A PROTON MAGNETIC RESONANCE STUDY OF THE EFFECT OF α - SUBSTITUENTS ON THE LONG - RANGE COUPLING CONSTANTS IN 2,6 - DICHLOROTOLUENE DERIVATIVES

by

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ABSTRACT

A short introduction to the quantum mechanical calculation of spin-spin coupling constants between protons is followed by a brief discussion of the mechanism of long-range coupling between protons separated by four, five, and six bonds. According to experiment, supported at least partially by theory, the coupling over five bonds between methyl and ring protons in toluene derivatives has contributions from both sigma and pi electrons. The analogous coupling over six bonds is dominated by a pi electron mechanism. Both couplings are quite insensitive to ring substitution but are evidently sensitive to the conformation of the C-H bonds in the methyl group.

In this thesis it is shown that α - substitution of 2,6 - dichlorotoluene changes the six - bond coupling but leaves the five - bond coupling unchanged. The six - bond coupling decreases in a roughly linear fashion as the electronegativity of the α - substituent increases. Extrapolation to the electronegativity of hydrogen yields a coupling of -0.3 Hz, half the observed value in 2,6 - dichlorotoluene. The value of -0.3 Hz for the six - bond coupling is consistent with a pi electron mechanism operating for a conformation of α - X - 2,6 - dichlorotoluene in which the C - X bond lies perpendicular to the plane of the aromatic ring.

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Introduction

1) Origin of Nuclear Spin - Spin Coupling

Nuclear spin - spin coupling arises through the perturbation by one nucleus of the valence electrons which then produce a small magnetic field at the other nucleus. The nuclear spin interacts with the electrons in three ways * (1).

a) The magnetic field of the nuclear dipole interacts with the orbital magnetic moments of the electrons. The Hamiltonian for this interaction is given by

$$H = g_e g_N \beta_N \beta \frac{\underline{L} \cdot \underline{I}}{r^3} \qquad 1.$$

where g_e and g_N are the Lande' g factors for the electron and for the nucleus, β_N is the nuclear magneton, β is the Bohr magneton, and r is the distance between the nucleus and the electron. $\underline{L}$ is the orbital angular momentum operator and $\underline{I}$ is the nuclear spin angular momentum operator. For an S electron this term is zero since $L = O$. The contribution made by this term to the overall coupling is considered to be small, about 3 Hertz (Hz), in the hydrogen molecule (2).

b) The nuclear dipole magnetic field interacts with the electronic spin dipole to polarize the electronic spins. This magnetic field of the electronic spins acts directly on the second nucleus. This interaction is analogous to the interaction between two magnetic dipoles. Selectrons, because of their spherical symmetry, do not experience

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* Sections 1 and 2 of this chapter follow the treatment of reference 1 closely.

this interaction. The contribution of the dipole - dipole interaction to the overall coupling has been estimated to be about 20 Hz in the hydrogen molecule (2).

c) The most important term is the contact term. An S electron has a finite density at the nucleus and the nuclear spin A, in Figure 1, tends to align the spin of electron A antiparallel to itself. By the Pauli principle electron B is aligned antiparallel to A and the spin of nucleus B will be antiparallel to the spin of nucleus A.

As an illustration of the calculation of coupling constants a simple calculation of the contact term contribution to the coupling constant in the hydrogen molecule is now given.

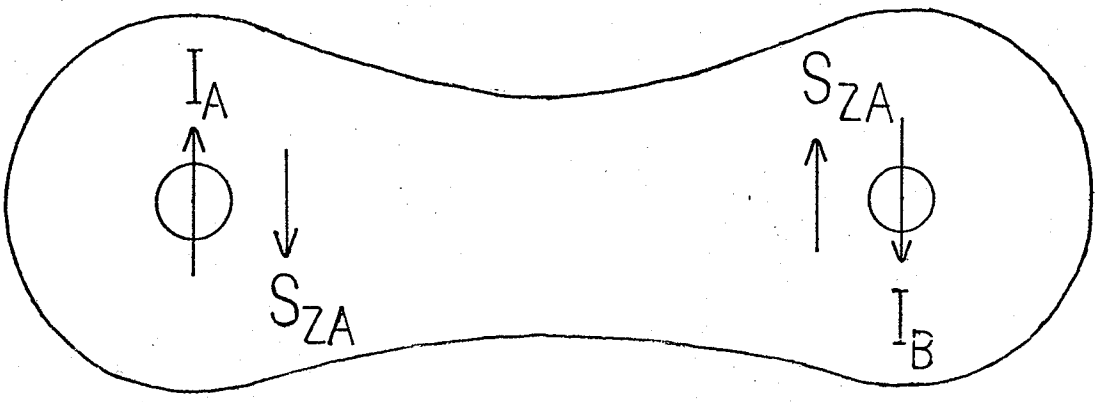


Figure 1

The Hydrogen molecule. I_A and I_B represent the nuclear spins and S_{ZA} and S_{ZB} represent the electron spins.

2) Nuclear Spin - Spin Coupling In The Hydrogen Molecule

The Hamiltonian for the contact term is given by

$$H = \frac{8}{3} \pi g_e \beta_e g_N \beta_N I_{ZA} S_{ZA} \qquad 2.$$

where $g_e, \beta_e, \beta_N, g_N$ have been defined previously. For convenience the spins are considered to be definitely quantized along the Z direction and only the Z portion of the operator $\underline{I} \cdot \underline{S}$ is retained. $\underline{I}$ is the nuclear spin angular momentum operator and $\underline{S}$ is the electronic spin angular momentum operator where

$$S_{ZA} = S_{Z1}\, \delta(\underline{r}_1 - \underline{r}_A) + S_{Z2}\, \delta(\underline{r}_2 - \underline{r}_A) \qquad 3.$$

is the "spin angular momentum density" of the two electrons at nucleus A. $\delta(\underline{r} - \underline{r}_A)$ is the Dirac delta function which requires the electron to be at nucleus A.

Taking ϕ_A and ϕ_B to be the hydrogen 1S orbitals of nuclei A and B then the simplest bonding and antibonding molecular orbitals are

$$\psi_b = \frac{1}{\sqrt{2}} (\phi_A + \phi_B) \qquad 4a.$$

$$\psi_a = \frac{1}{\sqrt{2}} (\phi_A - \phi_B) \qquad 4b.$$

Let α denote a spin $+\frac{1}{2}$ along with the z axis and let β denote a spin $-\frac{1}{2}$. The complete singlet state wave function of the hydrogen molecule to the zeroth order is

$$\psi_o = \frac{1}{\sqrt{2}} \psi_b(\underline{r}_1)\, \psi_b(\underline{r}_2)\, (\alpha_1\beta_2 - \beta_1\alpha_2) \qquad 5.$$

The contact interaction acts as a perturbation which mixes excited states with the ground state wave function. The first-order wave function is

$$\psi = \psi_o - \frac{8}{3}\pi g_e \beta g_N \beta_N I_{ZA} \sum_n \frac{\langle n | S_{ZA} | 0 \rangle}{E_n - E_o} \psi_n \qquad 6.$$

where ψ_n are excited states. The first order wave function now depends on the nuclear spin I_{ZA}.

To evaluate the electron spin angular momentum density at nucleus B the expression

$$\langle \psi | S_{ZB} | \psi \rangle \qquad 7.$$

must be evaluated, where

$$S_{ZB} = S_{Z1}\, \delta(\underline{r}_1 - \underline{r}_B) + S_{Z2}\, \delta(\underline{r}_2 - \underline{r}_B) \qquad 8.$$

and operates only on the spin functions.

$$\langle \psi | S_{ZB} | \psi \rangle = \langle \psi_o - \frac{8}{3}\pi g_e \beta g_N \beta_N I_{ZA} \sum_n \frac{\langle n | S_{ZA} | 0 \rangle}{E_n - E_o} \psi_n | S_{ZB}$$

$$\times | \psi_o - \frac{8}{3}\pi g_e \beta g_N \beta_N I_{ZA} \sum_n \frac{\langle n | S_{ZA} | 0 \rangle}{E_n - E_o} \psi_n \rangle \qquad 9.$$

$$= \langle \psi_o | S_{ZB} | \psi_o \rangle - 2 \langle \frac{8}{3}\pi g_e \beta g_N \beta_N I_{ZA} \sum_n \frac{\langle n | S_{ZA} | 0 \rangle}{E_n - E_o} \psi_n | S_{ZB} | \psi_o \rangle$$

$$+ \langle (\frac{8}{3}\pi g_e \beta g_N \beta_N)^2 I_{ZA}^2 \sum_n \frac{\langle n | S_{ZA} | 0 \rangle}{E_n - E_o} \psi_n | S_{ZB} | \sum_n \frac{\langle n | S_{ZA} | 0 \rangle}{E_n - E_o} \psi_n \rangle$$

10.

But, the first term in equation 10 is

$$\langle \psi_o | S_{ZB} | \psi_o \rangle = \tfrac{1}{2} \langle \left[\psi_b(\underline{r}_1)\, \psi_b(\underline{r}_2) \right]^2 \rangle \, X$$

$$< \alpha\beta - \beta\alpha \mid S_{Z1}\,\delta(\underline{r}_1 - \underline{r}_B) + S_{Z2}\,\delta(\underline{r}_2 - \underline{r}_B) \mid \alpha\beta - \beta\alpha > \qquad 11.$$

$$S_{Z1}(\alpha\beta - \beta\alpha) = \tfrac{1}{2}\ (\alpha\beta + \beta\alpha) \qquad 12a.$$

$$S_{Z2}(\alpha\beta - \beta\alpha) = -\tfrac{1}{2}\ (\alpha\beta + \beta\alpha) \qquad 12b.$$

Then, since $(\alpha\beta + \beta\alpha)$ is orthogonal to $(\alpha\beta - \beta\alpha)$

$$< \psi_o \mid S_{ZB} \mid \psi_o > = 0 \qquad 13.$$

The third term of equation 10 contains the matrix elements $< \psi_n \mid S_{ZB} \mid \psi_n >$. In the hydrogen molecule the most important excited state is a triplet state, where one electron has been promoted to the antibonding orbital ψ_a. The triplet spin function is symmetric but the overall function must be antisymmetric. Thus the first triplet state is

$$\psi_1 = \frac{1}{2}\left[\psi_b(\underline{r}_1)\,\psi_a(\underline{r}_2) - \psi_a(\underline{r}_1)\,\psi_b(\underline{r}_2)\right](\alpha\beta + \beta\alpha) \qquad 14a.$$

$$\psi_1' = \frac{1}{\sqrt{2}}\left[\psi_b(\underline{r}_1)\,\psi_a(\underline{r}_2) - \psi_a(\underline{r}_1)\,\psi_b(\underline{r}_2)\right](\alpha\alpha) \qquad 14b.$$

$$\psi_1'' = \frac{1}{\sqrt{2}}\left[\psi_b(\underline{r}_1)\,\psi_a(\underline{r}_2) - \psi_a(\underline{r}_1)\,\psi_b(\underline{r}_2)\right](\beta\beta) \qquad 14c.$$

Then the term

$$\begin{aligned} < \psi_1 \mid S_{ZB} \mid \psi_1 > &= K < \alpha\beta + \beta\alpha \mid S_{ZB} \mid \alpha\beta + \beta\alpha > \\ &= K < \alpha\beta + \beta\alpha \mid \alpha\beta - \beta\alpha > \\ &= 0 \end{aligned} \qquad 15.$$

where K is a constant. The other two triplets also give vanishing matrix elements. Similarly, any singlet excited state gives vanishing matrix elements.

The second term in equation ten which gives the electron spin polarization at nucleus B is

$$\left(-\frac{8}{3}\pi g_e \beta g_N \beta_N I_{ZA}\right)$$

$$\left[\sum_n \frac{\langle n|S_{ZA}|0\rangle}{E_n - E_o} \psi_n |S_{ZB}| \psi_o > + \langle \psi_o |S_{ZB}| \sum_n \frac{\langle n|S_{ZA}|0\rangle}{E_n - E_o} \psi_n \right] \quad 16.$$

where ψ_n is taken to be ψ_1, the first excited triplet state. The energy of the interaction of the spin polarization with nucleus B is given by

$$\frac{8}{3} \pi g_e \beta g_N \beta_N I_{ZB} \quad \langle \psi |S_{ZB}| \psi \rangle \qquad 17.$$

and it can be rewritten as

$$J I_{ZA} I_{ZB} = I_{ZA} I_{ZB} \left[\left(-\frac{8}{3} \pi g_e \beta g_N \beta_N\right)^2 \right.$$

$$\left. \frac{\left(\sum_n \langle n|S_{ZA}|0\rangle \langle \psi_n |S_{ZB}|\psi_o\rangle + \langle \psi_o |S_{ZB}|\psi_n\rangle \langle n|S_{ZA}|0\rangle\right)}{E_n - E_o} \right] \qquad 18.$$

Then

$$J = \left(-\frac{8}{3}\pi g_e \beta g_N \beta_N\right)^2 \sum_n \frac{\langle n|S_{ZA}|0\rangle \langle n|S_{ZB}|0\rangle + \langle 0|S_{ZB}|n\rangle \langle n|S_{ZA}|0\rangle}{E_n - E_o} \qquad 19.$$

and taking $\psi_n = \psi_1$

$$\langle 1|S_{ZA}|0\rangle = \langle \tfrac{1}{2}\left[\psi_b(\underline{r}_1)\psi_a(\underline{r}_2) - \psi_a(\underline{r}_1)\psi_b(\underline{r}_2)\right] (\alpha\beta + \beta\alpha)$$

$$x|\, S_{Z1}\, \delta(\underline{r}_1 - \underline{r}_A) + S_{Z2}\, \delta(\underline{r}_2 - \underline{r}_A)\,| \frac{1}{\sqrt{2}} \psi_b(\underline{r}_1)\psi_b(\underline{r}_2)(\alpha\beta - \beta\alpha)\rangle \qquad 20.$$

Using equation 12

$$\langle 1|S_{ZA}|0\rangle = \frac{1}{2\sqrt{2}} \langle \left[\psi_b(\underline{r}_1)\psi_a(\underline{r}_2) - \psi_a(\underline{r}_1)\psi_b(\underline{r}_2)\right| \delta(\underline{r}_1 - \underline{r}_A) - \delta(\underline{r}_2 - \underline{r}_A)$$

$$x\,|\, \psi_b(\underline{r}_1)\psi_b(\underline{r}_2)\rangle \qquad 21a.$$

$$= \frac{-1}{2\sqrt{2}} \left[\langle \psi_a(\underline{r}_2) | \delta(\underline{r}_2 - \underline{r}_A) | \psi_b(\underline{r}_2) \rangle + \langle \psi_a(\underline{r}_1) | \delta(\underline{r}_1 - \underline{r}_A) | \psi_b(\underline{r}_1) \rangle \right] \quad 21b.$$

$$= \frac{-1}{\sqrt{2}} \psi_a(\underline{r}_A) \psi_b(\underline{r}_A) \quad 21c.$$

Therefore

$$\langle 1 | S_{ZA} | 0 \rangle = \frac{-1}{2\sqrt{2}} \left(\phi_a^2(\underline{r}_A) - \phi_b^2(\underline{r}_A) \right) \quad 22.$$

$\phi_a^2(\underline{r}_A)$ will be the dominant term because ϕ_a is centred on A.

Then

$$\langle 1 | S_{ZA} | 0 \rangle = \frac{-1}{2\sqrt{2}} \phi_a^2(\underline{r}_A) \quad 23a.$$

and

$$\langle 1 | S_{ZB} | 0 \rangle = \frac{1}{2\sqrt{2}} \phi_b^2(\underline{r}_B) \quad 23b.$$

Therefore, in equation 19 the summation may be replaced by

$$\frac{2 \langle 1 | S_{ZA} | 0 \rangle \langle 1 | S_{ZB} | 0 \rangle}{E_n - E_o} = \frac{-\phi_a^2(\underline{r}_A) \phi_b^2(\underline{r}_B)}{4 (E_n - E_o)} \quad 24.$$

Then

$$J = \left(\frac{8}{3} \pi g_e \beta g_N \beta_N \right)^2 \frac{\phi_a^2(\underline{r}_A) \phi_b^2(\underline{r}_B)}{4 \Delta E} \quad 25.$$

$$= 174 \text{ Hz.}$$

The experimental value is 280 Hertz which is derived from the coupling in HD.

This calculation of the coupling in the hydrogen molecule illustrates the fact that couplings between nuclei are second order properties of a molecule and consequently their accurate calculation depends on a knowledge of accurate wave functions.

3) Valence Bond Approach To Couplings Over Many Bonds

A) Couplings Via σ - Bonds

The coupling constants over a number of bonds in saturated hydrocarbons can be described as follows:

1) The Propanic Fragment

Consider the example of coupling in a propanic fragment, Figure 2, as given by Barfield and Chakrabarti (3). The two coupled nuclei are H and H' where h and h' are their respective 1S orbitals. The expression for the coupling is given by

$$^4J_{HH'} = \frac{4185}{\Delta E} \{ p^o(h h') + \frac{3}{2} \left[p^o(h \sigma_1) p^o(\sigma_2 h') + p^o(h \sigma_2') p^o(\sigma_3' h') \right] - \frac{3}{2} \left[p^o(h c_2) p^o(c_2 h') + p^o(h c_2') p^o(c_2' h') \right] \} \quad 26.$$

where

$$p^o(hh') = \frac{1}{2} \left[\frac{K(hh') + K(cc') - K(ch') - K(c'h)}{K(hc) + K(c'h')} \right] \quad 26a.$$

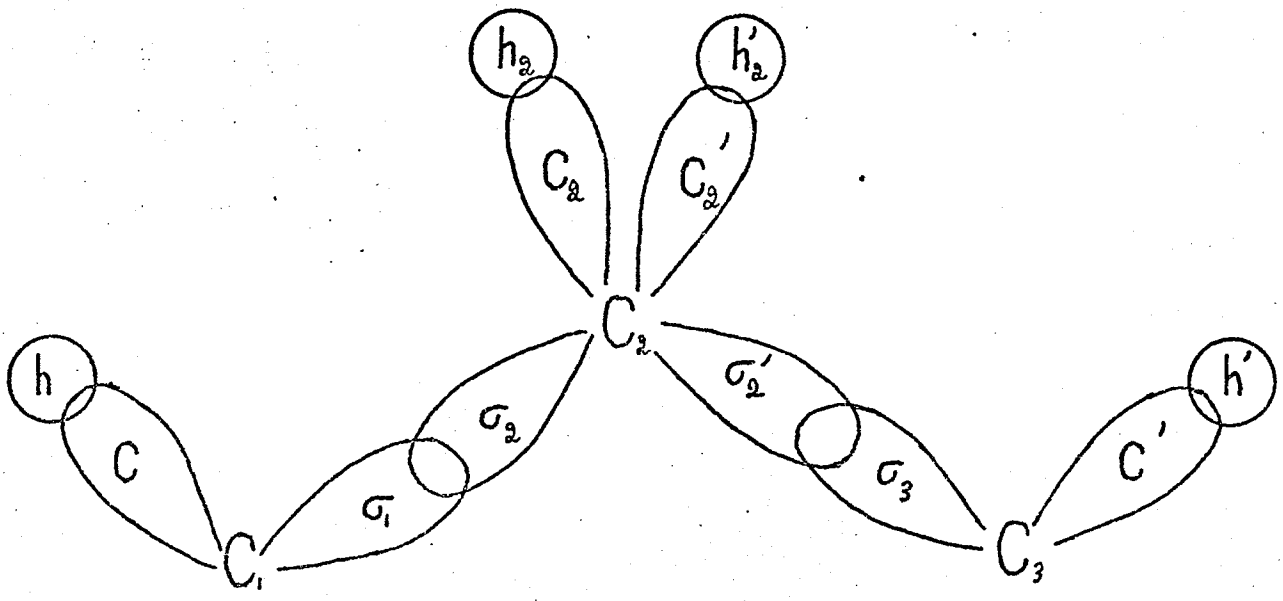
and

$$p^o(h \sigma_j) = \frac{1}{2} \left[\frac{K(h\sigma_j) + K(c\sigma_j') - K(h\sigma_j') - K(c\sigma_j)}{K(hc) + K(\sigma_j \sigma_j')} \right] \quad 26b.$$

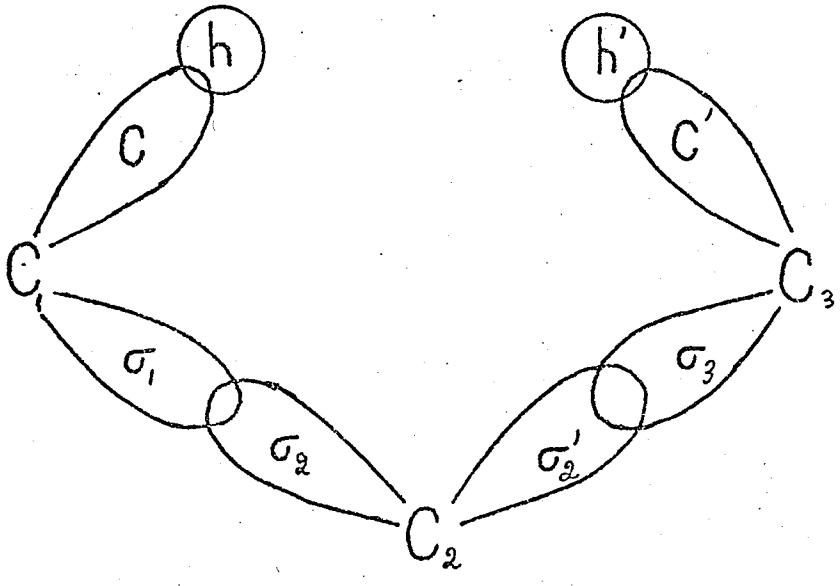
K denotes the two - electron valence bond exchange integral associated with the orbitals given in the argument. The first term in equation 26 represents the direct interaction between the two C-H bonds. The direct term is expected to depend on the conformation. In Figure 2b the direct term would be much more important than in Figure 2a. The next two terms give the geminal-vicinal coupling. The geminal term is independent of the dihedral angle but the vicinal term may be written as (3)

Figure 2

The propanic fragment. ϕ and ϕ' are the dihedral angles formed by the C - H and C - H' bonds respectively with the $C_1 - C_2 - C_3$ plane. In a) $\phi = \phi' = 180^o$ whereas in b) $\phi = \phi' = 0^o$. The direct interaction between the c - h and c' - h' bonds is expected to be more important in b) than in a) .



a)



b)

$$p^{o}(h\,\sigma_2') = A\cos^2\phi + B\cos\phi + C$$

$$p^{o}(\sigma_2 h') = A\cos^2\phi' + B\cos\phi' + C \qquad 27.$$

where ϕ and ϕ' denote the dihedral angles formed by the C-H and C-H' bonds, respectively, with the $C_1 - C_2 - C_3$ plane. In Figure 2a ϕ and ϕ' are 180^{o}. The last two terms in equation 26 give the indirect vicinal-vicinal coupling. These will again depend on the dihedral angle. Higher order terms could be included in equation 26 but these are expected to be negligible.

2) The Butanic Fragment

The butanic fragment (Figure 3) which is discussed by Barfield and Karplus (4) is a coupling over five-bonds. The indirect contributions are expected to be of major important here and can be written as

$$^{5}J_{H,H'} = \frac{4185}{\Delta E}\ \frac{3}{2}\ p^{o}(c\sigma)\,p^{o}(\sigma'c') \qquad 28.$$

Both $p^{o}(c\sigma)$ and $p^{o}(\sigma'c')$ are vicinal terms and are written as

$$p^{o}(c\sigma) = A\cos^2\phi + B\cos\phi + C$$

$$p^{o}(\sigma'c') = A\cos^2\phi' + B\cos\phi' + C \qquad 29.$$

where ϕ is the dihedral angle formed by the c-h bond with the $C_1-C_2-C_3$ plane and ϕ' is the dihedral angle formed by the c-h' bond with the $C_2-C_3-C_4$ plane. In Figure 3 $\phi = \phi' = 180^{o}$. Then $^{5}J_{H,H'}$ has an angular dependence of the form (3)

$$^{5}J_{HH'} = (A\cos^2\phi + B\cos\phi + C)\,(A'\cos^2\phi' + B'\cos\phi' + C)$$

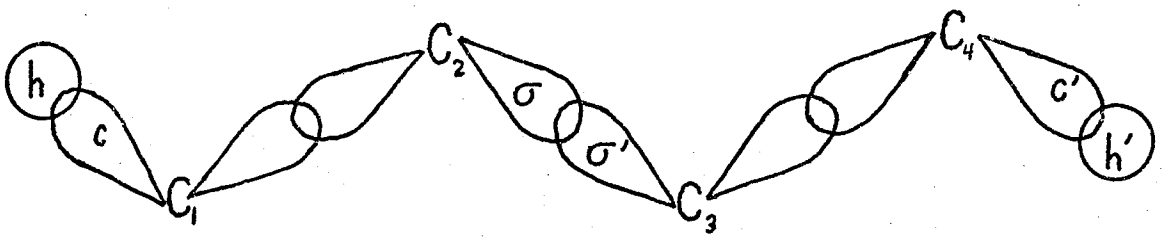
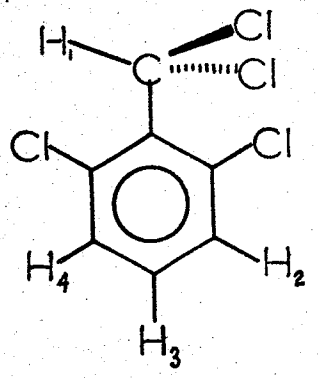


Figure 3

The butanic fragment. The main interaction is the vicinal-vicinal interaction. ϕ is the dihedral angle formed by the c - h bond with the $C_1 - C_2 - C_3$ plane and ϕ' is the dihedral angle formed by the c' - h' bond with the $C_2 - C_3 - C_4$ plane.

The maximum coupling occurs for $\phi = \phi' = 180^{o}$. $^{5}J_{HH'}$ is independent of the dihedral angle about the $C_2 - C_3$ bond in Figure 3.

Experimentally it has been observed that the trans-trans conformation gives a larger coupling than the trans-cis conformation. In I the methine



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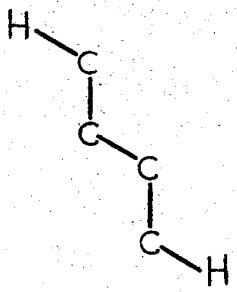
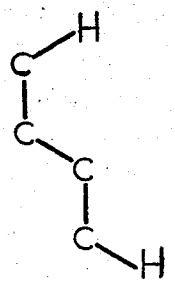


trans-trans



cis-trans

proton couples more strongly to proton 2 than to proton 4 (5). $J_{12} = 0.5$ Hz and $J_{14} = 0$ but both are 5 bond couplings. The coupling is strongest along the straightest zig-zag path (6, 7).

Couplings via σ bonds are attenuated rapidly, perhaps by as much as a factor of 10 for each additional intervening carbon-carbon bond separating the coupled nuclei (8). Few five bond couplings in saturated hydrocarbons have been reported (4) and those which have been reported involve multiple coupling paths (3).

B) Coupling Via π-Bonds

In unsaturated systems the coupling may be transmitted by the π bonds. This coupling, which is small and is much less rapidly attenuated than couplings through σ bonds, depends on the $\sigma - \pi$ configuration interaction (8) and may be written as (8, 9)

$$J_{\pi} = \frac{\beta^2 Q_{CH}^2 \rho_{NN'}^2}{h \quad \Delta E} \qquad 30.$$

β is the Bohr magneton, $\rho_{NN'}$ is the mobile bond order between carbon atoms bonded to the hydrogen atoms, ΔE is the average excitation energy to the triplet states. Q_{CH} corresponds to an effective isotropic coupling constant arising from the interaction between a π - electron in a carbon atomic orbital and an adjacent σ - proton. Q_{CH} depends on charge (10) and hybridization of the carbon atom (11) and is approximately equal to -24 gauss (12,13).

According to the treatment of Karplus (14) the coupling through a π system is positive over an odd number of bonds and is negative over an even number of bonds. It requires that replacement of an ethylenic proton by a methyl group will change the sign of the coupling but not the magnitude, and this is indeed observed. The proton-para proton coupling in benzene is +0.65 Hz (15), the methyl proton-para proton coupling in toluene is -0.62 Hz (16), and the methyl proton-methyl proton coupling in a para xylene derivative is +0.62 Hz (17).

When one ethylenic proton is replaced by a freely rotating methyl group the expression 30 can be rewritten as (9, 18)

$$J_{\pi} = \frac{\beta^2 Q_{CH} Q_{CCH} \rho_{NN'}}{h \quad \Delta E} \qquad 31.$$

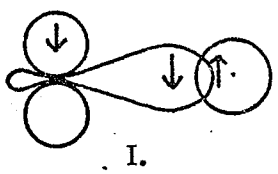
where Q_{CCH} is the effective isotropic splitting constant for the fragment $C - CH_3$ and is about +25 gauss.

Barfield has carried out calculations on the π contributions to long-range couplings using self-consistent-field molecular-orbital (S. C. F. M. O.) wave-functions where semi-empirical exchange integral parameters were used (19, 20). The calculations, which indicate that the coupling through the π-system is very sensitive to configuration interaction, show an excellent agreement with experiment for the proton-para proton coupling in benzene, the methyl proton- para proton coupling in toluene and the methylene proton-para proton coupling in acenaphthene.

4) Hyperconjugation And Spin Polarization In Benzylic Systems

The π -coupling mechanism in an unsaturated molecule such as a benzylic system may be discussed either in terms of spin polarization or hyperconjugation (21).

In the spin polarization model the electron spins are rearranged in the aliphatic bonds and spin density is transferred from the π -system to the σ -system through an exchange coupling (22). In Figure 4 the 1S electron on the benzylic proton has a spin state antiparallel to that of the benzylic proton because of the Fermi contact interaction. This electron spin polarizes the spin of the other electron in the C - H bond, so that these two electron spins are antiparallel in accordance with the Pauli principle. Next the electron in the benzylic carbon - aromatic carbon bond interacts with the electron belonging to the carbon atom in the C - H bond. By Hund's rule a parallel arrangement of the spins of these two electrons is slightly preferred energetically to an antiparallel arrangement. The other electron in the C - C bond has its spin aligned antiparallel to that of the first electron according to the Pauli principle. At this point the carbon - carbon σ -bond interacts with the π -orbital on the aromatic carbon atom. By Hund's rule the parallel arrangement of spins, I, is slightly preferred over the antiparallel arrangement, II, (22). In the aromatic ring the electron spins are successively paired as shown in



I.

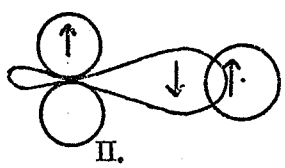


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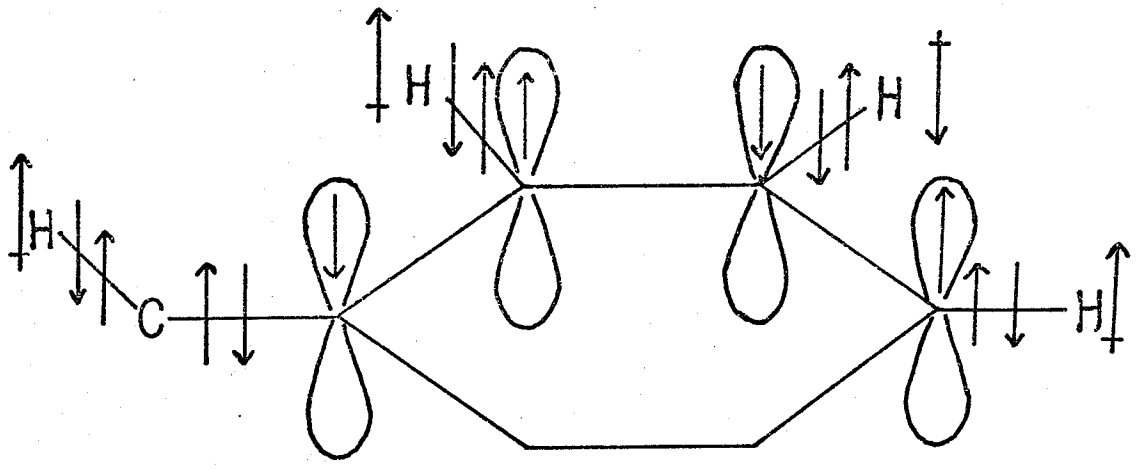
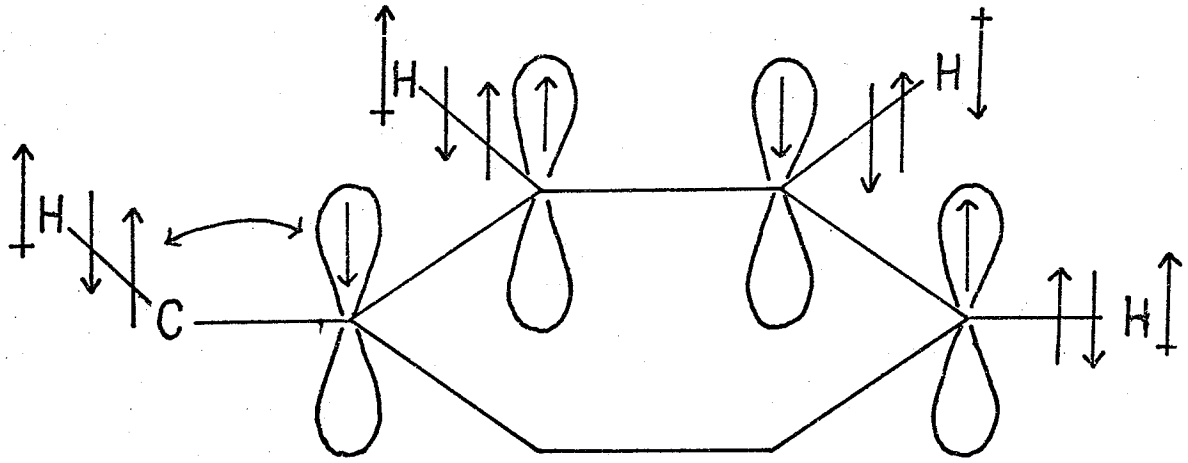
Figure 4

Spin Polarization and hyperconjugation in a benzylic system.



a) SPIN POLARIZATION



b) HYPERCONJUGATION

Figure 4. The π - system then interacts with the aromatic C - H bond, e.g., the para proton, polarizing the electron spins in the C - H bond and, as before, the spin information is transferred to the aromatic proton.

In the hyperconjugation description the π -orbitals overlap with the pseudo - π -orbitals of the σ -system (21). In Figure 4 the aromatic π -orbitals conjugate with the benzylic C - H bond so that the spin of the electron in the carbon π -orbital is antiparallel to the spin of the benzylic proton. This conjugation is angle - dependent and the Q_{CCH} term in equation 31 may be written as (23, 21)

$$Q_{CCH} \propto B \cos^2 \theta \qquad 32.$$

where $\theta = 0$ when the C - H bond lies in a plane with the adjacent carbon p - π orbital. In the aromatic ring the electron spins are successively paired and the rest of the interactions are exactly as described for the spin polarization mechanism.

The difference between the spin polarization description and the hyperconjugation description is that the former is independent of the dihedral angle θ, whereas the latter has a $\cos^2 \theta$ dependence. Colpa and de Boer (21), however, calculate that spin polarization makes only a minor contribution to the total coupling. Bearing in mind that a coupling constant is defined to be positive when the spins of the coupled nuclei are antiparallel and negative when the nuclear spins are parallel, both the spin polarization and hyperconjugation mechanisms correctly predict the signs of the coupling between the benzylic protons and the ortho-, meta -, and para - aromatic protons to be negative, positive and negative respectively (6, 16).

Chapter II

Long - Range Couplings In Benzylic Systems With Hindered Internal Rotation

1) Angular Dependence of Benzylic Couplings Over Five and Six Bonds.

In a benzylic system the benzylic proton - para proton coupling is transmitted by a π-mechanism (8, 9, 24) and it has an angular dependence which may be written as (21, 23)

$$^{6}J_{p}^{H,H'} = B \cos^{2} \theta \qquad 33.$$

where θ is the angle between the benzylic C - H bond and the axis of the first aromatic π - orbital. $\theta = 0$ when the benzylic C - H bond is perpendicular to the plane of the ring.

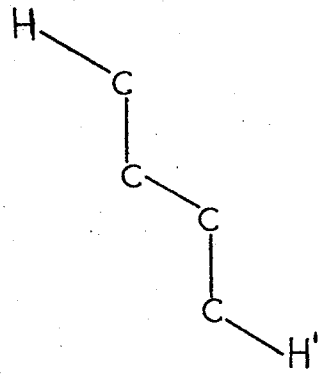
The benzylic proton - meta proton coupling is transmitted by both the σ - and π - mechanisms (4, 8, 24) so that the observed coupling may be expressed as

$$J_{m}^{H,H'} = J_{m}^{\pi} + J_{m}^{\sigma} \qquad 34.$$

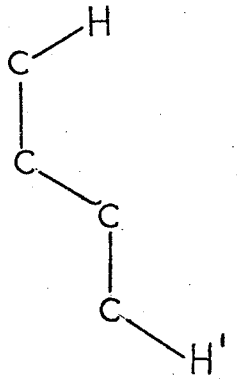
The π - contribution, J_{m}^{π}, which has the same angular dependence as the para coupling $J_{p}^{H,H}$ vanishes whenever the benzylic C - H bond lies in the plane of the ring. J_{m}^{σ}, which is a five - bond coupling similar to the butanic coupling may be expressed as

$$J_{m}^{\sigma} \alpha (A \cos^{2} \phi + B \cos \phi + C)(A' \cos^{2} \phi' + B \cos \phi' + C) \qquad 35.$$

where ϕ and ϕ' (see Figure 3) are the dihedral angles about the C_1-C_2 and C_3 - C_4 bonds respectively. $\phi = \phi' = 180^{o}$ in the trans - trans conformation but $\phi = 0$ and $\phi' = 180^{o}$ in the cis - trans conformation. As far as J_{m}^{σ} is concerned, the benzylic proton - meta proton system may be viewed as two butanic fragments where in compound I the $C_1 - C_2 - C_3 - C_4$ system



trans-trans

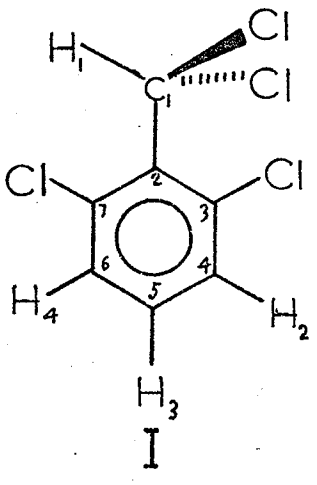


cis-trans

is in the trans - trans configuration with $\phi = \phi' = 180^{o}$ and the $C_1 - C_2 - C_7 - C_6$ system is in the cis - trans configuration with $\phi = 0$ and $\phi' = 180^{o}$. In both the trans - trans and the cis - trans arrangements $\phi' = 180^{o}$ so that the expression 35 may be rewritten as

$$J_m^{\sigma} = K (A \cos^2 \phi + B \cos \phi + C) \qquad 36.$$

where K is a constant. This expression predicts unequal couplings to the two meta - protons. The compound α, α, 2, 6 - tetrachlorotoluene, which at -40°C has the benzylic C - H bond in the plane of the ring, shows proton - proton coupling constants $J_{12} = .5$ Hz and $J_{14} = 0$ Hz (5). This coupling is considered



I

to be transmitted entirely via σ - bonds. Using these values for the coupling constants J_m^{σ} could be written as

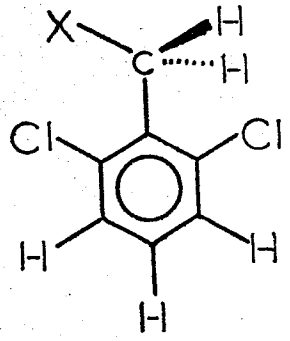
$$J_m^{\sigma} = .25 \cos^2 \phi - .25 \cos \phi \qquad 37.$$

2) $^{6}J_{p}^{H,CH_2}$ In Cases With Hindered Internal Rotation As Compared To Free Rotation.

The angular dependence of $^{6}J_{p}^{H,H}$ given by equation 33 can be applied to systems where there are more than one benzylic proton and where the benzylic group rotates. In toluene the methyl group rotates about the carbon-carbon bond axis where the barrier to this rotation is only .014 kcal./mole (25). The rotational kinetic energy is $\frac{1}{2}kT$ by the equipartition theorem, which at room temperature is about 0.3 kcal./mole. If therefore the rotation is considered to be free and if the frequency of this rotation is greater than the coupling between the benzylic proton and the para proton the coupling constant will be averaged over one revolution for each of the 3 methyl protons. Then

$$^{6}J_{p}^{H,CH_3} = \frac{1}{3} B \langle 3 \cos^2 \theta \rangle = \frac{1}{2} B \qquad 38.$$

The compound II, where X is a



II

substituent, is a case of hindered internal rotation. The methylene group and the frame both have a two - fold symmetry axis and so the rotational barrier will be symmetrical. The most preferred conformation will have the substituent X perpendicular to the ring (26), with each C - H bond lying

at 30° to the plane of the ring. If the rotational barrier, V_o, is high enough (V_o/kT about 5) it can be assumed to be a sinusoidal potential and the motion of the methylene rotor may be treated as simple harmonic (26). This approximation is valid provided the angular amplitude is small. Obviously, near the top of the barrier a simple harmonic oscillator is a very poor approximation. The angular displacement from equilibrium is given classically by (26)

$$\theta(t) = \theta_o + \phi' \sin\left(2\pi t/\tau\right) \qquad 39$$

where θ_o is the equilibrium angle made by the C - C - H plane with the p_z orbital on the first aromatic carbon atom. ϕ' is the maximum amplitude of the motion, and τ is the period of the oscillation.

If the frequency of oscillation is larger than the coupling of the benzylic proton with the para proton the coupling is given by

$$J_p^{H,CH_2} = B\langle\cos^2\theta(t)\rangle$$

$$= B\langle\cos^2(\theta_o + \phi' \sin(2\pi t/\tau))\rangle \qquad 40.$$

$$J_p^{H,CH_2} = B\,F(\phi', \theta_o) \qquad 41.$$

where

$$F(\phi', \theta_o) = \frac{1}{\pi}\int_{-\pi/2}^{+\pi/2} \cos^2(\theta_o + \phi' \sin x)\,dx \qquad 42.$$

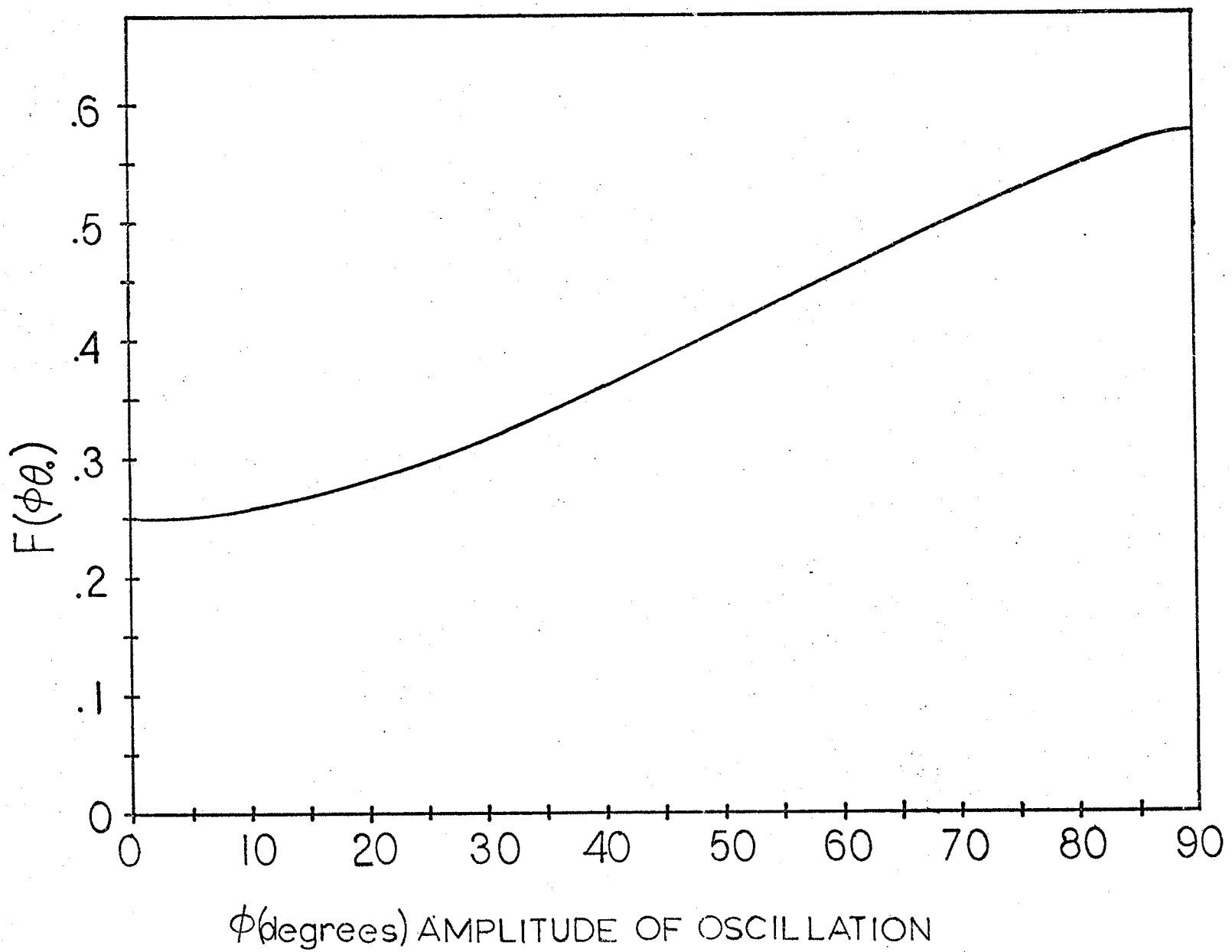
and

$$x = 2\pi t/\tau \qquad 43.$$

Equation 42 is graphed (in Figure 5) as a function of ϕ', the amplitude of oscillation, for $\theta_o = 60°$. Since the approximation of a simple harmonic

Figure 5

The classical motional factor $F(\phi,\theta_o)$ as a function of ϕ, the amplitude of the motion. θ_o is 60 degrees.


.6
.5
.4
.3
.2
.1
0
F(φθ₀)
0
10
20
30
40
50
60
70
80
90
φ(degrees) AMPLITUDE OF OSCILLATION

oscillator was used equation 42 and Figure 5 are valid for low values of ϕ. Figure 5 also shows that for small amplitudes of motion, about 15^{o} or less, the coupling constant is not sensitive to changes in the amplitude of motion, but for larger amplitudes it is sensitive to changes in amplitude. For small amplitudes of oscillation, then, $J_p^{H,CH_2} = \frac{1}{2} J_p^{H,CH_3}$ in toluene (equation 38).

If the frequency of oscillatory motion is less than $^{6}J_p^{H,H}$ the coupling constant will be constantly changing and broadened N. M. R. peaks will be observed.

Chapter III

The Problem

In toluene the methyl proton - ring proton couplings are transmitted by both σ -and π -mechanisms and are insensitive to ring substitution. J_p^{H,CH_3} in toluene is -0.62 Hz (16), in 2,6 - dichlorotoluene is -0.63 Hz, in 3,5 - dichlorotoluene is -0.59 Hz (40), and in 2, 3, 5, 6 - tetrachloro-toluene is -0.63 Hz (41). The spectrum of 2,6 - dichlorotoluene is much simpler and easier to work with than that of toluene. The effects on the coupling constants of inserting an α - substituent in 2,6 - dichlorotoluene should be similar to the corresponding effects in toluene itself. The aim of this thesis is the study of the influence of α - substituents on the σ - and π - coupling mechanisms.

Chapter IV

Experimental

1) Sources of Compounds

The compounds used in this study were obtained from the sources given in Table I. 2,6 - Dichloroethylbenzene was prepared by hydrogenation of 2,6 - dichlorostyrene. 3 Millilitres (ml.) of 2,6 - dichlorostyrene were dissolved in about 20 ml. of distilled methanol containing one drop of concentrated hydrochloric acid. 50 Milligrams of a palladium - on - charcoal catalyst (Matheson, Coleman, and Bell) were used. Air was swept out of the reaction vessel by repeatedly lowering the pressure in the vessel and then admitting hydrogen gas. The reaction vessel was left on a shaker overnight. The solvent was distilled off. 10 Ml. of chloroform were added and distilled off, and this procedure was repeated. Infrared and N. M. R. spectra of the resulting compound were taken and were consistent with the structure of 2,6 - dichloroethylbenzene. There were no impurity peaks.

2) Sample Preparation

The samples were prepared as 10 mole % solutions in benzene - d_6 (C_6D_6). A few drops of tetramethylsilane (TMS), about 7% by volume, were added. The samples were degassed by the freeze - pump - thaw technique and were then sealed in the sample tube.

3) Recording of Spectra

The spectra were recorded with a Varian DA - 60 I spectrometer using internal TMS as the lock signal. The spectra were taken using the

frequency mode at a sweep width of 50 Hertz (Hz) and a sweep time of 2500 seconds. The peaks were calibrated by counting the sweep frequency and manual oscillator frequency on either side of the peak, followed by interpolation. Each peak was recorded five times. The quoted errors in the parameters are standard deviations.

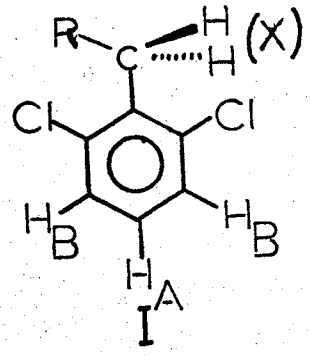
Table I

Sources of Compounds

Compound	Source
2,6 - dichlorobenzyl thiocyanate	K and K Laboratories
2,6 - dichlorobenzyl amine	K and K Laboratories
2,3,6 - trichloro-5 - nitro toluene	Alfred Bader Co.
2,6 - dichlorobenzyl cyanide	Aldrich Chemical Co.
2,6 - dichlorobenzyl bromide	Aldrich Chemical Co.
2,4,6 - trimethoxy toluene	Aldrich Chemical Co.
2,6 - dichlorobenzyl alcohol	Aldrich Chemical Co.
2,6 - dichlorostyrene	K and K Laboratories
deuterated benzene	Merck, Sharp and Dohme
deuterated toluene	Aldrich Chemical Co.
2,6 - dinitro - 3-methoxy - 4-tert. butyl toluene	Alfred Bader Co.
2,4,6 - triiodo - 3 - hydroxy toluene	Pfaltz and Bauer Inc.
2,6 - dichlorobenzyl chloride	Aldrich Chemical Co.
2,6 - dichlorotoluene	K and K Laboratories

4) Analysis of Spectra : AB_2X_2 Spectra

All compounds of the type I have AB_2X_2 spectra. Figure 6 shows



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the AB_2 part of an AB_2X_2 spectrum. There are 8 sets of triplets which are numbered from right to left. The centre peak of triplet 3, labelled H_A, gives the shift of the para proton. The splitting of this triplet is the benzylic proton-para proton coupling constant ${}^6J_p^{H,CH_2}$(27). The shift of the meta proton is midway between triplets 5 and 7. The benzylic proton - meta proton coupling constant ${}^6J_m^{H,CH_2}$ is half the sum of the splittings of triplets 5 and 7 (see Appendix I).

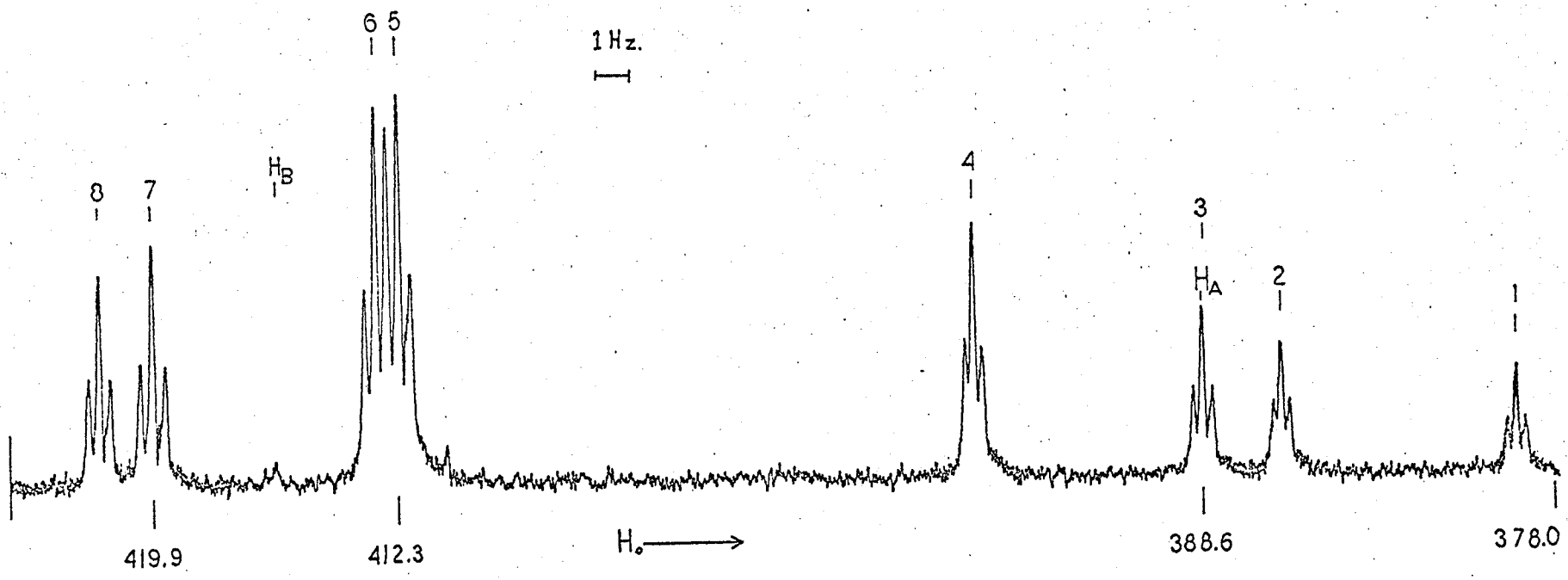
These long - range coupling constants can be obtained by direct measurement. These couplings were measured five times and the quoted errors are the calculated standard deviations.

AX_3 Spectra

The compound 2,3,6 - trichloro - 5 - nitro - toluene is an example of a system having an AX_3 type spectrum. The spectrum consists of doublet and a quartet with the relative shift about 300 times as large as the coupling constant. The coupling constant, J_{AX}, is given by the splitting of either the doublet or the quartet (28).

Figure 6

The AB_2 part of an AB_2X_2 spectrum for the compound 2,6 - dichloroethylbenzene. The scale is in Hertz with the field increasing to the right. The spectrum was recorded on a sweep width of 50 Hz. at a sweep time of 2500 seconds.


6 5
1 Hz.
8
7
H_B
4
3
H_A
2
1
419.9
412.3
H_o
388.6
378.0

A_2X_2 Spectra

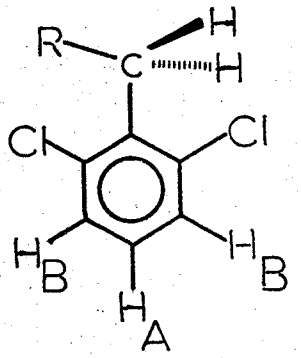
An A_2X_2 type spectrum is observed for 2,4,6 - tribromobenzylbromide. For this compound the ratio of the relative shift to the coupling constant is about 500 so that first order rules apply. The spectrum consists of two triplets and the splitting of each triplet is J_{AX} (29).

Chapter V

Results And Discussion

1) Spectral Parameters

The chemical shifts relative to internal TMS, ν_A, ν_B, ν_{CH_2}, and the coupling constants, J, for α - X - 2,6 - dichlorotoluene derivatives are given in Tables II and III. The subscripts A, B denote the ring protons in I, and the subscript CH_2 denotes the



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benzylic protons. $^6J_p^{H,CH_2}$, $^5J_m^{H,CH_2}$ and $^3J_o^{H,H}$ represent the benzylic proton - para proton coupling, the benzylic proton - meta proton coupling and the para proton - meta proton coupling constants, respectively. E_X is the group electronegativity of the α - substituent which was determined by Dailey and Shoolery from the shift difference between the methylene protons and the methyl protons in substituted ethanes (30). The chemical shifts of the para - protons and the benzylic protons move downfield somewhat as the α - substituent becomes more electronegative.

TABLE II

Chemical Shifts of α - x - 2,6 - Dichlorotoluene Derivatives

Compound	ν_A(Hz.)	ν_B(Hz.)	ν_{CH_2}(Hz.)	
2,6 - dichlorotoluene	-	-	-	
2,6 - dichloroethyl benzene	388.62 ± .03	416.21 ± .03	-	
2,6 - dichlorobenzyl cyanide	-	-	196.47 ± .2	
2,6 - dichlorobenzyl thiocyanate	390.58 ± .03	409.14 ± .03	231.31 ± .03	
2,6 - dichlorobenzyl bromide	384.85 ± .02	407.31 ± .03	262.48 ± .03	
2,6 - dichlorobenzyl amine	390.79 ± .03	414.85 ± .02	234.33 ± .03	ν_{NH_2} = 65.24 ± .03
2,6 - dichlorobenzyl chloride	—	—	—	
2,6 - dichloro - α - methoxy toluene	394.35 ± .03	416.24 ± .03	272.80 ± .04	ν_{OCH_3} = 191.13 ± .04
2,6 - dichlorobenzyl alcohol	388.50 ± .03	411.70 ± .03	280.96 ± .03	ν_{OH} = 111.10 ± .07
2,6 - dichlorobenzyl fluoride[a]	415.6 ± .1	401.4 ± .1	323.5 ± .2	

a) T. Schaefer, C. M. Wong, and K. C. Tam. Canad. J. Chem. 47 3688 (1969)

TABLE III

Coupling Constants Of α - x - 2,6 - Dichlorotoluene Derivatives

α - substituent	$^{6}J_{p}$ H, CH_2 (Hz.)	$^{5}J_{m}$ H, CH_2 (Hz.)	$^{3}J_{o}$ H, H (Hz.)	E_x [b]
- H	- .63 ± .01	.41 ± .03	-	2.10
- CH_3	- .29 ± .02	.36 ± .03	-	2.32
- CN	- .33 ± .02	.35 ± .04	8.14 ± .05	2.52
- SCN	- .27 ± .02	.34 ± .02	8.13 ± .035	2.70
- Br	- .21 ± .02	.36 ± .02	8.04 ± .03	2.94
- NH_2	- .20 ± .02	.35 ± .02	8.27 ± .03	2.99
- Cl	- .21 ± .02	.36 ± .04	-	3.19
- OCH_3	- .20 ± .02	.31 ± .02	8.07 ± .03	3.31
- OH	- .19 ± .034	.33 ± .02	8.07 ± .03	3.51
- F [a]	- .16 ± .02	.34 ± .04	8.14 ± .05	3.93

a) T. Schaefer, C. M. Wong, and K. C. Tam. Canad. J. Chem. 47 3688 (1969)

b) Electronegativities were taken from reference 30.

2) Benzylic Proton - Para Proton Coupling Constant, $^{6}J_{p}^{H,CH_2}$

$^{6}J_{p}^{H,CH_2}$ decreases sharply with the introduction of an α - substituent to 2,6 - dichlorotoluene and continues to decrease as the α - substituent becomes more electronegative. Since $^{6}J_{p}^{H,CH_2}$ has an angular dependence of

$$^{6}J_{p}^{H,H} = B \cos^2 \theta$$

it will also depend on the amplitude of the oscillatory motion of the methylene group.

A) $^{6}J_{p}^{H,H'}$ In 2,6 - Dichlorotoluene As Compared To 2,6 - Dichloroethylbenzene

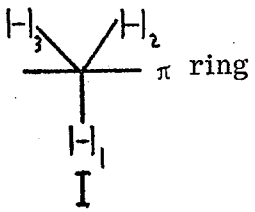
The 6 - fold rotational barrier of the methyl group in 2, 6 - dichlorotoluene should be small due to the relative phasing of the interactions between the 3 - fold symmetric methyl group and the 2 - fold symmetric aromatic ring (31). For example, ethane has a 3-fold barrier of 2.88 kcal./mole (32) whereas toluene has a 6-fold barrier of only .014 kcal./mole (25) and nitromethane has a 6-fold barrier of .006 kcal./mole (32) as compared to the kinetic energy of the rotor of $\frac{1}{2}kT$, about .3 kcal./mole at room temperature. Treating the rotation of the methyl group in 2,6 - dichlorotoluene as free the observed methyl proton - para proton coupling constant will be an average of the coupling of each of the methyl protons over one revolution. Then from equation 38

$$^{6}J_{p}^{H,CH_3} = \frac{1}{3}\left[3B < \cos^2 \theta >\right] = \frac{1}{2} B \qquad 44.$$

The replacement of an α - hydrogen atom in 2,6 - dichlorotoluene by a methyl group changes the 6 - fold barrier in toluene to a 2 - fold barrier in 2,6 - dichloroethylbenzene. This barrier is expected to be substantially larger. Treating the rotational motion of the methylene group as simple harmonic the benzylic proton-para proton coupling constant may be written as (26)

$$ {}^{6}J_{p}^{H,CH_2} = \tfrac{1}{2}\left[2B\langle\cos^2(60 + \phi\sin 2\pi t/\tau)\rangle\right] \qquad 45. $$

from equation 40. 60^{o} is the equilibrium angle made by the C - H bond with the axis of the π - orbital on the first aromatic carbon atom, and ϕ is the maximum amplitude of the motion. Figure 5 shows that as ϕ goes to zero the coupling constant ${}^{6}J_{p}^{H,CH_2}$ approaches $\frac{1}{4}B$ whereas with the free rotation in 2,6 - dichlorotoluene ${}^{6}J_{p}^{H,CH_3} = \frac{1}{2}B$. This means that if 2,6 - dichlorotoluene were locked in the conformation I, and if the proton H_1 were



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masked the observed benzylic proton - para proton coupling would decrease by a factor of 2. In fact, ${}^{6}J_{p}^{H,CH_3}$ in 2,6 - dichlorotoluene is -0.63 Hz and in ${}^{6}J_{p}^{H,CH_2}$ in 2,6 - dichloroethylbenzene is -0.29 Hz.

Therefore, to compare ${}^{6}J_{p}^{H,CH_3}$ in 2,6 - dichlorotoluene with ${}^{6}J_{p}^{H,CH_2}$ in the corresponding α - substituted compounds one of the methyl protons must be masked. For that reason in Figure 7 below, $\frac{1}{2}\ {}^{}J_{p}^{H,CH_3}$ is used for 2,6 - dichlorotoluene.

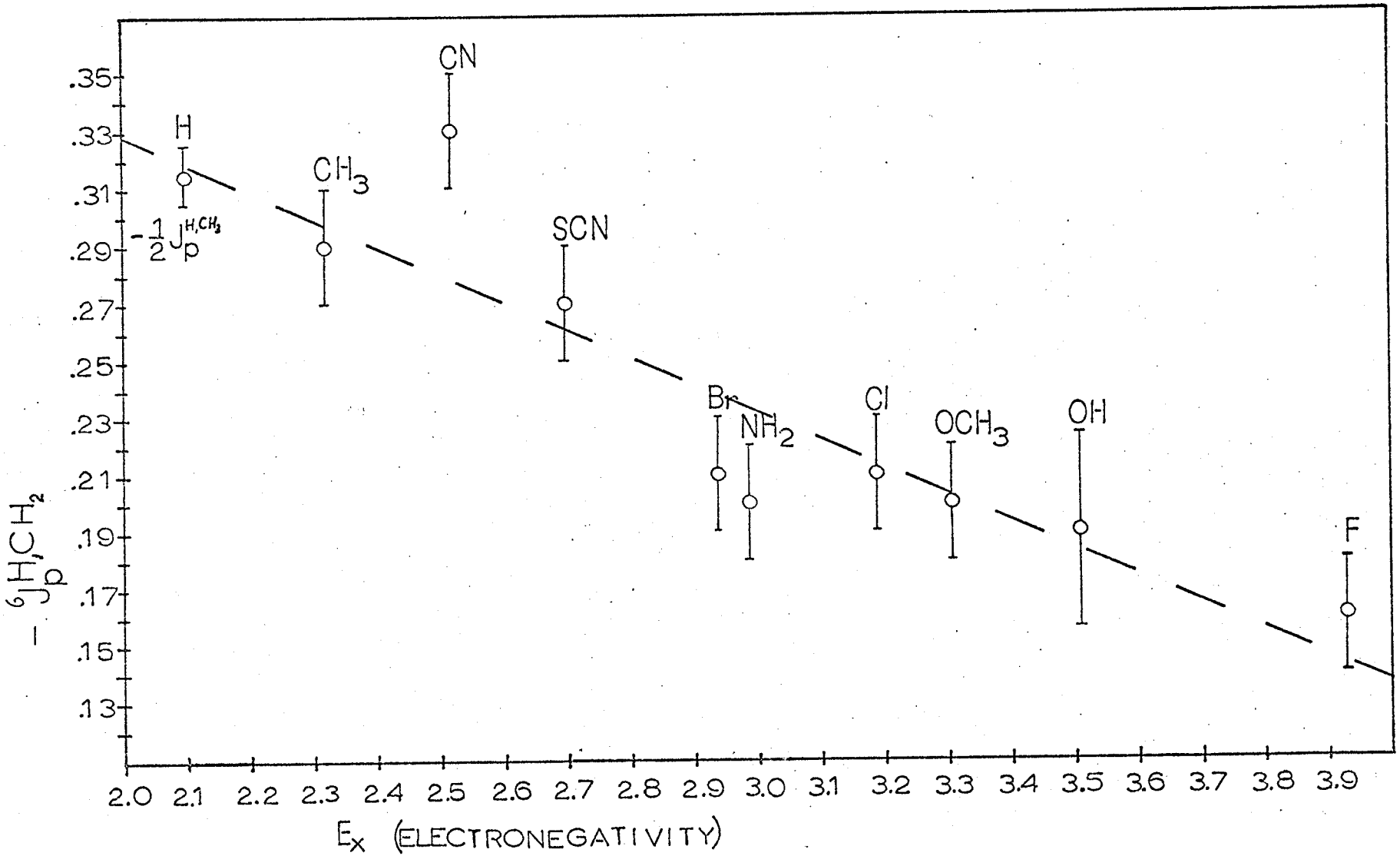
B) The Effect Of Electronegativity Of The α - Substituent

Figure 7 shows that as the α - substituent becomes more electronegative the magnitude of the benzylic proton - para proton coupling decreases. This coupling which is transmitted via π - bonds is proportional to Q_{CCH} (see equation 31). The electronegative group, tending to withdraw electrons, causes a decrease in the overlap between the methylene group and the aromatic ring resulting in less efficient transfer of spin information. Q_{CCH} decreases and hence $^{6}J_{p}^{H,CH_2}$ decreases.

Figure 7

The dependence of the magnitude of the benzylic proton - para proton coupling, $^{6}J_{p}^{H, CH_2}$, on the electronegativity of the α - substituent, E_X. The correlation coefficient is 0.915. If CN is omitted the correlation coefficient is 0.954.

The bars indicate the error limits in $^{6}J_{p}^{H, CH_2}$, but the circles are not intended as error limits in the electronegativity values.


CN
H
CH3
SCN
Br
NH2
Cl
OCH3
OH
F
-1/2 J_p^{H,CH3}
- 6JH,CH2
.35
.33
.31
.29
.27
.25
.23
.21
.19
.17
.15
.13
2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.9 3.0 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8 3.9
Ex (ELECTRONEGATIVITY)

Anomalous Effects of CN

In Figure 7 $^{6}J_{p}^{H,CH_2}$ for 2,6 - dichlorobenzyl cyanide is larger than expected on the basis of the electronegativity of CN. In methyl cyanide because of its two π -bonds the CN group displays considerable hyperconjugation with the methyl orbitals (33). With the additional aromatic system in 2,6 - dichlorobenzyl cyanide this compound can then behave as an extended hyperconjugated system with a larger overlap between the methylene group and the aromatic ring than if say, a halogen were present, resulting in a larger coupling constant, $^{6}J_{p}^{H,CH_2}$.

C) The Effect Of The Size Of The α -Substituent

From equation 41 and Figure 5 it can be seen that the benzylic proton-para proton coupling constant depends on the amplitude of the motion of the methylene group and therefore also depends on the size of the α -substituent. The van der Waals potential energy function which takes into account the steric interaction between the ring substituents and the alkyl group was used to calculate the barrier to rotation (34). These functions are shown for 2,6 - dichlorobenzyl bromide and 2,6 - dichlorobenzyl fluoride* in Figures 8 and 9. The fluorine group, being smaller than bromine, allows for a larger amplitude of motion which would tend to increase $^{6}J_{p}^{H,CH_2}$ (Figure 5). In spite of this, fluorine is electronegative enough to show the smallest coupling of all the compounds listed in Table III.

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* I am grateful to Mr. Brian Barber for calculating these barriers.

Figure 8

The van der Waals potential energy function for 2,6 - dichloro-benzyl bromide. The angle of rotation is 0^{o} when the C - Br bond eclipses a C - Cl bond. A is about 15 kcal./mole.

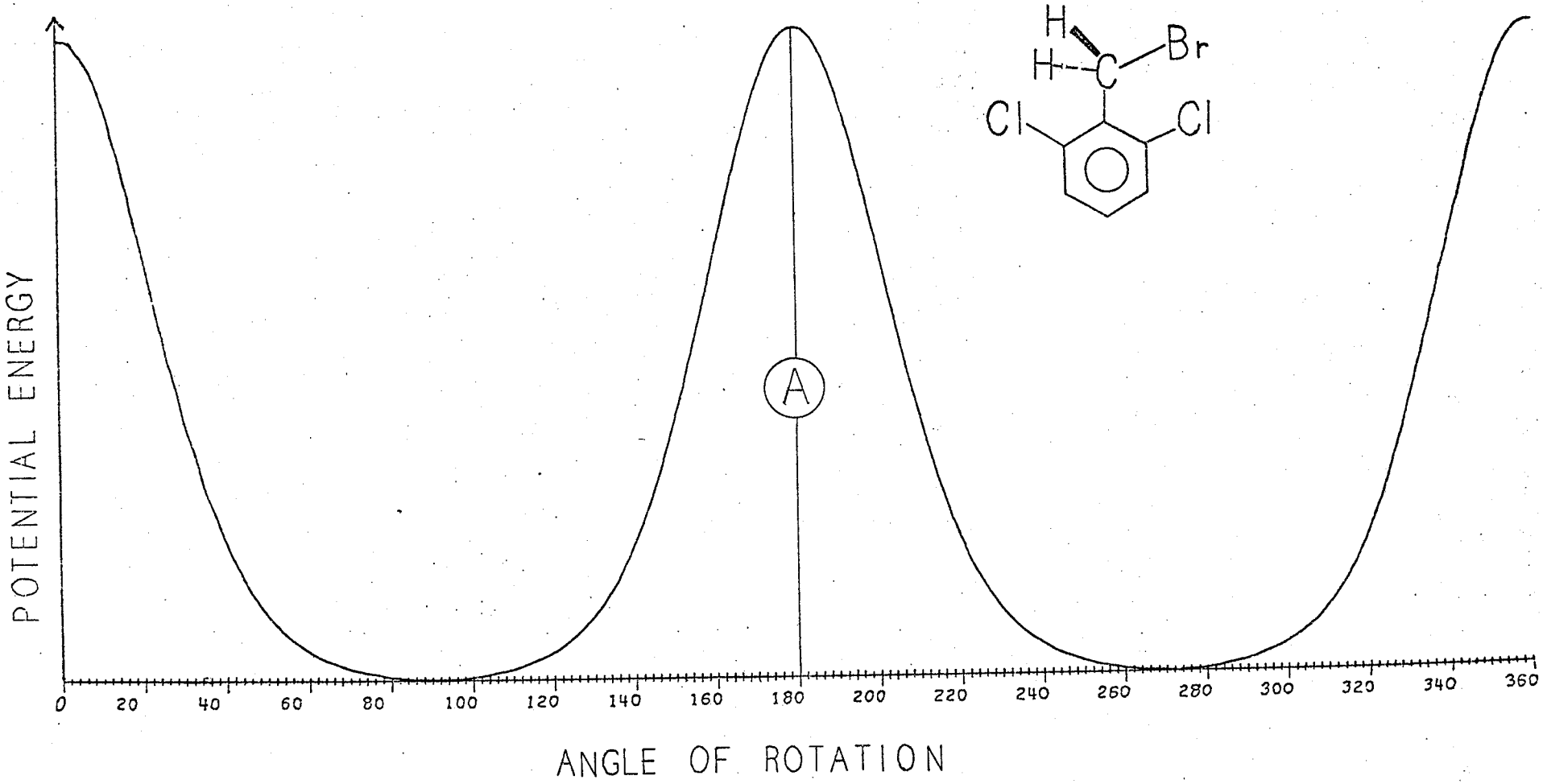
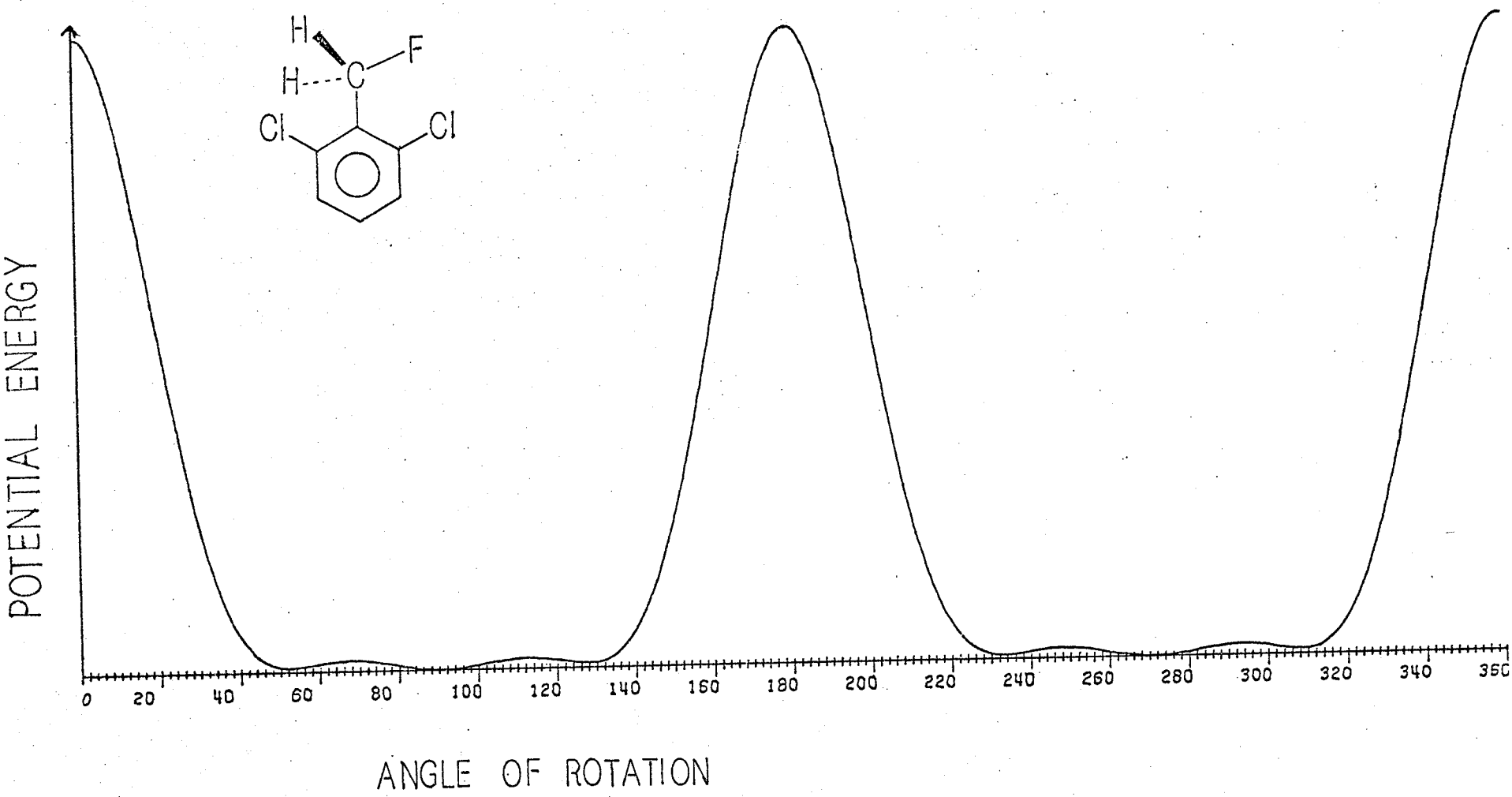
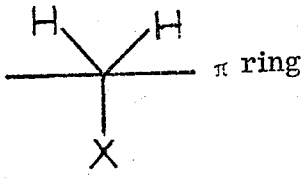

POTENTIAL ENERGY
A
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
ANGLE OF ROTATION
H
H
Br
C
Cl
Cl

Figure 9

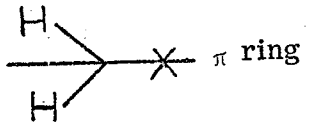
The van der Waals potential energy function for 2,6 - dichloro-benzyl fluoride. The angle of rotation is 0^{o} when the C-F bond eclipses the C - Cl bond. F is smaller than Br so the methylene rotor has a larger amplitude of motion.


H
F
H
C
Cl
Cl
POTENTIAL ENERGY
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
ANGLE OF ROTATION

In Figures 8 and 9 the most stable conformation occurs when the C - X bond is out of the plane of the ring as in I



I



II

with the high energy situation occurring when the C - X bond eclipses a C - Cl bond as in II. Allowing the C - Cl, C - X, C - H bonds to bend (tilt) from 0^{o} to 5^{o}, the barrier to rotation was calculated for each degree of tilt and the results for 2,6 - dichlorobenzyl bromide are listed in Table IV.

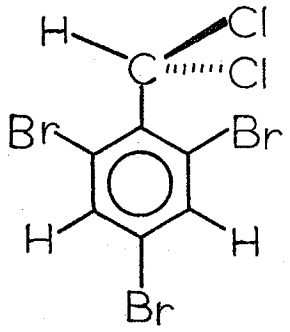
TABLE IV

Dependence Of The Rotational Barrier On Tilt

Of Bond Angles In 2, 6 - Dichlorobenzyl Bromide

tilt (degrees)	Barrier Height (kcal. /mole)
0	22.1
1	18.0
2	14.7
3	12.0
4	9.8
5	8.0

The rotational barrier in compound III



III

which also has Br and Cl groups interacting at distances similar to those in 2, 6 - dichlorobenzyl bromide, is 15.65 kcal. /mole (35). On this basis the rotational barrier, A, in 2, 6 - dichlorobenzyl bromide should be about 15 kcal. /mole which occurs for 2^{o} of tilt. In 2, 6 - dichlorobenzyl fluoride the barrier calculated by the van der Waals functions is 3 kcal. /mole for 0^{o} of tilt.

D) Temperature Dependence of $^6J_p^{H,CH_2}$

Considering that the kinetic energy of an internal rotor is $\frac{1}{2}kT$ and that possibly the amplitude of motion of the rotor changes with temperature the magnitude of $^6J_p^{H,CH_2}$ could be temperature dependent. The effect of temperature on the benzylic proton-para proton coupling constant in 2,6 - dichlorobenzylbromide dissolved in toluene-d_8 was studied. The results are listed in Table V. The coupling constant remains constant over a temperature range of 100°C. Therefore the amplitude of the oscillation of the methylene rotor does not change significantly over a temperature range of 100°C (see equation 40 and Figure 5).

TABLE V

Effects Of Temperature On $^6J_p^{H,CH_2}$

Temp. (°C)	$^6J_p^{H,CH_2}$ (Hz.)
+ 80	- .21 ± .02
+ 40	- .21 ± .02
+ 20	- .21 ± .02
0	- .21 ± .02
- 20	- .20 ± .02

3) Benzylic Proton - Meta Proton Coupling Constant $^5J_m^{H,CH_2}$

The methylene - meta coupling constant $^5J_m^{H,CH_2}$ has both a σ and a π contribution (4, 8, 24).

$$^5J_m^{H,CH_2} = J_m^{\pi} + J_m^{\sigma} \qquad 46.$$

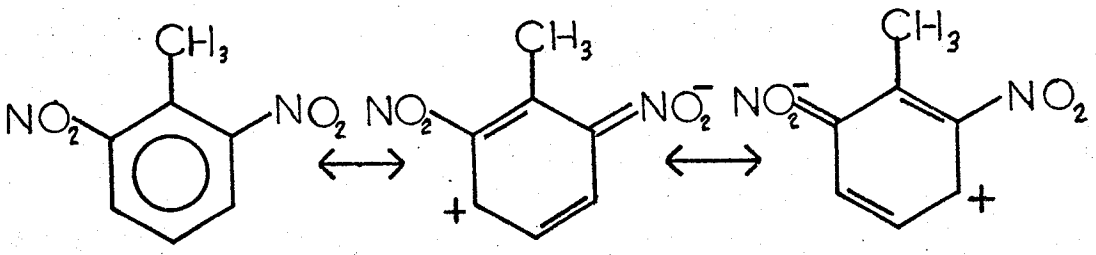
J_m^{σ} is known to be positive (5, 7) and J_m^{π} is positive because it occurs over an odd number of bonds. The experimental values for $^5J_m^{H,CH_2}$, Table III, are roughly independent of the α - substituent. J_m^{π} must decrease as the electronegativity of the α - substituent increases because $^6J_p^{H,CH_2}$ decreases. Therefore because $^5J_m^{H,CH_2}$ is independent of the α - substituent, J_m^{σ} apparently increases on α - substitution.

There is some evidence that α - substitution increases J^{σ} over five bonds in other systems. In benzene the five bond coupling $^5J_p^{H,H}$ is transmitted by the π - mechanism (see Chapter 1 Section B) and is .65 Hz. (15). Substituents apparently affect mainly the σ - electron framework and $^5J_p^{H,H}$ should then have a σ - component. An alternating effect of the electronegativity of the substituents is then observed (36). An electronegative β - substituent, as in fluorobenzene, decreases $^5J_p^{H,H}$ whereas an α - substituent, as in pyridine or the benzylic system (above) increases the coupling. $^5J_p^{H,H}$ in fluorobenzene is .43 Hz. (37) and in pyridine is .98 Hz. (38).

4) Effects Of Ring Substituents

In Table VI the methyl proton - ring proton coupling constants are listed for toluene and some ring substituted toluene derivatives. $^{6}J_{p}^{H,H}$ and $^{5}J_{m}^{H,H}$ are the methyl proton - para proton and methyl proton - meta proton coupling constants respectively. The chemical shifts are denoted by ν and all measurements are given in Hertz, The ring substituents show little effect on the long - range coupling constants as compared to the α - substituents, which is in agreement with a previous study (39). Comparing toluene with 2,6 - dichlorotoluene, 2,6 - dinitrotoluene and 2,6 - dimethoxy toluene the Cl substituents leave the long - range coupling constants unchanged whereas both nitro and methoxy substituents slightly increase the methyl proton - para proton coupling.

The nitro substituents increases $^{5}J_{m}^{H,H}$ while Cl and methoxy substituents hardly change it. Since carbon - nitrogen and carbon - oxygen double bonds are well known possibly structures such as



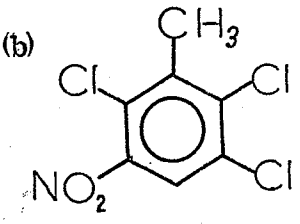
cause changes in the bond orders of the molecule and thereby could conceivably affect the coupling constants. Bromine shows no effect on the long-range couplings . The methyl proton - meta proton coupling in 2,6 - dichlorobenzyl bromide is identical with that in 2,4,6 - tribromobenzyl bromide.

TABLE VI

Spectral Parameters Of Ring - Substituted Toluene Derivatives

Compound	$^{6}J_{p}^{H,H}$ (Hz.)	$^{5}J_{m}^{H,H}$ (Hz.)
toluene [a]	-0.62 ± .02	+0.36 ± .01
2,6-dichloro toluene [b]	-0.63 ± .01	+0.41 ± .03
3,5-dichloro toluene [c]	-0.59 ± .02	-
2,3,5,6-tetrachlorotoluene [d]	-0.63 ± .02	-
2,3,4,6-tetrachorotoluene [d]	-	+0.36 ± .02

(b)

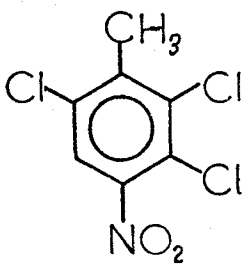


$\nu_{H} = 418.27 \pm .02$

$\nu_{CH_3} = 116.50 \pm .02$

-0.68 ± .02 | -

(b)

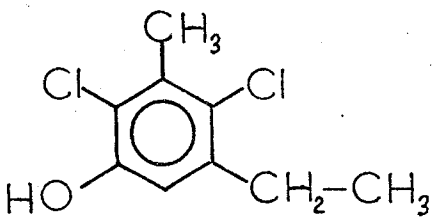


$\nu_{H} = 421.06 \pm .05$

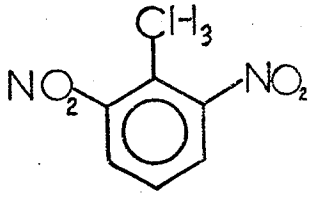
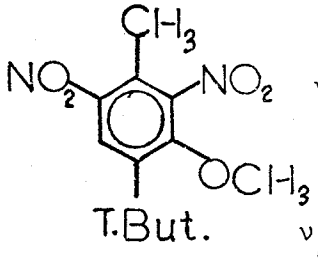
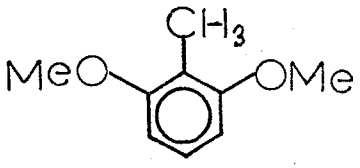
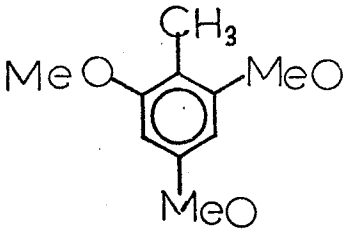
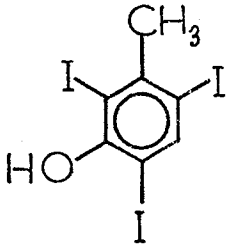
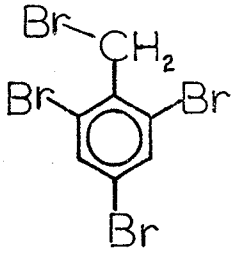
$\nu_{CH_3} = 117.85 \pm .04$

- | +0.41 ± .02

(e)



-0.61 ± .02 | -

		$^6J_{p}^{H,H}$ (Hz.)	$^5J_{m}^{H,H}$ (Hz.)
(b) 	$\nu_{CH_3} = 123.55 \pm .03$	$-0.66 \pm .02$	$+0.46 \pm .02$
(b) 	$\nu_{CH_3} = 124.28 \pm .03$ $\nu_{t.but.} = 67.38 \pm .02$ $\nu_{H} = 468.41 \pm .05$ $\nu_{OCH_3} = 205.70 \pm .03$		$+0.40 \pm .02$
(e) 		$-0.70 \pm .02$	$+0.38 \pm .02$
(b) 	$\nu_{H} = 367.06 \pm .04$ $\nu_{CH_3} = 139.55 \pm .03$ $\nu_{m\,MeO} = 205.47 \pm .03$ $\nu_{p\,MeO} = 208.19 \pm .03$		$+0.40 \pm .02$
(b) 	$\nu_{CH_3} = 145.18 \pm .03$ $\nu_{H} = 473.46 \pm .03$ $\nu_{OH} = 329.61 \pm .04$		$+0.38 \pm .02$
(b) 	$\nu_{CH_2} = 279.9$ $\nu_{H} = 458.9$		$+0.36 \pm .02$

continued...

(a) M. P. Williamson, R. J. Kostelnik, S. M. Castellano. J. Chem. Phys. 49 2218 (1968)

(b) This study

(c) R. Schwenk. M. Sc. Thesis. University of Manitoba, 1968

(d) S. Sternhell and R. H. Rottendorf Ref. 41

(e) R. Wasylishen. Private communication.

Chapter VI

Summary and Conclusions

In this study it has been found that:

1) in toluene derivatives the methyl proton - ring proton coupling constants are not sensitive to ring substitution.

2) α - x - 2,6 - dichlorotoluene compounds have a relatively large barrier to the rotation of the methylene group and the preferred conformation is one in which the substituent lies perpendicular to the plane of the ring.

3) as the α - substituent becomes more electron withdrawing the methylene proton - para proton coupling decreases in magnitude whereas the methylene proton - meta proton coupling remains approximately constant.

4) the α - substituent is responsible for other effects:

   a) with an α - CN group the benzylic proton - para proton coupling is larger than expected on the basis of electronegativity.

   b) a small group, such as F, allows the methylene rotor a larger amplitude of oscillation.

Chapter VII

Suggestions For Further Research

The problem of the effects of the α - substituents in benzylic systems could be investigated further by:

1) measuring the benzylic C^{13} - hydrogen coupling constant in α - substituted toluenes.

2) measuring the benzylic proton - ring proton coupling constants in α - x - 2,6 - dibromotoluene. Ring bromine substituents have little or no effect on the long - range coupling constants but bromine being larger than chlorine would cause a larger barrier to the rotation of the methylene group and the amplitude of the motion of the methylene group would be smaller.

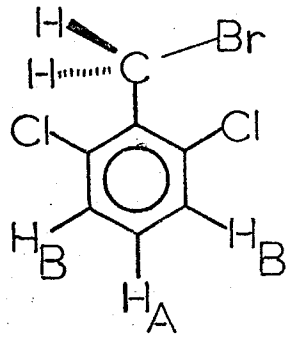
3) measuring the benzylic proton - para proton coupling in α - x - 3,5 - dichlorotoluene. Since these compounds have two ortho hydrogen substituents the methylene rotor would have a larger amplitude of motion as compared to α - x - 2,6 - dichlorotoluene.

4) Taking the ultraviolet spectra of the α - substituted toluene compounds. These spectra should show how the α - substituent influences the overlap between the methylene group and the aromatic ring (42).

APPENDIX I

Analysis of AB_2X_2 Spectra

A normal AB_2 spectrum consists of 8 peaks. In an AB_2X_2 system the X_2 protons split each of the AB_2 lines into a triplet so that the spectrum is composed of 8 sets of triplets. An example of an AB_2X_2 system is



The AB_2 portion of such a spectrum can be treated as 3 subspectra (27) where the shift in each subspectrum is given by

$$\nu_A(x) = \nu_A + xJ_{AX}$$
$$\nu_B(x) = \nu_B + xJ_{BX}$$

where $x = 1, 0, -1$. $\nu_A(x)$ denotes the shift of proton A in subspectrum X, J_{AX} and J_{BX} are the coupling constants. The line frequencies are given by the following expressions.

line 1 a. $\frac{1}{2}(\nu_A + \nu_B) + \frac{1}{2}(J_{AX} + J_{BX}) + 3/4\, J_{AB} + C^+_{+1}$

b. $\frac{1}{2}(\nu_A + \nu_B) + 3/4\, J_{AB} + C^+_0$

c. $\frac{1}{2}(\nu_A + \nu_B) - \frac{1}{2}(J_{AX} + J_{BX}) + 3/4\, J_{AB} + C^+_{-1}$

line 2 a. $\nu_B + J_{BX} + C^+_{+1} + C^-_{+1}$

b. $\nu_B + C^+_0 + C^-_0$

c. $\nu_B - J_{BX} + C^+_{-1} + C^-_{-1}$

line 3 a. $\nu_A + J_{AX}$

b. ν_A

c. $\nu_A - J_{AX}$

line 4 a. $\frac{1}{2}(\nu_A + \nu_B) + \frac{1}{2}(J_{AX} + J_{BX}) - 3/4\, J_{AB} + C^-_{+1}$

b. $\frac{1}{2}(\nu_A + \nu_B) \qquad - 3/4\, J_{AB} + C^-_0$

c. $\frac{1}{2}(\nu_A + \nu_B) - \frac{1}{2}(J_{AX} + J_{BX}) - 3/4\, J_{AB} + C^-_{-1}$

line 5 a. $\nu_B + J_{BX} + C^+_{+1} - C^-_{+1}$

b. $\nu_B \qquad + C^+_0 - C^-_0$

c. $\nu_B - J_{BX} + C^+_{-1} - C^-_{-1}$

line 6 a. $\frac{1}{2}(\nu_A + \nu_B) + \frac{1}{2}(J_{AX} + J_{BX}) + 3/4\, J_{AB} - C^+_{+1}$

b. $\frac{1}{2}(\nu_A + \nu_B) \qquad + 3/4\, J_{AB} - C^+_0$

c. $\frac{1}{2}(\nu_A + \nu_B) - \frac{1}{2}(J_{AX} + J_{BX}) + 3/4\, J_{AB} - C^+_{-1}$

line 7 a. $\nu_B + J_{BX} - C^+_{+1} + C^-_{+1}$

b. $\nu_B \qquad - C^+_0 + C^-_0$

c. $\nu_B - J_{BX} - C^+_{-1} + C^-_{-1}$

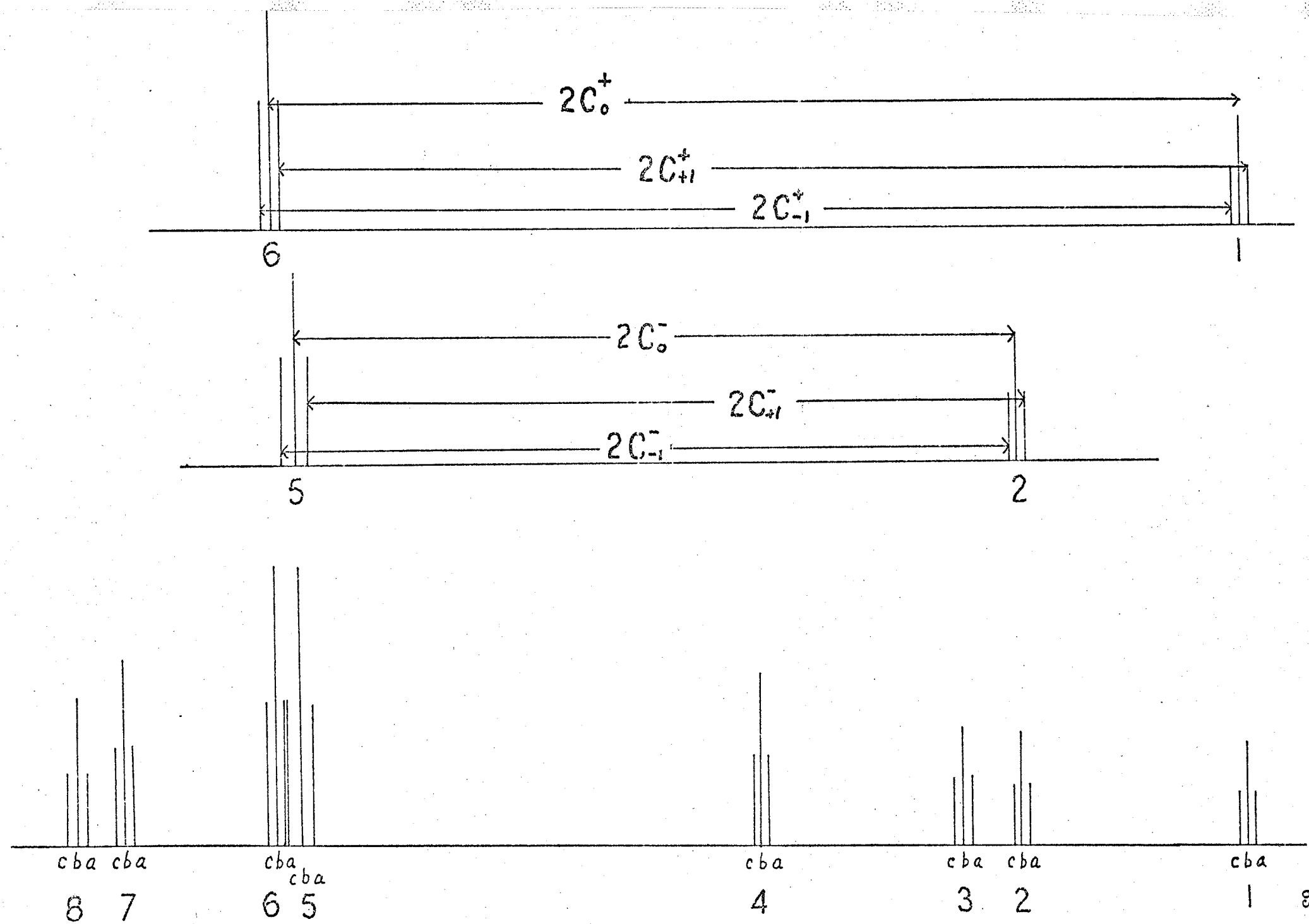
line 8 a. $\frac{1}{2}(\nu_A + \nu_B) + \frac{1}{2}(J_{AX} + J_{BX}) - 3/4\, J_{AB} - C^-_{+1}$

b. $\frac{1}{2}(\nu_A + \nu_B) \qquad - 3/4\, J_{AB} - C^-_0$

c. $\frac{1}{2}(\nu_A + \nu_B) - \frac{1}{2}(J_{AX} + J_{BX}) - 3/4\, J_{AB} - C^-_{-1}$

Figure 10

The AB_2 portion of a typical AB_2X_2 spectrum. The triplets are numbered 1 to 8 from right to left. The constants C_0^+, C_{-1}^+, C_{+1}^+, C_0^-, C_{-1}^-, C_{+1}^- take on the values shown.


$2C_0^+$
$2C_{+1}^+$
$2C_{-1}^+$
6
1
$2C_0^-$
$2C_{+1}^-$
$2C_{-1}^-$
5
2
c b a
c b a
c b a
c b a
c b a
c b a
c b a
8 7 6 5 4 3 2 1

The terms C_1^+, C_0^+, C_{-1}^+, C_1^-, C_0^-, C_{-1}^-, are constants which take on the values shown in Figure 10.

From these expressions it is seen that:

$$\nu_A = 3b$$

$$\nu_B = \frac{1}{2}\left[5b + 7b\right]$$

$$J_{AX} = \frac{1}{2}(3a - 3c)$$

$$J_{AB} = \frac{1}{3}\left[(8b - 6b) + (4b - 1b)\right]$$

$$J_{BX} = \frac{1}{4}\left[(5a - 5c) + (7a - 7c)\right]$$

This means that J_{AX} can be obtained directly by a single measurement of the splitting of triplet 3. In toluene J_{AX} and J_{BX} are negative and positive respectively (16).

In this case the nucleus A resonates to high field of nucleus B. If the order were reversed the observed spectrum would just be the mirror image of the one shown in Figure 6. The triplets 5 and 6 are not completely resolved. Peaks 5a and 6c are seen as a single peak.

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