

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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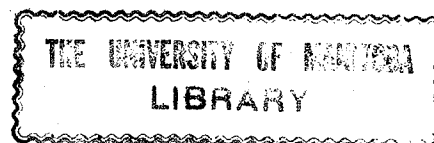
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ABSTRACT

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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Chapter I

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

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

where g_e and g_N are the Landé 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 $L = 0$. 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

* 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.

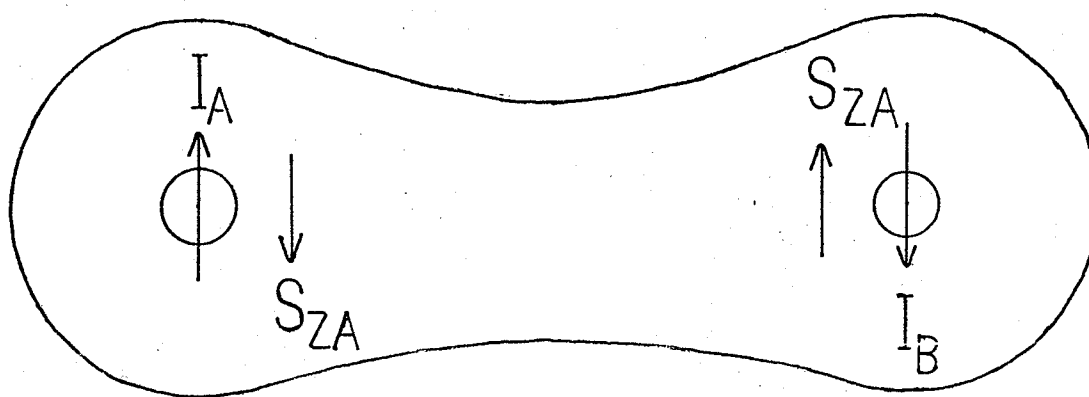


Figure 1

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

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

where $g_e, \beta_e, g_N, \beta_N$ 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

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

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

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

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

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

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

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

$$\psi = \psi_0 - \frac{8}{3} \pi g_e \beta g_N \beta_N I_{ZA} \sum_n \frac{\langle n | SZA | 0 \rangle}{E_n - E_0} \psi_n \quad 6.$$

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

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

must be evaluated, where

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

and operates only on the spin functions.

$$\begin{aligned} \langle \psi | S_{ZB} | \psi \rangle &= \langle \psi_0 - \frac{8}{3} \pi g_e \beta g_N \beta_N I_{ZA} \sum_n \frac{\langle n | SZA | 0 \rangle}{E_n - E_0} \psi_n | S_{ZB} | \psi_0 \\ &\quad - \frac{8}{3} \pi g_e \beta g_N \beta_N I_{ZA} \sum_n \frac{\langle n | SZA | 0 \rangle}{E_n - E_0} \psi_n \rangle \quad 9. \\ &= \langle \psi_0 | S_{ZB} | \psi_0 \rangle - 2 \langle \frac{8}{3} \pi g_e \beta g_N \beta_N I_{ZA} \sum_n \frac{\langle n | SZA | 0 \rangle}{E_n - E_0} \psi_n | S_{ZB} | \psi_0 \rangle \\ &\quad + \langle (\frac{8}{3} \pi g_e \beta g_N \beta_N)^2 I_{ZA}^2 \sum_n \frac{\langle n | SZA | 0 \rangle}{E_n - E_0} \psi_n | S_{ZB} | \sum_n \frac{\langle n | SZA | 0 \rangle}{E_n - E_0} \psi_n \rangle \quad 10. \end{aligned}$$

But, the first term in equation 10 is

$$\langle \psi_0 | S_{ZB} | \psi_0 \rangle = \frac{1}{2} \langle [\psi_b(\underline{r}_1) \psi_b(\underline{r}_2)]^2 \rangle_X$$

$$\langle \alpha\beta - \beta\alpha | S_{Z1} \delta(\underline{r}_1 - \underline{r}_B) + S_{Z2} \delta(\underline{r}_2 - \underline{r}_B) | \alpha\beta - \beta\alpha \rangle \quad 11.$$

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

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

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

$$\langle \psi_0 | S_{ZB} | \psi_0 \rangle = 0 \quad 13.$$

The third term of equation 10 contains the matrix elements $\langle \psi_n | S_{ZB} | \psi_n \rangle$. 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

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

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

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

Then the term

$$\begin{aligned} \langle \psi_1 | S_{ZB} | \psi_1 \rangle &= K \langle \alpha\beta + \beta\alpha | S_{ZB} | \alpha\beta + \beta\alpha \rangle \\ &= K \langle \alpha\beta + \beta\alpha | \alpha\beta - \beta\alpha \rangle \\ &= 0 \end{aligned} \quad 15.$$

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

$$\left(-\frac{8}{3} \pi g_e \beta g_N \beta_N I_{ZA} \right) \left[\sum_n \frac{\langle n | S_{ZA} | 0 \rangle}{E_n - E_0} \langle \psi_n | S_{ZB} | \psi_0 \rangle + \langle \psi_0 | S_{ZB} | \sum_n \frac{\langle n | S_{ZA} | 0 \rangle}{E_n - E_0} \psi_n \rangle \right] \quad 16.$$

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

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

and it can be rewritten as

$$J I_{ZA} I_{ZB} = I_{ZA} I_{ZB} \left[\left(-\frac{8}{3} \pi g_e \beta g_N \beta_N \right)^2 \frac{\left(\sum_n \frac{\langle n | S_{ZA} | 0 \rangle \langle \psi_n | S_{ZB} | \psi_0 \rangle + \langle \psi_0 | S_{ZB} | \psi_n \rangle \langle n | S_{ZA} | 0 \rangle}{E_n - E_0} \right)}{E_n - E_0} \right] \quad 18.$$

Then

$$J = \left(-\frac{8}{3} \pi g_e \beta g_N \beta_N \right)^2 \sum_n \frac{\langle n | S_{ZA} | 0 \rangle \langle n | S_{ZB} | 0 \rangle + \langle 0 | S_{ZB} | n \rangle \langle n | S_{ZA} | 0 \rangle}{E_n - E_0} \quad 19.$$

and taking $\psi_n = \psi_1$

$$\langle 1 | S_{ZA} | 0 \rangle = \frac{1}{2} \left[\psi_b(\underline{r}_1) \psi_a(\underline{r}_2) - \psi_a(\underline{r}_1) \psi_b(\underline{r}_2) \right] (\alpha\beta + \beta\alpha) \\ \times \left[S_{Z1} \delta(\underline{r}_1 - \underline{r}_A) + S_{Z2} \delta(\underline{r}_2 - \underline{r}_A) \right] \frac{1}{\sqrt{2}} \psi_b(\underline{r}_1) \psi_b(\underline{r}_2) (\alpha\beta - \beta\alpha) \quad 20.$$

Using equation 12

$$\langle 1 | S_{ZA} | 0 \rangle = \frac{1}{2\sqrt{2}} \left\langle \left[\psi_b(\underline{r}_1) \psi_a(\underline{r}_2) - \psi_a(\underline{r}_1) \psi_b(\underline{r}_2) \right] \delta(\underline{r}_1 - \underline{r}_A) - \delta(\underline{r}_2 - \underline{r}_A) \right. \\ \left. \times \left[\psi_b(\underline{r}_1) \psi_b(\underline{r}_2) \right] \right\rangle \quad 21a.$$

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

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

Therefore

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

$\phi_a^2(\underline{r}_A)$ 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

$${}^4J_{HH'} = \frac{4185}{\Delta E} \left\{ p^o(hh') + \frac{3}{2} \left[p^o(h\sigma_1) p^o(\sigma_2 h') + p^o(h\sigma_2) p^o(\sigma_1 h') \right] - \frac{3}{2} \left[p^o(hc_2) p^o(c_2 h') + p^o(hc_2') p^o(c_2' h') \right] \right\} \quad 26.$$

where

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

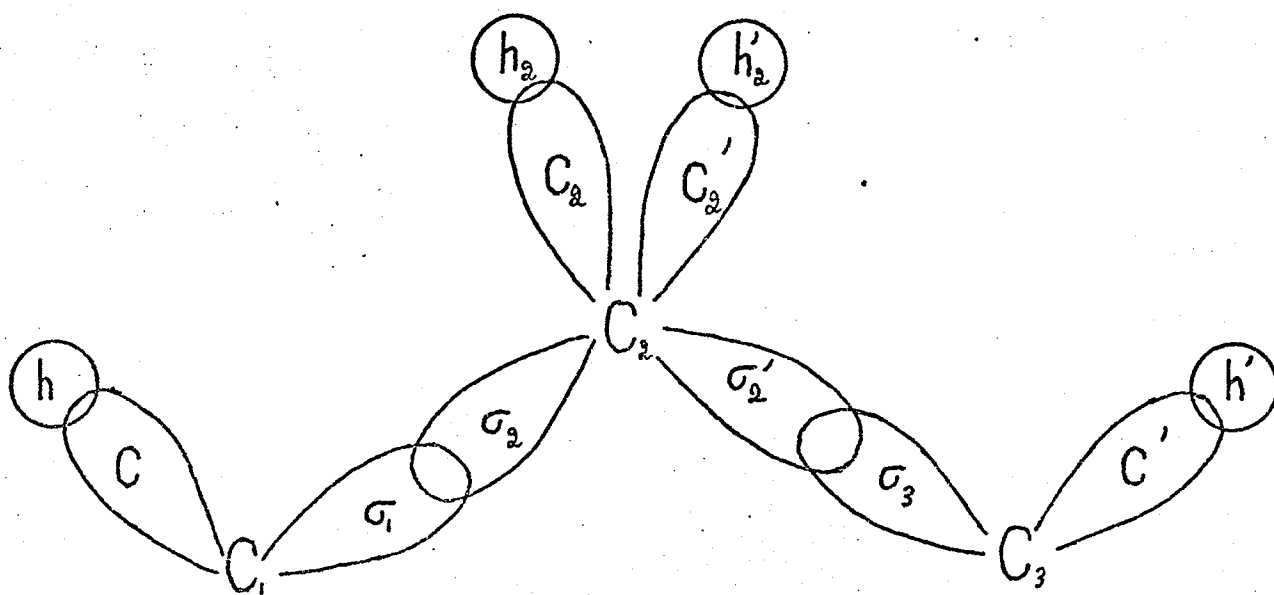
and

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

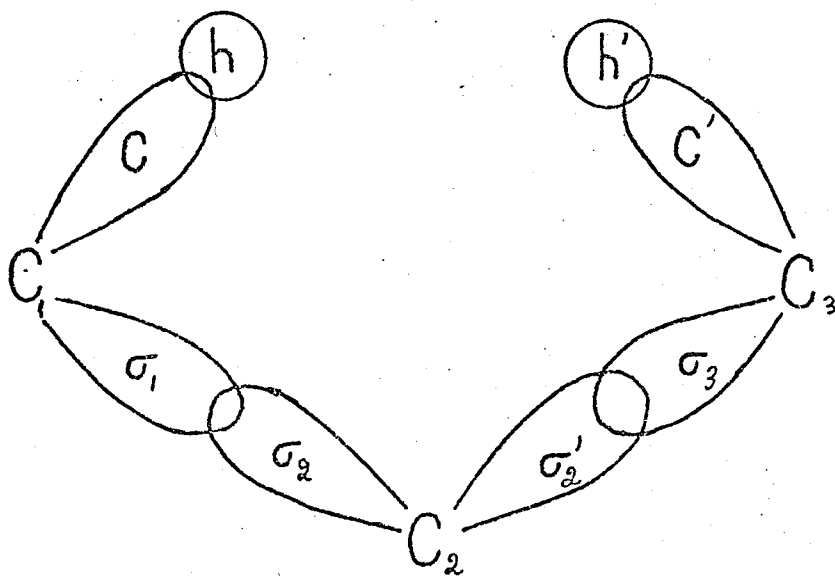
K denotes the two - electron valence bond exchange integral associated with the orbitals given in the argument. The first term in equation 26 represents the direct interaction between the two C-H bonds. The direct term is expected to depend on the conformation. In Figure 2b the direct term would be much 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. ϑ and ϑ' are the dihedral angles formed by the C - H and C - H' bonds respectively with the C₁ - C₂ - C₃ plane. In a) $\vartheta = \vartheta' = 180^\circ$ whereas in b) $\vartheta = \vartheta' = 0^\circ$. The direct interaction between the c - h and c' - h' bonds is expected to be more important in b) than in a) .



a)



b)

$$\begin{aligned}
 p^0(h \sigma_2') &= A \cos^2 \vartheta + B \cos \vartheta + C \\
 p^0(\sigma_2 h') &= A \cos^2 \vartheta' + B \cos \vartheta' + C
 \end{aligned}
 \tag{27}$$

where ϑ and ϑ' 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 ϑ and ϑ' are 180° . 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 importance here and can be written as

$${}^5J_{H, H'} = \frac{4185}{\Delta E} \frac{3}{2} p^0(c\sigma) p^0(\sigma'c')
 \tag{28}$$

Both $p^0(c\sigma)$ and $p^0(\sigma'c')$ are vicinal terms and are written as

$$\begin{aligned}
 p^0(c\sigma) &= A \cos^2 \vartheta + B \cos \vartheta + C \\
 p^0(\sigma'c') &= A' \cos^2 \vartheta' + B' \cos \vartheta' + C
 \end{aligned}
 \tag{29}$$

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

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

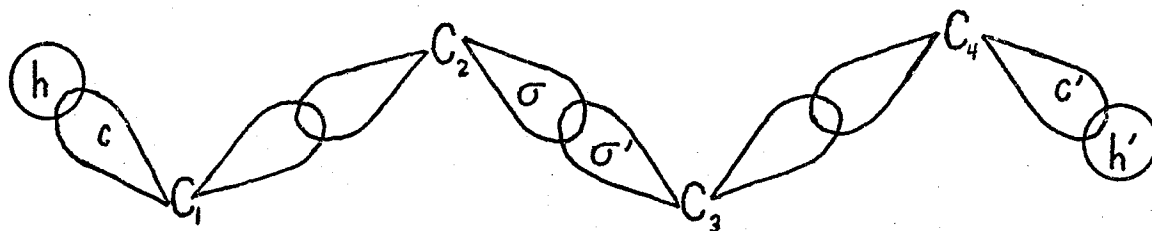
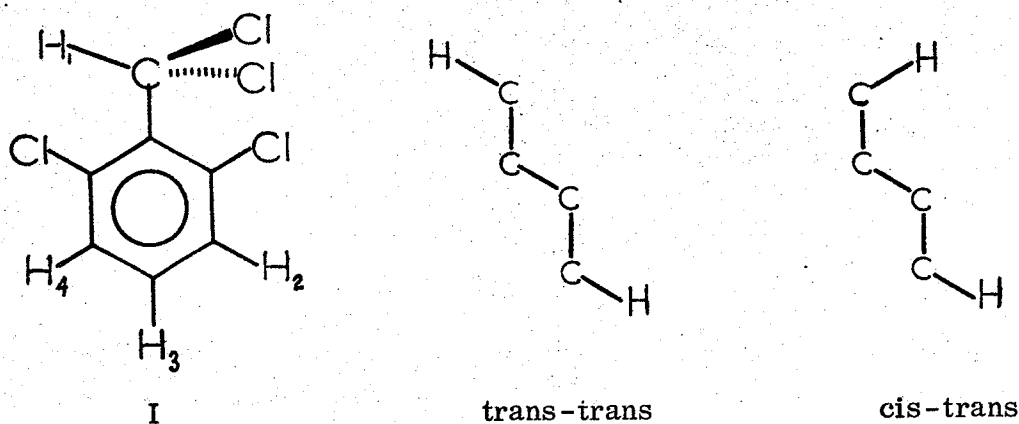


Figure 3

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 $\theta = \theta' = 180^\circ$. ${}^5J_{\text{HH}'}$ is independent of the dihedral angle about the $\text{C}_2 - \text{C}_3$ 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



proton couples more strongly to proton 2 than to proton 4 (5), $J_{12} = 0.5 \text{ Hz}$ 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 σ - π configuration interaction (8) and may be written as (8, 9)

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

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)

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

where Q_{CCH} is the effective isotropic splitting constant for the fragment C - CH₃ 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

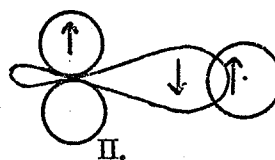
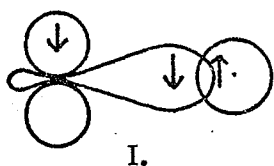
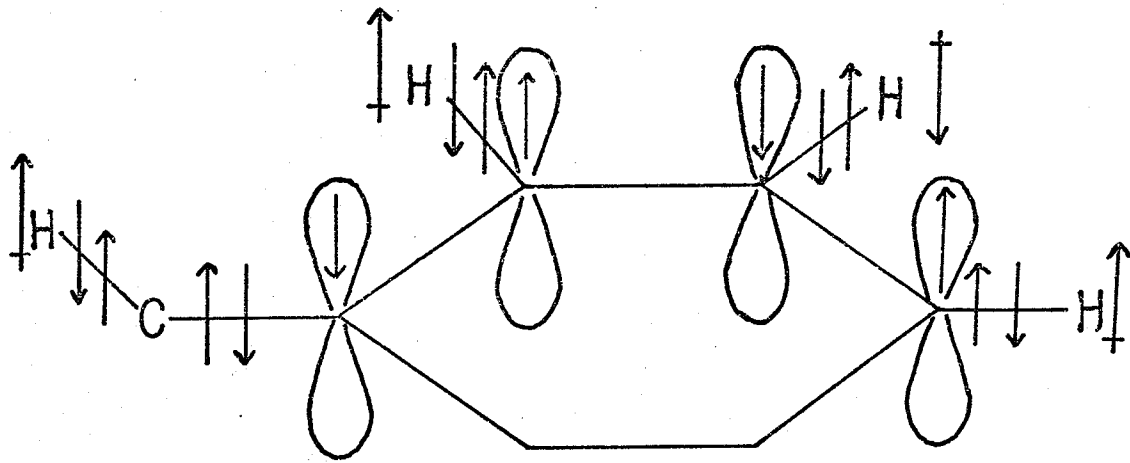
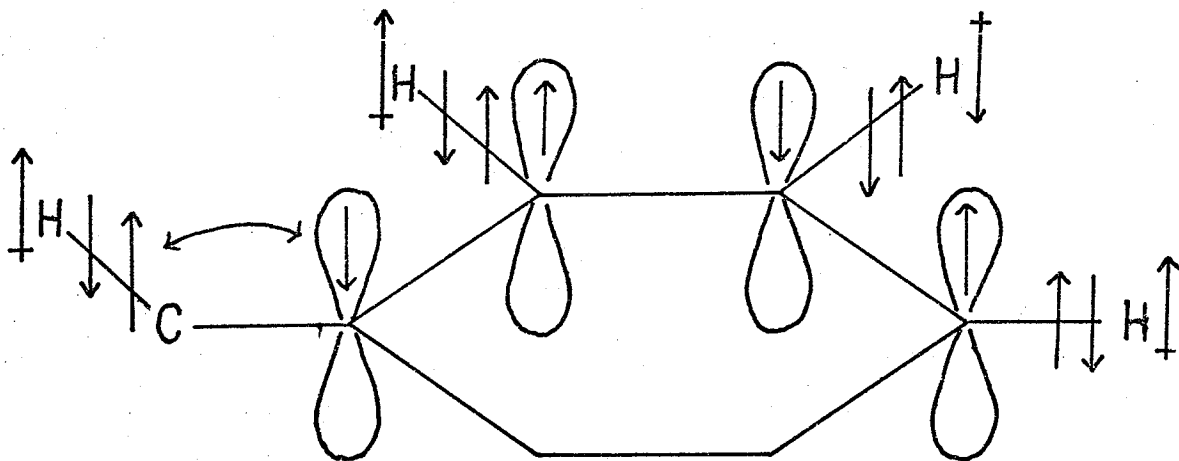


Figure 4

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)

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

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)

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

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.

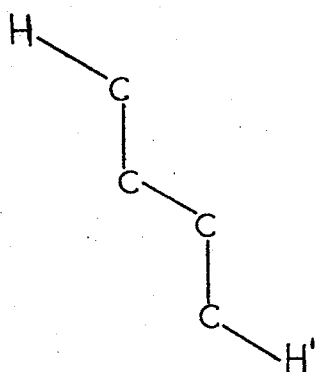
The benzylic proton - meta proton coupling is transmitted by both the σ - and π - mechanisms (4, 8, 24) so that the observed coupling may be expressed as

$$J_m^{H, H'} = J_m^{\pi} + J_m^{\sigma} \quad 34.$$

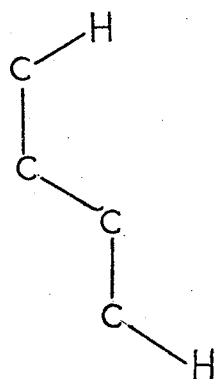
The π - contribution, J_m^{π} , which has the same angular dependence as the para coupling $J_p^{H, H'}$ vanishes whenever the benzylic C - H bond lies in the plane of the ring. J_m^{σ} , which is a five - bond coupling similar to the butanic coupling may be expressed as

$$J_m^{\sigma} \propto (A \cos^2 \vartheta + B \cos \vartheta + C) (A' \cos^2 \vartheta' + B \cos \vartheta' + C) \quad 35.$$

where ϑ and ϑ' (see Figure 3) are the dihedral angles about the $C_1 - C_2$ and $C_3 - C_4$ bonds respectively. $\vartheta = \vartheta' = 180^\circ$ in the trans - trans conformation but $\vartheta = 0$ and $\vartheta' = 180^\circ$ 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 $\theta = \theta' = 180^\circ$ and the $C_1 - C_2 - C_7 - C_6$ system is in the cis - trans configuration with $\theta = 0$ and $\theta' = 180^\circ$. In both the trans - trans and the cis - trans arrangements $\theta' = 180^\circ$ so that the expression 35 may be rewritten as

$$J_m^\sigma = K (A \cos^2 \theta + B \cos \theta + C) \quad 36.$$

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

