0.29	

[a]ref. 16.

[b]Solvent is shown in parentheses.

[c]Hz

transmitted by a σ-π mechanism. These requirements can be investigated by inspecting the proton-fluorine coupling constants of benzal fluoride (16), 3,5-dichlorobenzal fluoride (16), and p-methylbenzal fluoride.

The ortho and para ring proton to side-chain fluorine couplings in benzal fluoride and 3,5-dichlorobenzal fluoride are listed below. The chlorine substituents in the 3 and 5 positions should have

	ϕCHF_2	3,5-diCl-ϕCHF_2	ϕ=phenyl
${}^4J_o^{H,CF_2}$	-1.16 Hz	-1.02	
${}^6J_p^{H,CF_2}$	-1.14 Hz	-0.95	

minimal, if any, effect on the barrier. Hence, ${}^6J_p^{H,CF_2}$ should be almost the same in the two compounds, which it is not. A similar difference in the coupling magnitude is noted for the four-bond ortho coupling, ${}^4J_o^{H,CF_2}$. Thus, there is a substantial effect on the ring proton-side-chain fluorine couplings by meta substituents.

A condition which indicates that a coupling is transmitted solely by a σ-π mechanism is the constancy in magnitude of the coupling between the protons of a methyl top and a para proton, and the same coupling when the para proton is replaced by another methyl top. Thus, the fact that $|{}^6J_p^{H,CH_3}|$ in toluene is equal to $|{}^7J_p^{CH_3,CH_3}|$ in p-xylene shows that this is a σ-π coupling. Similarly, a sole σ-π mechanism is found for the para coupling in benzyl bromide where ${}^7J_p^{CH_3,CH_2} = 0.34$ Hz in p-methylbenzyl bromide (58) and ${}^{6}J_{p}^{H,CH_2} = -0.32$ in 3,5-dichlorobenzyl bromide (21). The equality within experimental error of the coupling constants also indicates the negligible intrinsic substituent effect of the _meta_ substituents on the _para_ coupling.

Some proton-fluorine and proton-proton couplings in p-methylbenzal fluoride and benzal fluoride (16) are listed in table 8 for comparison. The four and five-bond proton-fluorine couplings are equal within experimental errors in the two compounds, and show that _para_ methyl substitution has negligible effect on these couplings. Similarly, _para_ methyl substitution has no effect on the proton-proton couplings.

That the _para_ six-bond coupling between the ring proton and the α proton is transmitted solely by a σ-π mechanism is shown by the equality of $|{}^{6}J_{p}^{H,CH}|$ and $|{}^{7}J_{p}^{CH_3,CH}|$. However, the large discrepancy in the magnitude of the _para_ ring proton to fluorine couplings in the two compounds indicates a sizeable non-σ-π component to the coupling transmission mechanism. This component can be estimated by assuming that the seven-bond coupling, ${}^{7}J_{p}^{CH_3,CF_2}$, is due solely to a σ-π mechanism. The observed six-bond coupling, ${}^{6}J_{p}^{H,CF_2}$, then has a σ-π component equal in magnitude by opposite in sign to ${}^{7}J_{p}^{CH_3,CF_2}$ plus the non-σ-π component, denoted ~σ-π. Thus, $-1.14 = -1.46 + {\sim}\sigma\text{-}\pi$ or ${\sim}\sigma\text{-}\pi = +0.30$ Hz. The dependence of this non-σ-π component on the angle of internal rotation is unknown.

table 8. Long-range side-chain to ring proton-proton and proton-fluorine coupling constants in benzal fluoride and p-methylbenzal fluoride.

	ϕ-CHF_2[a]	p-CH_3-ϕ-CHF_2
$^4J_o^{H,CF_2}$	-1.16[b]	-1.17
$^4J_o^{H,CH}$	-0.46	-0.46
$^5J_m^{H,CF_2}$	0.92	0.89
$^5J_m^{H,CH}$	0.26	0.25
$^6J_p^{H,CH}$	-0.25	
$^7J_p^{CH_3,CH}$		0.23
$^6J_p^{H,CF_2}$	-1.14	
$^6J_p^{CH_3,CF_2}$		1.46

[a]ref. 16; ϕ = phenyl

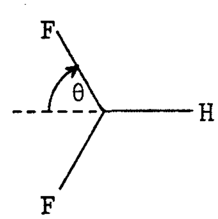
[b]in Hz.

${}^6J_p^{H,CH}$ can be used to determine the rotational barrier because the negligible intrinsic effect of ring substitution on the coupling allows easier estimation of ${}^6J_{90}^{H,CH}$, and a sole σ-π coupling mechanism implies the observed coupling is angle dependent and follows a $\langle \sin^2\theta \rangle$ relationship. ${}^6J_p^{H,CF_2}$ does not meet these requirements and, hence, is not as good as ${}^6J_p^{H,CH}$ for use in barrier determinations.

However, ${}^6J_p^{H,CF_2}$ does indicate some consistency within the context of the J method as the following considerations show. The angular dependence of ${}^6J_p^{H,CF_2}$ in benzal fluoride is given by the same equation as that of ${}^6J_p^{H,CH}$, namely

$$ {}^6J_p^{H,CF_2} = {}^6J_0^{H,CF_2} + {}^6J_{90}^{H,CF_2} \langle \sin^2\theta_F \rangle \qquad [29] $$

where θ_F is now the dihedral angle between one of the C-F bonds and a C_1-$C_{\underline{ortho}}$ ring bond, as in 37, which also illustrates the minimum energy conformation



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as deduced above. ${}^6J_p^{H,CF_2}$, the coupling transmitted by a non-σ-π mechanism, is assumed to be angle independent, and can be assigned a value of −0.30 Hz, as determined above.

In p-methylbenzal fluoride, the non-σ-π contribution to the coupling is assumed zero, and ${}^6J_{90}^{CH_3,CF_2} = -{}^6J_{90}^{H,CF_2}$. The observed seven-bond coupling, ${}^7J_p^{CH_3,CF_2}$ is 1.46 Hz, and thus, for a barrier of 1.1 kcal/mol for which $\langle\sin^2\theta_F\rangle = 0.60$, ${}^6J_{90}^{H,CF_2} = -1.46/0.60 = -2.43$ Hz. Then, equation [28] becomes

$${}^6J_p^{H,CF_2} = 0.30 - 2.43 \langle\sin^2\theta_F\rangle$$

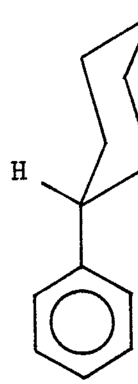
The range of $\langle\sin^2\theta_F\rangle$ from zero barrier to infinite barrier, where <u>37</u> is the rigid conformation, is 0.5 to 0.75, respectively, and for a very large barrier ${}^6J_p^{H,CH}$ is predicted to be $0.30 - 2.43 \times (0.75) = -1.52$ Hz. The barrier in 2,6-dichlorobenzal fluoride (16) is high and <u>37</u> is the minimum energy conformation. The value of ${}^6J_p^{H,CF_2}$ in this compound is -1.25 Hz, where the predicted value is -1.52 HZ. However, as discussed above, there is an intrinsic substituent effect on this coupling from ring substituents. Thus, the magnitude of ${}^6J_p^{H,CF_2}$ is reduced from -1.14 Hz in benzal fluoride to -0.95 in 3,5-dichlorobenzal fluoride, the same trend and nearly the same difference as in the predicted and observed values for 2,6-dichlorobenzal fluoride.

In summary, the barriers to rotation in benzal fluoride, bromide, and chloride were predicted by the J method. The problem of determining the effect of α-substituent electronegativity on ${}^6J_{90}^{H,CH}$ required theoretical calculations to be used in the barrier determinations, and, hence, was not completely solved. The INDO MO FPT method provided a value for ${}^6J_{90}^{H,CH}$ in benzal fluoride and, with an assumed linear dependence of this coupling on electronegativities, yielded barriers of 1.1, 2.2, and 3.5_5 kcal/mole in benzal fluoride, chloride and bromide, respectively. An *ab initio* STO-3G calculation of the barrier in benzal fluoride gave a value of 0.18 kcal/mole. This barrier was used to determine $^6J_{90}^{H,CH}$, and with a linear dependence of this parameter on substituent electronegativities, yielded barriers of 0.18, 1.6, and 2.9 kcal/mole for the benzal fluoride, chloride, and bromide, respectively. An experimental determination by another method, of the barrier in a benzal halide, preferably the fluoride, would aid greatly in bettering the accuracy of the barriers predicted for these compounds by the J method.

The use of $^6J_p^{H,CF_2}$ as another probe of the barrier in benzal fluoride was found to be unsuitable. Both a non-σ-π contribution to the coupling and an intrinsic ring substituent effect on $^6J_{90}^{H,CF_2}$ was evident in the experimental NMR data. However, use of the J method, and quantitative estimates of these effects gave results consistent with the experimental data.

3. 3,5-Dichlorophenyl Derivatives of Cyclohexane, 1,3-Dithiane, 1,3-Dioxane, and 1,3-Dioxolane

The J method was successful in predicting barriers to internal rotation and minimum energy conformations in such compounds as ethylbenzene (40), isopropylbenzene, styrene (59), and phenylcyclopropane (60). The rotational barriers in isopropylbenzene and phenylcyclopropane were found to be equal within experimental errors, implying that α,α-dialkyl substitution in toluene produced the same rotational barriers. A likely molecule to test this hypothesis is phenylcyclohexane, 38, which has a structure similar to phenylcyclopropane. The investigation of phenylcyclohexane suggested a series of similar molecules, ones in which the same heteroatom occurred at the 1 and 3 positions of a saturated ring. These were 2-phenyl-1,3-dithiane, 39, 2-phenyl-1,3-dioxane, 40, and 2-phenyl-1,3-dioxolane, 41. The rotational barriers of these molecules were also determined and compared.



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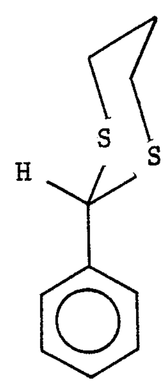

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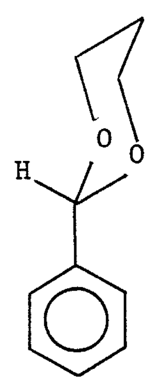

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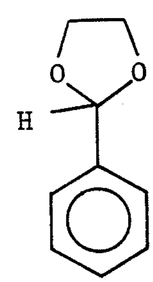

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The spectral dispersions of the ring proton resonances in 38 to 41 were too small for accurate analysis. Hence, as in the case of ethylbenzene and isopropylbenzene, halogen atoms were substituted in the 3 and 5 positions of the aromatic rings to yield the molecules 3,5-dichlorophenylcyclohexane, 2-(3,5-dichlorophenyl)-1,3-dithiane, 2-(3,5-dichlorophenyl)-1,3-dioxane, and 2-(3,5-dichlorophenyl)-1,3-dioxolane. The chlorine substituents, as discussed previously, were assumed to have a negligible effect on the intrinsic six-bond *para* proton-proton coupling and the actual barrier to rotation. Thus the barrier determined in, say 3,5-dichlorophenylcyclohexane, is taken to be the same as in the parent phenylcyclohexane.

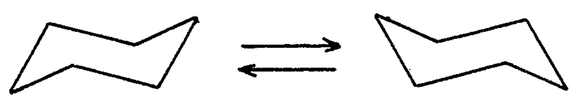
i) spectral analysis

The 3,5-dichlorophenylcyclohexane, and the 2-(3,5-dichlorophenyl)-1,3-dioxane and -1,3-dioxolane, were prepared as 10 mole % solutions in C_6D_6. The 2-(3,5-dichlorophenyl)-1,3-dithiane was prepared as a 10 mol % solution in CS_2. The NMR spectra of the compounds were recorded on a Varian HA 100 spectrometer. Only the aromatic ring proton resonances were calibrated for analysis, the ones of the saturated ring, including those of the methine proton, being unresolvable as individual peaks. No coupling was observable from the saturated ring protons to the aromatic ring except for the important methine proton.

The aromatic ring proton spectrum was analyzed, with the use of the program LAME, as an AB_2 subspectrum of a AB_2X spectrum, the X referring to the methine proton. Although the frequencies of the methine proton resonances could not be assigned, the *para* proton resonances were well resolved and allowed the determination of $^6J_p^{H,CH}$. The phenyl ring spectrum of 3,5-dichlorophenylcyclohexane is reproduced in figure 7 and the phenyl ring and methine proton spectrum of 2-(3,5-dichlorophenyl)-1,3-dioxolane in figure 8, with the simulated spectra for comparison. The spectral parameters of the four compounds are listed in table 9.

ii) 3,5-dichlorophenylcyclohexane

Cyclohexane is known to exist mainly in the chair conformation, and to interconvert, by ring inversion, between two chair conformations as illustrated below. The kinetic parameters, $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$,



for this interconversion were determined by Anet and Bourne (61) in a classic dynamic nuclear magnetic resonance experiment and found to be 10.3, 10.8 kcal/mole, and 2.9 cal/mol deg, respectively.

Although not indicated in the diagram, chair-chain inversion results in an exchange of the protons between the axial and equatorial positions on the ring. Thus, the equatorial protons in one chair conformation become the axial protons after the inversion to the other chair conformation. The chair-chair interconversion also occurs for many mono-substituted cyclohexane molecules with the concomitant dynamic equilibration of the substituent between the equatorial and axial positions. For phenylcyclohexane there is an

Figure 7. The observed and calculated ring proton magnetic resonance spectra at 100 MHz of a 10 mole % solution of 3,5-dichlorophenylcyclohexane in C_6D_6. The spectral parameters used in the simulation are given in table 9.

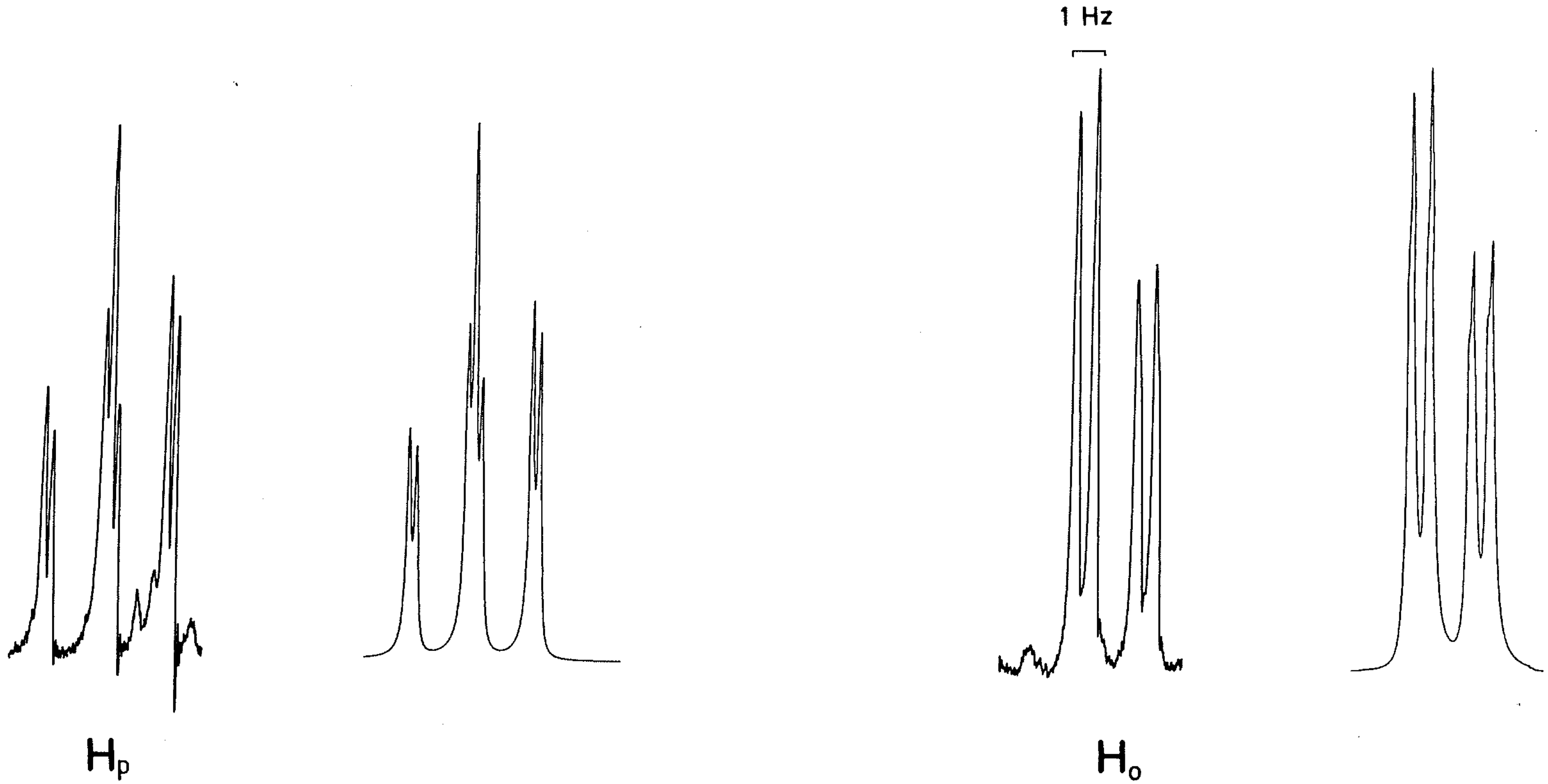

1 Hz
H_p
H_o

Figure 8. The observed and calculated ring and side-chain proton magnetic resonance spectra at 100 MHz of a 10 mole % solution of 2-(3,5-dichlorophenyl)-1,3-dioxolane in C_6D_6. The experimental peak of the α-proton shows the coupling from the protons of the saturated heterocyclic ring which are not included in the calculated resonance peaks. The spectral parameters used in the simulation are given in table 9.

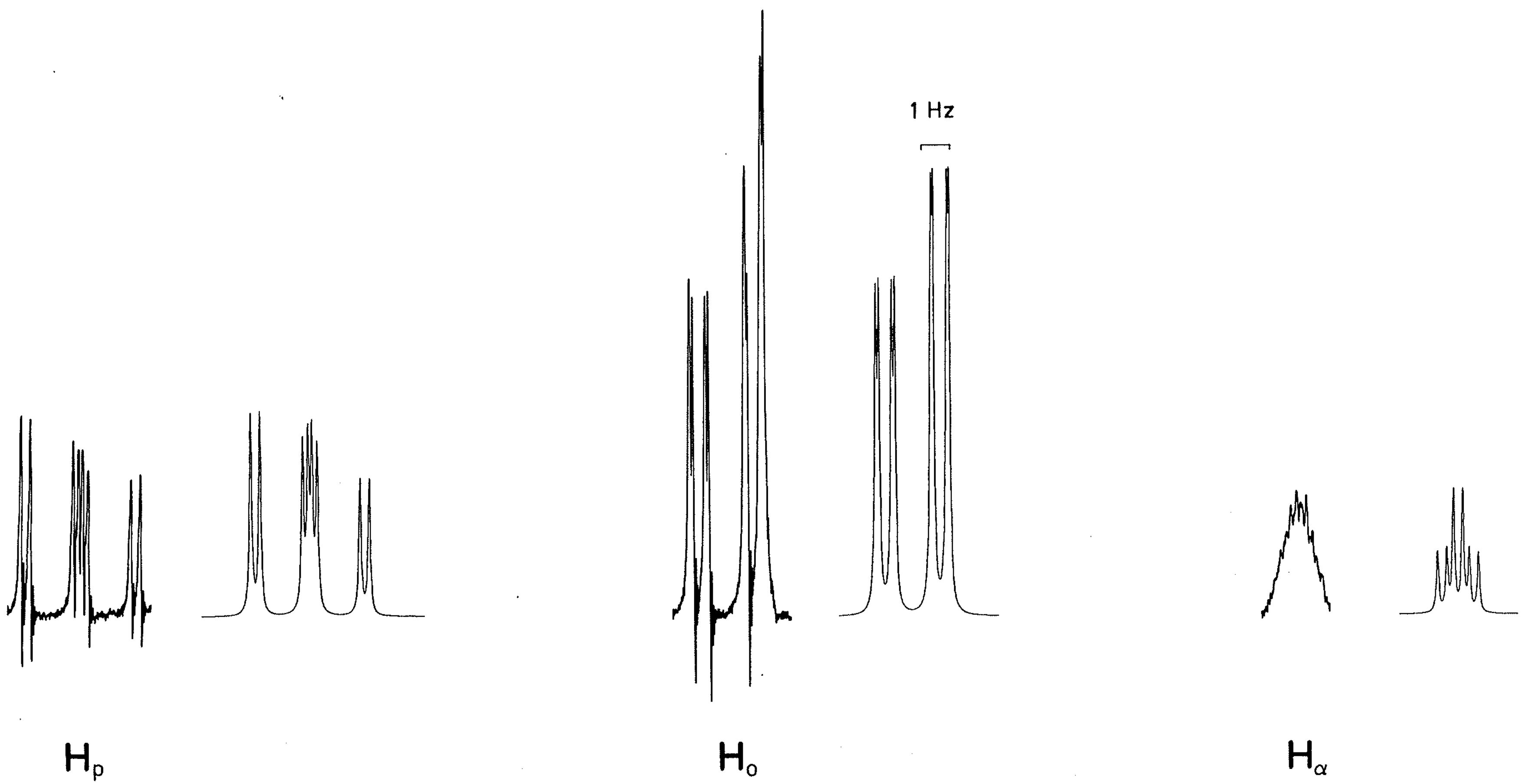
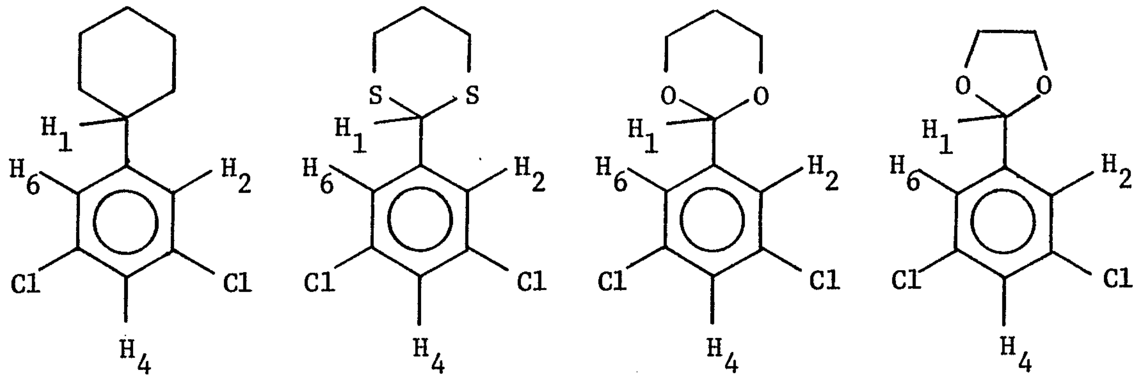

1 Hz
H_p
H_o
H_α

Table 9. NMR spectral parameters of 3,5-dichlorophenylcyclohexane and 2-(3,5-dichlorophenyl)-1,3-dithiane, -1,3-dioxane, and 1,3-dioxolane.

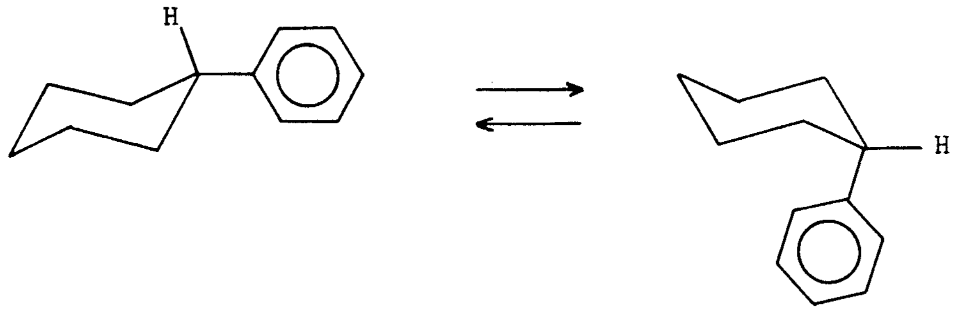


ν_1 [a]	206.7	498.2	498.5	542.9
$\nu_2 = \nu_6$	687.586(5)	729.792(3)	739.270(8)	729.053(4)
ν_4	704.515(5)	719.423(3)	708.483(6)	709.202(4)
$J_{12} = J_{16}$ [b]	-0.576(11)	-0.481(6)	-0.727(16)	-0.572(8)
J_{14}	-0.233(11)	-0.218(7)	-0.399(11)	-0.329(5)
$J_{24} = J_{46}$	1.911(6)	1.908(4)	1.981(7)	1.967(5)
RMS error	0.013	0.007	0.012	0.010

[a] In Hz at 100.001 MHz to low field of internal tetramethylsilane: chemical shifts.

[b] Coupling constants in Hz; numbers in parentheses give standard deviations in the last or second last place.

equilibrium between the two conformations, 42 and 43, the free energy difference between the two being 3.1 kcal/mole (62) at 298 K



42 43

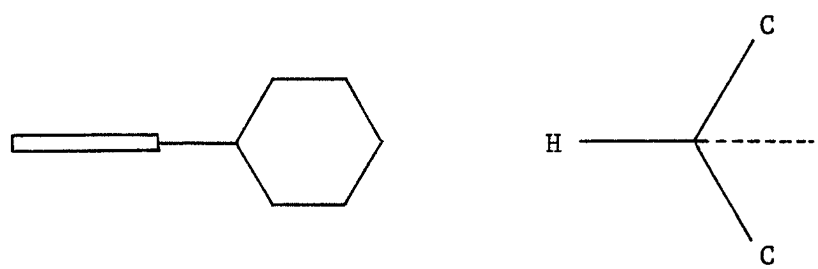
and 42 having the lower energy. The relative populations, n_A/n_B, of the two conformations are given by the expression

$$\frac{n_A}{n_B} = \exp\left(\frac{-\Delta G_{AB}}{RT} \right) \qquad [29]$$

where A and B are two chemical species in equilibrium, ΔG_{AB} is the free energy difference between the species, R is the universal gas constant constant, and T is the temperature. At 305 K, over 99% of the phenylcyclohexane molecules have the phenyl substituent in the equatorial position.

If the rate of inversion of the cyclohexyl group in phenylcyclohexane is assumed to be comparable to that in cyclohexane, and because $\Delta H^{\ddagger}$ can be associated with the barrier to interconversion, then the rate of inversion of the cyclohexyl group is much smaller than the rate of internal rotation about the C_{phenyl}-C_α bond ($\Delta H^{\ddagger}$(inversion) ≈ 10 kcal/mole; $\Delta H^{\ddagger}$(internal rotation) ≈ 2 kcal/mole (see below)). Thus, the following discussion concerning the internal rotation in 3,5-dichlorophenylcyclohexane will be for a non-inverting equatorial conformation.

The observed six-bond coupling, ${}^6J_p^{H,CH}$, in 3,5-dichlorophenylcyclohexane is $-0.23_3 \pm 0.02$ Hz. To find $<\sin^2\theta>$, a value of ${}^6J_{90}^{H,CH}$ is required. Because the α-substituents of the benzal top are alkyl groups a value of -1.24 Hz is suggested. This is the value found in toluene and used in the determination of the barriers in phenylethane (40) and isopropylbenzene. With this value and the experimental coupling constant, $<\sin^2\theta> = -0.233/-1.24 = 0.188$, and a plot of $<\sin^2\theta>$ versus V_2 indicates a barrier of 2.1 kcal/mole. The $<\sin^2\theta>$ values as a function of V_2 were calculated for a temperature of 305 K and a reduced moment of inertia of 1.72×10^{-38} g cm^2. The reduced moment was calculated for an equatorial conformation and an orientation of the cyclohexyl moiety where $\theta_{min} = 0°$. The reduced



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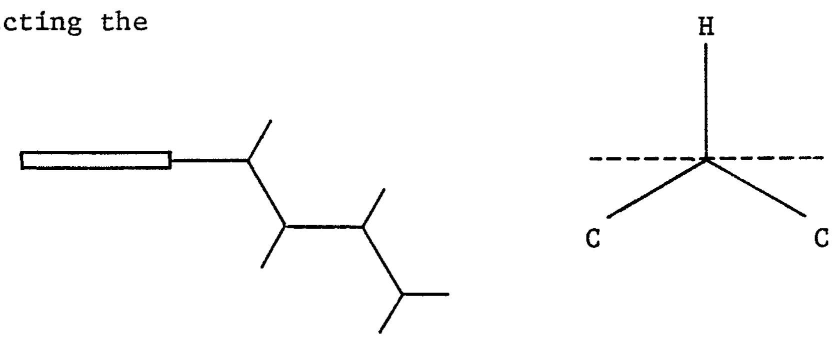
moment changes to 1.80×10^{-38} g cm^2 for the $\theta = 90°$ orientation 43, but this relatively small change is completely negligible when constructing the



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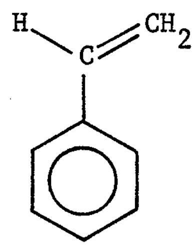
$\langle \sin^2\theta \rangle$ versus V_2 plot because of the insensitivity of $\langle \sin^2\theta \rangle$ to the reduced moment.

${}^6J_{90}^{H,CH}$ is transmitted by a σ-π mechanism and so the magnitude of the coupling can be affected by factors which change the overlap of the C_α-H bond with the ring π system. One such factor is the electronegativity of the α-substituents, as seen in the case of the benzal halides. Another is the bond angle, denoted by C_1-C_α-H, between the C_1-C_α bond and the C_α-H bond. In toluene, and in phenylethane and isopropylbenzene, the bond angle was assumed to be the tetrahedral angle (109.5^o). In styrene, 44, where the standard C_1-C_α-H angle is 120^o, overlap of the C_α-H bond with



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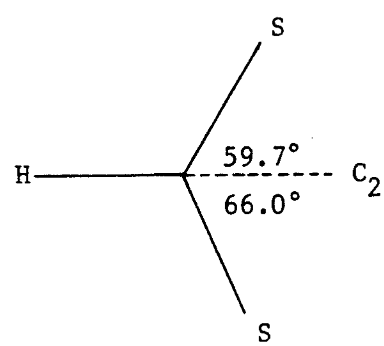
the π system is less and, hence, the magnitude of ${}^6J_{90}^{H,CH}$ is expected to be less. This prediction is verified by INDO MO FPT calculations using standard geometries (14) which gave a value of -1.05 Hz for ${}^6J_{90}^{H,CH}$. When an experimentally determined geometry (63) of styrene was used, ${}^6J_{90}^{H,CH}$ was calculated to be -1.00 Hz. In cyclopropane, where the C_1-C_α-H angle is between the 109.5^o of toluene and 120^o of styrene, INDO calculations gave a value of -1.11 Hz, using a geometry determined by an electron diffraction method (64). The INDO calculated values of ${}^6J_{90}^{H,CH}$ are assumed accurate for these compounds because of the agreement between the calculated and experimentally determined value of ${}^{6}J_{90}^{H,CH_3}$ in toluene, i.e. -1.24 Hz.

The bond angles in cyclohexane are not perfect tetrahedral angles, which the standard geometry predicts. The ring angles, C-C-C, are actually 111.55° (65), which impiles that the H-C-H angles decrease from 109.5°. An experimental value for this angle in cyclohexane was 107.5 ± 1.5° (66) while another was 110° (67). The C_1-C_α-H angle in phenylcyclohexane, which corresponds to the H-C-H angle in cyclohexane is taken to be 2° more or less than the tetrahedral angle. The fractional change in ${}^{6}J_{90}^{H,CH}$ with angle can be estimated by taking the difference of the ${}^{6}J_{90}^{H,CH}$ values for styrene and toluene, calculated by the INDO program, over the difference in the C_1-C_α-H angle, which results in 0.0181 Hz/deg. The possible error in taking -1.24 Hz as ${}^{6}J_{90}^{H,CH}$ in 3,5-dichlorophenylcyclohexane is ± 2 x 0.0181 = +0.036 or ± 2.9%. The experimental error in ${}^{6}J_{p}^{H,CH}$ = -0.233 Hz is ±0.02 Hz or ±8.6%, for a total error in the couplings of ±11.5%. This corresponds to an error in $\langle \sin^2\theta \rangle$ of 0.1879 x ± 0.216 and an error in the barrier of ± 0.3 kcal/mole. Thus, the barrier in 3,5-dichlorophenylcyclohexane, as determined by the J method, is 2.1 ± 0.3 kcal/mole.

Allinger and Tribble (68) calculated, by a molecular mechanics method, the energies of the phenylcyclohexane conformations which have the phenyl group in the equatorial position, and the phenyl ring plane oriented perpendicular (θ_{min} = 90°) and parallel (θ_{min} = 0°) to the mirror plane of the cyclohexane ring which includes the bond connecting the two rings. The energy difference between the two conformations, which can be taken as the barrier to internal rotation, was 3.92 kcal/mole with the $\theta = 0^{o}$ conformation having the lower energy.

iii) 2-(3,5-dichlorophenyl)-1,3-dithiane

An X-ray crystallographic (69) study of 2-phenyl-1,3-dithiane found that the dithiane ring had a flattened chair conformation and that the phenyl group was in an equatorial position, with an orientation almost perpendicular to the "plane" of the dithiane ring. In fact, the dihedral angles between the C_{α}-S bonds and the C_1-C_2 bond in the phenyl ring were 59.7 and 66.0^{o}, as shown in 45. The 6^{o} difference



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from 60^{o} was not considered significant as the standard deviation in the dihedral angles was about 2.5^{o}.

A gas-phase electron diffraction study (70) of 1,3-dithiane found no significant evidence for any conformations other than the chair. The sensitivity of the detection was 10% so that if any other conformation were present its population would be below this value. An equilibrium study of substituted 1,3-dithianes in chloroform solutions (71) found that the free energy difference between the chair and boat conformations in 1,3-dithiane itself was 1.8 kcal/mole at 298 K. This implies a chair conformation population of about 95%.

The free-energy difference between the axial and equatorial forms of 2-phenyl-1,3-dithiane in chloroform and pyridine solutions (72) was predicted to be 1.7 kcal/mol in favour of the equatorial conformation. A subsequent dipole moment study of 2-(p-chlorophenyl)-1,3-dithiane in benzene and carbon tetrachloride (73), verified this value as 1.7 $\pm$ 0.3 kcal/mole showing that the p-chlorophenyl group was largely (>90%) in the equatorial position.

The chair-chair interconversion barrier in 1,3-dithiane was found to be 9.4 kcal/mole (71). If this is close to the value in 2-phenyl-1,3-dithiane, which it is assumed to be, then the interconversion is much slower than the internal rotation about the $C_{1,phenyl}-C_{\alpha}$ bond. Thus, the discussion concerning this internal rotation is for a noninterconverting, equatorially substituted dithiane ring.

The observed six-bond coupling $^6J_p^{H,CH}$ in 2-(3,5-dichlorophenyl)-1,3-dithiane is -0.21_8 Hz, and for a $^6J_{90}^{H,CH}$ value of -1.24 Hz, $\langle \sin^2\theta \rangle = 0.1758$. From a plot or tables of $\langle \sin^2\theta \rangle$ versus V_2, with a temperature of 305 K and a reduced moment of 2.48×10^{-38} g cm^2, the barrier to rotation about the C_1-C_{α} bond was found to be 2.22 kcal/mole.

In the previous section it was seen that both the electronegativity of the α-substituents and the C_1-C_α-H bond angle would affect the magnitude of ${}^6J_{90}^{H,CH}$. A carbon α-substituent, that is, a simple alkyl group such as methyl, cyclopropyl, or cyclohexyl, was deduced to have a negligible effect on ${}^6J_{90}^{H,CH}$ of toluene. The sulphur atom has almost the same electronegativity as carbon, 2.58 compared to 2.55 on the Pauling scale (74), and so should have a negligible effect on ${}^6J_{90}^{H,CH}$ in the phenyldithiane derivative. A previous application of the J method to benzyl mercaptan used the value in toluene, -1.24 Hz, for ${}^6J_{90}^{H,CH}$ in this compound (56).

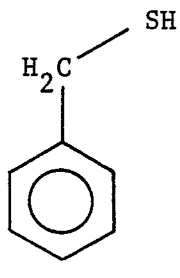
The bond angle, C_1-C_α-H in 2-phenyl-1,3-dithiane is not known with any certainty. If the bond angle, S-C-S, is greater than the tetrahedral angle, 109.5°, then the H-C(S,S)-H bond angle is expected to be less than the tetrahedral angle. Some support for this prediction can be found by considering cyclohexane, where the C-C-C angle was determined the be 111.5° (65) and H-C-H angle reported as $107.5 \pm 1.5^\circ$ (66). The S-C-S angle in 1,3-dithiane, from the gas-phase electron diffraction study (70), was $115.0 \pm 0.3^\circ$. In the same study the H-C-H angle was determined to be $104._1 \pm 4._5^\circ$ but this value was constrained to be the same for all the H-C-H angles in the data analysis. However, the C-C-S and C-C-C angles, in which the centre carbon also appears in the H-C-H angle, were all approximately 114°; suggesting that the individual H-C-H angles would not differ much from 104°. The S-C-S angle in 2-phenyl-1,3-dithiane as determined in the X-ray analysis (69), is 115.2°, very close to the 115.0° in 1,3-dithiane, which implies that the C_1-C_α-H angle in 2-phenyl-1,3-dithiane is close to the H-C-H angle in 1,3-dithiane.

Hence, the C_1-C_α-H angle is predicted to be approximately 104°.

If the C_1-C_α-H angle is 104°, the C_α-H bond would have a greater overlap with the ring π system, and ${}^6J_{90}^{H,CH}$ would increase from the -1.24 Hz value associated with the tetrahedral angle. A decrease of 5.5° of the angle should increase the magnitude of the coupling by 5.5 x 0.0181 = 0.10 Hz. The conversion factor was estimated in the preceding section. The new value of $\langle \sin^2\theta \rangle$ is -0.218/-1.34 = 0.1627 which yields a barrier of 2.4_9 kcal/mole in 2-(3,5-dichlorophenyl)-1,3-dithiane.

This barrier is greater than the value of 2.1 kcal/mole determined for phenylcyclohexane above. Space filling models of phenylcyclohexane and 2-phenyl-1,3-dithiane indicate lesser steric interaction in the phenyldithiane with respect to the internal rotation, a conclusion also reached if the van der Waals radii of a methyl group (200 pm) and a sulphur atom (180 pm) are compared. If the barrier arises mainly from steric interactions, then these considerations imply that 2.5 kcal/mole is an overestimation.

On the other hand, the rotational barriers in benzyl mercaptan (56), 46, and in ethylbenzene (40), 47, were found to be 1.8 and



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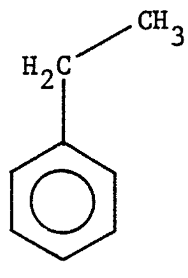

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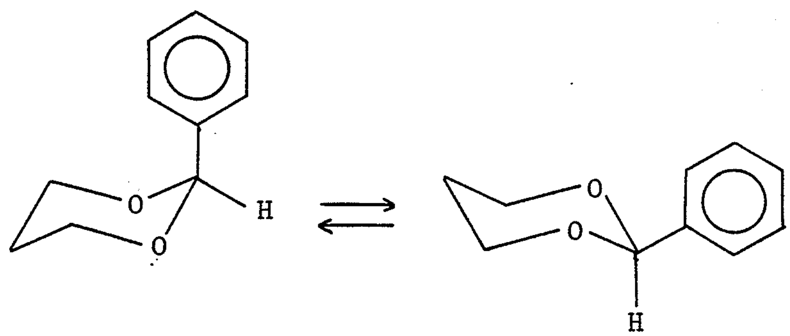
1.2 kcal/mole, respectively, by the J method. Substitution of another methyl group on the α-carbon of ethylbenzene produces isopropylbenzene with a barrier of 2.0 kcal/mole, comparable to the 2.1 kcal/mole in phenylcyclohexane. Thus, there is a sizeable increase in the barrier on the substitution of a second methyl group and this could also be the case for the substitution of a second sulphur group. The increase of the barrier on a second methyl substitution is 0.8 kcal/mole, and if this value also applies to substitution of a second sulfur moiety, then 2.6 kcal/mol is predicted for the rotational barrier in the phenyldithiane, not far from the 2.5 kcal/mole determined.

The increase of $^6J_{90}^{H,CH}$ with a decrease in the C_1-C_α-H angle is an extrapolation, and as such has a higher risk of error than an interpolation. Because of this fact and the large error in the H-C-H angle used to predict C_1-C_α-H in the 2-(3,5-dichlorophenyl)-1,3-dithiane, the barrier to rotation is reported as the mean of the two possible barriers, $2.3_5 \pm 0.4$ kcal/mole. The error represents both the experimental error in $^6J_p^{H,CH}$ of $\pm$ 0.02 Hz and the possible error in $^6J_{90}^{H,CH}$, $\pm$0.10 Hz.

As in the phenylcyclohexane, the observed coupling, $^6J_p^{H,CH}$ implies a minimum energy conformation in which the C_α-H bond is in the plane of the benzene ring, $\theta_{min} = 0^o$. If the minimum energy conformation were either of those with $\theta_{min} = 60^o$ or 90^o, then the observed coupling would have to be greater than 0.5 x 1.24 = 0.62 Hz. In both cases $|^6J_p^{H,CH}|$ would increase with the barrier from the zero barrier limit of 0.62 Hz. The $\theta_{min} = 0^o$ conformation is found to be the stable conformation in the solid 2-phenyl-1,3-dithiane, as mentioned above (69).

iv) <u>2-(3,5-dichlorophenyl)-1,3-dioxane</u>

The dioxane ring in 2-phenyl-1,3-dioxane undergoes ring inversion, between the conformation where the phenyl substituent is in the axial position, 48, and the one where the substituent is in the equatorial position, 49. The equatorial conformation,



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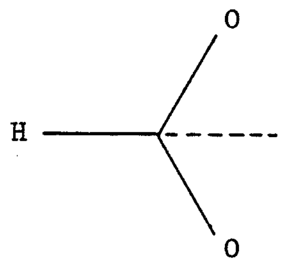
49, is favoured by a free energy of -3.12 $\pm$ 0.02 kcal/mole (75) at 298 K, and so, over 99% of the 2-phenyl-1,3-dioxane molecules exist in this conformation.

As well as ring inversion, internal rotation occurs about the bond joining the phenyl ring to the dioxane ring. This bond will be denoted as the C_1-C_α bond where C_1 is the aromatic ring carbon and C_α is the dioxane ring carbon at the 2 position. The two possible minimum energy rotational conformations are those with the C_α-H bond in the plane of the phenyl ring, or the C_α-H bond perpendicular to the plane of the phenyl ring, as in 50 and 51, respectively. These two conformations



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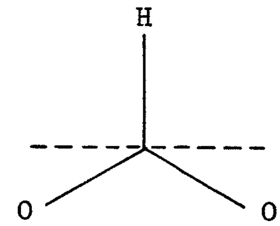

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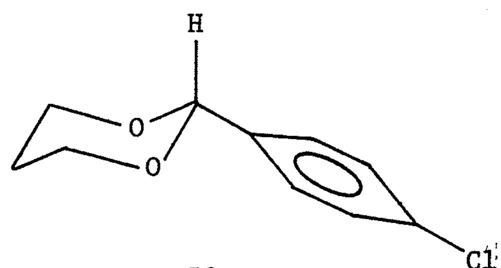
will be referred to as the $\theta_{min} = 0^{o}$ conformation and the $\theta_{min} = 90^{o}$ conformation, respectively, where θ is the angle defining the dihedral angle between the C_{α}-H bond and a C_1-$C_{\underline{ortho}}$ bond.

There is experimental evidence that the rotational barrier between 50 and 51 is very small or even non-existent. In the X-ray analysis of 2-(p-chlorophenyl)-1,3-dioxane (76), 52, the phenyl moiety was in the equatorial position and was rotationally



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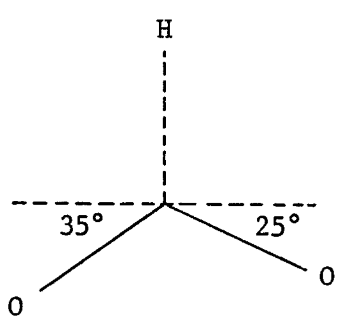
oriented nearly in the $\theta_{min} = 90^{o}$ position, 53. The α-hydrogen



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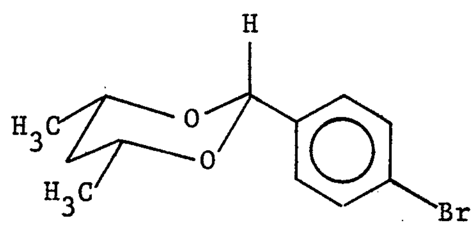
dihedral angle was not determined. On the other hand X-ray analysis of the equatorially substituted isomer of r-2-(p-bromophenyl)-C-4, C-6-dimethyl-1,3-dioxane (77a,b), 54, reported the rotational conformation 54 to be nearly the $\theta_{min} = 0^{o}$ one, the dihedral angle being actually 29^{o} as shown in 55.



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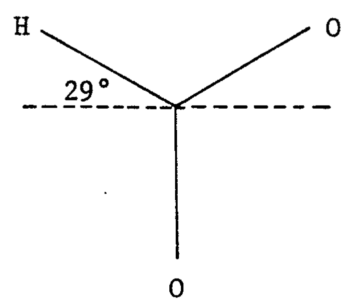

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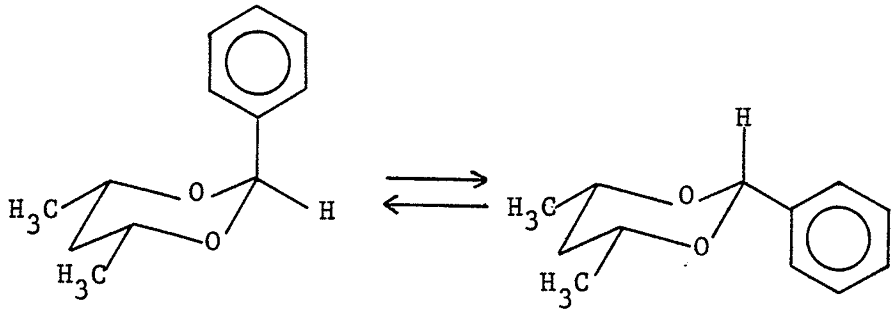
These results suggest that there is very little intrinsic preference for either rotational conformation, that is, the rotational barrier is very small, and that the orientation of the phenyl group is determined mainly by packing forces in the solid state.

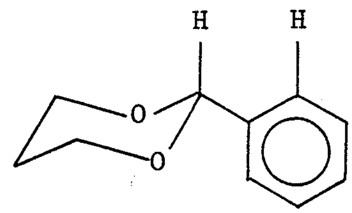
A zero rotational barrier was proposed by Bailey et al. (75) from calorimetric measurements of the heat of acid-catalyzed isomerization of axial 2-phenyl-C-4,C-6-dimethyl-1,3-dioxane, 56, to its equatorial epimer, 57. A large conformational



56 57

entropy, ΔS^{o} = 3.9 cal/mol deg favouring the equatorial isomer was found and was proposed to result from a large difference in the hindrance to internal rotation of the phenyl group about the C_1-C_α bond in the axial and equatorial isomers. The entropies associated with the internal rotation of each of the axial and equatorial isomers were calculated, and for the equatorial 2-phenyl-1,3-dioxane, the simplest model consistent with the experimental data was that for free rotation.

A theoretical calculation of the barrier to rotation in the equatorial isomer of 2-phenyl-1,3-dioxane was performed by Allinger and Chung (78) using a molecular mechanics method. The calculations yielded a zero barrier due to the cancellation of repulsive interactions in the rotational conformations. In the $\theta_{min} = 0^{o}$ conformation there is a severe repulsion between an _ortho_ hydrogen and an α hydrogen, 58,



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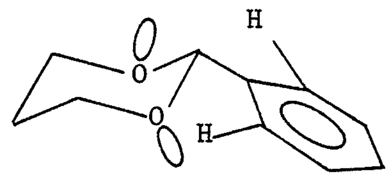
while in the $\theta_{min} = 90^{\circ}$ conformation there are moderately severe repulsions between the ortho hydrogens and the equatorial lone pairs on the oxygens, 59.



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In order to determine the rotational barrier in 2-(3,5-dichlorophenyl)-1,3-dioxane, the six-bond coupling between the α proton and the *para* proton, ${}^{6}J_{90}^{H,CH}$, must be estimated. The two factors which affect this coupling are the electronegativity of the α-substituents and the C_1-C_α-H bond angle. The X-ray diffraction studies of the 2-phenyl-1,3-dioxane derivatives (76,77) found the O-C-O angle to be 111° which is almost exactly the value for the corresponding angle in cyclohexane. The H-C-H angle in cyclohexane is either 107.5° (66) or 110° (67), and 107° is given as the C_1-C_α(O,O)-H angle in 2-phenyl-1,3-dioxane in one of the X-ray studies (77). The uncertainty of the C_1-C_α-H angle in phenylcyclohexane and the small effect of, at most, a 2^{o} difference in the C_1-C_α-H angle from the tetrahedral, justified the use of -1.24 Hz, the toluene value, for $^6J_{90}^{H,CH}$. Any variation in $^6J_{90}^{H,CH}$ due to the angle difference was incorporated into the reported error for the barrier. Because of the similarity in the relevant angles in cyclohexane and 1,3-dioxane, $^6J_{90}^{H,CH}$ is assumed to be unaffected by changes in the C_1-C_α-H angle.

The electronegativity of oxygen on the Pauling scale is 3.44, substantially greater than that of hydrogen or methyl. Hence, $^6J_{90}^{H,CH}$, should be reduced in magnitude by the electronegativity effect. An inverse linear dependency was proposed for the $^6J_{90}^{H,CH}$ coupling in the benzal halides on the α-substituent electronegativity, E_X, and illustrated in figure 6, above. The limits on the $^6J_{90}^{H,CH}$ scale were the INDO MO FPT calculated values in toluene and benzal fluoride. $^6J_{90}^{H,CH}$ for a benzal compound with α-substituents, X, can be interpolated if E_X falls between E_H and E_F.

For E_O = 3.44, the interpolated value of $^6J_{90}^{H,CH}$ is -0.98 Hz. The six-bond observed coupling, $^6J_p^{H,CH}$, is -0.39_9 Hz. These couplings then give $\langle \sin^2\theta \rangle = 0.407$ for a rotational barrier height of 0.48 kcal/mole. The error in the observed coupling is $\pm$ 0.02 Hz, and an estimated error in $^6J_{90}^{H,CH}$ due to a deviation of the C_1-C_α-H angle from the tetrahedral is $\pm$ 0.04 Hz. The combined deviations given an error in the barrier of $\pm$ 0.20 kcal/mole. Thus the rotational barrier in 2-(3,5-dichlorophenyl)-1,3-dioxane is predicted to be 0.5 $\pm$ 0.2 kcal/mole.

The plot of $<\sin^2\theta>$ versus V_2 used to determine the barrier is for a $\theta_{min} = 0^o$ minimum energy conformation. The value of $<\sin^2\theta>$ calculated from the experimental data is only within the $<\sin^2\theta>$ range of this conformation. For the other possible minimum energy conformation, where $\theta_{min} = 90^o$, the experimental $<\sin^2\theta>$ would have to be in the range 0.5 to 1.0, which it is not.

Free rotation in the 2-(3,5-dichlorophenyl)-1,3-dioxane would imply that $^6J_{90}^{H,CH}$ is -0.399/0.5 = -0.80 Hz which is rather low in magnitude. It is lower than $^6J_{90}^{H,CH}$ in benzal fluoride, which is calculated by INDO to be -0.87 Hz.

v) <u>2-(3,5-dichlorophenyl)-1,3-dioxolane</u>

The saturated six-membered rings considered so far have had only a few thermodynamically stable conformations, among which they equilibrate. For the compounds studied the most stable conformation had a chair form for the alicyclic ring with the phenyl substituent in the equatorial position. This conformation was in equilibrium with a second, in which the phenyl substituent was in the axial position, and the two forms interconverted through a chair-chair inversion. The equatorially substituted conformation was present in solution at over 95% and the high activation energies of the inversion indicated that the NMR parameters were for a non-inverting equatorially substituted molecule.

The large amplitude internal motions of five-membered rings do not have the high thermodynamic and activation energies of the six-membered rings. The cyclopentane molecule is puckered, having out-of-plane conformations such as the "envelope", 60, or the "half-chair" form, 61. The out-of-plane bending and twisting occur for

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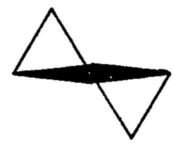

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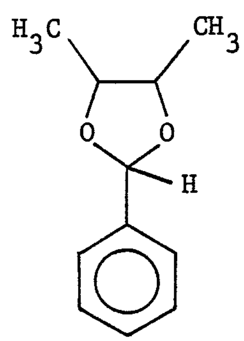
each atom in the ring and produce new conformations which are minimum energy conformations but are separated, in the case of internal (hetero-atom) or external substitution, by very small energies. The activation energies between the conformations are also small so that the five-membered rings are in a constant conformational flux called pseudorotation. The pseudorotational motion can be described by a hamiltonian, and the energies and eigenfunctions calculated. Transitions between the energy levels have been observed in the far-infrared region of five-membered rings in the gas phase, one being 1,3-dioxolane (79). The effect of a barrier to rotation on the transitions, allowed an estimation of the barrier in 1,3-dioxolane of about 50 cm^{-1} or 0.14 kcal/mole.

Extensive equilibration experiments on substituted 1,3-dioxolanes (80), showed that the ring in most of the compounds was highly flexible, even when triply substituted. Carbon-13 chemical shifts in some methyl-substituted 1,3-dioxolanes (81) also confirm that the ring is highly flexible and is a dynamic mixture of various conformations. For a single substituent, as in the case of

2-(3,5-dichlorophenyl)-1,3-dioxolane, the pseudorotational motion of the alicyclic ring is assumed to be much faster than the internal rotation about the C_1-C_α bond, and the six-bond para coupling, ${}^6J_p^{H,CH}$, applies to a dynamically averaged alicyclic ring structure.

The six-bond para coupling, ${}^6J_p^{H,CH}$, in 2-(3,5-dichlorophenyl)-1,3-dioxolane is -0.33 Hz. If ${}^6J_{90}^{H,CH}$ = -0.98, as estimated for the phenyldioxane derivative, then $\langle\sin^2\theta\rangle$ = 0.337. The only $\langle\sin^2\theta\rangle$ versus V_2 curve which includes this value is the one for the θ_{min} = 0^o minimum energy conformation. The barrier to rotation in 2-(3,5-dichlorophenyl)-1,3-dioxolane is then $0.8_5 \pm 0.3$ kcal/mole, where the error has contributions from the experimental error in ${}^6J_p^{H,CH}$ of $\pm$ 0.02 Hz and the uncertainty in the exact magnitude of ${}^6J_{90}^{H,CH}$ of $\pm$ 0.04 Hz.

The other possible minimum energy conformation, where θ_{min} = 90^o, requires that ${}^6J_{90}^{H,CH}$ be -0.66 Hz or less in magnitude, decidedly unlikely. That the C_α-H bond lies in the plane of the phenyl ring is supported by chemical shift data reported in the equilibrium study of the 1,3-dioxolane derivatives (80). Thus, in 2-phenyl-cis-4,cis-5-dimethyl-1,3-dioxolane, 62, in CCl_4, the chemical shift of the 2 or α proton was at 338.8 Hz from TMS, whereas, in 2,cis-4,cis-5-trimethyl-1,3-dioxolane, 63, the α proton was at 292.5 Hz.



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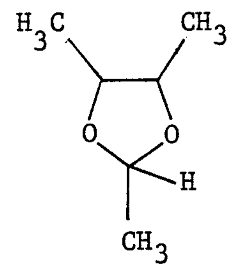

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Thus, the replacement of a methyl group by a phenyl group at the 2 position of 1,3-dioxolane produces a downfield shift of the 2 or α proton which indicates a deshielding of this proton. Deshielding of nuclei by a phenyl ring occurs when the nucleus is in or near the plane of the phenyl ring.

vi) summary

The barriers to rotation of the phenyl substituted alicycles and some related compounds, as determined by the J method, are listed in table 10. The similarity of the barriers in the phenylcyclohexane, phenylcyclopropane, and isopropylbenzene derivatives suggests that, if the barriers result mainly from steric interactions of the α-substituents with the ortho protons of the phenyl ring, then the cyclohexyl, cyclopropyl, and dimethyl substituents have similar steric requirements. Because of the similarity of the barriers in the phenylcyclohexane and phenyldithiane derivatives the dithiane ring is assumed to have steric requirements similar to the three groups listed above. Furthermore, if it is the groups at the 1,3 positions table 10. Rotational barriers of derivatives of phenylcyclohexane and related compounds.

Compound	Barrier (kcal/mol)[b]
3,5-dichlorophenylcyclohexane	2.1 ± 0.3 [c]
phenylcyclopropane[a]	2.0 ± 0.3
3,5-dibromoisopropylbenzene	2.0 ± 0.3
2-(3,5-dichlorophenyl)-1,3-dithiane	$2.3_5 \pm 0.4$
2-(3,5-dichlorophenyl)-1,3-dioxane	0.5 ± 0.2
2-(3,5-dichlorophenyl)-1,3-dioxolane	$0.8_5 \pm 0.3$

[a] ref. 60.

[b] For all molecules the minimum energy conformation was that with the C_α-H bond in the plane of the benzene ring, or the $\theta = 0^\circ$ conformation.

[c] All values of the barrier were determined by the J method.

of the saturated rings which interact sterically with the <u>ortho</u> protons of the phenyl ring, then the steric requirements actually apply to the methyl group and the methylene and sulfur fragments.

4. 3,5-Dichloro Derivatives of Benzyl Alcohol and Selenol

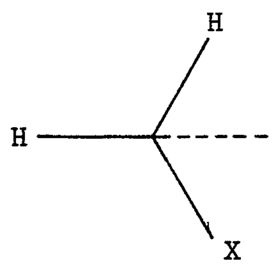
Up to this point the compounds discussed have been benzal compounds, that is, those with two identical substituents on the methyl top of toluene. The compounds now to be discussed, including the present benzyl alcohol and selenol are all benzyl compounds, those with one substituent on the methyl top. For both benzyl and benzal cases the barrier to internal rotation is interpolated from $<\sin^2\theta>$ versus V_2 plots or tables, where the $<\sin^2\theta>$ values are calculated as a function of reduced moment of inertia and temperature. The tables and resulting plots are also calculated for a particular minimum energy conformation. Sample tables and plots are given in Appendixes I and II.

In benzal compounds the observed coupling, ${}^6J_p^{H,CH}$, results from the $<\sin^2\theta>$ dependence of the long-range coupling between the one α proton and the para ring proton. On the other hand, in benzyl compounds the observed coupling, ${}^6J_p^{H,CH_2}$, results from the couplings between the two α protons with the para proton, each coupling having a $<\sin^2\theta>$ dependence. The internal rotational motion averages the two couplings to the one observed coupling, and, if ${}^6J_{90}^{H,CH_2}$ is assumed the same for the coupling protons, the observed coupling is given by the expression

$$ {}^6J_p^{H,CH_2} = {}^6J_{90}^{H,CH_2} <\sin^2\theta> \qquad [29] $$

where $<\sin^2\theta>$ is the average of $<\sin^2\theta>_1$ and $<\sin^2\theta>_2$ for the two α proton-para proton couplings. For a particular minimum energy conformation, the program EXPECT calculates the average of $<\sin^2\theta>_1$

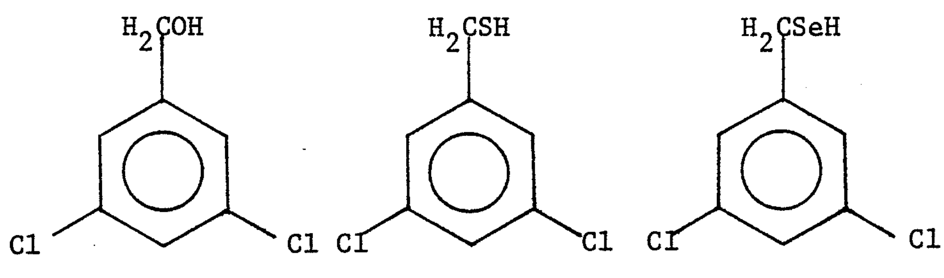
and $<\sin^2\theta>_2$ which are themselves calculated for the angles θ_{min1} and θ_{min2}, less than 90^o, which the plane formed by each of the C_1-C_α-H fragment makes with the benzene ring plane. As an example, if 64 is a minimum energy conformation, $\theta_{min1} = 0^o$ and $\theta_{min2} = 60^o$.



64

Thus, the observed coupling constant, $^6J_p^{H,CH_2}$, and a plot of $<\sin^2\theta>$ versus V_2 for benzyl compounds allows the determination of the barrier to rotation, exactly as for the benzal compounds.

The rotational barrier in 3,5-dichlorobenzyl mercaptan, 66, has been determined previously by the J method to be 1.8 $\pm$ 0.2 kcal/mole (56). The thiol moiety, SH, can be replaced by an alcohol or a selenol moiety to yield 3,5-dichlorobenzyl alcohol, 65 or selenol, 67. The three compounds form a series in which the



65 66 67

first three atoms of group 6B of the periodic table are substituted at the α position of toluene. If steric factors predominantly influence the rotational barriers, then the barrier is predicted to increase from the alcohol to the thiol to the selenol. The rotational barriers in the first and last of these compounds, and the minimum energy conformation, are determined by the J method and compared with those of the benzyl mercaptan.

i) spectral analysis

The NMR samples were prepared as 1 and 5 mol % solutions of 3,5-dichlorobenzyl alcohol in CS_2 and C_6D_6, respectively, and a 10 mol % solution of 3,5-dichlorobenzyl selenol in C_6D_6. A small amount of TMS was added to the solutions as a reference and a lock. The spectra of the solutions were recorded on a Varian HA100D spectrometer, and were analyzed by means of the computer program LAME (33, 34). The spectra were analyzed as an AB_2X_2R spin system. The spectral parameters of the benzyl alcohol and selenol compounds are listed in table 11. The spectrum of 3,5-dichlorobenzyl selenol is illustrated in figure 9 together with the simulated spectrum.

ii) 3,5-dichlorobenzyl alcohol

In order to determine the barrier and infer the minimum energy rotational conformation of 3,5-dichlorobenzyl alcohol, a value of $<\sin^2\theta>$ is required. This is calculated as the ratio of the couplings $^6J_p^{H,CH_2}$ and $^6J_{90}^{H,CH_2}$, the latter being the long-range coupling between the para ring proton and the C_α-H proton when the C_α-H bond is parallel to the axis of the p-orbitals constituting the π

Figure 9. The observed and calculated proton magnetic resonance spectra at 100 MHz of a 10 mole % solution of 3,5-dichlorobenzyl selenol in C_6D_6. The spectral parameters used in the simulation are given in table 11.

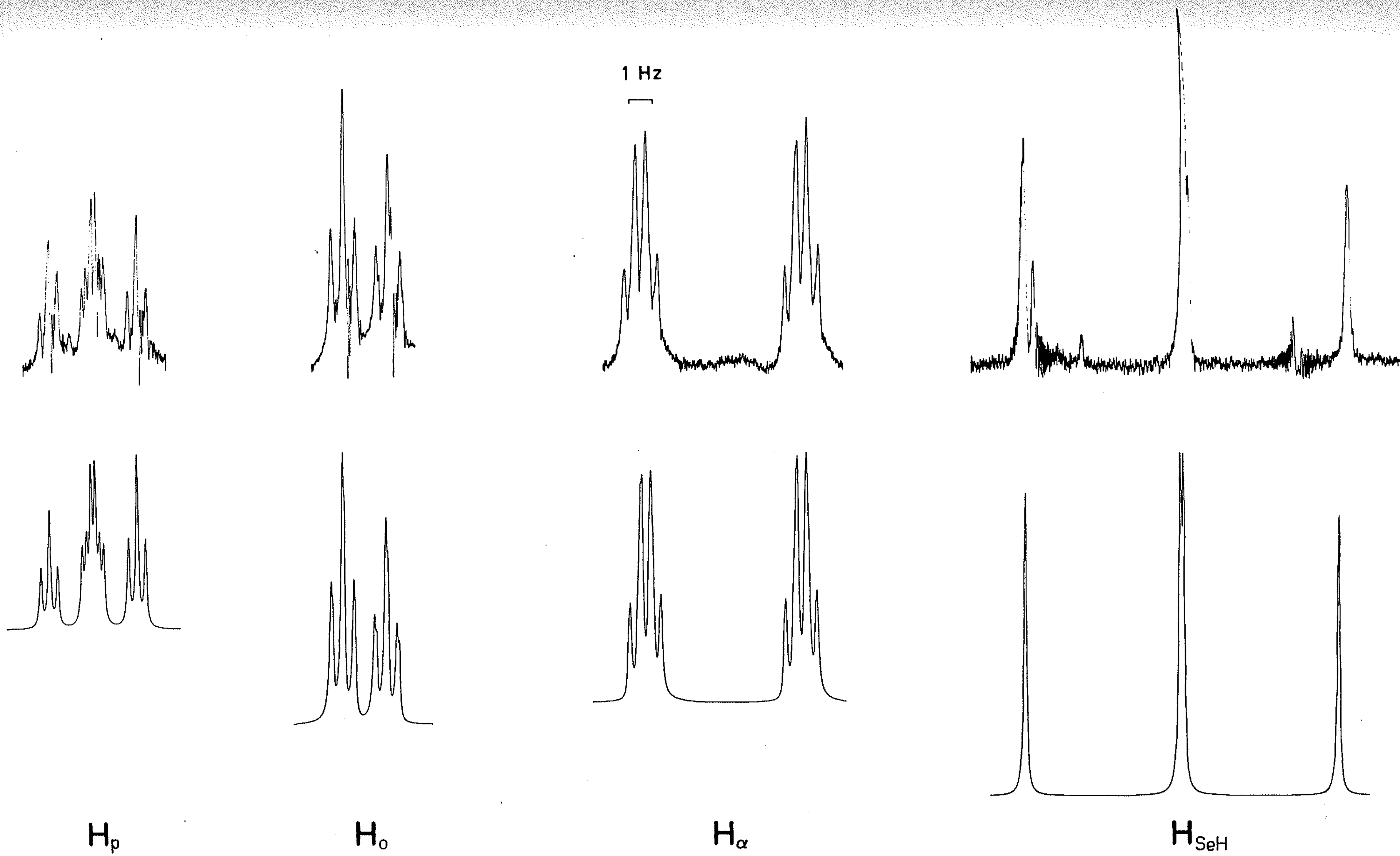
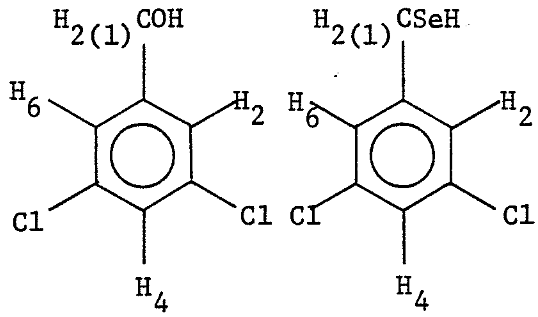

1 Hz
H_p
H_o
H_α
H_{SeH}

table 11. NMR spectral parameters of 3,5-dichlorobenzyl alcohol and selenol.



ν_1[a]	456.130(6)	298.829(4)
$\nu_2 = \nu_6$	712.593(5)	674.949(3)
ν_4	714.956(5)	694.668(2)
ν_{XH}	195.020(5)	-40.299(3)[c]
$J_{12} = J_{16}$[b]	-0.775(6)	-0.487(4)
J_{14}	-0.588(7)	-0.368(3)
$J_{1,XH}$	5.951(6)	6.804(3)
$J_{24} = J_{46}$	1.917(5)	1.894(3)
RMS Error	0.019	0.012

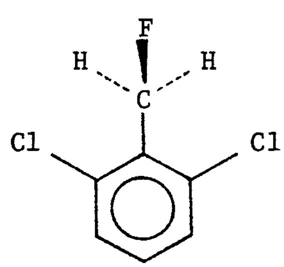
[a]Chemical shift in Hz at 100.001 MHz to low field of internal TMS and 305 K; the number in parentheses give the standard deviations in the last place.

[b]Coupling constants in Hz.

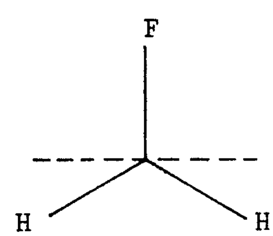
[c]The chemical shift is to high field of internal TMS.

orbitals of the benzene ring. Substituents on the α-carbon can affect the $^{6}J_{90}^{H,CH_2}$ coupling if they have an electronegativity much different from that of hydrogen, the atom which they replace. In most cases the electronegativity of the substituents is greater than or equal to that of hydrogen. Thus, the more electronegative substituent will polarize the C_α-H bond(s), decreasing the delocalization and the overlap with the π orbitals. Because the magnitude of the coupling increases with the overlap, a decrease in the overlap will decrease $|^{6}J_{90}^{H,CH_2}|$, where the vertical bars represent the absolute value or magnitude of the coupling. The decrease in $|^{6}J_{90}^{H,CH_2}|$ with increasing α substituent electronegativity has already been shown and discussed for the benzal halides above. The two substituents of benzal compounds have a greater effect on $^{6}J_{90}^{H,CH}$ than the one substituent of the respective benzyl compound. Thus, data for benzyl halides will be used to predict the effect of electronegativity on $^{6}J_{p}^{H,CH_2}$ in benzyl compounds.

The six-bond coupling, $^{6}J_{90}^{H,CH_2}$, in 3,5-dichlorobenzyl fluoride was established by the following reasoning (39). In 2,6-dichlorobenzyl fluoride, 68, the ortho chlorine substituents were assumed



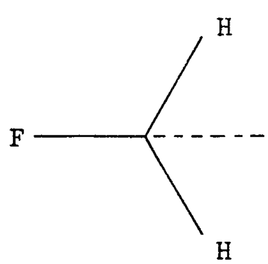
68



69

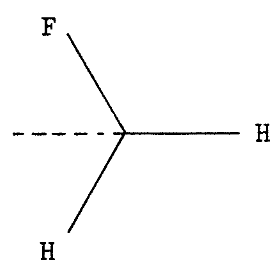
to produce a large barrier to rotation of the fluoromethyl top because of steric hindrance, and to hold the top in the minimum energy conformation <u>69</u>, where the C-F bond is perpendicular to the plane of the benzene ring (19). The six-bond proton - fluorine coupling was assumed to be transmitted by a σ-π mechanism, just like the proton-proton coupling, and, hence, the observed coupling in <u>68</u>, ${}^{6}J_{p}^{H,CF}$ = -2.43 Hz, was taken to be equal to ${}^{6}J_{90}^{H,CF}$, $<\sin^2\theta>$ being equal to 1.0. The angle θ is the dihedral angle between the C_α-F bond and a C_1-$C_{\underline{ortho}}$ bond.*

The observed six-bond proton - fluorine coupling, ${}^{6}J_{p}^{H,CF}$, in 3,5-dichlorobenzyl fluoride was -1.11 Hz and, with ${}^{6}J_{90}^{H,CF}$ = -2.43 Hz, gave $<\sin^2\theta>$ = 0.457, which implied a minimum energy conformation, <u>70</u>, where the C_α-F bond was in the plane of the benzene ring. The other possible minimum energy conformations, <u>71</u> and <u>72</u>, would have required $<\sin^2\theta>$ to be greater than 0.5. From a plot



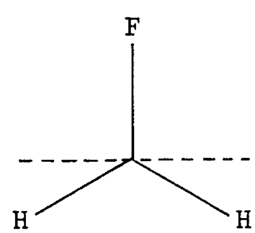
θ_{min} = 0°

<u>70</u>



θ_{min} = 60°

<u>71</u>



θ_{min} = 90°

<u>72</u>

of $<\sin^2\theta>$ versus V_2 for the $\theta_{min} = 0^\circ$ conformation, a reduced moment of 0.52 x 10^{-38} g cm^2, and a temperature of 305 K, the barrier to rotation was found to be 0.22 kcal/mole.

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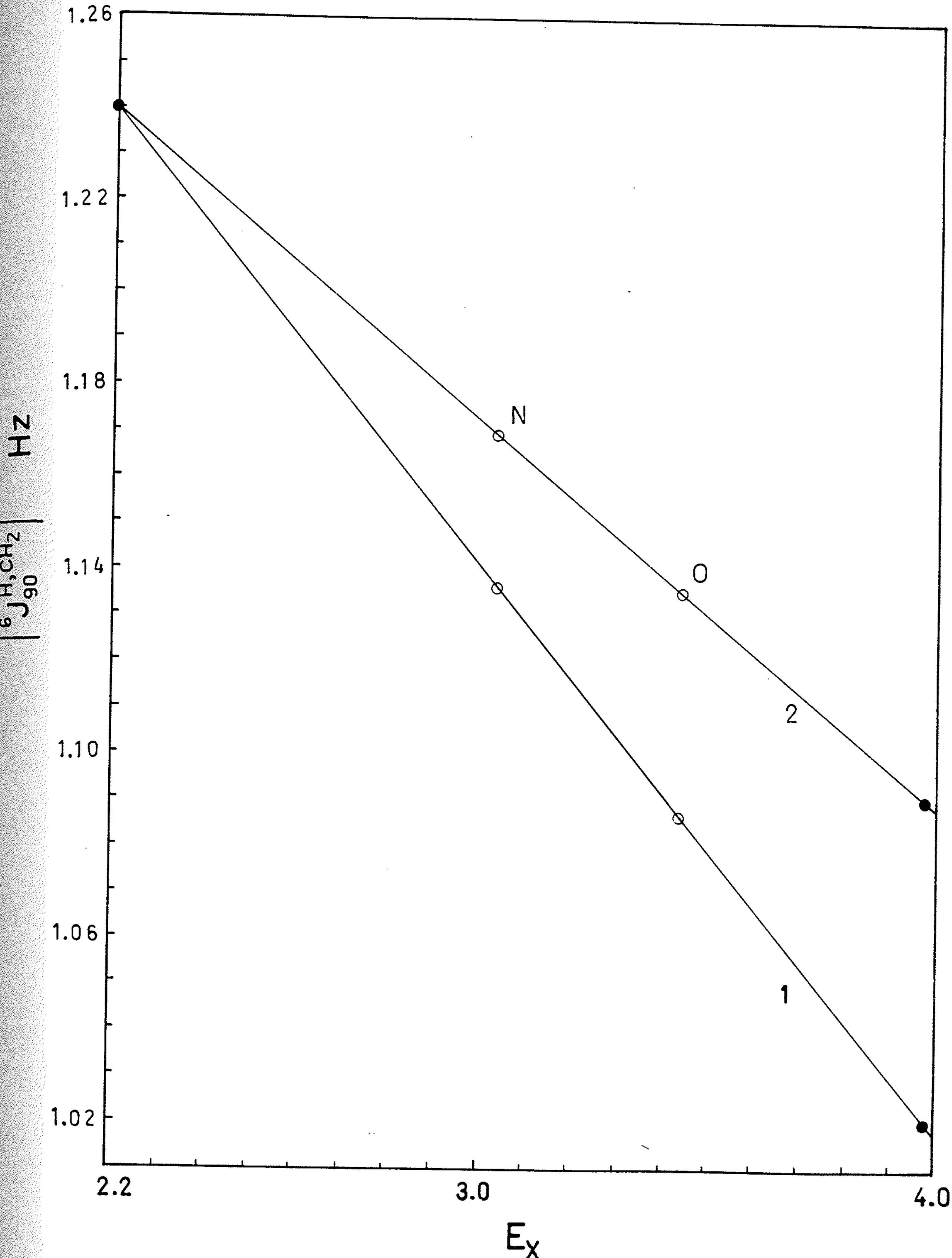
* See note on page 134

The value of ${}^6J_{90}^{H,CH_2}$ in 3,5-dichlorobenzyl fluoride was then predicted by reversing the above procedure. From a plot of $\langle\sin^2\theta\rangle$ versus V_2 for minimum energy conformation 70, but with $\theta_{min} = (60^\circ, 60^\circ)$, where θ was the angle, less than 90°, between the planes formed by the benzene ring and the two C_1-C_α-H fragments, a value of 0.522 was interpolated from the barrier of 0.22 kcal/mole. The six-bond coupling, ${}^6J_p^{H,CH_2}$, was observed to be -0.53 Hz, and so ${}^6J_{90}^{H,CH_2}$ was -0.53/0.522 = -1.02 Hz. Considerations as to the effect of torsional motions, intrinsic substituent effects of dichloro substitution and the variation of the C-C-F angle in 2,6-dichlorobenzyl fluoride suggested that 0.22 kcal/mole was the lower limit of the rotational barrier in 3,5-dichlorobenzyl fluoride. These factors, however, introduce no more than a decrease in magnitude of 0.02 Hz to the predicted value of ${}^6J_{90}^{H,CH_2}$, and, as such, the variation is written as an uncertainty, i.e., ${}^6J_{90}^{H,CH_2} = -1.02 \pm 0.02$ Hz.

If $|{}^6J_{90}^{H,CH_2}|$ is decreased to 1.02 Hz by a fluorine substituent, and the decrease is a linear function of the electronegativity, then for the two points of hydrogen, $E_H = 2.20$, $|{}^6J_{90}^{H,CH_2}| = 1.24$ Hz, and fluorine, $E_F = 3.98$, $|{}^6J_{90}^{H,CH_2}| = 1.02$ Hz, ${}^6J_{90}^{H,CH_2}$ in 3,5-dichlorobenzyl alcohol can be interpolated as -1.09 Hz for $E_{OH} = 3.44$. The observed ${}^6J_p^{H,CH_2}$ in benzyl alcohol is -0.588 Hz for a $\langle\sin^2\theta\rangle$ value of -0.588/-1.09 = 0.539. The interpolated barrier to rotation from a $\langle\sin^2\theta\rangle$ versus V_2 plot for an assumed minimum energy conformation, 73, where $\theta_{min} = (60^\circ, 60^\circ)$, is 0.4 ± 0.2 kcal/mole,

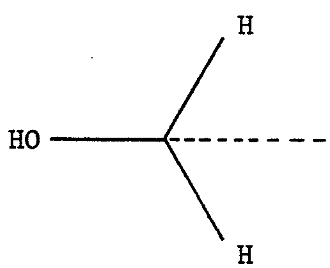
Figure 10. The plot of the linear relationship between $|{}^6J_{90}^{H,CH_2}|$ and E_X, the α-substituent electronegativity. The solid circles indicate $|{}^6J_{90}^{H,CH_2}|$ for toluene and two estimates of this coupling in benzyl fluoride. One estimate is deduced from the six-bond coupling between the side-chain fluorine and the para ring proton in 3,5-dichlorobenzyl fluoride which results in line 1. The other estimate is the INDO calculated value of ${}^6J_{90}^{H,CH_2}$ in benzyl fluoride which results in line 2. The open circles show the interpolation of $|{}^6J_{90}^{H,CH_2}|$ for nitrogen and oxygen substituents.


1.26
1.22
1.18
1.14
1.10
1.06
1.02
$|{}^{6}J_{90}^{H,CH_2}|$ Hz
N
O
2
1
2.2
3.0
4.0
E_X

where the error in the barrier results from the error in both $^{6}J_{p}^{H,CH_2}$ and $^{6}J_{90}^{H,CH_2}$ of $\pm$ 0.02 Hz.

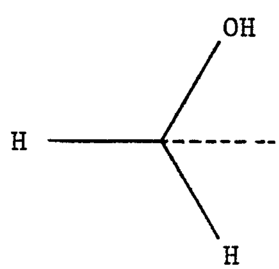
$^{6}J_{90}^{H,CH_2}$ in benzyl fluoride was calculated by the INDO MO FPT method (39) and found to be -1.09 Hz. As discussed previously, these calculations predict the observed six-bond coupling between the <u>para</u> proton and a methyl proton in toluene when the C_{α}-H orientation is perpendicular to the ring plane. Again, an assumed linear dependency of $^{6}J_{90}^{H,CH_2}$ on the α substituent electronegativity predicts $^{6}J_{90}^{H,CH_2}$ in benzyl alcohol to be -1.14 Hz. The data used in estimating this and the previous value are listed in table 12 and the procedure is illustrated in figure 10. The barrier to rotation is interpolated from the $\langle \sin^2\theta \rangle$ value of -0.588/-1.14 = 0.516, and is found to be 0.2 $\pm$ 0.2 kcal/mole.

In both cases the minimum energy conformation is taken to be <u>73</u>. The other possible minimum energy conformations are <u>74</u> and <u>75</u>. For both conformations $\langle \sin^2\theta \rangle$ must be less than 0.5 for any barrier.



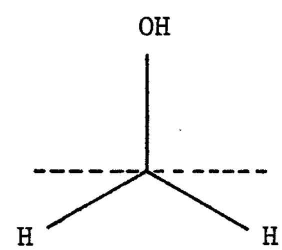
θ_{min} = (60°,60°)

<u>73</u>



θ_{min} = (0°,60°)

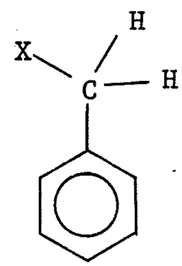
<u>74</u>



θ_{min} = (30°,30°)

<u>75</u>

Thus $|^{6}J_{90}^{H,CH_2}|$ must be greater than 0.588/0.5 = 1.18 Hz if one of these is the minimum energy conformation. A maximum barrier can be estimated for each conformation from the observed six-bond table 12. The dependence of $^{6}J_{90}^{H,CH_2}$ on α substituent electronegativities.



I^{a}	X	E_x [b]	$^{6}J_{90}^{H,CH_2}$ [c]
	H	2.20	-1.24
	F	3.98	-1.02
	O	3.44	-1.09
II	H	2.20	-1.24
	F	3.98	-1.09
	O	3.44	-1.14

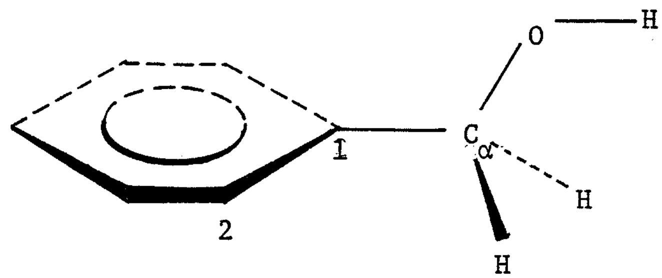
[a] The value of $^{6}J_{90}^{H,CH_2}$ for F was determined from $^{6}J_{p}^{H,CH_2}$ in 3,5-dichlorobenzyl fluoride in I, and from INDO MO FPT calculations in II.

[b] Electronegativities were from Inorganic Chemistry, 2nd Ed., J. E. Huheey, Harper, and Row, New York, N.Y. 1978.

[c] Coupling constants in Hz.

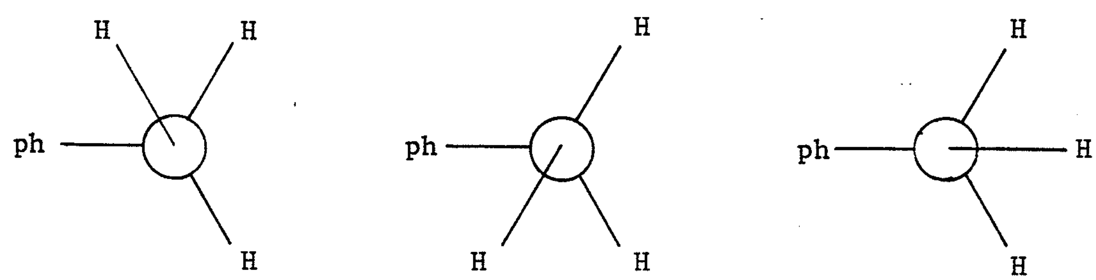
coupling constant by assuming that $^{6}J_{90}^{H,CH_2}$ has the toluene value of -1.24 Hz. Then $\langle \sin^2\theta \rangle = -0.588/-1.24 = 0.474$ and $V_2 = 0.5 \pm 0.2$ kcal/mole for 74 or 0.3 ± 0.2 kcal/mole for 75.

Abraham and Bakke (82) have used NMR to investigate the conformations of benzyl alcohol in a solution of CCl_4 and DMSO. If the benzyl alcohol molecular structure is as shown in 76, then the



76

dihedral angle ϕ for the fragment C_1-C_α-O-H can specify two different rotational conformations designated endo, 77a,b, and exo, 78, and for each of which the vicinal proton-proton coupling, $^{3}J^{OH,CH_2}$, can



77a 77b 78

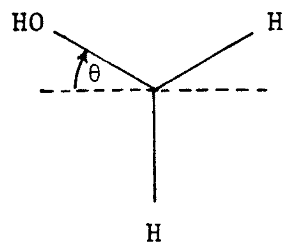
be predicted. The observed vicinal coupling, $^{3}J_{obs}^{OH,CH_2}$, indicated that benzyl alcohol is approximately 90% in the endo conformation in CCl_4.

The chemical shift of the OH proton and the geminal coupling constant between the methylene protons were then used to predict the stable rotational conformation of the CH_2OH rotor about the phenyl ring. The possible minimum energy conformations are shown by 73, 74, and 75. Abraham and Bakke determined the chemical shift of several aliphatic alcohols, 0.70 $\pm$ 0.05 δ, and benzyl alcohol, 1.09 $\pm$ 0.05 δ, at infinite dilution. The chemical shift of the benzyl alcohol proton, OH, was 0.39 ppm downfield of the aliphatic alcohol proton chemical shifts, the deshielding arising from the ring current effect. The ring current shift of the alcoholic proton was calculated for the various conformations from Johnson and Bovey tables (83) and a dipole formula developed by Abraham et al. (84). For the conformations 73, 74, and 75 with the OH proton in the *endo* position, the calculated shifts were 0.50, 0.39, and 0.15 ppm, respectively. The ring current shift calculated for 74, $\theta_{min} = (0^{\circ}, 60^{\circ})$, is exactly the same as the observed ring current shift. However, the average of the shifts for 73 and 75, 0.33 ppm, which would arise for free rotation of the CH_2OH top, is within the error limit of the observed shift of 0.39 ppm.

The geminal coupling constant, $^{2}J^{H,H}$, of the methylene protons of the CH_2OH top was calculated from the formula

$$^{2}J^{H,H} = A + B\cos\theta + C\cos(2\theta)$$

where A, B, and C are empirical constants and θ is the dihedral angle of the C_2-C_1-C_α-O fragment as illustrated in 79. For the *endo* conformation A = -14.8 Hz, B = 2.5 Hz, and C = -4.3 Hz, and



79

the calculated values for 73, 74, and 75 were -16.7, -11.5, and -10.6 Hz, respectively. The experimental value of $^{2}J^{H,H}$ was calculated from the observed value of $^{2}J^{H,D}$ in α-monodeuterobenzyl alcohol and the gyromagnetic ratios of hydrogen and deuterium, and found to be $\pm 12.4 \pm 0.3$ Hz. Again, $^{2}J^{H,H}_{calc}$ in 74 was closest to $^{2}J^{H,H}_{obs}$, although the average of $^{2}J^{H,H}_{calc}$ for 73 and 75, 13.7 Hz, was not so far removed from the experimental value as to have been rejected. Thus, benzyl alcohol in solution was predicted to have either a barrier to internal rotation about the C_1-C_α bond with 74, $\theta_{min} = (0^\circ, 60^\circ)$, as the minimum energy conformation, or a zero barrier or free rotation of the CH_2OH moiety.

A gas electron diffraction study (85) of benzyl alcohol found that 74 was the stable conformation, with the dihedral angle of the C_2-C_1-C_α-O fragment being 54°. The J method does not exclude 74 as the minimum energy conformation, although the experimental data imply that it is unlikely. Free rotation would require $^{6}J_{90}^{H,CH_2}$ to be -1.18 Hz, and 74 as a stable conformation would require even a greater magnitude for this coupling. The larger electronegativity of oxygen compared to that of hydrogen strongly suggests that the magnitude of ${}^6J_{90}{}^{H,CH_2}$ is below -1.18 Hz, and that 73 is the stable conformation with a barrier to rotation of 0.3 ± 0.2 kcal/mole, the average of the two values found from the two different estimates of ${}^6J_{90}{}^{H,CH_2}$.

In support of the minimum energy conformation of the benzyl alcohol predicted by the J method are *ab initio* molecular orbital calculations at the STO-3G level (36). With the molecule described by standard geometries (14), the energy difference between the conformations in which the C-OH bond was in the ring plane, and perpendicular to the ring plane, was 0.22 kcal/mole, the former conformation being more stable. The O-H bond was oriented *exo*, 78. When the O-H bond was oriented *endo*, 77a,b, the energy difference was 1.92 kcal/mole with the C-OH bond in plane conformation more stable. The energy difference between the O-H *exo* and *endo* conformations for the C-OH bond in plane was 0.06 kcal/mole, the O-H *exo* conformation being more stable.

It is observed that the long-range six-bond coupling, ${}^6J_p{}^{H,CH_2}$, is unchanged in going from a 1 mol % solution in CS_2 to a 5 mol % solution in C_6D_6, a five-fold increase in concentration. Thus, intermolecular association seems ineffective in changing this coupling, and, hence, the barrier to rotation, in non-polar solvents.

iii) 3,5-dichlorobenzyl selenol

The observed six-bond coupling, ${}^6J_p{}^{H,CH_2}$, in 3,5-dichlorobenzyl selenol is -0.368 Hz. The electronegativity of selenium is exactly that of carbon, 2.55, and so ${}^6J_{90}{}^{H,CH_2}$ is assumed to be -1.24 Hz.

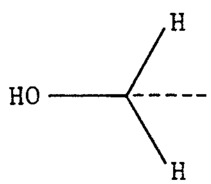
Then, $<\sin^2\theta> = -0.368/-1.24 = 0.297$, and V_2 is interpolated to be 3.8 ± 0.7 kcal/mole. The error arises solely from the uncertainty in ${}^6J_p^{H,CH_2}$ of ± 0.02 Hz.

If figure 10 is used to interpolate a ${}^6J_{90}^{H,CH_2}$ value for an electronegativity of 2.55, then the values interpolated are 1.20 and 1.21 Hz from curves 1 and 2, and yield barriers of 3.3 and 3.4 kcal/mole, respectively. A median value of 3.6 ± 1.0 kcal/mole is then a reasonable barrier to rotation in 3,5-dichlorobenzyl selenol, where the error incorporates both the uncertainty in the choice of ${}^6J_{90}^{H,CH_2}$, and the experimental error in ${}^6J_p^{H,CH_2}$. This large error in V_2 occurs because of the insensitivity of $<\sin^2\theta>$ to V_2 for barriers greater than about 3.0 kcal/mole. A small variation in $<\sin^2\theta>$ corresponds to a large variation in V_2.

The barrier is interpolated from $<\sin^2\theta>$ versus V_2 data calculated for the minimum energy conformation <u>75</u> (OH replaced by SeH), $\theta_{min} = (30^\circ, 30^\circ)$. The range of $<\sin^2\theta>$ for this conformation, and for barriers of zero to infinite magnitude, is 0.5 to 0.25, respectively. The experimentally determined $<\sin^2\theta>$ falls within this range, but not within the range for <u>73</u>, $\theta_{min} = (60^\circ, 60^\circ)$, of 0.5 to 0.75, or <u>74</u>, $\theta_{min} = (0^\circ, 60^\circ)$, of 0.5 to 0.375.

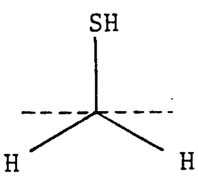
iv) <u>summary</u>

A previous study in this laboratory of 3,5-dichlorobenzyl mercaptan determined the barrier to rotation in this compound to be 1.8 ± 0.2 kcal/mole with the minimum energy conformation as <u>81</u>. In the present work the barriers to rotation in 3,5-dichlorobenzyl alcohol and selenol are found to be 0.3 ± 0.2 and 3.6 ± 1.0 kcal/mole, respectively. The former compound has 80 as the minimum energy conformer, while the latter has 82.



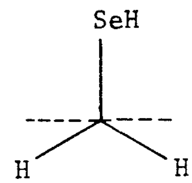
V_2 = 0.3

80



1.8

81



3.6 kcal/mole

82

The barrier in both the mercaptan and the selenol compounds would seem to arise mainly from steric interactions. The minimum energy conformation for both is the one with the C_α-SH or C_α-SeH bond perpendicular to the ring plane; where there is a minimum steric interaction between the substituent and the ortho protons. The greatest steric interaction would be for the S or Se atom in the plane of the ring, and the greater interaction of the two should be for the bulkier Se atom, implying that the barrier in the selenol should be greater than that in the mercaptan.

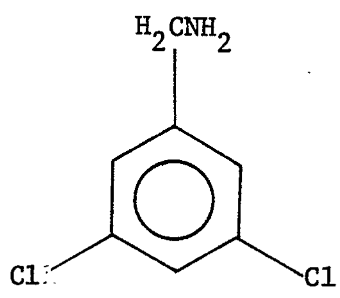
A mainly steric origin of the barrier would suggest that the barrier in benzyl alcohol is smaller than the ones in the benzyl mercaptan or selenol because of the smaller size of the oxygen atom than either the sulphur or selenium atoms, and this is found to be the case. However, the minimum energy conformation of the benzyl alcohol is predicted, by the J method, to be the one with the oxygen atom in the plane of the aromatic ring where the steric interactions between the oxygen and an ortho proton should be a maximum. Thus, interactions other than steric must be stabilizing the conformation.

note: In 2,6-dichlorobenzyl fluoride, 68, the observed proton-proton six-bond coupling was inferred to be anomalously small in magnitude. The explanation for this conclusion was that the tetrahedral geometry of the CH_2F top was distorted, with the C_1-C_α-H bond angles being greater than 109.5° and the C_1-C_α-F bond angle less than 109.5°. Thus, the hyperconjugative interaction of the C_α-F bond with the π system of the phenyl ring would increase $|{}^6J_{90}^{H,CF}|$ over the value in 3,5-dichlorobenzyl fluoride where the CH_2F group is assumed to have tetrahedral geometry.

The magnitude of ${}^6J_{90}^{H,CF}$ is used to determine the barrier to rotation in 3,5-dichlorobenzyl fluoride, and from the barrier to predict a value for ${}^6J_{90}^{H,CH_2}$. That the barrier predicted by ${}^6J_{90}^{H,CF}$ is a reasonable value is supported by data resulting from the application of the J method to 4-methylbenzyl fluorides (118). The barriers in 3,5-dichloro- and 3,5-dibromo-4-methylbenzyl fluoride were equal to the barrier in 3,5-dichlorobenzyl fluoride within experimental error. Thus, the possible distortion of the C_1-C_α-F bond angle seems to have a negligible effect on the determination of the rotational barrier and the consequent prediction of ${}^6J_{90}^{H,CH_2}$ in 3,5-dichlorobenzyl fluoride.

5. <u>3,5-Dichloro Derivatives of Benzylamine, Benzyldimethylamine, and Benzyldimethylarsine</u>

The compounds discussed in the previous section had group 6B α substituents, namely OH, SH, and SeH. In the present section are discussed benzyl compounds with α substituents of group 5B, specifically the amine, 83, the dimethylamine, 84, and the dimethylarsine, 85. The 3,5-dichlorobenzyldimethyl derivatives were prepared because of the ease of synthesis of these derivatives, and in the case of the arsine, a previous determination of the low energy conformation (86) with which the results from the J method could be compared. A synthesis of 3,5-dichlorobenzylphosphine or dimethylphosphine could not be accomplished.



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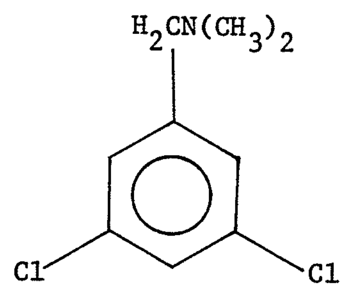

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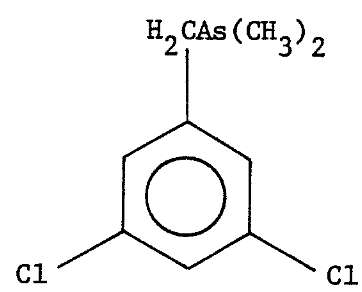


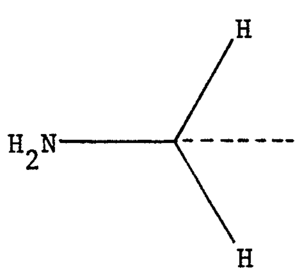
85

i) <u>spectral analysis</u>

The NMR samples were prepared as a 10 mol % solution of 3,5-dichlorobenzylamine in C_6D_6, and 5 mol % solutions of 3,5-dichlorobenzyldimethylamine and arsine in CS_2, with a small amount of TMS added as a reference standard and internal lock. The NMR spectra of all solutions were recorded on a Varian HA-100 spectrometer, and analyzed by means of the computer program LAME (33,34). No peaks for either the proton or methyl groups bonded to the nitrogen were assigned in the LAME iteration. Nor were resonance peaks assigned for the methylene protons in the spectra of the benzyldimethyl derivatives, but methylene proton resonance lines were assigned in the benzylamine analysis. The spectral parameters of the three compounds are listed in table 13 and the observed spectrum of 3,5-dichloro-benzyldimethylarsine with the simulated spectrum is displayed in figure 11.

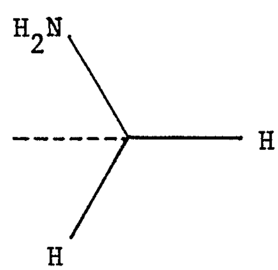
ii) 3,5-dichlorobenzylamine

The observed six-bond coupling, ${}^6J_p^{H,CH_2}$, in 3,5-dichlorobenzyl-amine is $0.57_9 \pm 0.02$ Hz. If ${}^6J_{90}^{H,CH_2}$ is taken to be -1.24 Hz, then $\langle \sin^2\theta \rangle = -0.579/-1.24 = 0.467$. From a plot of $\langle \sin^2\theta \rangle$ versus V_2, for a reduced moment $I_r = 0.6 \times 10^{-38}$ g cm^2 and a temperature of 305 K, V_2 is interpolated to be 0.4 ± 0.3 kcal/mole for an assumed minimum energy conformation 88



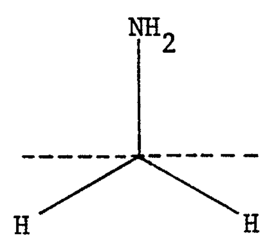
$\theta_{min} = (60°, 60°)$

86



$\theta_{min} = (0°, 60°)$

87



$\theta_{min} = (30°, 30°)$

88

Figure 11. The observed and calculated proton magnetic resonance spectrum of a 5 mole % solution of 3,5-dichlorobenzyldimethylarsine in CS_2. The methylene and methyl proton resonances were not considered in the spectral analysis and were not simulated. The spectral parameters used in the simulation of the ring proton resonances are given in table 13.

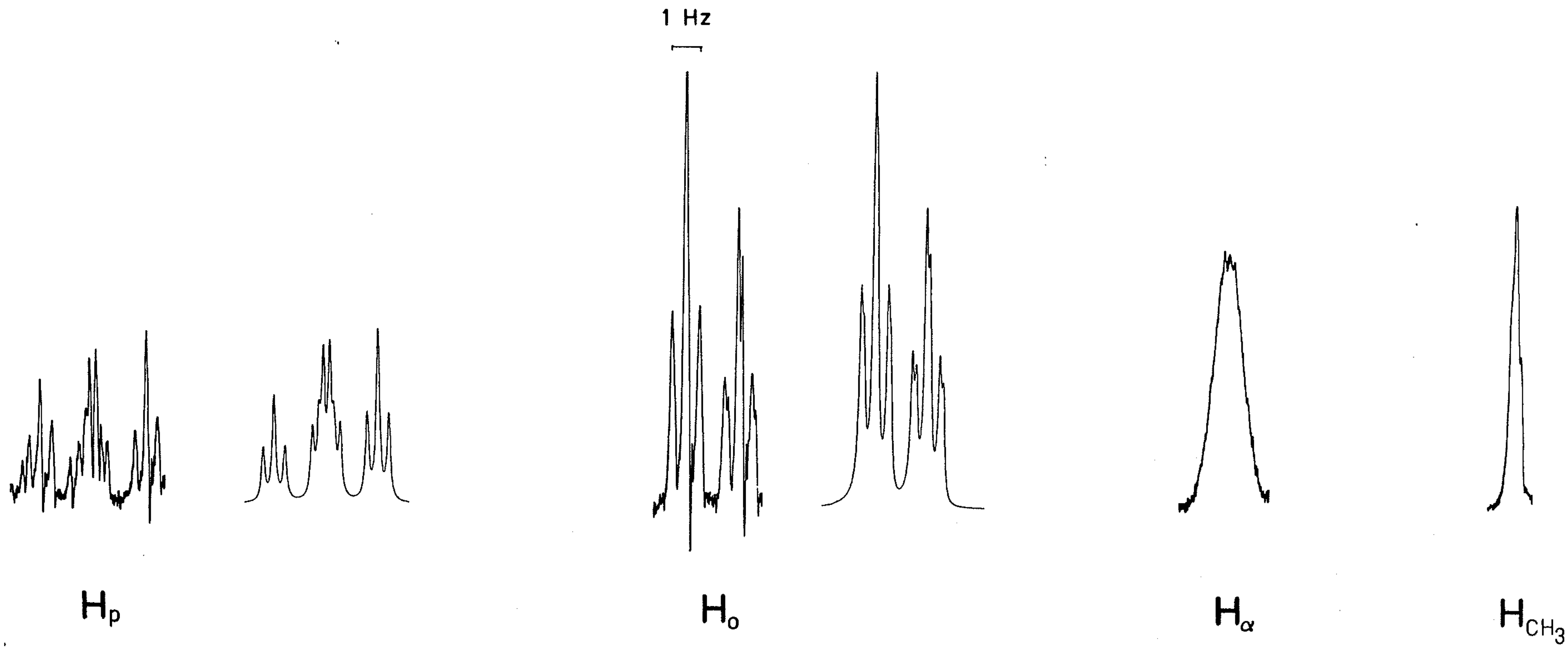
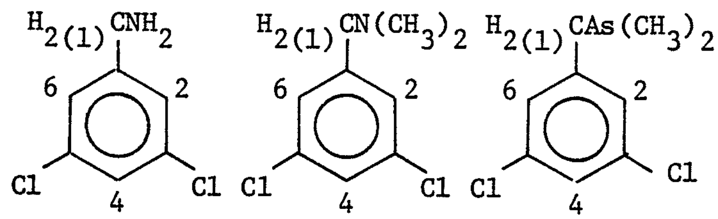

1 Hz
H_p
H_o
H_α
H_{CH_3}

table 13. Spectral parameters of 3,5-dichloro derivatives of benzylamine, benzyldimethylamine, and benzyldimethylarsine.



ν_1[a]	325.243(3)	331.23	265.95
$\nu_2 = \nu_6$	691.940(3)	714.711(4)	687.065(4)
ν_4	705.753(3)	712.041(5)	702.828(3)
ν_{NH_2} or $\nu_{X(CH_3)_2}$	73.7	218.48	89.05
$J_{12} = J_{16}$[b]	-0.773(3)	-0.732(6)	-0.492(5)
J_{14}	-0.579(4)	-0.512(7)	-0.391(4)
$J_{24} = J_{46}$	1.953(3)	1.961(4)	1.896(3)
RMS error	0.0127	0.0121	0.0088

[a]Chemical shift in Hz at 100.001 MHz to low field of internal TMS; numbers in parentheses give the standard deviation in the last place.

[b]Coupling constants in Hz.

The observed $\langle \sin^2\theta \rangle$ falls in the range of $\langle \sin^2\theta \rangle$ of 0.5 to 0.25 for zero to infinite barrier in this conformation. It also falls within the range of 0.5 to 0.375 for the conformation 87 where it yields a barrier of 0.7 $\pm$ 0.3 kcal/mole. The observed $\langle \sin^2\theta \rangle$ is not within the range of 0.5 to 0.75 for conformation 86, which is, thus, not a possible minimum energy conformation.

$^6J_{90}^{H,CH_2}$ in benzyl compounds depends on the electronegativity of the α substituent. The electronegativity of nitrogen on the Pauling scale is 3.04 and, hence, should decrease the magnitude of $^6J_{90}^{H,CH_2}$ from its value in toluene and ethylbenzene of -1.24 Hz. However, a photoelectron spectroscopy study (87) of pyrrole, thiophene, and selenophene derivatives found that the NH group had an electronegativity approximately equal to that of the sulphur atom. A large polarity of the N-H bond leads to a large reduction of the effective electronegativity of the NH group compared with the nitrogen atom. Thus, if the electronegativity of the NH_2 group is almost equal to that of sulphur, which itself has an electronegativity near that of carbon, then $^6J_{90}^{H,CH_2}$ in benzylamine can be taken as -1.24 Hz, the value in ethylbenzene, and the barrier and low energy conformation are as found above.

Ab initio molecular orbital calculations at the STO-3G level predict the low energy conformation of benzylamine as 88, and an energy difference between 88 and 86, the maximum energy conformation, of 3.7 kcal/mole (36). The minimum energy conformation is consistent with the results of the J method. The calculated barrier to rotation is rather high, but as in the case of ethylbenzene in the same study where the barrier is reduced substantially from 4.7 kcal/mole to 2.2 kcal/mole by geometry optimization of bond angles, the barrier could be similarly reduced in the benzylamine.

The low energy conformation can be only 88 for values of ${}^6J_{90}^{H,CH_2}$ between -1.24 Hz and -0.579/0.5 = -1.16 Hz, where the latter value implies free rotation. This range supports a reduced electronegativity for the NH_2 substituent, as the value of 3.04 for the electronegativity of nitrogen interpolates a value of -1.14 Hz for ${}^6J_{90}^{H,CH_2}$, as shown in figure 10 above. This value gives $\langle \sin^2\theta \rangle$ as 0.508, implying 86 as the minimum energy conformation, opposite to the *ab initio* results, and a barrier of 0.1 kcal/mole. The ${}^6J_{90}^{H,CH_2}$ value is interpolated from the straight line plot arrived at by assuming ${}^6J_{90}^{H,CH_2}$ = -1.02 Hz in benzyl fluoride as inferred from the observed six-bond proton - fluorine coupling in a derivative of this compound. The other straight line plot in figure 10 arises from the value of -1.09 Hz for ${}^6J_{90}^{H,CH_2}$ in benzyl fluoride predicted by INDO MO FPT calculations. An electronegativity of 3.04 for the nitrogen atom yields ${}^6J_{90}^{H,CH_2}$ = -1.17 Hz on this second line, with a resulting $\langle \sin^2\theta \rangle$ of -0.579/-1.17 or 0.495, and a barrier of 0.05 $\pm$ 0.20 kcal/mole for 88 as the low energy conformer; or 0.10 $\pm$ 0.20 kcal/mole for 87 as the low energy conformer. The quoted error in the barriers results solely from the error in ${}^6J_p^{H,CH_2}$ of $\pm$ 0.02 Hz.

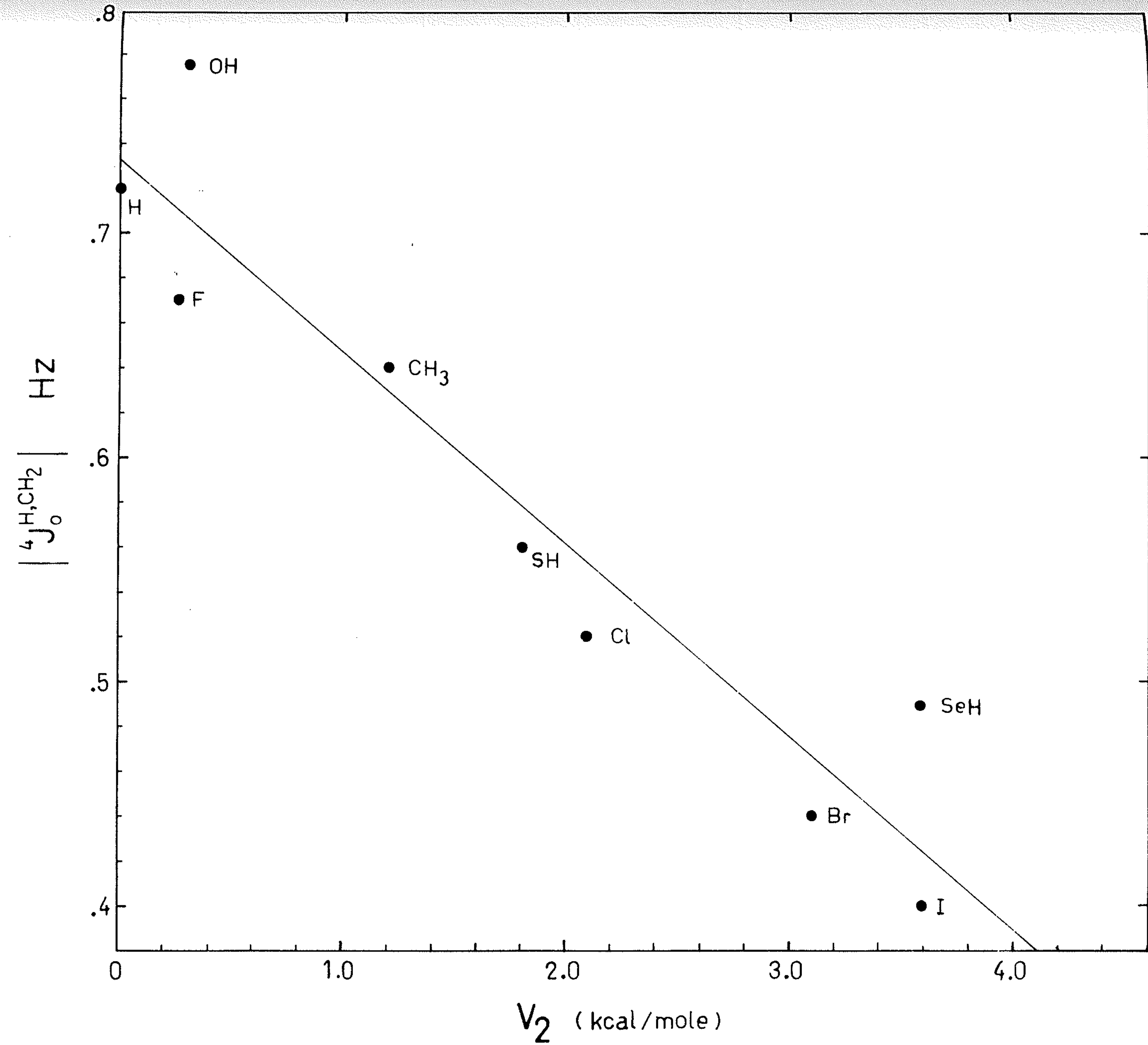
If E_{NH_2} is taken as a median value between E_N and E_S, say 2.75, and line 1 of figure 10 is used to interpolate ${}^6J_{90}^{H,CH_2}$, then ${}^6J_{90}^{H,CH_2}$ = -1.17 Hz, exactly as above for E_N = 3.04 and line 2, resulting in the same barriers, 0.05 $\pm$ 0.20 or 0.10 $\pm$ 0.30 kcal/mole for 88 or 87 as the minimum energy conformers, respectively. Because of the uncertainty in the actual dependence of $^6J_{90}^{H,CH_2}$ on electronegativity demonstrated by the two straight line plots of figure 10, and in the estimation for NH_2, the barrier in 3,5-dichlorobenzylamine is put forward as 0.3 ± 0.3 kcal/mole and the minimum energy conformation as 88.

A qualitative indication of the barrier in benzylamine can be had by considering the four-bond ortho coupling between the side-chain protons and the ring protons. This coupling, $^4J_o^{H,CH_2}$, is plotted against the barrier to rotation, V_2, for some 3,5-dichlorobenzyl compounds as determined from $^6J_p^{H,CH_2}$. The data which are plotted are listed in table 14 and the plot is displayed in figure 12.

INDO MO FPT calculations of the coupling constants in toluene (13) as a function of the angle of rotation of the methyl group, indicated that the four-bond coupling between the ortho protons and the methyl protons resulted from spin information transmitted through both the σ and π systems. The π coupling was predominant and introduced a $\sin^2\theta$ dependency on the overall coupling, which, however, was modified by the component transmitted through the σ system. Separation of the σ and π contributions to the coupling was impossible with the information at hand and, hence, quantitative values of the π coupling from which $\langle\sin^2\theta\rangle$ could be found, were not extracted.

The plot of $^4J_o^{H,CH_2}$ versus V_2 for the 3,5-dichlorobenzyl derivatives does show a rough correlation between the four-bond coupling and the barrier, the magnitude of the coupling generally decreasing

Figure 12. The plot of $|{}^4J_o^{H,CH_2}|$ versus V_2 for some 3,5-dichlorobenzyl compounds. The straight line is for a linear least squares fit to the data.



OH
H
F
CH_3
SH
Cl
SeH
Br
I
.8
.7
.6
.5
.4
0
1.0
2.0
3.0
4.0
$|{}^4J_o^{H,CH_2}|$ Hz
V_2 (kcal/mole)

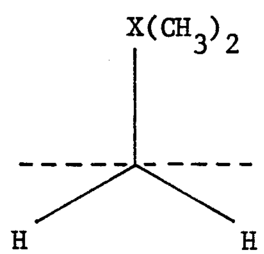
table 14. Rotational barriers and four-bond *ortho* coupling constants of some 3,5-dichlorobenzyl compounds.

X (in CH_2X)	$^4J_o^{H,CH_2}$ (Hz)	V_2 (kcal/mole)	reference
H	0.72	0.014	21
F	0.67	0.26	39
CH_3	0.64	1.2	40
Cl	0.52	2.1	21
OH	0.77_5	0.30	this work
SH	0.56	1.8	56
Br	0.44	3.1	21
I	0.40	3.6	21
SeH	0.49	3.6	this work

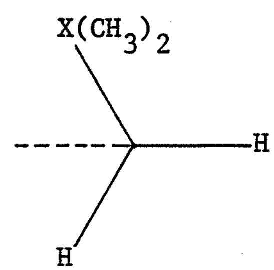
with increasing barrier. The deviation of some points from the least squares straight line shows the difficulty of predicting an angular dependence, if any, of the σ coupling component or the effect of the side-chain substituent on this coupling. ${}^4J_o^{H,CH_2}$ in 3,5-dichlorobenzylamine is equal to ${}^4J_o^{H,CH_2}$ in 3,5-dichlorobenzyl alcohol, which suggests from the plot, figure 12, that the barrier is very small.

iii) <u>3,5-dichlorobenzyldimethylamine</u>

${}^6J_p^{H,CH_2}$ in 3,5-dichlorobenzyldimethylamine is $-0.51_2 \pm 0.02$ Hz. If ${}^6J_{90}^{H,CH_2}$ is assumed to be -1.24 Hz, then $\langle \sin^2\theta \rangle = 0.413$. This value falls into the range of $\langle \sin^2\theta \rangle$ of 0.5 to 0.25 or 0.5 to 0.375 for the zero to infinite barrier limit of possible minimum energy conformations 89 and 90, where X represents N. The reduced moments of



89



90

inertia of all the possible conformations of 3,5-dichlorobenzyldimethylamine range from 1.2 to 1.9×10^{-38} g cm^2. The variation in the reduced moment has a negligible effect on $\langle \sin^2\theta \rangle$ compared to the error in ${}^6J_{90}^{H,CH_2}$, and, hence, plots and tables of $\langle \sin^2\theta \rangle$ versus V_2 were produced for an I_r of 1.5×10^{-38} g cm^2, a temperature of 305 K, and for conformations 89 and 90. If 89 is the low energy conformation and ${}^6J_{90}^{H,CH_2} = -1.24$ Hz, then $V_2 = 0.9 \pm 0.2$ kcal/mole, and if 90 then $V_2 = 2.5 \pm 2.0$ kcal/mole. The large error in the latter barrier arises from the insensitivity of $\langle\sin^2\theta\rangle$ to V_2 as $\langle\sin^2\theta\rangle$ asymptotically approaches the limiting value of 0.375.

The value of -1.24 Hz for ${}^6J_{90}^{H,CH_2}$ implies that the $N(CH_3)_2$ substituent does not perturb the coupling from its value in toluene or ethylbenzene, and that the electronegativity of this substituent is nearly that of S or CH_3 as postulated for the NH_2 fragment. If $|{}^6J_{90}^{H,CH_2}|$ for the benzyldimethylamine derivative is allowed to decrease to 1.17 Hz as for the amino group, then $\langle\sin^2\theta\rangle$ is 0.438; giving $V_2 = 0.6 \pm 0.2$ kcal/mole for 89, or $V_2 = 1.4 \pm 0.6$ kcal/mole for 90 as the minimum energy conformation.

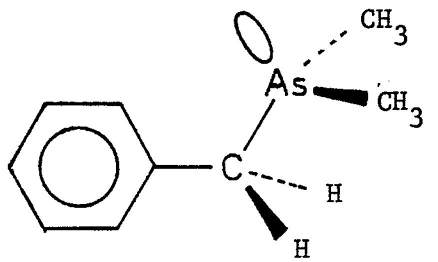
It is unlikely that the barrier is as high as those predicted for 90 as the low energy conformation. All benzyl compounds having elements of the first row of the periodic table as α substituents, and for which barriers have been determined by the J method, have barriers less than about 1.2 kcal/mole, certainly less than the barriers determined for the benzyldimethylamine with 90 as the low energy conformer. Furthermore, the correlation between the four-bond *ortho* coupling, ${}^4J_o^{H,CH_2}$, and the barrier, as discussed above, suggests a very low barrier corresponding to the ${}^4J_o^{H,CH_2}$ value of -0.73 Hz, as can be seen from inspection of figure 12. Thus, the rotational barrier in 3,5-dichlorobenzyldimethylamine is estimated as 0.8 ± 0.3 kcal/mole, a median value between the two barriers determined above. The error is assumed sufficient to represent the experimental error in ${}^6J_p^{H,CH_2}$ and the uncertainty in ${}^6J_{90}^{H,CH_2}$. The minimum energy conformation is 89, where the C_α-N bond is oriented perpendicular to the plane of the aromatic ring.

iv) 3,5-dichlorobenzyldimethylarsine

${}^6J_p^{H,CH_2}$ in 3,5-dichlorobenzyldimethylarsine is $-0.39_1 \pm 0.02$ Hz. The electronegativity of arsenic and hydrogen are almost equal and, thus, ${}^6J_{90}^{H,CH_2}$ for the benzyldimethylarsine can be taken unequivocally as -1.24 Hz. Then $\langle \sin^2\theta \rangle$ is -0.391/-1.24 or 0.315, which eliminates 90 (X = As) as a possible minimum energy conformation. The range of $\langle \sin^2\theta \rangle$ for 90 has a lower limit of 0.375 for infinite barrier. Thus, 89 is the only rotational conformation having a range which includes the $\langle \sin^2\theta \rangle$ value determined above.

The range of reduced moments for the possible conformations of 3,5-dichlorobenzyldimethylarsine with respect to rotation about the C_1-C_α bond is 2.4 to 3.1 x 10^{-38} g cm^2, and a table and plot of $\langle \sin^2\theta \rangle$ versus V_2 were produced for an I_r = 3.0 x 10^{-38} g cm^2, a temperature of 305 K, and conformation 89. The barrier for $\langle \sin^2\theta \rangle$ = 0.315 is 3.0 ± 0.7 kcal/mole.

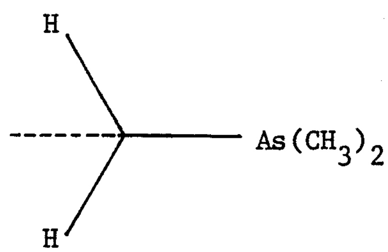
A theoretical and ultraviolet photoelectron spectroscopy study (86) predicted the minimum energy conformation of benzyldimethylarsine to have an n-cis, As-cis orientation. The n-cis designation refers to the dihedral angle of the C_1-C_α-As-n fragment, pictured in 91, where n refers to the lone or non-bonding electron pair of arsenic



91

and the As-n direction is the axis of the non-bonding orbital. The orientation is n-cis for a dihedral angle of 0^{o}, and n-trans for a dihedral angle of 180^{o}.

The As-cis designation refers to the dihedral angle for the C_2-C_1-C_α-As fragment. This is also the angle of internal rotation considered by the J method. Thus, the two conformations, 89 (X = As) and 92 are designated As-gauche and As-cis, respectively.



92

The theoretical calculations were based on a CNDO/2 method extended to the third row elements of the periodic table (88). When the $As(CH_3)_2$ group was in the n-cis orientation, 92 was calculated to have the minimum energy while 89 had the maximum energy.

When the $As(CH_3)_2$ group was in the n-trans orientation 89 was calculated to have the minimum energy. Standard bond lengths and angles were used except that the C_1-C_α-As angle was increased to 115° for one series of calculations which did not change the conclusions as to the minimum energy conformation.

The photoelectron spectroscopy data were used to confirm the n-cis, As-cis conformation as being the minimum energy conformation of benzyldimethylarsine. The photoelectron spectrum of benzyldimethylarsine did not show a separation of the doubly degenerate π ion states of the phenyl ring, as would have been expected for a hyperconjugative interaction between the C_α-As bond and the π system of the aromatic ring. This interaction was expected to occur when the C_α-As bond was oriented perpendicular to the benzene ring plane but not when the bond was in the ring plane. Also, a lower ionization potential was observed for the n state in benzyldimethylarsine than in trimethylarsine or phenyldimethylarsine. The n state refers to the non-bonding orbital of arsenic. The lower ionization potential was ascribed to the interaction of the n orbital of the arsenic with the C_{ortho}-H bond of the phenyl ring when benzyldimethylarsine was in the n-cis, As-cis conformation, that is, 92.

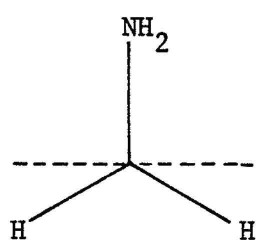
The J method predicts 89 as the minimum energy conformation to a high degree of probability. In order for $\langle \sin^2\theta \rangle$ to be within the range for zero to infinite barrier of 0.5 to 0.75 for conformation 92, $|{}^6J_{90}^{H,CH_2}|$ must be at most 0.782 Hz and for any sizeable barrier must be even less. This value is highly unlikely on any grounds discussed for a decrease in $|{}^6J_{90}^{H,CH_2}|$.

Now, 89 is considered the rotational conformation in which the least steric interactions occur. Thus, for 2,6-dichlorobenzyl derivatives (19), where steric interactions between α substituents and the chlorine atoms are large, 89, the conformation where the C_{α}-X bond is oriented perpendicular to the phenyl ring plane, is preferred with very large barriers to rotation. The arsenic atom has a relatively large van der Waals radius, resulting in a large steric interaction between the As atom and the *ortho* protons of the ring, which should favour 89 as the minimum energy conformation.

The disagreement between the J method and the photoelectron study is unexplained.

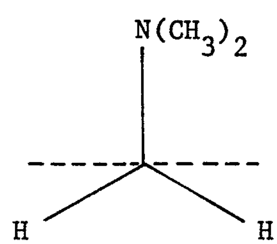
v) summary

The J method predicts the barriers to internal rotation and the minimum energy conformations to be as illustrated in 93 to 95.



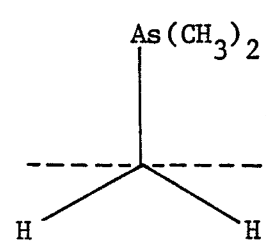
$V_2 = 0.3 \pm 0.3$

93



0.8 ± 0.3

94



3.0 ± 0.7 kcal/mole

95

The magnitude of the barriers follow the trend found for the benzyl alcohol, mercaptan, and selenol, that is, increasing barrier with increasing atomic size of the directly bonded α substituent. Steric factors seem to dominate the contributions to the rotational barrier. The benzylamine is found in the low energy conformation which minimizes steric interactions; unlike the benzyl alcohol which prefers the conformation where the OH group is in the plane of the phenyl ring.

Replacement of the amino hydrogens in benzylamine by the bulkier methyl groups increases the barrier, which also increases when the nitrogen in benzyldimethylamine is replaced by arsenic to produce benzyldimethylarsine. Both these trends indicate steric factors are a large part of the barrier in this series of compounds.

6. Derivatives of Para-fluorotoluene

To this point the J method has required an observed six-bond ring proton - side-chain proton coupling constant in order to determine $\langle \sin^2\theta \rangle$ and to interpolate the barrier to rotation, V_2. Proton-fluorine coupling constants are also commonly measured, and, perhaps, could be used in the same way as the proton-proton couplings in the J method. In fact, the six-bond proton-fluorine coupling $^6J_p^{H,CF}$ in 3,5-dichlorobenzylfluoride (39) was used to determine the barrier in this compound and to infer the effect of a side-chain fluorine substituent on the six-bond proton-proton coupling, $^6J_{90}^{H,CH_2}$.

Rather than the side-chain fluorine to para proton coupling, the side-chain proton to para fluorine coupling would have more versatility of use. A para fluorine substituent simplifies the spectral analysis of the ring resonances, and the large magnitude of the coupling, almost twice that of a similar proton-proton coupling, increases the relative accuracy of the coupling constant and the resultant barrier to rotation. On the other hand, the six-bond proton-fluorine coupling, like the six-bond proton-proton coupling, depends on the σ-π interaction and it is not certain that either side-chain or ring substituents have no effect on this coupling. Hence, para-fluoro derivatives of the compounds, toluene, benzyl bromide, benzyl chloride, benzyl cyanide, isopropylbenzene, and benzal chloride are investigated, and compared with the respective non-para-fluorinated compounds in order to determine the suitability of using $^6J_p^{F,CH_n}$ in the J method.

i) spectral analysis

The NMR samples of all the para-fluoro toluene derivatives were prepared as 10 mol % solutions in CS_2 with a small amount of TMS added as a lock and reference. The 3,5-dichlorobenzyl cyanide was insufficiently soluble in CS_2 to allow observation of a spectrum suitable for calibration. However, the benzyl cyanide derivative was soluble in a mixture of CS_2, $CDCl_3$, and CS_2 to approximately 5 mol % concentration.

The spectra were recorded on a Varian HA-100 spectrometer at 305 K. The sign of the long-range coupling, ${}^6J_p^{F,CH_n}$ was determined by low-amplitude double irradiation methods (31) and was found to be the same as ${}^3J^{H,F}$, which is positive (89).

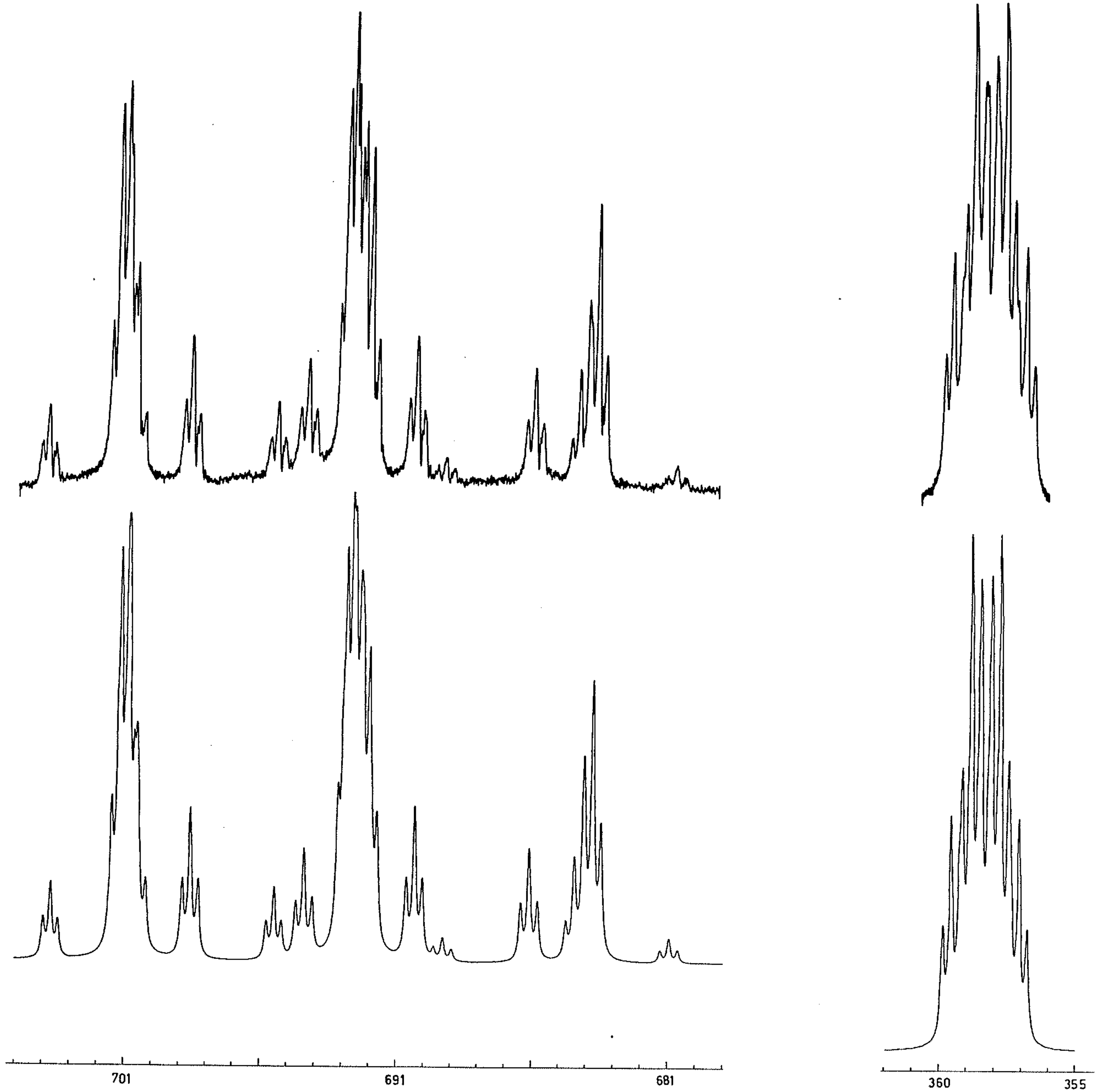
The spectra were analyzed by means of the computer program LAME (33,34). The spectral parameters of the 3,5-dichlorobenzyl cyanide are listed in table 15, while those of the para-fluoro derivatives are listed in table 16. An example of a spectrum is that of p-fluorobenzyl cyanide shown in figure 13.

ii) para-fluorotoluene

a) σ-π mechanism in p-fluorotoluene

The analog of toluene for the p-fluoro compounds is p-fluorotoluene. The arguments which lead to the conclusion that the six-bond coupling in toluene is transmitted solely by a π mechanism are also applicable to p-fluorotoluene.

Figure 13. The observed and calculated proton magnetic resonance spectra at 100 MHz of a 10 mole % solution of p-fluorobenzyl cyanide in CS_2. The spectral parameters used in the simulation are given in table 16.


701
691
681
360
355

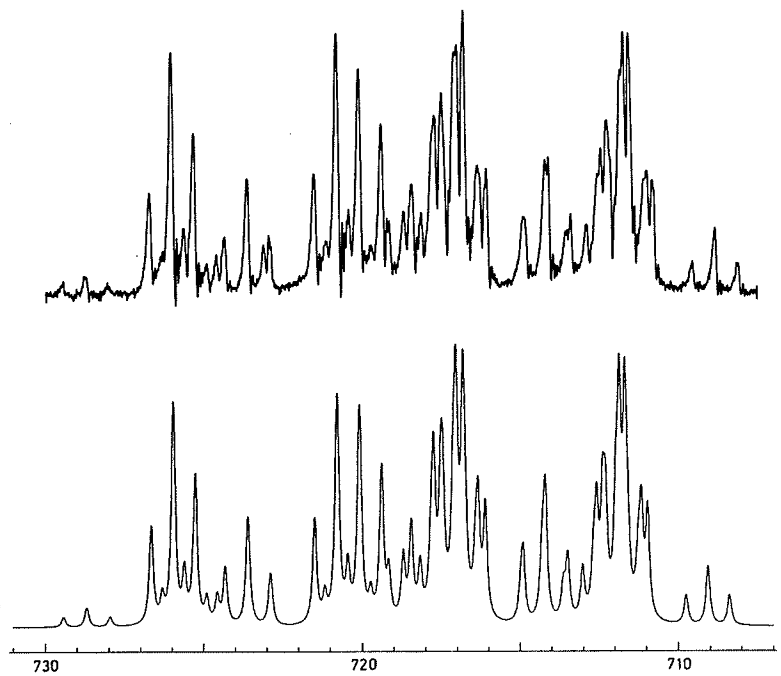
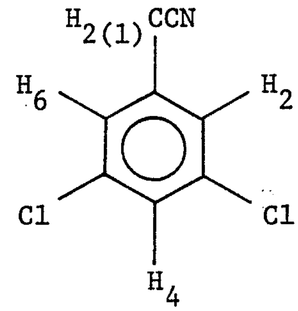

730
720
710

table 15. Spectral parameters of 3,5-dichlorobenzyl cyanide.



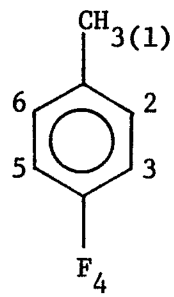
ν_1[a]	290.412(3)[b]
$\nu_2 = \nu_6$	682.374(4)
ν_4	709.925(3)
$J_{12} = J_{16}$[c]	-0.762(4)
J_{14}	-0.602(3)
$J_{24} = J_{46}$	1.851(3)
RMS error	0.015

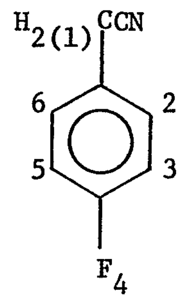
[a]Chemical shift in Hz at 100.001 MHz to low field of internal TMS.

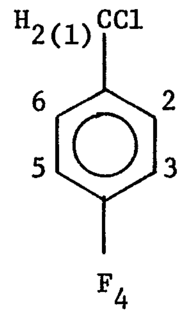
[b]Number in parentheses give the standard deviation in the last place.

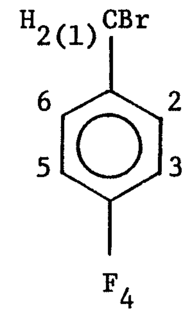
[c]Coupling constant in Hz.

table 16. Spectral parameters of <u>para</u>-fluorotoluene and some derivatives.







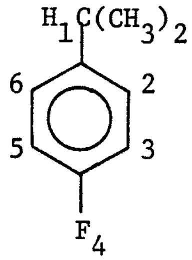
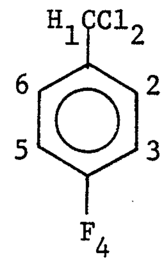


ν_1	226.166(2)[a]	[225.387(2)][b]	358.368(4)	444.945(2)	435.720(3)
$\nu_2 = \nu_6$	712.750(2)		718.141(3)	724.142(2)	725.582(3)
$\nu_3 = \nu_5$	693.272(2)		693.143(3)	691.189(2)	690.109(3)
ν_4					
$J_{12} = J_{16}$[c]	-0.720(3)	[-0.714(3)]	-0.736(4)	-0.492(2)	-0.432(3)
$J_{13} = J_{15}$	0.343(2)	[0.360(3)]	0.330(3)	0.290(2)	0.288(3)
J_{14}	1.149(3)	[1.122(4)]	1.058(7)	0.652(4)	0.545(7)
$J_{23} = J_{56}$	8.439(2)		8.522(5)	8.535(3)	8.500(4)
$J_{24} = J_{46}$	5.431(3)		5.078(6)	5.204(4)	5.184(6)
$J_{25} = J_{36}$	0.389(2)		0.392(4)	0.392(3)	0.373(4)
J_{26}	2.390(2)		2.838(5)	2.770(4)	2.751(5)
$J_{34} = J_{45}$	8.965(3)		8.365(6)	8.416(4)	8.351(6)
J_{35}	2.877(3)		2.486(5)	2.423(4)	2.453(5)
RMS error	0.0140	0.0219	0.0257	0.0159	0.0254

[a]Ref. 90; Chemical shift in Hz downfield of TMS; the value in parentheses is standard dev. in the last value.

[b]Only the methyl resonances were assigned in the LAME analysis. [c]Coupling constants in Hz

table 16. (cont.) spectral parameters of <u>para</u>-fluorotoluene and some derivatives.

		
ν_1	281.785(4)	658.866(5)
$\nu_2 = \nu_6$	705.311(5)	746.693(5)
$\nu_3 = \nu_5$	682.124(4)	697.233(5)
ν_4		
$J_{12} = J_{16}$	-0.581(5)	-0.436(6)
$J_{13} = J_{15}$	0.309(5)	0.241(6)
J_{14}	0.557(8)	0.220(10)
$J_{23} = J_{56}$	8.482(7)	8.653(7)
$J_{24} = J_{46}$	5.321(10)	5.026(9)
$J_{25} = J_{36}$	0.411(6)	0.382(8)
J_{26}	2.750(10)	2.738(9)
$J_{34} = J_{45}$	8.498(9)	8.172(11)
J_{35}	2.501(10)	2.527(9)
RMS error	0.0222	0.0259

The J method depends on the fact that the six-bond side-chain to ring proton-proton coupling in toluene and its derivatives is transmitted by a π mechanism, and that the coupling is solely due to this mechanism. As discussed previously, the six-bond coupling is given by the expression

$$^6J_p^{H,CH_n} = {}^6J_0^{H,CH_n} + {}^6J_{90}^{H,CH_n} \langle \sin^2\theta \rangle \qquad [5]$$

where $^6J_0^{H,CH_n}$ is the coupling not transmitted through the π system and, hence, associated with spin information transmitted through the σ system. $^6J_{90}^{H,CH_n}$ is the coupling transmitted through the π system when the C_α-H bond of the methyl side-chain is oriented perpendicular to the aromatic ring plane. A theoretical calculation of the coupling constants in toluene (13) gave a value of -0.075 Hz for the six-bond para coupling when the C_α-H bond was oriented in the plane of the phenyl ring, and was taken to be $^6J_0^{H,CH_3}$, and -1.219 Hz for the coupling when the C_α-H bond was perpendicular to the plane of the phenyl ring, i.e. $^6J_{90}^{H,CH_3}$. The methyl group is assumed to be freely rotating in toluene (V_6 = 0.0134 kcal/mole (18)) and so $\langle \sin^2\theta \rangle$ would be 0.5. Then the observed coupling, $^6J_p^{H,CH_3}$, is predicted to be -0.61 Hz if $^6J_0^{H,CH_3}$ is assumed zero. This is exactly the same value, within experimental error, determined by experiment, which was -0.62 $\pm$ 0.02 Hz (9). The calculated value of $^6J_0^{H,CH_3}$ was small and if included in equation [5] predicted $^6J_p^{H,CH_3}$ to be -0.65 Hz, not a large difference from the value when $^6J_p^{H,CH_3}$ is neglected. The theoretical calculations also show the profile of the calculated ${}^{6}J_{p}^{H,CH_3}$ versus θ plot to have close to a $\sin^2\theta$ dependence.

A sole π mechanism for the six-bond coupling in toluene is verified by experimental data on p-xylene. Thus, a sole π mechanism is predicted to result in a seven-bond coupling of the same magnitude but of opposite sign when the <u>para</u> ring proton of toluene is replaced by a methyl group, to form p-xylene. The observed coupling, ${}^{7}J_{p}^{CH_3,CH_3}$, in a derivative of p-xylene (10) is +0.62 ± 0.03 Hz, and in p-xylene itself (91) is 0.62 ± 0.03 Hz, again equal in magnitude to the value for ${}^{6}J_{p}^{H,CH_3}$ found for toluene.

Theoretical calculations of the long-range coupling between the side-chain protons and the ring fluorine were also performed for p-fluorotoluene (13). ${}^{6}J_{0}^{F,CH_3}$ was calculated to be -0.008 Hz and ${}^{6}J_{90}^{F,CH_3}$ as +1.872 Hz. As can be seen, the magnitude of ${}^{6}J_{0}^{F,CH_3}$ was even smaller than ${}^{6}J_{0}^{H,CH_3}$ in toluene, and was assumed zero. Because the rotational barrier in p-fluorotoluene, 0.0138 kcal/mole (92), was the same as the barrier in toluene, $\langle\sin^2\theta\rangle$ was 0.5 and ${}^{6}J_{p}^{F,CH_3}$ was calculated to be 1.872 x 0.5 = 0.94 Hz. The experimental value of ${}^{6}J_{p}^{F,CH_3}$ has been determined to be 1.15 ± 0.02 Hz (90), which was close to the theoretically predicted value. The calculated ${}^{6}J_{p}^{F,CH_3}$ versus θ profile showed a close $\sin^2\theta$ dependency, the same as for toluene.

Confirmation of a sole π mechanism for the transmission of the six-bond methyl proton to fluorine coupling in p-fluorotoluene cannot be had by replacement of the coupling nucleus by a methyl group as in toluene. However, the premises which were used to predict the outcome of replacing a proton by a methyl group showed that a sole π mechanism was consistent with the experimental six-bond coupling constant in p-fluorotoluene, as discussed below.

McConnell (7,8) predicted that if spin information was transmitted only through the π system of the phenyl ring then the coupling constant was proportional to the product of two hyperfine interaction constants. Thus, for the six-bond coupling in toluene the proportionality is

$$^{6}J_{p}^{H,CH_3} \propto Q_{CH}\, Q_{CCH} \qquad [30]$$

where Q_{CH} is the hyperfine interaction constant between the proton and the electron in the π orbital centred on the carbon to which the proton is bonded. Q_{CCH} is the hyperfine constant between a proton bonded to an α carbon and the π electron centred on the carbon to which the α carbon is bonded. If the <u>para</u> proton of toluene is replaced by a methyl group, then the proportionality is

$$^{7}J_{p}^{CH_3,CH_3} \propto Q_{CCH}\, Q_{CCH} \qquad [31]$$

and the coupling constant in p-xylene can be predicted from the ratio of [30] and [31]

$$^{7}J_p^{CH_3,CH_3} = \frac{Q_{CCH}}{Q_{CH}}\ ^{6}J_p^{H,CH_3} \qquad [32]$$

if the constant of proportionality is assumed the same for both. Macdonald and Reynolds (10) used equation [32] with the following values: $Q_{CH} = -23G$, $Q_{CCH} = +25G$, and $^{6}J_p^{H,CH_3} = -0.62$ Hz, and the experimental value of $^{7}J_p^{CH_3,CH_3} = +0.62$ to conclude that the six and seven-bond coupling in toluene and p-xylene results solely from a π mechanism.

For the six-bond coupling in p-fluorotoluene a similar expression to [30] can be written

$$^{6}J_p^{F,CH_3} \propto Q_{CF}\, Q_{CCH} \qquad [33]$$

where Q_F is the hyperfine interaction constant between the fluorine nucleus and the π electron centred on the carbon of the phenyl ring to which the fluorine is bonded. The ratio of [33] and [31] will then yield an expression for $^{6}J_p^{F,CH_3}$ in terms of Q_{CH}, Q_{CF} and $^{6}J_p^{H,CH_3}$

$$^{6}J_p^{F,CH_3} = \frac{Q_{CF}}{Q_{CH}}\ ^{6}J_p^{H,CH_3} \qquad [34]$$

Wasylishen and Schaefer (6) found that equation [34] predicted a value of 1.16 Hz for $^{6}J_p^{F,CH_3}$ with the following values: $Q_{CH} = -22.5G$, $Q_{CF} = 41.1G$ and $^{6}J_p^{H,CH_3} = -0.62$ Hz. The Q_{CF} used was the value found for p-fluorophenyl groups in nickel (II) aminotroponeimineate derivatives (93). The experimentally determined value of $^{6}J_p^{F,CH_3}$ in acetone solution was +1.15 Hz. This excellent agreement between predicted and observed values strongly supports a sole π mechanism for the spin transmission of $^{6}J_p^{F,CH_3}$ in p-fluorotoluene.

b) $^6J_{90}^{F,CH_n}$ in para-fluorotoluene

As mentioned previously, the rotational barrier in p-fluorotoluene was found to be 0.0138 kcal/mole (92) and such a low barrier results in almost free rotation of the methyl top. In that case $\langle \sin^2\theta \rangle$ = 0.5. The equation which describes the observed six-bond side-chain proton-ring fluorine coupling in p-fluorotoluene and side-chain substituted derivatives of p-fluorotoluene is

$$^6J_p^{F,CH_n} = {^6J_0^{F,CH_n}} + {^6J_{90}^{F,CH_n}} \langle \sin^2\theta \rangle \qquad [35]$$

The terms in this equation are defined exactly as in equation [5] for the analogous proton-proton coupling, including $\langle \sin^2\theta \rangle$. From the above discussion of the σ-π mechanism in p-fluorotoluene, where it was indicated that $^6J_p^{F,CH_3}$ is transmitted solely by a π mechanism, $^6J_0^{F,CH_n}$ can be assumed zero and equation [35] becomes

$$^6J_p^{F,CH_n} = {^6J_{90}^{F,CH_n}} \langle \sin^2\theta \rangle \qquad [36]$$

A value of $^6J_{90}^{F,CH_n}$ can be determined from the ratio of $^6J_p^{F,CH_n}$ and $\langle \sin^2\theta \rangle$.

A previous determination of the spectral parameters of p-fluorotoluene in acetone solution (90) found $^6J_p^{H,CH_3} = 1.15 \pm 0.02$ Hz. A redetermination of the long-range side-chain proton to ring proton and fluorine couplings of p-fluorotoluene in a CS_2 solution found $^6J_p^{F,CH_3} = 1.12 \pm 0.02$ Hz. This value will be used for determining $^6J_{90}^{F,CH_3}$ because all the other p-fluorotoluene derivatives were prepared as CS_2 solutions. The high dielectric constant of acetone might produce a slightly larger double bond character of the

C-F bond and increase the coupling, although the two values observed are equal within experimental error. Thus, ${}^6J_{90}^{F,CH_3} = 1.12/0.5 =$ 2.24 Hz.

iii) substituent effects on ${}^6J_{90}^{F,CH_n}$

${}^6J_{90}^{H,CH_n}$ in toluene is known to be affected by the type and number of α substituents. Thus, the value of -1.24 Hz remains the same for simple alkyl or dialkyl α substituents, whereas the magnitude decreases to -1.14 Hz and -1.05 Hz for α-chloro and α,α-dichloro substituents, respectively. These values are predicted by assuming an inverse linear relationship between the electronegativity of the substituent and the magnitude of the coupling. INDO MO FPT calculations show a decrease in $|{}^6J_{90}^{H,CH_n}|$ for both benzyl (39) and benzal fluoride (16), and a comparison of ${}^6J_{90}^{H,CF}$ and ${}^6J_{90}^{H,CH_2}$ in benzyl fluoride also indicates a decrease in the magnitude of the latter coupling to 1.02 Hz. The effect of the electronegativity of the α substituents is assumed to be the same on ${}^6J_{90}^{F,CH_n}$ as on ${}^6J_{90}^{H,CH_n}$, and the fractional change predicted for the latter coupling is taken to be the same for ${}^6J_{90}^{F,CH_n}$. Thus,

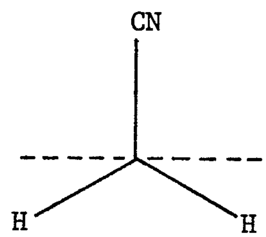
$$ {}^6J_{90}^{F,CH_n} = \frac{{}^6J_{90}^{H,CH_n}}{-1.24} \times 2.24 \text{ Hz} \qquad [37] $$

where -1.24 and 2.24 Hz are the unperturbed values of ${}^6J_{90}^{H,CH_n}$ and ${}^6J_{90}^{F,CH_n}$, respectively.

iv) 3,5-dichlorobenzyl cyanide

Of the p-fluorotoluene derivatives studied only the p-fluorobenzyl cyanide does not have a parent benzyl cyanide investigated previously. Hence, the rotational barrier and ground state rotational conformation in 3,5-dichlorobenzyl cyanide are determined in order to compare them with the ones inferred for p-fluorobenzyl cyanide.

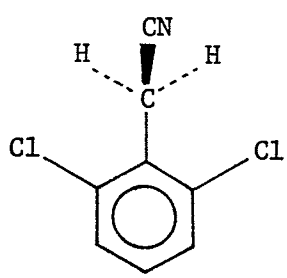
$^{6}J_{p}^{H,CH_2}$ in 3,5-dichlorobenzyl cyanide is found to be -0.60 $\pm$ 0.02 Hz. If the CN substituent is assumed to have the same electronegativity as the CH_3 group, then $^{6}J_{p}^{H,CH_2}$ can be assumed to be -1.24 Hz, resulting in $\langle\sin^2\theta\rangle = 0.484$. From a plot of $\langle\sin^2\theta\rangle$ versus V_2, and a minimum rotational energy conformation of <u>95</u>, the barrier is



<u>95</u>

interpolated to be 0.16 $\pm$ 0.16 kcal/mole. The dichloro substituents are assumed not to affect the coupling as deduced from the equal values for $^{6}J_{p}^{H,CH_3}$ in toluene and 3,5-dichlorotoluene (21).

However, the minimum energy conformation of 2,6-dichlorobenzyl cyanide, <u>96</u>, is also <u>95</u>, but



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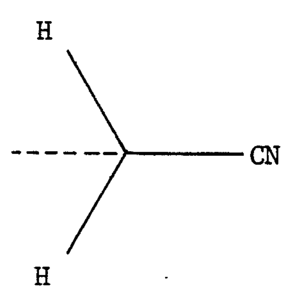
this compound has a much larger barrier (19) so that $<\sin^2\theta>$ is approximately 0.25. Then, for the observed coupling, ${}^6J_p^{H,CH_2}$ = -0.33, and $<\sin^2\theta>$ = 0.25, ${}^6J_{90}^{H,CH_2}$ is -0.33/0.25 = -1.32 Hz. This is a larger magnitude than -1.24 Hz and might arise from stronger hyperconjugation in the presence of the CN groups. If this value is taken for ${}^6J_{90}^{H,CH_2}$ in 3,5-dichlorobenzyl cyanide, $<\sin^2\theta>$ = -0.60/-1.32 = 0.455 and the rotational barrier becomes 0.46 ± 0.16 kcal/mole. Because of the uncertainty as to the value of ${}^6J_{90}^{H,CH_n}$ a compromise value of 0.3 ± 0.2 kcal/mole is considered to be the barrier to rotation in 3,5-dichlorobenzyl cyanide, and 95 as the minimum energy conformation.

A molecular polarizability study (94) of some α,α'-disubstituted p-xylenes and the correspondingly substituted toluenes determined a dihedral angle of the C_2-C_1-C_α-CN fragment of 44° in benzyl cyanide from molecular Kerr constant data. The data was also consistent with free rotation of the CH_2CN top, which implies, if not free rotation, then at least a small barrier, as found by the J method.

Ab initio molecular orbital calculations were performed for benzyl cyanide. With standard geometries (14) the difference in energies between the two rotational conformers, 95 and 97, yielded a



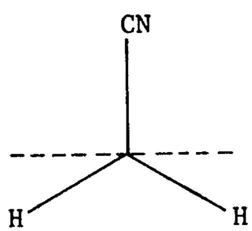
97

value of 1.98 kcal/mole. A partial geometry optimization was performed on the C_1-C_α-CN angle for each rotational conformer. The energy minimum occurred for the angle 114.4° in 97 and 112.1° in 95. The energy difference between the two conformations was now 0.98 kcal/mole. The results of the calculation are listed in table 17. A full geometry optimization of all the bond angles and bond lengths, including the benzene ring, would probably reduce the energy difference to a value nearer to the barrier determined by the J method.

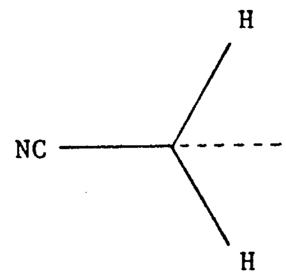
v) determination of the rotational barriers

The barriers determined for both the various α substituted toluenes and the corresponding p-fluorotoluenes are listed in table 18. ${}^6J_p^{H,CH_n}$ and ${}^6J_p^{F,CH_n}$ were the experimentally determined six-bond side-chain - ring proton or fluorine coupling constants. ${}^6J_{90}^{H,CH_n}$ was chosen as the more likely value if more than one value had been postulated as in the case of benzal chloride. However, because the comparison of the barriers is more important at present, and because ${}^6J_{90}^{F,CH_n}$ depends on ${}^6J_{90}^{H,CH_n}$, discussion of the merits of different ${}^6J_{90}^{H,CH_n}$ values is reserved for determinations of the actual magnitude of the barriers. ${}^6J_{90}^{F,CH_n}$ was calculated by means of equation [37] and is directly proportional to ${}^6J_{90}^{H,CH_n}$.

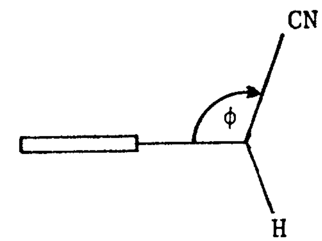
The $\langle\sin^2\theta\rangle$ values were determined from plots and tables of $\langle\sin^2\theta\rangle$ versus V_2 calculated for a reduced moment of 0.60×10^{-38} g cm^2, a temperature of 305 K and the two minimum energy conformations, 98 and 99, the former assumed for the benzyl table 17. Partial geometry optimization of benzyl cyanide.



perpendicular



parallel



Conformation[a]	ϕ(deg)	E(Hartree)	at STO-3G level
perpendicular	109.47	-357.017097267	
parallel	109.47	-357.013942495	ΔE = -0.003154772 Hartree = -1.9796 kcal/mole
perpendicular	110.0	-357.017231734	
	111.1	-357.017402692	minimum energy [b]
	112.0	-357.017468517	= -357.017469279 at 112.1°
	113.0	-357.017428372	
	114.0	-357.017282143	
parallel	113.0	-357.015755211	minimum energy
	114.0	-357.015893645	= -357.015905527 at 114.4°
	115.0	-357.015879185	
	116.0	-357.015724001	ΔE min = .001563752 Hartree = 0.9813 kcal/mole

[a]Standard geometries used for complete molecular geometry except ϕ.

[b]Minimum energy and angle found by Lagrange interpolation of data points.

table 18 . Barriers to rotation from $^6J_p^{H,CH_n}$ and $^6J_p^{F,CH_n}$ in some benzyl and benzal compounds.

cpd	$^6J_p^{H,CH_n}$ [a]	$^6J_{90}^{H,CH_n}$	$^6J_p^{F,CH_n}$	$^6J_{90}^{F,CH_n}$	$\langle \sin^2\theta \rangle_{H,H}$	$\langle \sin^2\theta \rangle_{H,F}$	$V_2(H,H)$	$V_2(H,F)$
CH_2CN [c]	-0.60 [b]	-1.24	1.06	2.24	0.484	0.473	0.16 ± 0.16	0.27 ± 0.10
	-0.60	-1.32	1.06	2.38	0.445	0.445	0.46 ± 0.16	0.56 ± 0.09
CH_2Cl [e]	-0.40	-1.14	0.65	2.06	0.351	0.316	1.88 ± 0.37	2.87 ± 0.40
CH_2Br [e]	-0.32	-1.16	0.55	2.17	0.276	0.253	>4	>4
$CH(CH_3)_2$ [d]	-0.25	-1.24	0.56	2.24	0.202	0.250	1.88 ± 0.17	1.45 ± 0.07
$CH(Cl_2)$	-0.18	-1.05	0.22	1.96	0.171	0.112	2.23 ± 0.25	3.30 ± 0.27

[a] All values of the average are in Hz.

[b] The error in all the experimental couplings is ± 0.02 Hz.

[c] Minimum energy conformation of all benzyl compounds has $C_\alpha H_2$-X bond oriented perpencidular to aromatic plane.

[d] Minimum energy conformation of all benzal compounds has $C_\alpha X_2$-H bond in the aromatic plane.

[e] Ref. 21.

compounds, and the latter for benzal compounds. These curves and tables are given in Appendices I and II. All of the compounds had reduced moments of inertia at most different by a factor of three from 0.6×10^{-38} g cm^2. Because $<\sin^2\theta>$ is grossly insensitive to this parameter any variation of the barrier from the value listed in table 18 is adequately compensated for by the quoted error.

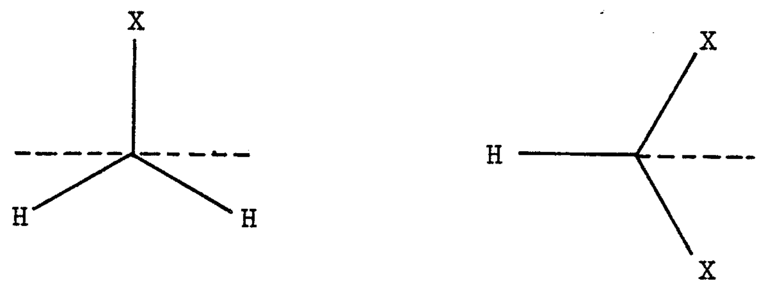
The barriers listed in table 18 have a higher accuracy than is usually warranted. The errors for the barriers are calculated only for an error of $\pm$ 0.02 Hz in the experimental coupling constant. The uncertainty in $^6J_{90}^{H,CH_n}$ and, hence, $^6J_{90}^{F,CH_n}$, is usually greater than the experimental error in $^6J_p^{H,CH_n}$ and $^6J_p^{F,CH_n}$, especially for highly polar α substituents.

The error for the barrier can be seen to vary for a constant error in the coupling with the position of the barrier on the $<\sin^2\theta>$ versus V_2 curve. Also, the error is smaller for a barrier determined from the fluorine-proton coupling than from the proton-proton coupling. This is, of course, due to the larger magnitude of the former coupling constant for the same experimental error.

vi) comparison of barriers

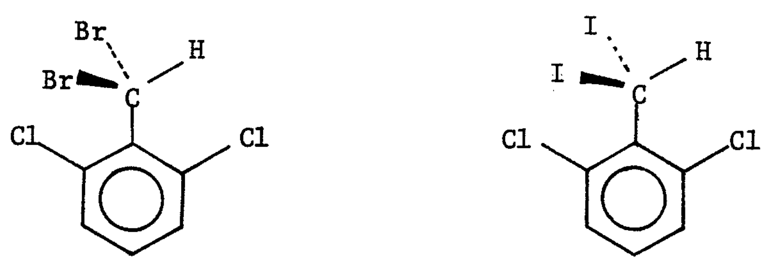
Comparison of the barriers found for the two different couplings shows significant differences. The barriers determined from the proton-proton coupling are assumed to be the more accurate for the following reasons.

That $^6J_p^{H,CH_n}$ is transmitted via a σ-π mechanism through the π system is experimentally verified by methyl group replacement. Thus, the para coupling in toluene, ${}^{6}J_{p}^{H,CH_3}$, is equal in magnitude but opposite in sign to the para coupling in p-xylene, ${}^{7}J_{p}^{CH_3,CH_3}$, as predicted for a σ-π mechanism. Furthermore, in compounds where 99 is the minimum



98 99

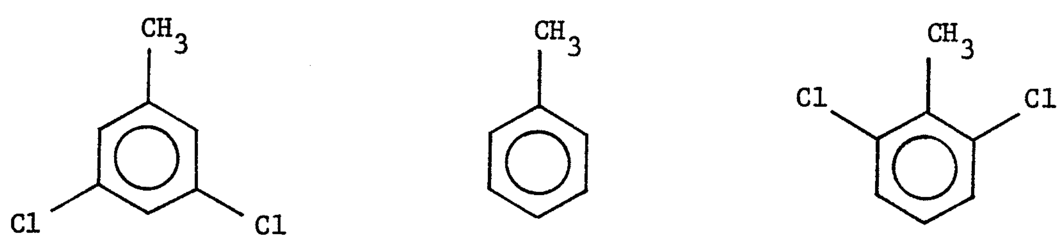
energy conformation (15,50), such as α,α-dibromo-2,6-dichlorotoluene (2,6-dichlorobenzal bromide), 100, and α,α-diiodo-2,6-dichlorotoluene (2,6-dichlorobenzal iodide), 101, and the barrier to rotation is extremely high, the coupling



100 101

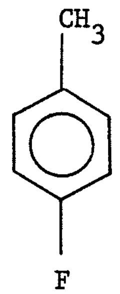
of the α proton, which is held fairly rigidly in the plane of the benzene ring by the large potential, to the para proton, ${}^{6}J_{p}^{H,CH}$, is so small as to be considered equal to zero. This coupling is usually taken to be ${}^{6}J_{0}^{H,CH_n}$, a non-σ-π contribution to the observed coupling, and because it is zero, a sole σ-π mechanism is inferred for the observed six-bond side-chain to <u>para</u> proton coupling. Both of these experimental verifications of the σ-π mechanism are not available for p-fluorotoluene derivatives, and so a non-σ-π contribution to the coupling cannot be ruled out. In fact, for the six-bond coupling from the side-chain fluorine to the <u>para</u> proton in benzal fluoride, ${}^{6}J_{p}^{H,CF}$ was found to have a non-σ-π component of almost 20%.

It is also not certain that ${}^{6}J_{p}^{F,CH_n}$ is independent of intrinsic substituent effects from the side-chain substituent of interest. If ${}^{6}J_{p}^{F,CH_n}$ is assumed transmitted by a sole π mechanism, then by equation [33] it depends on Q_{CF}, which appears to vary more from system to system than does Q_{CH} (95,96). Thus, if actual coupling constants are compared, ${}^{6}J_{p}^{H,CH_3}$ is -0.60, -0.62 and -0.63 Hz (9, 21) in 3,5-dichlorotoluene <u>102</u>, toluene <u>103</u>, and 2,6-dichlorotoluene <u>104</u>, respectively, all equal within experimental error, whereas ${}^{6}J_{p}^{F,CH_3}$

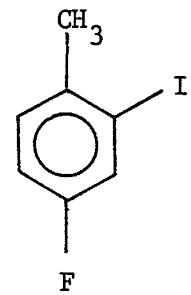


<u>102</u> <u>103</u> <u>104</u>

is 1.15 and 1.2_8 Hz (90,95) in p-fluorotoluene <u>105</u> and 4-fluoro-2-iodotoluene <u>106</u>, respectively. These values differ by more than



105



106

the experimental error and probably indicate a substituent effect on the coupling. This substituent effect from ring substituent, suggests a possible substituent effect from the side-chain substituents.

A last consideration as to the difference in barriers determined by the two couplings is that the fluorine substituent actually changes the magnitude of the barrier, either by changing the maximum or minimum energy rotational conformations. Now, in 3,5-dichloro derivatives of benzal fluoride and chloride (above), $^{6}J_{p}^{H,CH}$ was about 0.03 Hz greater in magnitude than the corresponding coupling in the parent compounds. This difference was explained as an experimental error, an unrecognized solvent effect, or a slightly different barrier in the derivative and parent compound. If this last explanation is in fact the case, a <u>para</u> fluorine can influence the rotational barrier of the substituted methyl top.

vii) <u>summary</u>

There is a significant difference between the barriers to rotation determined from $^{6}J_{p}^{F,CH_n}$ and those from $^{6}J_{p}^{H,CH_n}$. The differences probably arise from a combination of the effects outlined above. Although the barriers are different, both couplings yield the same minimum energy conformation. Hence, α substituted p-fluorotoluene derivatives can be used to predict the minimum energy rotational conformation and a rough value of the barrier to internal rotation.

7. Derivatives of Diphenylmethane

The J method has been applied to several compounds in which the side-chain carbon atom of toluene has been bonded to a carbon atom of the α substituent group. These types of molecules were ethylbenzene, isopropylbenzene, styrene (59), and phenylcyclohexane. Another compound of this type is diphenylmethane which has an aromatic ring as the α substituent. Because of the complexity of the ^1H NMR spectrum of diphenylmethane, derivatives rather than the parent compound are used in the analysis.

Two of the derivatives are 3,5-dibromodiphenylmethane and 4,4'-difluorodiphenylmethane. The former compound is used to find the barrier from the observed proton-proton coupling, $^6J_p^{H,CH_2}$ while the latter allows a barrier determination from the observed proton-fluorine coupling, $^6J_p^{F,CH_2}$. Because the magnitude of the long-range fluorine-proton coupling is almost twice the magnitude of the corresponding proton-proton coupling, an investigation of the temperature dependence of $^6J_p^{F,CH_2}$ is possible. It can then be used to support the minimum energy conformation and rotatonal barrier of the diphenylmethane derivative deduced from $^6J_p^{H,CH_2}$.

i) spectral analysis

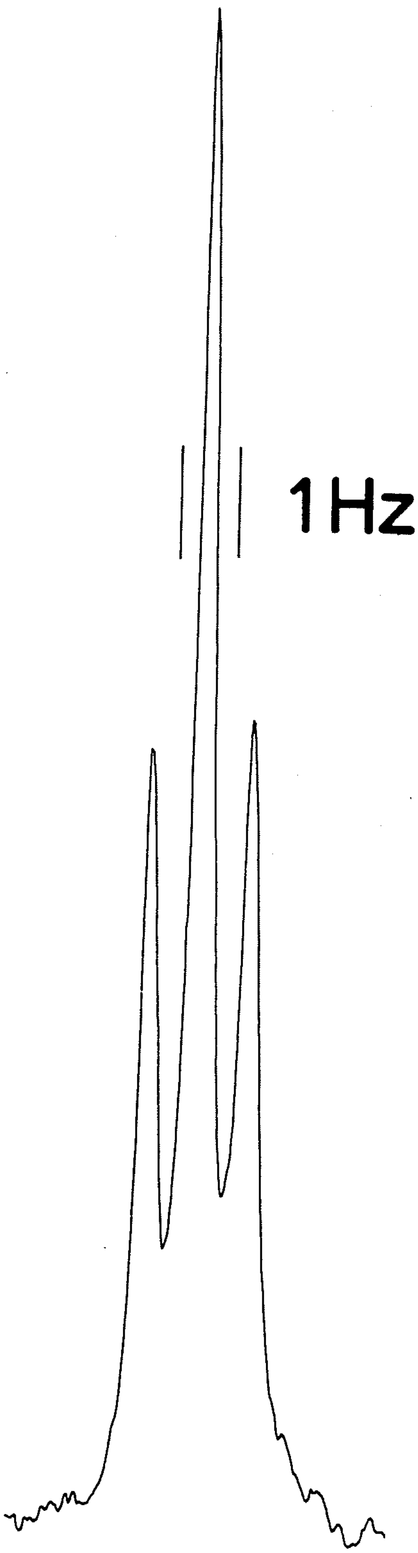
The 4-aminodiphenylmethane, 3,5-dibromodiphenylmethane, and 4,4'-difluorodiphenylmethane were prepared as 5 mol %, 5 mol %, and 10 mol % solutions in toluene-d_8, respectively, with a small amount of TMS added as a lock for the HA 100 spectrometer, and as a proton reference. The deuterated solvent was used as a lock for the WH90 FT spectrometer.

The spectra of the amino and dibromo derivatives were recorded on a Varian HA 100 spectrometer at a probe temperature of 305 K. The spectra of the fluoro derivative were recorded, on a Bruker WH-90 spectrometer in the FT mode at four temperatures between 250 and 370 K, inclusive. The instrumental parameters required for recording the spectra are given in the Experimental Methods section.

The fluorine spectrum of 4,4'-difluorodiphenylmethane is very complex because of the small internal shifts of the ring protons. The width of the ring proton resonances was only about 10 Hz and the resonances were well removed from the methylene proton resonances, by 2.7 ppm to low field. This allowed selective decoupling of the ring protons by a decoupling field having an amplitude low enough not to affect the methylene proton transitions as observed in the fluorine spectrum. The decoupled fluorine spectrum at 370 K is illustrated in figure 14. As can be seen, the spectrum is a 1:2:1 triplet, the splitting being due to ${}^{6}J_{p}^{F,CH_2}$.

The proton spectra of 4-aminodiphenylmethane and 3,5-dibromodiphenylmethane were analyzed by means of the computer program LAME (33,34). In the analysis of the amino compound only the transitions of the ring protons were assigned frequencies. Because of coupling to all the ring protons, the methylene proton resonances occurred as a single broadened peak from which no individual lines could be identified or resolved. Cross-ring coupling constants were found to be negligible, if present at all, and the spectrum

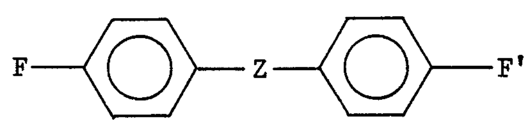
Figure 14. The ring proton decoupled fluorine magnetic resonance spectrum at 84.69 MHz of a 10 mole % solution of 4,4'-difluorodiphenylmethane in toluene-d_8. The temperature was 370 K.


1Hz

was treated as a six-spin system consisting of the four protons on the amino substituted ring and the methylene protons.

The spectrum of 3,5-dibromodiphenylmethane was treated as a five spin system in the analysis. Again, cross-coupling was negligible and the dibromo substitution produced sufficient dispersion to allow separation and identification of the ring proton resonances from the different phenyl groups. No methylene proton transitions were assigned in the analysis. The spectral parameters of the amino and the dibromo derivatives are given in table 19.

The proton decoupled fluorine spectrum of 4,4'-difluorodiphenylmethane was assumed to be a first order spectrum. Analysis of some 4,4'-difluorodiphenyl compounds (97) of the type 107

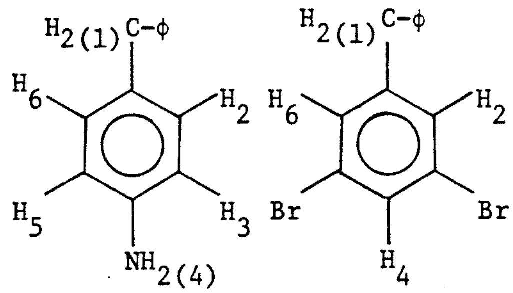


107

show that compounds very similar to diphenylmethane (Z = O, S, CH(OH)) have negligible coupling between the fluorine nuclei. Thus, the coupling constant, $^{6}J_{p}^{F,CH_2}$, is just the measured splitting. The coupling constant and the temperature at which it was measured are given in table 20.

ii) stable conformations of diphenylmethane

The rotational conformations of diphenylmethane can be described by specifying two angles, ψ and ψ', which refer to the rotation of the phenyl ring about the C_1-C_7 or $C_{1'}$-C_7 bond. The angles are both zero when the two rings are co-planar. The table 19. Spectral parameters of 4-aminodiphenylmethane and 3,5-dibromodiphenylmethane.



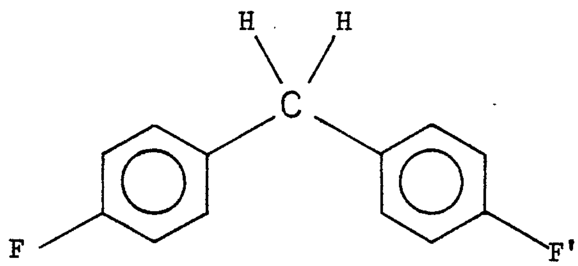
ν_1 [a]	368.7	339.9
$\nu_2 = \nu_6$	679.690(3) [c]	698.094(7)
$\nu_3 = \nu_5$	623.269(3)	
ν_4	287.5	730.117(8)
$J_{12} = J_{16}$ [b]	-0.612(4)	-0.636(10)
$J_{13} = J_{15}$	0.283(4)	
J_{14}		-0.498(11)
$J_{23} = J_{56}$	7.887(4)	
$J_{24} = J_{46}$		1.775(8)
$J_{25} = J_{36}$	0.426(5)	
J_{26}	2.571(4)	
$J_{34} = J_{45}$		
J_{35}	2.163(4)	
RMS error	0.009	0.025

[a]Chemical shifts in Hz at 100.001 MHz to low field of internal TMS.

[b]Coupling constants in Hz.

[c]Numbers in parentheses give the standard deviation in the last significant figure.

table 20. $^{6}J_{p}^{F,CH_2}$ in 4,4'-difluorodiphenylmethane as a function of the temperature.



$^{6}J_{p}^{F,CH_2}$	Temperature (K)
0.80_8 [a]	250 [b]
0.82_5	296
0.85_4	343
0.87_9	370

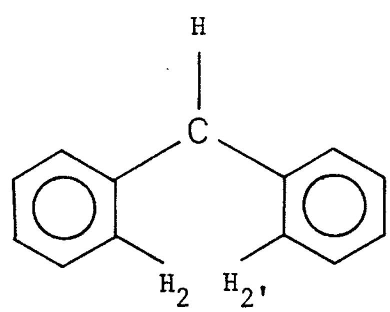
[a] Hz; reproducability of J is about 0.01 Hz.

[b] Temperature is accurate to $\pm$ 1 K.

rotation is positive when the phenyl ring is rotated clockwise when viewed along the rotation axis from H_4 to C_7, or when it is rotated counter-clockwise when viewed along the rotation axis from $H_{4'}$ to C_7. The sense of these positive rotations is illustrated in figure 15.

There are certain conformations for which the symmetry would suggest that it is a minimum energy conformation. They are best visualized by use of molecular models, which can also indicate whether the conformation is sterically favoured or not.

Five conformations can be formed by rotating the phenyl groups about the rotation axes. The first, conformation 1, occurs when the phenyl rings are co-planar($\psi=0^{\circ},\psi'=0^{\circ}$). This conformation is

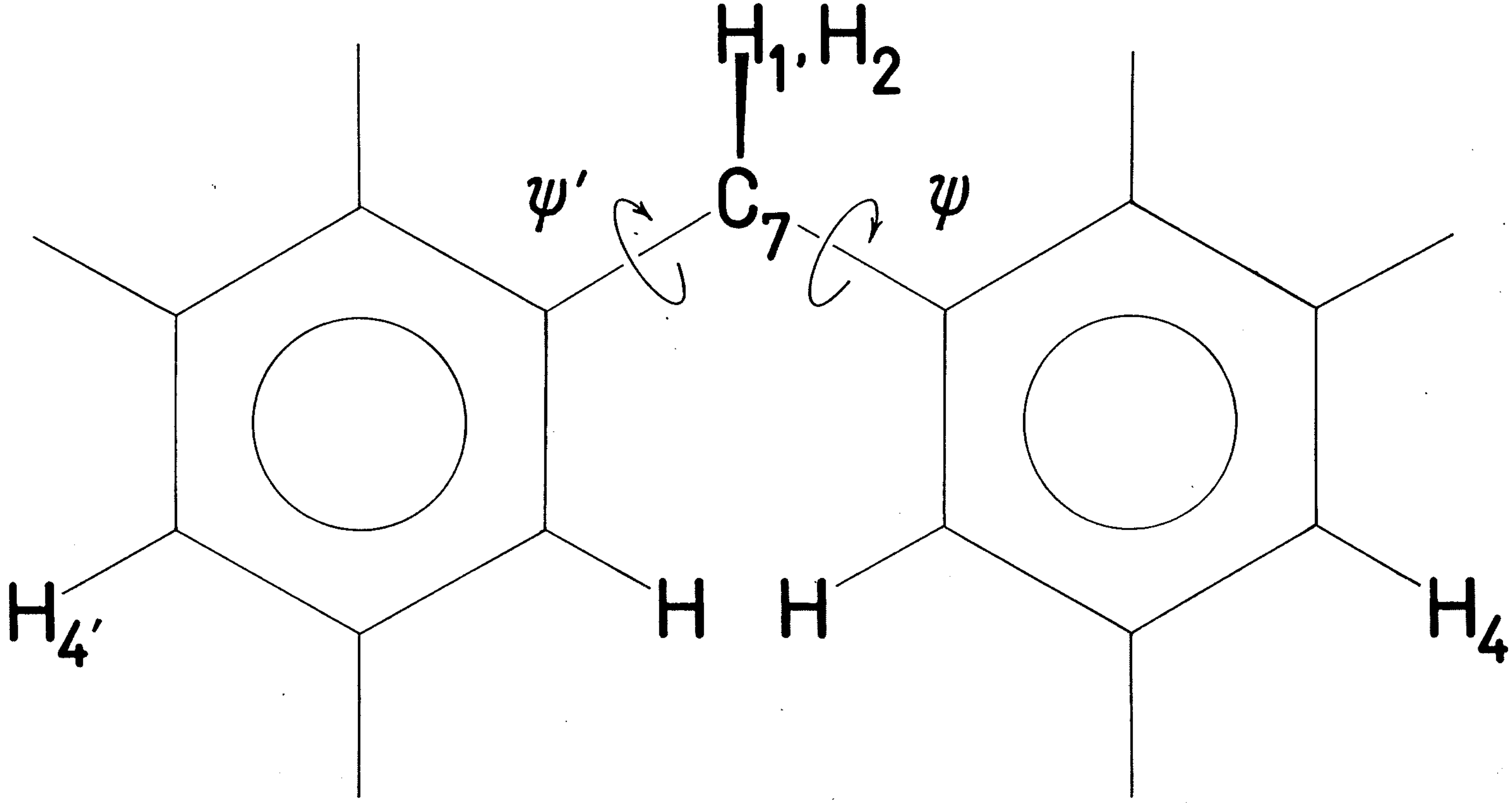


1

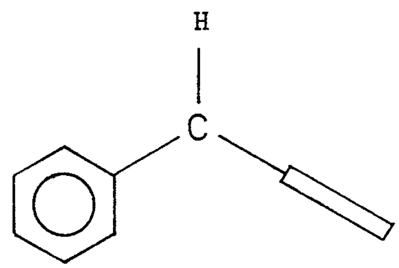
assumed to have a fairly high energy because of the strong non-bonded interactions between the ortho C-H groups of the two phenyl rings. It will not be considered as a possible minimum energy conformation.

Conformation 2, referred to as the perpendicular conformation, is formed by rotating one of the phenyl rings by 90° ($\psi=90^{\circ},\psi'=0^{\circ}$).

Figure 15. The diphenylmethane molecule showing the angles ψ and ψ' and their sense of rotation.



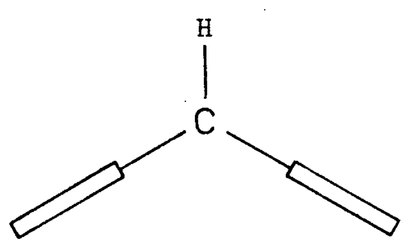
H_1, H_2
ψ'
C_7
ψ
$H_{4'}$
H
H
H_4



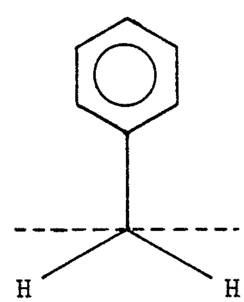
2

It has C_s symmetry and is often considered a possible stable conformation of diphenylmethane. However, the ortho hydrogen atom of the $\psi'=0^{\circ}$ ring penetrates the π cloud of the neighboring ring and this process is assumed to involve an increase in the energy of the molecule. Hence, conformation 2 is not regarded as a possible minimum energy conformation.

Conformation 3 is referred to as the gable conformation and results from the rotation of the $\psi'=0^{\circ}$ phenyl ring in conformation 2 by 90° ($\psi=90^{\circ},\psi'=90^{\circ}$). The gable conformation has C_{2v} symmetry.



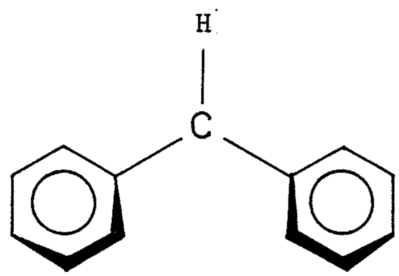
3a



3b

The sum of the van der Waals radii of the pairs of opposed *ortho* hydrogen atoms is a much smaller value than the actual distance between the proton centres and so no steric interactions are indicated. This conformation, then, is a possible minimum energy conformation.

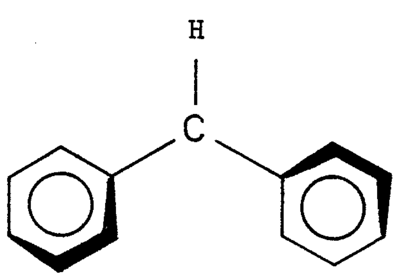
Another conformation 4 can be formed by rotating each phenyl group 60° in the positive sense (ψ=60°, ψ'=60°). Molecular models show that in this conformation one pair of *ortho* hydrogen



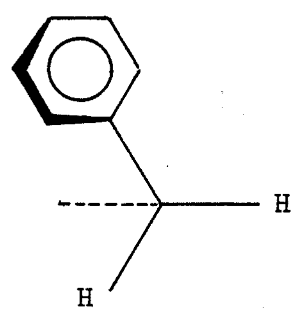
4

atoms on opposite rings come into contact which implies a high energy in the molecule. This conformation can safely be rejected as being of low energy.

A final conformation, 5, can be formed by rotating one phenyl group by 60° in the positive sense and the other phenyl group by 60° in the negative sense (ψ=60°,-ψ'=60°). This conformation



5a



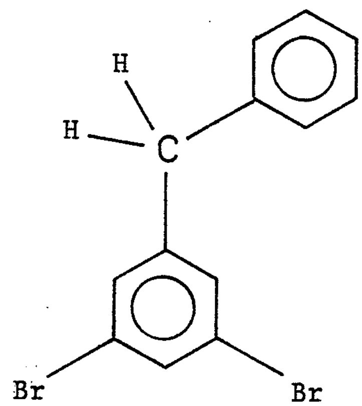
5b

is called the skew or helical conformation, has C_2 symmetry, and not having a rotation-reflection axis, is chiral. The aromatic plane of each phenyl ring contains one C_7-H bond. Molecular models show no obvious steric interactions and so conformation 5 is a possible minimum energy conformation.

Whereas in many discussions concerning the stable conformations of diphenylmethane (98), 2 and 5, the perpendicular and helical conformations are considered the two possible choices for the minimum energy conformation; in the present study, 3, the gable conformation, and 5 are considered the possible choices for the stable conformation, with 2 qualitatively predicted to have a higher energy than either of the other two.

The conformations discussed so far have involved the implicit assumption that the methyl carbon atom has a tetrahedral geometry. This assumption is substantiated by the observed one-bond methylene carbon-proton coupling constant, $^1J(^{13}C,H)$, in diphenylmethane, which has a value of 126.0 Hz (100). The one bond methyl coupling is 125 Hz in methane (99) and 126.0 Hz in toluene (100-102), showing that this parameter varies negligibly when one or two phenyl groups are substituted on the methane. This coupling is correlated with the carbon orbital hybridization in simple hydrocarbon systems having low polarity (103-106), and the near constancy of $^1J(^{13}C,H)$ in methane, toluene, and diphenylmethane indicates nearly the same hybridization in each, namely sp^3. Thus, the bond angles are inferred to be close to the tetrahedral angle in diphenylmethane in solution.

iii) 3,5-dibromodiphenylmethane

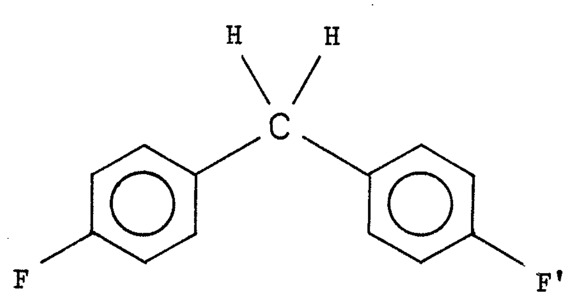


Because of the complexity of the diphenylmethane spectrum, a 3,5-dibromo derivative was prepared in order to make the spectrum amenable to analysis. This procedure of selective substitution has been applied to many of the compounds studied by the J method. If the barrier in benzyl and benzal compounds arises mainly from steric interactions between the rotor substituents and the *ortho* C-H bonds, then substitution of halogen atoms in the *meta* positions would not perturb the barrier to any great degree, and this is assumed to be the case. Thus, the rotational barrier about the C_1-C_α bond in 3,5-dibromophenylethane determined by the J method (40) agrees exactly with the barrier in phenylethane given by low resolution microwave (107) and heat capacity data (108).

If the rotational potential about the C_1-$C_{7(\alpha)}$ bond in 3,5-dibromodiphenylmethane is assumed to be two-fold in character, then the barrier to rotation, V_2, can be found by the J method. ${}^6J_{90}^{H,CH_2}$ is taken to be -1.24 Hz, the value in toluene and benzyl and benzal compounds having simple alkyl α substituents such as phenylethane, isopropylbenzene, and phenylcyclohexane. $^6J_p^{H,CH_2}$ = $-0.49_8 \pm 0.02$ Hz and so $\langle \sin^2\theta \rangle = -0.498/-1.24 = 0.402$. From tables or plots of $\langle \sin^2\theta \rangle$ versus V_2 calculated for a particular minimum energy conformation, various reduced moments of inertia and a temperature of 305 K (see appendices I and II), the barrier can be extrapolated. Because $\langle \sin^2\theta \rangle$ is so insensitive to the reduced moment, the variation of I_r with the rotational angle has a negligible affect. If the minimum energy conformation is <u>3</u>, the gable conformation, then for a reduced moment of 2×10^{-38} g cm^2, the barrier is extrapolated to be 1.1 ± 0.2 kcal/mole.

If the minimum energy conformation is <u>5</u>, the helical conformation, then V_2 is 3.5 ± 1.5 kcal/mole. Inspection of molecular models of phenylethane, in which the barrier is 1.2 kcal/mole (40, 108), and diphenylmethane, show that both have similar steric properites with respect to rotation about the exocyclic sp^2-sp^3 bond, and that 3.5 kcal/mole seems an unreasonably high value for the barrier. Hence, the gable conformation, <u>3</u>, which implies a barrier comparable to the one in phenylethane is predicted to be the minimum energy conformation of 3,5-dibromodiphenylmethane in a toluene solution.

iv) <u>4,4'-difluorodiphenylmethane</u>

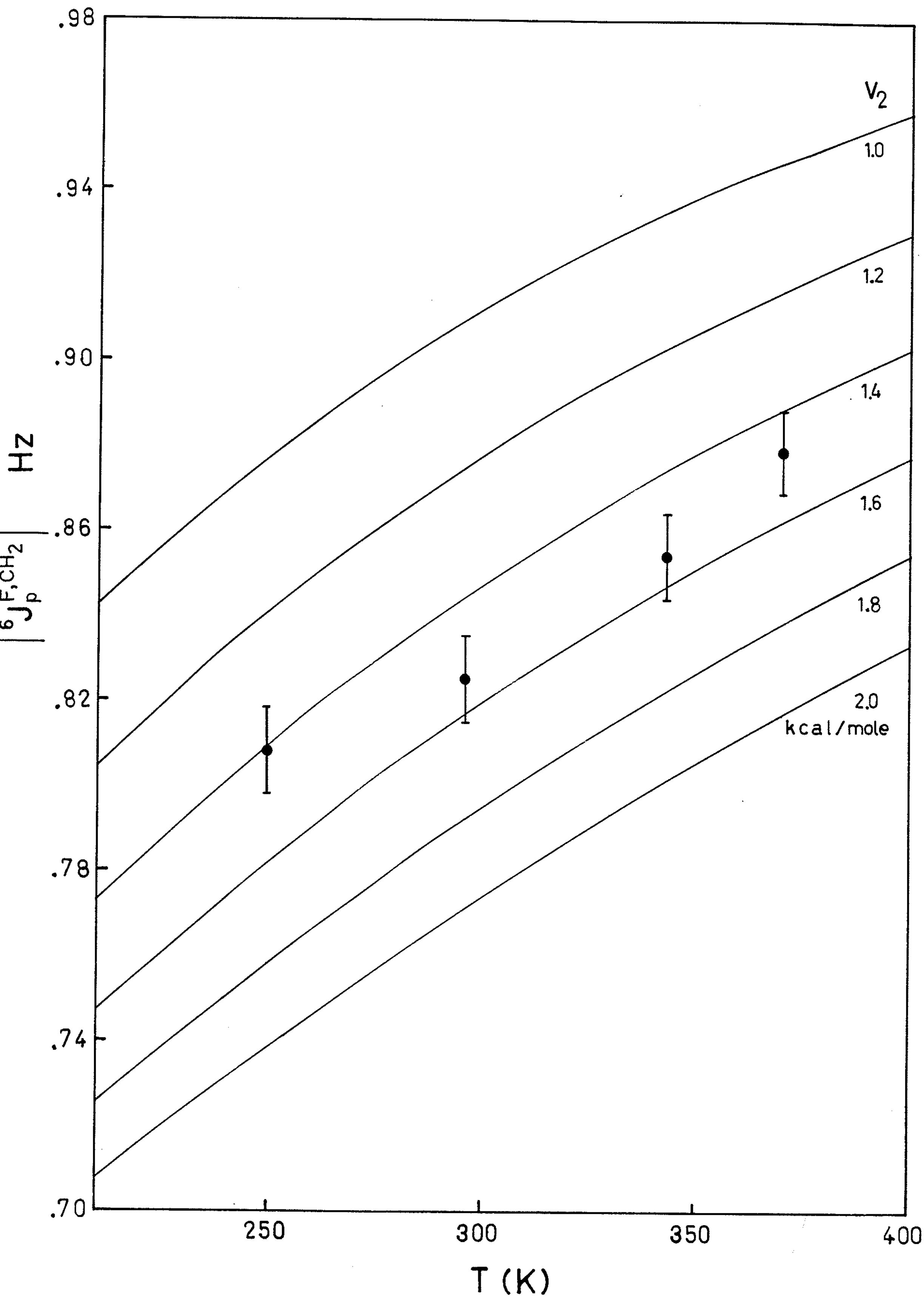


In the study of p-fluorotoluene derivatives the observed six-bond fluorine-proton coupling constant, ${}^6J_p^{F,CH_n}$, was inferred to follow the same type of angle-dependent relationship as the six-bond proton-proton coupling, ${}^6J_p^{H,CH_n}$ (equations [36] and [6]). ${}^6J_{90}^{H,CH_n}$ is 2.24 Hz in p-fluorotoluene and is assumed to be the same value in compounds with simple alkyl α substituents including 4,4'-difluorodiphenylmethane. Then, from $\langle\sin^2\theta\rangle$ versus V_2 data and equation [36], ${}^6J_p^{F,CH_3}$ can be calculated as a function of the temperature for various barriers. The curves, calculated for 3 as the minimum energy conformation, are shown in figure 16. The experimental values of ${}^6J_p^{F,CH_2}$ at the different temperatures, listed in table 20, are also plotted. The temperature dependence of the experimental points are consistent with a barrier of 1.5 ± 0.2 kcal/mole.

If 5 is considered the minimum energy conformation, then the ${}^6J_p^{H,CH_2}$ values predict an extremely high barrier. In fact, the experimental $\langle\sin^2\theta\rangle$ for the first two temperatures are lower than the limiting value of $\langle\sin^2\theta\rangle$, 0.375, for an infinite barrier and independent of the temperature. It is highly improbable that the barrier in diphenylmethane is so high and, thus, the six-bond fluorine-proton couplings confirm the gable conformation as the minimum energy conformer of diphenylmethane in solution, as predicted by ${}^6J_p^{H,CH_2}$.

The results for 4,4'-difluorodiphenylmethane are consistent with the conclusions from the study of the p-fluorotoluene derivatives. The barrier determined from ${}^6J_p^{F,CH_2}$ is generally larger

Figure 16. The calculated and observed temperature dependence of $|{}^6J_p^{F,CH_2}|$ in 4,4'-difluorodiphenylmethane. $|{}^6J_p^{F,CH_2}|$ was calculated from $|{}^6J_{90}^{F,CH_2}|$ and $\langle \sin^2\theta \rangle$ for a series of temperatures and barriers to rotation. The experimental values of $|{}^6J_p^{F,CH_2}|$ are shown with the error of $\pm$ 0.02 Hz indicated by error bars.



.98
.94
.90
.86
.82
.78
.74
.70
$|{}^6J_p^{F,CH_2}|$ Hz
V2
1.0
1.2
1.4
1.6
1.8
2.0
kcal/mole
250
300
350
400
T (K)

than the one determined from $^6J_p^{H,CH_2}$ but the inferred minimum energy conformation is the same for both couplings. The barrier from $^6J_p^{H,CH_2}$ is considered the more reliable of the two because of the reasons stated in the p-fluorotoluene derivatives study.

The larger magnitude of $^6J_p^{F,CH_2}$ compared to $^6J_p^{H,CH_2}$ allowed the determination of the temperature dependence of the former coupling. However, a change of 120^o in the temperature produced only a 0.07 Hz change in the coupling. Although the uncertainty in the barrier determined from the temperature dependence data was no better than a barrier determined at a single temperature, the fact that a barrier can be determined by the former method adds support for the consistency in the formalism of the J method.

v) $^4J_o^{H,CH_2}$ and the barrier to rotation

The four bond side-chain proton to ortho ring proton coupling, $^4J_o^{H,CH_2}$, in benzyl compounds has been shown to have a rough correlation with the barrier to rotation of the side-chain top. A plot of $|^4J_o^{H,CH_2}|$ versus V_2 for various benzyl compounds studied by the J method is given in figure 10, with the least squares determined straight line drawn through the points. The value of $|^4J_o^{H,CH_2}|$ in 4-aminodiphenylmethane and 3,5-dibromodiphenylmethane is 0.61_2 and 0.63_6 Hz, respectively. Interpolation of these points results in barriers of 1.4 and 1.1 kcal/mole for the 4-aminodiphenylmethane and the 3,5-dibromodiphenylmethane, respectively. The values, of course, are only rough estimates, but do support the barriers determined from the six-bond coupling in 4-fluorodiphenylmethane and 3,5-dibromodiphenylmethane which are 1.5 and 1.1

kcal/mole, respectively, remarkably close to the values interpolated from figure 10.

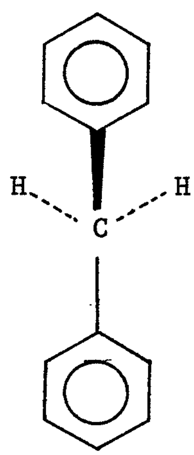
vi) theoretical calculations

The diphenylmethane molecule is too large for *ab initio* molecular orbital calculations by the programs available in this laboratory. However, semi-empirical INDO molecular orbital calculations can be performed for diphenylmethane. Standard geometries (14) are used in all cases and the total energy of the gable conformation 3, the helical conformation 5, and the perpendicular conformation 2 are calculated. The gable conformation has the lowest energy and is, thus, predicted to be the minimum energy conformation. The helical conformation is the next lowest in energy, and the perpendicular conformation has the highest total energy. The calculation results are shown immediately below.

conformation	total energy	energy difference
helical	-98.1638164720a.u.	
gable	-98.1655247713a.u.	0.0017082993a.u. = 1.07 kcal/mole
perpendicular	-98.1623586177a.u.	
gable	-98.1655247713a.u.	0.0031661536a.u. = 1.99 kcal/mole

In a recent crystal and molecular structure study of diphenylmethane (109), the authors performed empirical force field (EFF), empirical force field-molecular orbital (EFF-EHMO, EHT), and molecular orbital (MNDO) calculations, on the three conformations, 2, 3, and 5, of diphenylmethane. All these calculations confirm the INDO results that the gable conformation has the lowest energy. Both the EFF and MNDO calculations also confirm that the helical conformation has the next highest, and the perpendicular conformation the highest energy, while the EHT calculations reverse the order of the energies, that is, perpendicular next highest, helical highest.

If the internal rotation is governed by a simple two-fold symmetric potential, and the gable conformation is the minimum energy conformation, then the perpendicular conformation 109 is



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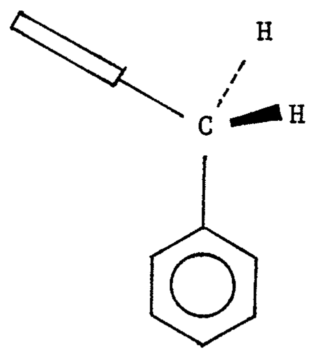

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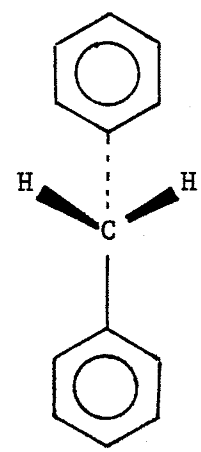


110

seen to be the transitional conformation as the benzyl top rotates about the phenyl ring. The difference in energy between the two conformers can then be thought of as the barrier to rotation.

The INDO calculation gives 1.99 kcal/mole, the EFF calculation, 1.57 kcal/mole, and the MNDO calculation, 2.26 kcal/mole for the difference. These results are only semi-quantitative but they do indicate that the barriers determined by the J method are not unreasonable.

The assumption of a two-fold symmetric potential is problematic as both rings can rotate simultaneously and these motions probably perturb the symmetry of the potential. However, if there is only one minimum and maximum energy conformation, the potential would remain two-fold and V_2 would still be the dominant term in the potential energy expansion, equation [3], although the other expansion terms would now have some small non-zero values.

vii) comparison with other experimental data

A recent X-ray crystallographic study of diphenylmethane by Barnes et al. (109) found the molecule to have a helical conformation in the crystal with orientational angles $\psi=63.9^{\circ}$, $-\psi'=71.1^{\circ}$. Other crystallographic studies of diphenylmethane derivatives (109) indicate that the derivative molecules prefer the helical conformation but can have perpendicular or gable conformations when the rings are suitably substituted. The above authors comment (109) that their theoretical calculations show that the gable and helical conformations are almost isoenergetic, which implies a very shallow torsional potential minimum where the ground state conformation can be easily influenced by its environment. Thus, crystal packing forces are, no doubt, important in the energetics governing the minimum energy conformation in the crystal.

Investigations of diphenylmethane in solution predict both helical and gable conformations as having the lowest energy. Helical conformations are deduced by Raleigh scattering (110), Kerr constant (111-113), and IR intensity measurements (114). The gable conformation is predicted by other Raleigh scattering data (115) although the orientational angles are proposed to be $\psi=-\psi'=81 \pm 4^{o}$, not the 90^{o} assumed in the J method.

No acutal barriers to rotation have been experimentally determined. However, a Raman line shape anlaysis of toluene, diphenylmethane, and triphenylmethane (116) determined the reorientational correlation times of the three molecules. The relative magnitudes of these correlation times suggested an interaction between the two phenyl groups in diphenylmethane, which hinders the orientational motion of the phenyl groups more so than in toluene. Thus, a hindering potential to internal rotation is predicted for the diphenylmethane molecule, and this potential must be larger than in toluene.

viii) summary

A rotational barrier of $V_2 = 1.1 \pm 0.2$ kcal/mole was found for 3,5-dibromodiphenylmethane by the J method in the usual way. A barrier of $V_2 = 1.5 \pm 0.2$ kcal/mole was found for 4,4'-difluorodiphenylmethane from the observed temperature dependence of $^{6}J_{p}^{F,CH_2}$, by a variation of the J method. The former value may be the more reliable of the two barriers. The gable conformation was concluded to be the stable conformation of both the derivatives in solution.

Rough estimates of the barrier in 4-aminodiphenylmethane and 3,5-dibromodiphenylmethane were found by applying the observed $|^4J_o^{H,CH_2}|$ to the empirical correlation of $|^4J_o^{H,CH_2}|$ versus V_2 of some benzyl compounds investigated by the J method. These barriers were almost the same as those found from $^6J_p^{H,CH_2}$ and $^6J_p^{F,CH_2}$, and, thus, add support to the assumptions made in predicting the values.

INDO MO calculations confirmed the gable conformation as having the lowest energy of the three conformations, gable, helical and perpendicular. Other calculations such as the empirical force field, molecular orbital, and a hybrid of the two, also gave the gable conformation the lowest energy.

X-ray crystallographic studies found that diphenylmethane preferred the helical conformation in the solid state, unless it was substituted in such a way as to force a perpendicular or gable conformation. The orientational angles were usually not the standard angles used in the description of the conformations.

Most studies of diphenylmethane in solution found a helical conformation as the one of low energy. A Raleigh scattering study predicted a gable conformation for the minimum energy of the diphenylmethane, also predicted by the J method. The conflicting results concerning the low energy conformation of diphenylmethane in solution suggests that more studies by different methods be attempted in order to resolve the question.

SUMMARY AND CONCLUSIONS

A new method for the determination of rotational barriers in side-chain substituted toluene derivatives, commonly referred to as benzyl and benzal compounds, has been developed in this laboratory and called the J method. The technique requires that the potential hindering the internal rotation be two-fold symmetric and the six-bond coupling between the side-chain proton(s) and the *para* ring proton be measureable. Then, because the coupling is transmitted solely by a π mechanism, it has a $\sin^2\theta$ dependence, where θ is the dihedral angle in the $C_{ortho}-C_1-C_\alpha-H$ fragment. The observed coupling, ${}^6J_p^{H,CH_n}$, is related to the maximum magnitude of the coupling, ${}^6J_{90}^{H,CH_n}$, occurring when $\theta = 90°$, by the expression

$$ {}^6J_p^{H,CH_n} = {}^6J_{90}^{H,CH_n} \langle \sin^2\theta \rangle \qquad [6] $$

where $\langle \sin^2\theta \rangle$ is the ensemble average of $\sin^2\theta$ over the hindered rotor states. This average value is a function of the reduced moment of inertia, the temperature, and the rotational barrier, V_2, and specific minimum energy conformation, and can be numerically calculated by a computer program. Hence, a $\langle \sin^2\theta \rangle$ value determined from the observed six-bond coupling constant by means of equation [6] can be compared to $\langle \sin^2\theta \rangle$ values calculated for a specific reduced moment of inertia, temperature, and low energy conformation, and for a series of rotational barriers, in order to infer the barrier in the molecule. Very often the conformation of the ground state rotamer can also be established. Tables and plots of $<\sin^2\theta>$ versus V_2 are shown in Appendices I and II.

In order to test the J method, rotational barriers determined by this method and by other methods were compared for similar molecules. A test molecule of the benzal type was isopropylbenzene which had the advantage of having α substituents with electronegativity about the same as the hydrogen atom, and having the barrier to rotation determined in a number of different studies.

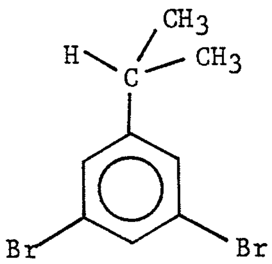
Because of the complexity of the spectrum of isopropylbenzene itself, the derivative 3,5-dibromoisopropylbenzene was used in the J method study. The barrier was assumed to arise mainly from steric interactions between the *ortho* hydrogen atoms and the side-chain substituents, and that 3,5-substituents would not substantially perturb the barrier magnitude from its value in the parent compound. This argument also applies to the barriers determined by other methods which were all for derivatives of isopropylbenzene.

The rotational barrier and minimum energy conformation of 3,5-dibromoisopropylbenzene determined by the J method compared favourably with those determined by other methods (mostly by an ESR method very similar to the J method) and, hence, was concluded to be a good and suitable method of determining rotational barriers in solution. The rotational barriers of the compounds investigated in this study and determined from ${}^{6}J_{p}^{H,CH_n}$ are shown in figure 15.

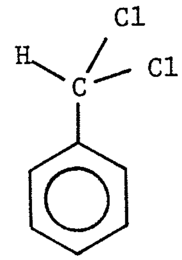
If a side-chain hydrogen atom of toluene is replaced by a substituent with electronegativity greater than that of hydrogen, then the magnitude of the six-bond _para_ coupling, ${}^{6}J_{90}^{H,CH_n}$, is expected to decrease because of the increased polarization of the remaining C_α-H bond(s). This decrease was assumed to be a linear function of the electronegativity and was estimated from the two values of ${}^{6}J_{90}^{H,CH_n}$ deduced for toluene and benzyl fluoride, and toluene and benzal fluoride. This relationship between ${}^{6}J_{90}^{H,CH_n}$ and α-substituent electronegativity was used to estimate the rotational barriers in benzal chloride and benzal bromide which were found to increase with the atomic size of the α-substituent. This trend supports the assumption that it is largely the steric interaction between the _ortho_ hydrogen atoms and the side-chain substituents which influence the barrier magnitude.

A series of benzal compounds in which the α carbon was incorporated into a saturated ring system was the 3,5-dichloro derivatives of phenylcyclohexane, 2-phenyl-1,3-dithiane, 2-phenyl-1,3-dioxane, and 2-phenyl-1,3-dioxolane. The phenylcyclohexane was found to have a barrier very similar to the ones in isopropylbenzene and phenylcyclopropane. Thus, the steric requirements

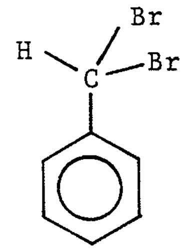
Figure 17. The rotational barriers of the benzyl and benzal compounds determined in the present study. Only the barriers found by means of $^{6}J_{p}^{H,CH_n}$ are shown. All the barriers have values of kcal/mole.



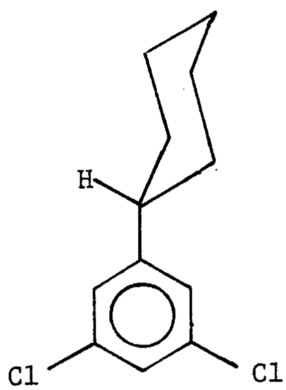
2.0 ± 0.2



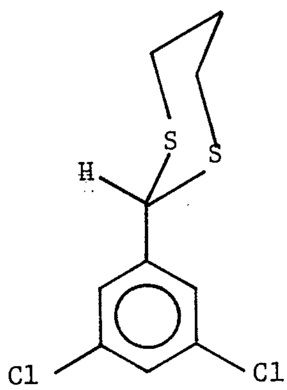
2.2 ± 0.3



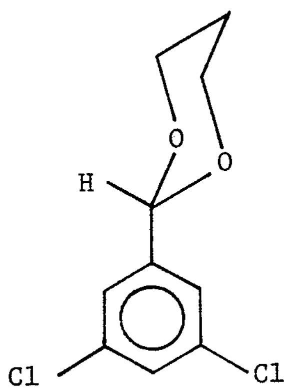
$3.5_5 \pm 0.6$



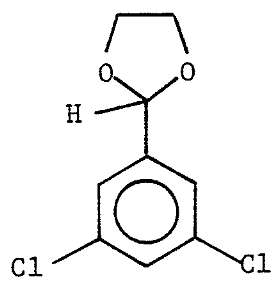
2.1 ± 0.3



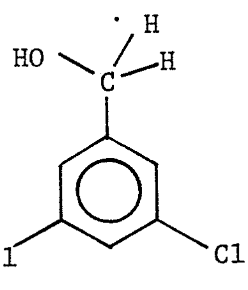
$2.3_5 \pm 0.4$



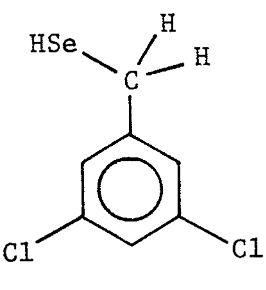
0.5 ± 0.2



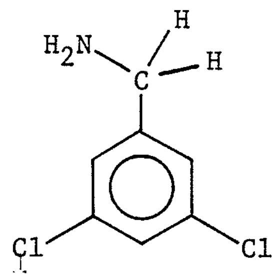
$0.8_5 \pm 0.3$



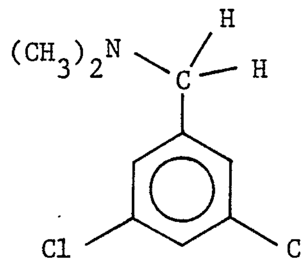
0.3 ± 0.2



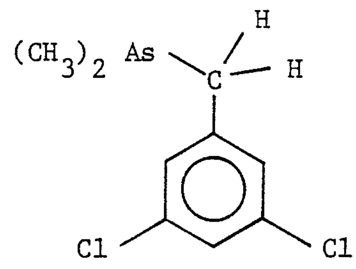
3.6 ± 1.0



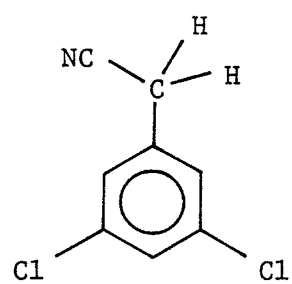
0.3 ± 0.3



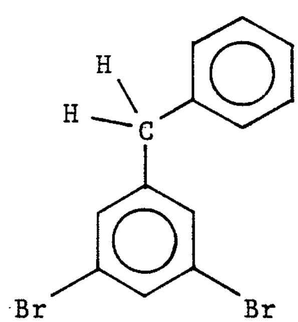
0.8 ± 0.3



3.0 ± 0.7



0.3 ± 0.2



1.1 ± 0.2

for saturated carbon substituents were considered to be similar and that only the directly bonded groups actually influenced the barrier magnitude.

The barriers in the phenyl-substituted heterocycles showed the same trend as in the benzal halides, that is, increasing barrier with increasing atomic size of the α-substituent. The phenyldithiane had a larger barrier than either the phenyldioxane or phenyldioxolane. ${}^{6}J_{90}^{H,CH_n}$ was estimated from the linear relationship between substituent electronegativity and the coupling as already mentioned.

In all the benzal compounds the minimum energy conformation was found to be the one in which the C_α-H bond occupied the plane of the aromatic ring.

The benzyl compounds studied had α-substituents of group 5B and 6B of the periodic table, and were 3,5-dichloro derivatives of benzyl alcohol and selenol, and benzylamine, benzyldimethylamine, and benzyldimethylarsine. ${}^{6}J_{90}^{H,CH_n}$ for the compounds was again estimated from the linear relationship of the coupling with the α-substituent electronegativity. The barriers showed that the bulkier the α-substituent the greater the barrier.

All but one of the compounds had a minimum energy conformation in which the C_α-X bond, where X is the substituent, was oriented perpendicular to the aromatic ring plane. The exception was benzyl alcohol where this bond preferred the aromatic plane in the rotational ground state. Thus, most of the benzyl compounds were found in the rotational conformation in which the steric interaction between the *ortho* hydrogen atoms and the α-substituent are minimized, implying that steric interactions are the dominant component of the rotational potential energy.

Because $^6J_p^{H,CH_n}$ had a $\sin^2\theta$ dependence on the $C_{\underline{ortho}}$-C_1-C_α-H dihedral angle, the same dependence was thought to occur for the long-range side-chain proton to *para* ring fluorine coupling, $^6J_p^{F,CH_n}$, in p-fluorotoluene derivatives, and that this coupling was described by a similar expression

$$^6J_p^{F,CH_n} = {}^6J_{90}^{F,CH_n} \langle \sin^2\theta \rangle . \qquad [36]$$

Rotational barriers determined from $^6J_p^{F,CH_n}$ in a series of p-fluorobenzyl and -benzal compounds were compared to the barriers in non-fluorinated compounds with the same side-chain substituents and determined from $^6J_p^{H,CN_n}$. The barriers from the proton-fluorine couplings were generally larger than those from the proton-proton couplings which were taken to be the more reliable for a number of reasons. However, the proton-fluorine coupling gave a rough estimate of the barrier and predicted the same minimum energy conformation in all cases as those predicted from the proton-proton coupling.

Finally, derivatives of diphenylmethane were investigated and the rotational barrier determined from both $^6J_p^{H,CH_2}$ and $^6J_p^{F,CH_2}$. The proton-proton coupling was used to find the barrier in 3,5-dibromodiphenylmethane while the proton-fluorine coupling was used to find the barrier in 4,4'-difluorodiphenylmethane. The barrier in the latter compound was inferred from the temperature dependence of the coupling, $^6J_p^{F,CH_2}$. As found for the p-fluorotoluene derivatives, the barrier in the 4,4'-difluorodiphenylmethane was larger than the barrier in 3,5-difluorodiphenylmethane. Whether the difference originated in unknown influences on the coupling constants or from an actual difference in the barriers could not be deduced. The gable conformation of diphenylmethane was predicted by both couplings as the ground state rotational conformer.

The J method seems to be a good technique for measuring rotational barriers of some benzyl and benzal compounds in solution. Many of the compounds which have been studied by the J method have not been investigated by any other method and those which have often show contradictory results, either in the barrier or predicted low energy conformer. More studies of benzyl and benzal compounds by different methods would be desirable in order to resolve some of the contradictions.

FUTURE CONSIDERATIONS

Several possibilities occur for future experiments involving the J method, especially with the high field and heteronuclear capabilities of present day NMR spectrometers.

In the present study, the majority of the molecules had either chlorine or bromine substituted at the 3 and 5 positions of the benzene ring. This was necessary to simplify the spectrum from the unsubstituted compound which often had a very small spectral dispersion. The use of a spectrometer with a higher field would separate the resonances of the parent compound, perhaps sufficiently enough for an analysis. The effect of _meta_ substituents on the rotational barrier, which had been assumed negligible, could then be identified.

The only couplings considered in the present work to be transmitted solely by a σ-π mechanism, and, thus, allowing rotational barrier determinations, are the six-bond couplings between the side-chain proton(s) of α-substitued toluene and the ring _para_ proton or fluorine nucleus. Theoretical INDO calculations of the five-bond coupling constant between the side-chain proton and the ring _para_ carbon atom, ${}^{5}J_{p}^{C,CH_n}$, (117) have indicated a $\sin^2\theta$ dependence for this coupling, and a σ-π mechanism for the coupling transmission. Then, a rotational barrier and the ground state rotational conformation might be extracted by the J method. This coupling might not be affected by substituents at the <u>para</u> positionand, if so, can be used to determine the barrier in <u>para</u>-fluoro compounds, which generally show higher values for the barriers than the unsubstituted compounds. A measurement of the barrier from the coupling independent of the six-bond proton-fluorine coupling would indicate whether or not the barrier is actually greater in the <u>para</u>-fluoro compounds.

Another coupling which could have a $\sin^2\theta$ dependence and could be used in the J method is the one between a β carbon atom, that is, one bonded to the α carbon, and the benzene ring <u>para</u> proton or fluorine atom, $^6J_p^{H,CC_n}$ or $^6J_p^{F,CC_n}$.

All these couplings can be investigated by means of high-field multinuclear FT spectrometers.

Finally, the J method could be extended to asymmetric potentials. In this case the Fourier expansion of the potential hindering internal rotation,

$$V(\alpha) = \sum_{n=0}^{\infty} \frac{V_n}{2} [1 - \cos(n\alpha)] \qquad [3]$$

would have the coefficients, V_n, of comparable magnitude. Then, two or more different couplings would be required to determine the same number of coefficients. As was suggested above, there can be a number of stereospecific couplings in a substituted toluene molecule which could be used to determine the V_n coefficients.

APPENDIX I

This appendix lists $<\sin^2\theta>$ versus V_2 for various parameters.

The first table lists $<\sin^2\theta>$ at 305 K for a rotational conformation in which $\theta_{min} = 0°$; for a reduced moment of inertia, I_r, from 0.5 to 4.0 x 10^{-38} g cm^2, and a rotational barrier, V_2, from 0.0 to 4.0 kcal/mole.

The second table lists $<\sin^2\theta>$ at 305 K for a rotational conformation in which $\theta_{min} = (30°,30°)$. The increments of I_r have been reduced because of the insensitivity of $<\sin^2\theta>$ to V_2. All other parameters are as described for the first table.

The remaining tables list $<\sin^2\theta>$ for a rotational conformation in which $\theta_{min} = 0°$; and I_r = 1.0 to 4.0 x 10^{-38} g cm^2, V_2 = 0.0 to 4.0 kcal/mole, and the temperature, T, varies from 250 to 350 K.

The tables can be used to calculate $<\sin^2\theta>$ for any minimum enrgy conformation angle, θ_{min}, from the expression

$$<\sin^2\theta> = \cos^2\theta_{min} <\sin^2\alpha> + \sin^2\theta_{min} <\cos^2\alpha> \qquad [A1]$$

where $<\sin^2\alpha> = <\sin^2\theta>$ when $\theta_{min} = 0°$ and $<\cos^2\alpha> = 1 - <\sin^2\alpha>$.

For benzal compounds, equation [A1] gives $<\sin^2\theta>$ directly for any value of θ_{min}. For benzyl compounds, where two different values of θ_{min}, say θ_{min1} and θ_{min2}, are possible, $<\sin^2\theta>$ is given by the expression

$$<\sin^2\theta> = \frac{<\sin^2\theta>_{\theta_{min1}} + <\sin^2\theta>_{\theta_{min2}}}{2} . \qquad [A2]$$

If $\theta_{min1} = 0°$ and $\theta_{min2} = 60°$ then

$$<\sin^2\theta> = 0.25 <\sin^2\alpha> + 0.375 .$$

Thirty and thirty-one expansion terms were used for the odd and even expansion functions in the calculation of the $<\sin^2\theta>$ values.

$\theta_{min} = 0^o$ $T = 305$ K

I_r =	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
V_2								
0.0	0.5000	0.5000	0.5000	0.5000	0.5000	0.5000	0.5000	0.5000
0.1	0.4794	0.4794	0.4794	0.4795	0.4795	0.4795	0.4795	0.4796
0.2	0.4590	0.4590	0.4590	0.4590	0.4591	0.4591	0.4592	0.4592
0.3	0.4387	0.4387	0.4387	0.4388	0.4389	0.4389	0.4390	0.4391
0.4	0.4188	0.4187	0.4188	0.4189	0.4190	0.4191	0.4191	0.4192
0.5	0.3992	0.3992	0.3992	0.3994	0.3995	0.3996	0.3997	0.3998
0.6	0.3801	0.3801	0.3802	0.3803	0.3804	0.3806	0.3807	0.3808
0.7	0.3616	0.3615	0.3616	0.3618	0.3619	0.3621	0.3622	0.3623
0.8	0.3437	0.3436	0.3437	0.3439	0.3441	0.3442	0.3444	0.3445
0.9	0.3264	0.3263	0.3265	0.3267	0.3268	0.3270	0.3272	0.3273
1.0	0.3099	0.3098	0.3099	0.3101	0.3103	0.3105	0.3107	0.3108
1.1	0.2941	0.2940	0.2941	0.2943	0.2945	0.2947	0.2949	0.2951
1.2	0.2790	0.2789	0.2790	0.2793	0.2795	0.2797	0.2799	0.2800
1.3	0.2647	0.2646	0.2647	0.2650	0.2652	0.2654	0.2656	0.2658
1.4	0.2511	0.2510	0.2512	0.2514	0.2517	0.2519	0.2521	0.2523
1.5	0.2383	0.2382	0.2384	0.2386	0.2389	0.2391	0.2393	0.2395
1.6	0.2263	0.2262	0.2263	0.2266	0.2268	0.2271	0.2273	0.2274
1.7	0.2149	0.2148	0.2150	0.2152	0.2155	0.2157	0.2159	0.2161
1.8	0.2043	0.2042	0.2043	0.2046	0.2048	0.2051	0.2053	0.2055
1.9	0.1943	0.1942	0.1943	0.1946	0.1949	0.1951	0.1953	0.1955
2.0	0.1850	0.1848	0.1850	0.1852	0.1855	0.1858	0.1860	0.1862
2.1	0.1762	0.1761	0.1762	0.1765	0.1768	0.1770	0.1772	0.1774
2.2	0.1681	0.1679	0.1681	0.1683	0.1686	0.1688	0.1690	0.1692
2.3	0.1604	0.1603	0.1604	0.1607	0.1610	0.1612	0.1614	0.1616
2.4	0.1533	0.1531	0.1533	0.1536	0.1538	0.1541	0.1543	0.1545
2.5	0.1466	0.1465	0.1466	0.1469	0.1472	0.1474	0.1476	0.1478
2.6	0.1404	0.1403	0.1404	0.1407	0.1409	0.1412	0.1414	0.1416
2.7	0.1346	0.1345	0.1346	0.1349	0.1351	0.1354	0.1356	0.1357
2.8	0.1292	0.1290	0.1292	0.1294	0.1297	0.1299	0.1301	0.1303
2.9	0.1241	0.1240	0.1241	0.1244	0.1246	0.1248	0.1251	0.1252
3.0	0.1194	0.1192	0.1194	0.1196	0.1199	0.1201	0.1203	0.1205
3.1	0.1150	0.1148	0.1149	0.1152	0.1154	0.1157	0.1159	0.1160
3.2	0.1108	0.1107	0.1108	0.1110	0.1113	0.1115	0.1117	0.1119
3.3	0.1069	0.1068	0.1069	0.1071	0.1074	0.1076	0.1078	0.1080
3.4	0.1033	0.1031	0.1033	0.1035	0.1037	0.1039	0.1041	0.1043
3.5	0.0999	0.0997	0.0998	0.1001	0.1003	0.1005	0.1007	0.1008
3.6	0.0966	0.0965	0.0966	0.0968	0.0971	0.0973	0.0975	0.0976
3.7	0.0936	0.0934	0.0936	0.0938	0.0940	0.0942	0.0944	0.0946
3.8	0.0907	0.0906	0.0907	0.0909	0.0912	0.0914	0.0916	0.0917
3.9	0.0881	0.0879	0.0880	0.0883	0.0885	0.0887	0.0888	0.0890
4.0	0.0855	0.0854	0.0855	0.0857	0.0859	0.0861	0.0863	0.0864

θ_{min} = (30°,30°) T = 305 K

I_r = V_2	1.0	2.0	3.0	4.0
0.0	0.5000	0.5000	0.5000	0.5000
0.1	0.4897	0.4898	0.4898	0.4898
0.2	0.4795	0.4795	0.4796	0.4796
0.3	0.4693	0.4694	0.4695	0.4695
0.4	0.4594	0.4594	0.4595	0.4596
0.5	0.4496	0.4497	0.4498	0.4499
0.6	0.4400	0.4401	0.4403	0.4404
0.7	0.4308	0.4309	0.4310	0.4312
0.8	0.4218	0.4219	0.4221	0.4222
0.9	0.4132	0.4133	0.4135	0.4137
1.0	0.4049	0.4051	0.4053	0.4054
1.1	0.3970	0.3972	0.3974	0.3975
1.2	0.3894	0.3896	0.3899	0.3900
1.3	0.3823	0.3825	0.3827	0.3829
1.4	0.3755	0.3757	0.3759	0.3761
1.5	0.3691	0.3693	0.3696	0.3697
1.6	0.3631	0.3633	0.3635	0.3637
1.7	0.3574	0.3576	0.3579	0.3581
1.8	0.3521	0.3523	0.3525	0.3527
1.9	0.3471	0.3473	0.3476	0.3478
2.0	0.3424	0.3426	0.3429	0.3431
2.1	0.3380	0.3383	0.3385	0.3387
2.2	0.3339	0.3342	0.3344	0.3346
2.3	0.3301	0.3303	0.3306	0.3308
2.4	0.3266	0.3268	0.3270	0.3272
2.5	0.3232	0.3234	0.3237	0.3239
2.6	0.3201	0.3203	0.3206	0.3208
2.7	0.3172	0.3174	0.3177	0.3179
2.8	0.3145	0.3147	0.3150	0.3152
2.9	0.3120	0.3122	0.3124	0.3126
3.0	0.3096	0.3098	0.3100	0.3102
3.1	0.3074	0.3076	0.3078	0.3080
3.2	0.3053	0.3055	0.3057	0.3059
3.3	0.3034	0.3036	0.3038	0.3040
3.4	0.3016	0.3017	0.3020	0.3021
3.5	0.2998	0.3000	0.3002	0.3004
3.6	0.2982	0.2984	0.2986	0.2988
3.7	0.2967	0.2969	0.2971	0.2973
3.8	0.2953	0.2955	0.2957	0.2958
3.9	0.2940	0.2941	0.2943	0.2945
4.0	0.2927	0.2929	0.2931	0.2932

$\theta_{min} = 0°$ T = 250 K

I_r	1.0	2.0	3.0	4.0
V_2				
0.0	0.5000	0.5000	0.5000	0.5000
0.1	0.4749	0.4749	0.4750	0.4750
0.2	0.4500	0.4501	0.4502	0.4503
0.3	0.4255	0.4256	0.4257	0.4258
0.4	0.4015	0.4016	0.4018	0.4019
0.5	0.3782	0.3783	0.3786	0.3788
0.6	0.3557	0.3559	0.3561	0.3564
0.7	0.3342	0.3344	0.3347	0.3349
0.8	0.3137	0.3139	0.3142	0.3145
0.9	0.2943	0.2945	0.2948	0.2951
1.0	0.2760	0.2762	0.2765	0.2769
1.1	0.2588	0.2590	0.2594	0.2598
1.2	0.2427	0.2430	0.2434	0.2437
1.3	0.2278	0.2280	0.2285	0.2288
1.4	0.2139	0.2142	0.2146	0.2150
1.5	0.2011	0.2013	0.2018	0.2021
1.6	0.1892	0.1895	0.1899	0.1903
1.7	0.1783	0.1785	0.1790	0.1794
1.8	0.1682	0.1685	0.1689	0.1693
1.9	0.1589	0.1592	0.1596	0.1600
2.0	0.1504	0.1506	0.1511	0.1515
2.1	0.1426	0.1428	0.1432	0.1436
2.2	0.1354	0.1356	0.1360	0.1364
2.3	0.1287	0.1289	0.1294	0.1297
2.4	0.1226	0.1228	0.1232	0.1236
2.5	0.1170	0.1172	0.1176	0.1180
2.6	0.1118	0.1120	0.1124	0.1127
2.7	0.1070	0.1072	0.1076	0.1079
2.8	0.1026	0.1028	0.1031	0.1035
2.9	0.0985	0.0986	0.0990	0.0994
3.0	0.0946	0.0948	0.0952	0.0955
3.1	0.0911	0.0913	0.0917	0.0920
3.2	0.0878	0.0880	0.0884	0.0887
3.3	0.0847	0.0849	0.0853	0.0856
3.4	0.0819	0.0820	0.0824	0.0827
3.5	0.0792	0.0794	0.0797	0.0800
3.6	0.0767	0.0769	0.0772	0.0775
3.7	0.0743	0.0745	0.0748	0.0751
3.8	0.0721	0.0723	0.0726	0.0729
3.9	0.0700	0.0702	0.0705	0.0708
4.0	0.0681	0.0682	0.0685	0.0688

$\theta_{min} = 0°$ $T = 270$ K

I_r	1.0	2.0	3.0	4.0
V_2				
0.0	0.5000	0.5000	0.5000	0.5000
0.1	0.4768	0.4768	0.4768	0.4769
0.2	0.4537	0.4537	0.4538	0.4539
0.3	0.4309	0.4310	0.4311	0.4313
0.4	0.4085	0.4087	0.4088	0.4090
0.5	0.3867	0.3869	0.3871	0.3873
0.6	0.3656	0.3658	0.3661	0.3663
0.7	0.3452	0.3454	0.3457	0.3460
0.8	0.3257	0.3259	0.3263	0.3266
0.9	0.3071	0.3073	0.3077	0.3080
1.0	0.2894	0.2897	0.2901	0.2904
1.1	0.2727	0.2730	0.2734	0.2737
1.2	0.2569	0.2572	0.2577	0.2580
1.3	0.2422	0.2425	0.2429	0.2433
1.4	0.2283	0.2286	0.2291	0.2295
1.5	0.2154	0.2157	0.2162	0.2166
1.6	0.2034	0.2037	0.2042	0.2046
1.7	0.1922	0.1925	0.1930	0.1934
1.8	0.1818	0.1821	0.1826	0.1830
1.9	0.1722	0.1725	0.1730	0.1734
2.0	0.1633	0.1636	0.1641	0.1645
2.1	0.1551	0.1554	0.1558	0.1562
2.2	0.1474	0.1477	0.1482	0.1486
2.3	0.1404	0.1407	0.1411	0.1415
2.4	0.1338	0.1341	0.1346	0.1350
2.5	0.1278	0.1281	0.1285	0.1289
2.6	0.1222	0.1225	0.1229	0.1233
2.7	0.1170	0.1173	0.1177	0.1181
2.8	0.1122	0.1124	0.1129	0.1132
2.9	0.1077	0.1079	0.1084	0.1087
3.0	0.1035	0.1038	0.1042	0.1045
3.1	0.0996	0.0999	0.1003	0.1006
3.2	0.0960	0.0963	0.0967	0.0970
3.3	0.0926	0.0929	0.0933	0.0936
3.4	0.0895	0.0897	0.0901	0.0904
3.5	0.0865	0.0868	0.0872	0.0875
3.6	0.0838	0.0840	0.0844	0.0847
3.7	0.0812	0.0814	0.0818	0.0821
3.8	0.0787	0.0789	0.0793	0.0796
3.9	0.0764	0.0766	0.0770	0.0773
4.0	0.0742	0.0745	0.0748	0.0751

$\theta_{min} = 0°$ $T = 290$ K

I_r	1.0	2.0	3.0	4.0
V_2				
0.0	0.5000	0.5000	0.5000	0.5000
0.1	0.4784	0.4784	0.4784	0.4785
0.2	0.4568	0.4569	0.4570	0.4571
0.3	0.4356	0.4357	0.4358	0.4359
0.4	0.4146	0.4148	0.4150	0.4151
0.5	0.3942	0.3944	0.3946	0.3948
0.6	0.3743	0.3745	0.3747	0.3749
0.7	0.3550	0.3552	0.3555	0.3558
0.8	0.3364	0.3366	0.3370	0.3372
0.9	0.3185	0.3188	0.3192	0.3195
1.0	0.3015	0.3018	0.3022	0.3025
1.1	0.2853	0.2856	0.2860	0.2864
1.2	0.2699	0.2702	0.2707	0.2710
1.3	0.2554	0.2557	0.2562	0.2565
1.4	0.2417	0.2420	0.2425	0.2429
1.5	0.2288	0.2292	0.2296	0.2300
1.6	0.2167	0.2171	0.2176	0.2180
1.7	0.2054	0.2058	0.2063	0.2067
1.8	0.1948	0.1952	0.1957	0.1961
1.9	0.1850	0.1854	0.1858	0.1862
2.0	0.1758	0.1762	0.1767	0.1771
2.1	0.1672	0.1676	0.1681	0.1685
2.2	0.1593	0.1596	0.1601	0.1605
2.3	0.1518	0.1522	0.1527	0.1531
2.4	0.1449	0.1453	0.1458	0.1462
2.5	0.1385	0.1389	0.1394	0.1397
2.6	0.1325	0.1329	0.1334	0.1338
2.7	0.1270	0.1273	0.1278	0.1282
2.8	0.1218	0.1222	0.1226	0.1230
2.9	0.1170	0.1173	0.1178	0.1181
3.0	0.1125	0.1128	0.1133	0.1136
3.1	0.1083	0.1086	0.1091	0.1094
3.2	0.1043	0.1047	0.1051	0.1055
3.3	0.1007	0.1010	0.1014	0.1018
3.4	0.0972	0.0975	0.0980	0.0983
3.5	0.0940	0.0943	0.0947	0.0951
3.6	0.0910	0.0913	0.0917	0.0920
3.7	0.0881	0.0884	0.0888	0.0892
3.8	0.0855	0.0858	0.0862	0.0865
3.9	0.0829	0.0832	0.0836	0.0839
4.0	0.0805	0.0808	0.0812	0.0815

$\theta_{min} = 0°$ $T = 310$ K

I_r	1.0	2.0	3.0	4.0
V_2				
0.0	0.5000	0.5000	0.5000	0.5000
0.1	0.4797	0.4798	0.4798	0.4799
0.2	0.4596	0.4597	0.4598	0.4599
0.3	0.4397	0.4398	0.4399	0.4400
0.4	0.4200	0.4202	0.4203	0.4205
0.5	0.4007	0.4009	0.4011	0.4013
0.6	0.3819	0.3821	0.3824	0.3826
0.7	0.3636	0.3639	0.3642	0.3644
0.8	0.3459	0.3462	0.3465	0.3468
0.9	0.3288	0.3291	0.3295	0.3298
1.0	0.3124	0.3128	0.3131	0.3134
1.1	0.2967	0.2971	0.2975	0.2978
1.2	0.2818	0.2821	0.2826	0.2829
1.3	0.2675	0.2679	0.2684	0.2687
1.4	0.2540	0.2544	0.2549	0.2553
1.5	0.2413	0.2417	0.2422	0.2425
1.6	0.2292	0.2296	0.2301	0.2305
1.7	0.2179	0.2183	0.2188	0.2192
1.8	0.2072	0.2076	0.2081	0.2085
1.9	0.1972	0.1976	0.1981	0.1985
2.0	0.1878	0.1882	0.1887	0.1891
2.1	0.1790	0.1794	0.1799	0.1803
2.2	0.1707	0.1712	0.1717	0.1721
2.3	0.1630	0.1635	0.1640	0.1644
2.4	0.1558	0.1563	0.1568	0.1572
2.5	0.1491	0.1495	0.1501	0.1504
2.6	0.1428	0.1432	0.1438	0.1441
2.7	0.1369	0.1374	0.1379	0.1382
2.8	0.1314	0.1319	0.1324	0.1327
2.9	0.1263	0.1267	0.1272	0.1276
3.0	0.1215	0.1219	0.1224	0.1228
3.1	0.1170	0.1174	0.1179	0.1182
3.2	0.1128	0.1132	0.1136	0.1140
3.3	0.1088	0.1092	0.1097	0.1100
3.4	0.1051	0.1055	0.1059	0.1063
3.5	0.1016	0.1020	0.1024	0.1028
3.6	0.0983	0.0987	0.0991	0.0995
3.7	0.0952	0.0956	0.0960	0.0964
3.8	0.0923	0.0927	0.0931	0.0935
3.9	0.0896	0.0899	0.0904	0.0907
4.0	0.0870	0.0873	0.0878	0.0881

$\theta_{min} = 0°$ T = 330 K

I_r	1.0	2.0	3.0	4.0
V_2				
0.0	0.5000	0.5000	0.5000	0.5000
0.1	0.4810	0.4810	0.4811	0.4811
0.2	0.4620	0.4621	0.4622	0.4623
0.3	0.4433	0.4434	0.4435	0.4436
0.4	0.4247	0.4249	0.4251	0.4252
0.5	0.4065	0.4067	0.4070	0.4071
0.6	0.3887	0.3889	0.3892	0.3894
0.7	0.3713	0.3716	0.3719	0.3721
0.8	0.3544	0.3547	0.3550	0.3553
0.9	0.3380	0.3384	0.3388	0.3390
1.0	0.3223	0.3226	0.3230	0.3233
1.1	0.3071	0.3075	0.3079	0.3082
1.2	0.2926	0.2930	0.2934	0.2938
1.3	0.2787	0.2791	0.2796	0.2799
1.4	0.2654	0.2659	0.2664	0.2667
1.5	0.2528	0.2533	0.2538	0.2542
1.6	0.2409	0.2414	0.2419	0.2422
1.7	0.2296	0.2301	0.2306	0.2309
1.8	0.2189	0.2194	0.2199	0.2203
1.9	0.2088	0.2093	0.2098	0.2102
2.0	0.1992	0.1997	0.2003	0.2007
2.1	0.1903	0.1908	0.1913	0.1917
2.2	0.1819	0.1824	0.1829	0.1833
2.3	0.1739	0.1744	0.1750	0.1754
2.4	0.1665	0.1670	0.1675	0.1679
2.5	0.1595	0.1600	0.1605	0.1609
2.6	0.1529	0.1534	0.1540	0.1544
2.7	0.1468	0.1473	0.1478	0.1482
2.8	0.1410	0.1415	0.1420	0.1424
2.9	0.1356	0.1361	0.1366	0.1370
3.0	0.1305	0.1310	0.1315	0.1319
3.1	0.1257	0.1262	0.1267	0.1271
3.2	0.1212	0.1217	0.1222	0.1225
3.3	0.1170	0.1175	0.1179	0.1183
3.4	0.1130	0.1135	0.1140	0.1143
3.5	0.1093	0.1097	0.1102	0.1106
3.6	0.1058	0.1062	0.1067	0.1070
3.7	0.1024	0.1029	0.1033	0.1037
3.8	0.0993	0.0997	0.1002	0.1005
3.9	0.0963	0.0968	0.0972	0.0976
4.0	0.0935	0.0940	0.0944	0.0947

$\theta_{min} = 0°$ T = 350 K

I_r	1.0	2.0	3.0	4.0
V_2				
0.0	0.5000	0.5000	0.5000	0.5000
0.1	0.4821	0.4821	0.4822	0.4822
0.2	0.4642	0.4643	0.4644	0.4645
0.3	0.4465	0.4466	0.4467	0.4468
0.4	0.4290	0.4291	0.4293	0.4294
0.5	0.4117	0.4119	0.4121	0.4123
0.6	0.3948	0.3950	0.3953	0.3955
0.7	0.3782	0.3785	0.3788	0.3790
0.8	0.3621	0.3624	0.3627	0.3630
0.9	0.3464	0.3468	0.3471	0.3474
1.0	0.3312	0.3316	0.3320	0.3323
1.1	0.3166	0.3170	0.3174	0.3177
1.2	0.3025	0.3029	0.3034	0.3037
1.3	0.2890	0.2894	0.2899	0.2902
1.4	0.2760	0.2765	0.2769	0.2773
1.5	0.2636	0.2641	0.2646	0.2649
1.6	0.2518	0.2523	0.2528	0.2532
1.7	0.2406	0.2411	0.2416	0.2420
1.8	0.2299	0.2304	0.2310	0.2313
1.9	0.2198	0.2203	0.2208	0.2212
2.0	0.2102	0.2107	0.2113	0.2117
2.1	0.2011	0.2017	0.2022	0.2026
2.2	0.1926	0.1931	0.1936	0.1940
2.3	0.1845	0.1850	0.1856	0.1860
2.4	0.1768	0.1774	0.1779	0.1783
2.5	0.1696	0.1702	0.1707	0.1711
2.6	0.1629	0.1634	0.1639	0.1643
2.7	0.1565	0.1570	0.1576	0.1579
2.8	0.1504	0.1510	0.1515	0.1519
2.9	0.1448	0.1453	0.1459	0.1462
3.0	0.1394	0.1400	0.1405	0.1409
3.1	0.1344	0.1349	0.1355	0.1358
3.2	0.1297	0.1302	0.1307	0.1311
3.3	0.1252	0.1257	0.1262	0.1266
3.4	0.1210	0.1215	0.1220	0.1224
3.5	0.1170	0.1175	0.1180	0.1184
3.6	0.1133	0.1138	0.1143	0.1146
3.7	0.1097	0.1102	0.1107	0.1111
3.8	0.1064	0.1069	0.1073	0.1077
3.9	0.1032	0.1037	0.1042	0.1045
4.0	0.1002	0.1007	0.1011	0.1015

APPENDIX II

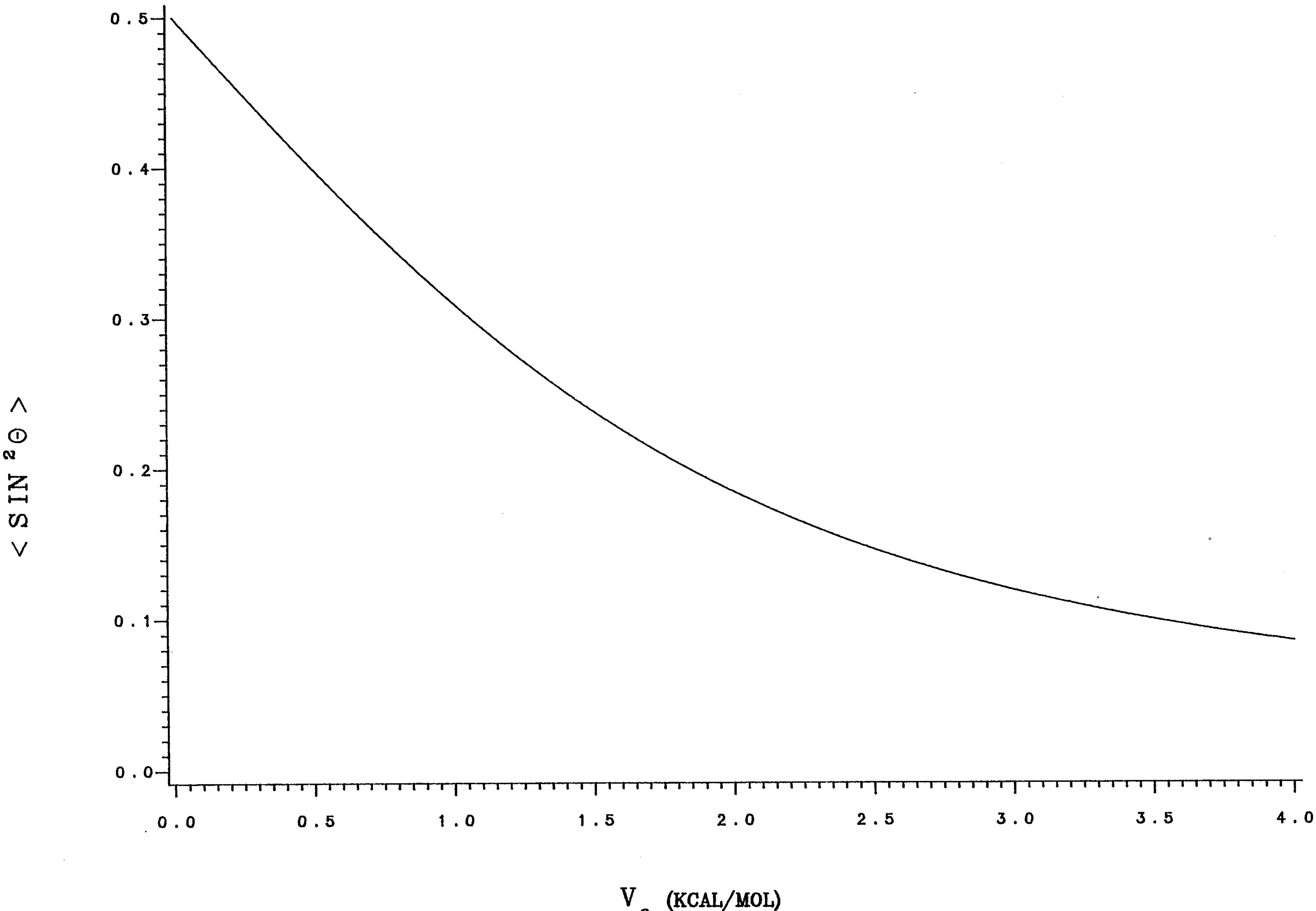
The following are plots of $<\sin^2\theta>$ versus V_2, taken from the data of Appendix I.

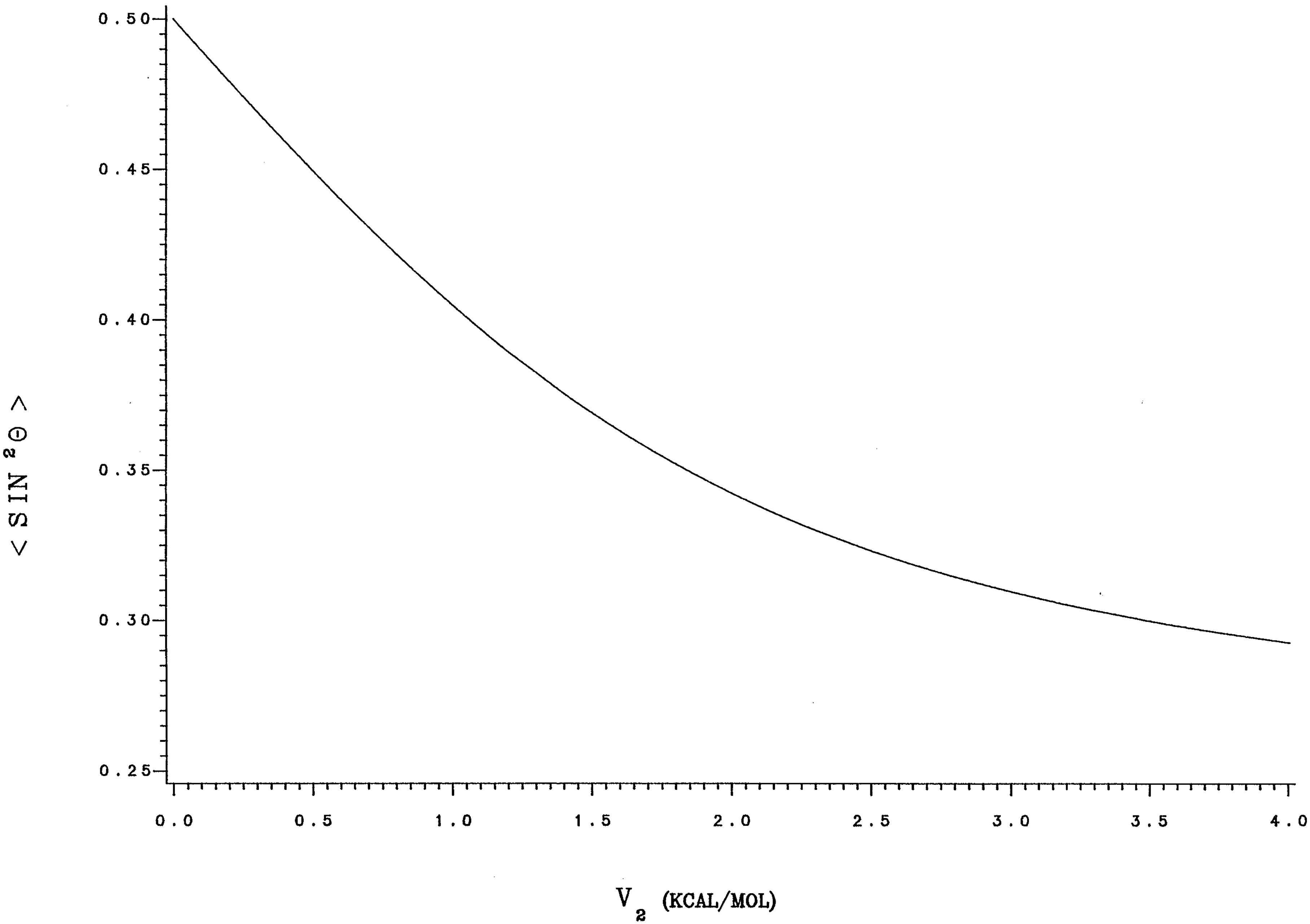
The first graph is a plot of $<\sin^2\theta>$ versus V_2 for a minimum energy conformation having $\theta_{min} = 0°$, $I_r = 1.0 \times 10^{-38}$ g cm^2, and T = 305 K.

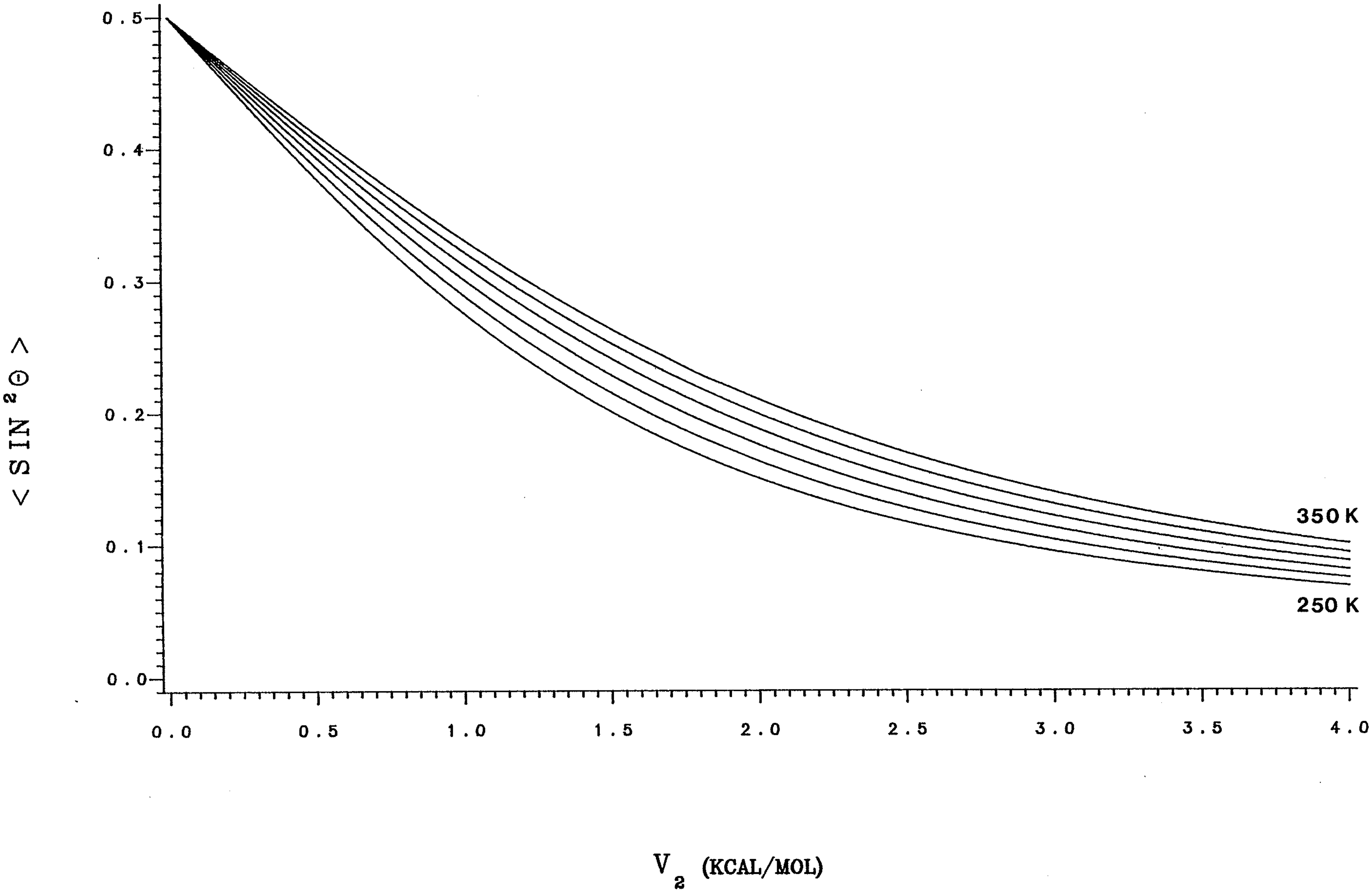
The second graph is a plot of $<\sin^2\theta>$ versus V_2 for a minimum energy conformation having $\theta_{min} = (30°, 30°)$, $I_r = 1.0 \times 10^{-38}$ g cm^2, and T = 305 K.

The third graph is a plot of $<\sin^2\theta>$ versus V_2 for a minimum energy conformation having $\theta_{min} = 0°$, $I_r = 1.0 \times 10^{-38}$ g cm^2, and for six temperatures: 250, 270, 290, 310, 330, and 350 K.

The program EXPECT allows a plot of $<\sin^2\theta>$ versus V_2 to be generated for any value of the reduced moment of inertia, I_r, and the temperature, T.


0.5
0.4
0.3
0.2
0.1
0.0
< SIN ²Θ >
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
V₂ (KCAL/MOL)


0.50
0.45
0.40
0.35
0.30
0.25
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
< $SIN^2\Theta$ >
V_2 (KCAL/MOL)



0.5
0.4
0.3
0.2
0.1
0.0
< SIN ²Θ >
350 K
250 K
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
V₂ (KCAL/MOL)

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