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Carbon-13 Magnetic Resonance. VII.[1] Steric Perturbation of the Carbon-13 Chemical Shift

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Abstract: The chemical shifts of sterically perturbed carbon atoms are generally found at higher magnetic fields than for similar carbons which are not spatially crowded. The magnitude of these shifts, however, exhibits a strong dependence upon the conformational geometry existing between the C–H bonds in the two interacting groups. These substituent shifts are found to be directly related to the force component along the H–C^{13} bond associated with nonbonded hydrogen–hydrogen repulsive interactions. Based on sterically induced charge polarization in the perturbed H–C^{13} bond, a model is discussed which rationalizes the angular and distance features accompanying the interacting, proximate hydrogen atoms.

In a study of the methylbenzenes, Woolfenden and Grant[2] proposed that the carbon-13 magnetic resonance spectra of the methyl carbons could be interpreted with additive parameters which reflect conformational features existing between adjacent methyl groups. The three configurations required to rationalize these spectral data and the corresponding substituent parameters are given as structures I–III in Figure 1. Two of the values have relatively sizable magnitudes while one of them does not deviate greatly from zero. It is well to emphasize, however, that the small value assigned to III is conceptually just as important as the two larger parameters. This conclusion follows from the manner in which all three structures were included, with equal importance, in the normalization of the populational factors used in the regressional analysis. Contained also in Figure 1 as structure IV is a substituent shift[3] which arises from the interaction of *gauche* 1,4-carbon atoms. This parameter was determined in several methylcyclohexanes of known structure which have axial methyl groups. The steric shift results from a *gauche* interaction between the hydrogens on an axial methyl at C-1 and the axial hydrogens in the 3 and 5 positions of the cyclohexane ring.

It is suggested that these conformational parameters can best be explained with a model which emphasizes the steric interactions existing between proximate hydrogens on two sterically perturbed carbon–hydrogen groups. It will be shown that the substituent parameters reflect the angular and distance dependence of nonbonded hydrogen–hydrogen repulsive forces. The recent work of Cignitti and Allen[4] contains an extensive survey of existing methods for treating such nonbonded interactions, and we have selected the simple valence bond (VB) approach to describe these steric features. The experimental hydrogen–hydrogen energies of Tobias and Vanderslice[5] are used to approximate the pertinent hydrogen–hydrogen integrals. As the empirical values are in good agreement with the theoretical results of Dalgarno and Lynn,[6] further confidence can be placed in the experimental quantities.

Results and Discussion

A. Structural and Geometric Parameters. Summarized in Table I are the substituent shift per pair of interacting hydrogens, the proton–proton distance (r), and the cosine of the H′H and HC^{13} angle for each of the

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[1] Previous paper in this series: T. D. Alger, D. M. Grant, and E. G. Paul, *J. Am. Chem. Soc.*, **88**, 5397 (1966).

[2] W. R. Woolfenden and D. M. Grant, *ibid.*, **88**, 1496 (1966).

[3] D. K. Dalling and D. M. Grant, *ibid.*, in press.

[4] M. Cignitti and T. L. Allen, *J. Phys. Chem.*, **68**, 1292 (1964).

[5] I. Tobias and J. T. Vanderslice, *J. Chem. Phys.*, **35**, 1852 (1961).

[6] A. Dalgarno and N. Lynn, *Proc. Phys. Soc.* (London), **A69**, 821 (1956).

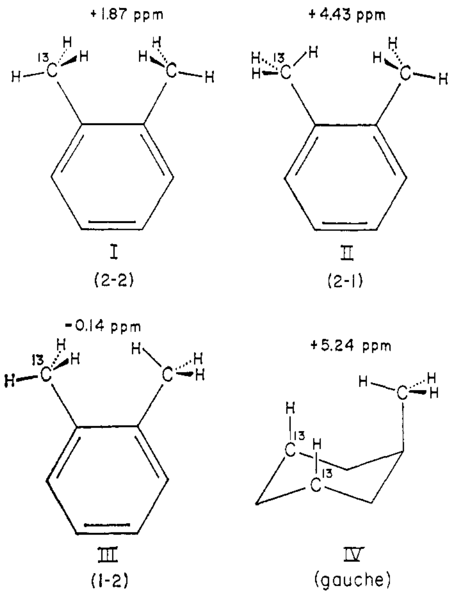

Figure 1. Carbon-13 chemical shift substituent parameters are given for the four specified conformations.

configurations given in Figure 1. The substituent parameters for the methyl conformations in the *o*-xylenes, which involve two hydrogen–hydrogen steric interactions each, are reduced by a factor of 2 to make them directly comparable with the *gauche* configuration where only one pair of proximate protons are interacting significantly. The values contained in Table I were obtained by assuming that the normal 109° 29′ and 120° angles exist for the tetrahedral and trigonal carbon atoms, respectively. The carbon–hydrogen bond distance was taken as 1.095 A[7] in each structure, and the carbon–carbon bond distances are 1.542 A[7] in the *gauche* configuration, 1.52 A[8] for the methyl-carbon-ring-carbon separation, and 1.392 A[8] for the carbon–carbon distance in the aromatic ring. A 60° angle was assumed for all of the dihedral angles in the staggered arrangement of atoms depicted by structure IV. In structures I–III the several dihedral angles are either 0 or 60°. The two varieties of dihedral angles can be easily visualized from Figure 1. Symmetry preserves all of the dihedral angles with the values indicated except for the dihedral angles existing in the cyclohexane ring. It may well be that the axial methyl group flattens the cyclohexane chair structure sufficiently to lead to minor deviations in these dihedral angles. As a working hypothesis these deviations are not considered to be important for the present.

Table I. Structural Parameters and Carbon-13 Substituent Shifts for Molecular Moieties Given in Figure 1

Structure	r, A	cos θ	$F_1(r)$, dynes	$\delta_{C^{13}}$,[a] ppm
I	2.383	0.2416	$+0.540 \times 10^{-6}$	+0.94
II	2.148	0.4944	$+2.068 \times 10^{-5}$	+2.22
III	2.148	−0.0592	-0.248×10^{-6}	−0.07
IV	1.881	0.4304	$+3.672 \times 10^{-5}$	+5.24

[a] These steric parameters reflect the shift in ppm for each interacting set of hydrogen atoms. Thus, the values given in Figure 1 for structures I–III have all been reduced by a factor of 2.

B. Nonbonded Hydrogen–Hydrogen Interactions. In a simple VB formulation that ignores deviations from perfect pairing, nonbonded interaction energies may be introduced directly into the total molecular energy as the sum of the Coulombic integral, $Q(r)$, and $-{}^1/_2$ times the exchange integral, $K(r)$. If one now makes the additional simplifying assumption that the molecular energy varies only with the appropriate hydrogen–hydrogen integrals as the distance between these hydrogens is altered, then the steric force can be written as

$$F(r) = -\frac{d}{dr}[Q(r) - K(r)/2] \qquad (1)$$

Values for $Q(r)$ and $K(r)$ may be evaluated in the VB formulation from the singlet (${}^1\Sigma_g$) and triplet (${}^3\Sigma_u$) state energies of the hydrogen molecule as

$$\begin{aligned} Q(r) &= \frac{1}{2}(E_s + E_t) + \frac{S^2}{2}(E_s - E_t) \\ K(r) &= \frac{1}{2}(E_s - E_t) + \frac{S^2}{2}(E_s + E_t) \end{aligned} \qquad (2)$$

where S is the overlap integral between the two hydrogen orbitals, and E_s and E_t are, respectively, the singlet- and triplet-state energies. As a proper means of simplification, S may be taken as zero for the relatively large internuclear distances encountered in this study, and thus $Q(r)$ and $K(r)$ become $^1/_2$ times the sum and difference of E_s and E_t, respectively. Using the very accurate singlet and triplet energy curves calculated by Kolos and Roothaan[9] for H_2, it was found that Q was 17% of E_s at the maximum distance (r = 1.852 A) for which these workers give energy values for E_t. Furthermore, the percentage of Q in E_s, as calculated from (2) with $S = 0$, does not vary greatly (±3%) from this 17% figure over the range 1.058–1.852 A. The unavailability of good triplet-state energies for distances exceeding 1.852 A prevents us from using (2) to calculate $Q(r)$ and $K(r)$ directly, but using 17% of $E_s(r)$ as an approximate value for $Q(r)$ allows us to evaluate (1) from a good, existing[5] singlet-state energy curve as

$$Q(r) - [K(r)/2] = 0.17E_s(r) - (0.83/2)E_s(r) = -0.25E_s(r) \qquad (3)$$

In order to use the numerical data of Tobias and Vanderslice[5] in (3) as an approximation of $E_s(r)$, the experimental values are fit with a simple mathematical expression of the following form.

$$E_s(r) = A\exp(-\alpha r) \qquad (4)$$

The success of a least-squares fit yielding $A = -1.943 \times 10^{-10}$ erg and $\alpha = 2.671$ A^{-1} can be seen in Figure 2 for the range in which nonbonded steric interactions are important. The simple exponential law proposed in (4) begins to break down seriously for $r < 1.7$ A, but agreement between this simple expression and the experimental data is quite satisfactory in the range 1.7 A $< r < \infty$ where normal nonbonded repulsions are important.

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(7) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Chapter 7.

(8) S. H. Bauer and P. Anderson, *Ann. Rev. Phys. Chem.*, 4, 236 (1953), quoting F. A. Keidel in ref 7. See also L. E. Sutton, "Interatomic Distances," Burlington House, London, 1958, p M214.

(9) W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 219 (1960).

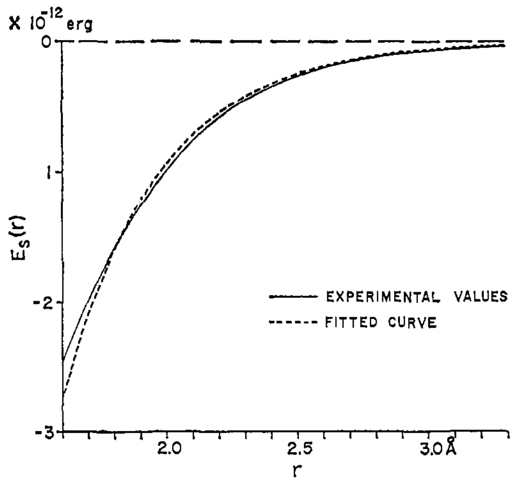

Figure 2. The hydrogen-hydrogen interaction energies of Tobias and Vanderslice[5] are compared with the simple expression, $V = 1.943 \times 10^{-10} \exp(-2.671r)$, in the range 1.6 to 3.3 A.

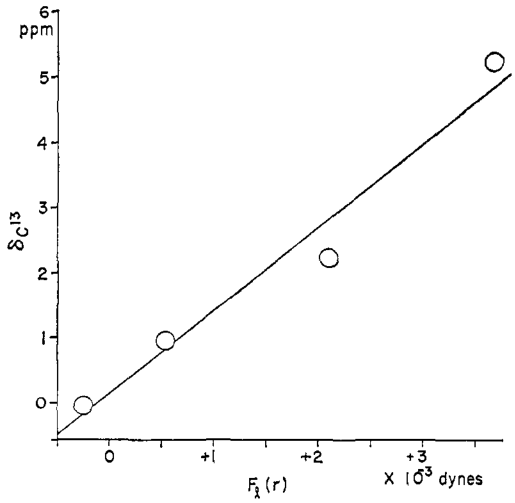

Figure 3. The carbon-13 substituent parameter, $\delta_{C^{13}}$, is plotted against F_l, the steric force directed along the H-C^{13} bond.

Equations 1, 3, and 4 and the above constants combine to give the following force relationship in units of dynes.

$$F(r) = 0.25\frac{dE_s(r)}{dr} = 1.297 \times 10^{-2} \exp(-2.671r) \quad (5)$$

The force vector is parallel to the hydrogen-hydrogen axis and is repulsive in nature as indicated by the plus sign.

C. Carbon-13 Substituent Shifts and Hydrogen-Hydrogen Steric Forces. The component of repulsive force $F_l(r)$ directed along the HC^{13} bond is given by

$$F_l(r) = F(r)\cos\theta \quad (6)$$

and its values are also presented in Table I. Figure 3 contains a plot of $\delta_{C^{13}}$ *vs.* $F_l(r)$, and within the limits of errors inherent in the treatment a linear relationship is obtained with a slope of 1.30×10^5 ppm/dyne. The scatter in data points is felt to be minimal when one considers the approximate nature of the simple VB theory along with the inaccuracies which exist in the values used for r and cos θ. Although there is no reason to believe that the structural parameters used to calculate the values in Table I are in serious error, exact bond distances and angles are nevertheless unavailable for the several compounds that are being considered, and some distortions in the distances and angles which have been used is unavoidable. The least-squares intercept (+0.12 ppm) for the best fit in Figure 3 does not differ from zero by much more than the experimental error in the substituent parameters. This would suggest that any change in the chemical shift arising from inductive effects through the skeletal carbon structure must be relatively small, and the proposal is supported that these substituent shifts are due primarily to steric interaction of otherwise remote groups which have coiled back upon one another. Considering that the steric effects studied here represent quite a variety of molecular orientations and of proton-proton distances, it is felt that the empirical correlation is unusually satisfactory. This is further emphasized by the success of the model in rationalizing completely the somewhat unexpected nonreciprocal relationship existing between the substituent parameters for conformations II and III. As the proton-proton distance is identical for these two configurations, it is encouraging that the difference in the two substituent values can be explained with the angular dependence of the steric interaction.

It would appear from the success of the above correlation that the carbon-13 chemical shift parameter is reflecting distance and angular features of steric interactions not previously enumerated in such an intricate manner by other physical measurements. The importance of such a relationship in studies of molecular conformation is apparent, and an expression relating the structural parameters with the carbon-13 shifts would be desirable. Utilizing the slope of Figure 3 along with (5) and (6), the following empirical expression is proposed for predicting the angular and distance dependence of sterically altered carbon-13 chemical shifts

$$\delta_{C^{13}}(\text{ppm}) = +1680\cos\theta\exp(-2.671r) \quad (7)$$

where r is the proximate proton-proton distance, θ is the angle between the proton-proton axis and the perturbed HC^{13} bond, and $\delta_{C^{13}}$ is the sterically induced carbon-13 chemical shift.[10]

D. The Nature of the Steric Effects on the Chemical Shift of Carbon. Several possible models suggest themselves as ways for explaining the sterically induced shifts in carbon-13 magnetic resonance spectra. The first which needs to be discussed, because of its general popularity, is one which has been used many times for explaining remote substituent effects in proton magnetic resonance spectra—the existence of anisotropy in the magnetic susceptibility[11,12] of the perturbing molecular moiety. This possibility might well be expected to

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(10) Alger, Grant, and Paul[1] used an expression of identical form with eq 7 but with different constants to predict a +5.9-ppm shift in the sterically perturbed C-4 position in phenanthrene. The expression used by these authors was derived from a Morse curve potential in which the exponential α value is 1.96 A^{-1}. As Cignitti and Allen[4] have pointed out, the negative Morse potential is too large in magnitude, and the force is too soft in its distance dependence in the region of interest. Thus we now realize that the previous chemical shift expression suffers from these errors which are embodied in the approximations used earlier. Using eq 7 of this paper the steric shift for phenanthrene at C-4 calculates to be +7.8 ppm for $\theta = 60°$ and $r = 1.75$ A. This steric shift is of comparable magnitude with that reported before for phenanthrene, and this revised estimate therefore does not change the conclusions proposed in ref 1.

(11) H. M. McConnell, *J. Chem. Phys.*, 27, 226 (1957).

(12) J. A. Pople, *Proc. Roy. Soc.* (London), **A239**, 550 (1957).

exhibit intricate conformational features but is excluded from major consideration on the basis that anisotropic terms describe field effects which are a property of the perturbing group and not of the nuclei under observation. Since no steric shifts of the magnitude observed here for carbon-13 nuclei have ever been noted for protons in the same general spatial orientations, one must conclude that anisotropic effects are relatively small and will not account for the steric effects under consideration.

Alteration of electron spin-pairing schemes can also lead to rather sizable effects upon the chemical shift parameter by changing the degree of admixture of excited paramagnetic states into the ground-state description of a molecule in a static magnetic field. In MO treatments of aromatic hydrocarbons, it has been recognized[1,13] that changes in the spin-pairing scheme, as reflected by variations in the bond-order parameter, can explain a large part of the range noted in the chemical shifts observed for these compounds. Likewise, VB estimates[14] of deviations from the classical bond structure, a similar way of considering variations in spin pairing of electrons, can rationalize some measurable shifts in the chemical screening values recorded for the simple alkanes. Thus, some changes in the screening constant might be expected from sterically induced alterations of the bonding scheme. We have made several attempts to estimate the magnitude of such terms along the lines suggested in ref 14, but the best estimates based on a simple VB calculation of spin-pairing effects fail to account for more than a small fraction of the substituent parameters given for the conformations contained in Figure 1. Pending additional work it is felt that this term can be excluded from consideration for the time being.

A highly speculative model for explaining the steric effect which is favored at the present time involves a steric polarization of the valence electrons in the molecule. It has already been proposed[1,13–15] that minor changes in the electron density about a nucleus create variations in the repulsion between electrons, and this should be reflected in the so-called "effective nuclear charge" parameter. Changes in the "effective nuclear charge" parameter alter the $\langle 1/r^3 \rangle$ term which is important in the paramagnetic portion of the chemical shift expression. For example, an increase of negative charge would be associated with a general electron expansion about the nucleus, and the smaller value for $\langle 1/r^3 \rangle$ would decrease the paramagnetic term, causing the resonance position to shift upfield. Thus, it is proposed that the upfield steric shifts are due to induced polarization of charge along the HC^{13} bond, and an attempt will now be made to estimate the magnitude of such a sterically induced polarization of electronic charge.

If the longitudinal bond polarizability constant, α_l, is used to approximate the degree of induced charge polarization, one may write

$$\mu_{\mathrm{HC}^{13}} = qeR \approx \frac{\alpha_l F_l(r)}{e} \qquad (8)$$

where $\mu_{\mathrm{HC}^{13}}$ is the sterically induced dipole moment, R is the HC^{13} bond distance, q is the fractional charge in electron units shifted along the HC^{13} bond, with $F_l(r)$, r, and θ having the same definitions as before.[16] Rearranging (8) and investigating the dependence of q upon $F_l(r)$ one obtains

$$\frac{\mathrm{d}q}{\mathrm{d}F_l(r)} \approx \frac{\alpha_l}{e^2R} \qquad (9)$$

One may also write

$$\frac{\mathrm{d}\delta_{\mathrm{C}^{13}}}{\mathrm{d}F_l(r)} = \frac{\mathrm{d}\delta_{\mathrm{C}^{13}}}{\mathrm{d}q}\frac{\mathrm{d}q}{\mathrm{d}F_l(r)} \approx \frac{\mathrm{d}\delta_{\mathrm{C}^{13}}}{\mathrm{d}q}\frac{\alpha_l}{e^2R} \qquad (10)$$

The value[17] for α_l is 0.79×10^{-24} cm^3 and R equals[7] 1.095×10^{-8} cm. Experimental values for $\mathrm{d}\delta_{\mathrm{C}^{13}}/\mathrm{d}q$ equal to 160[18] and 200 ppm/e[19] have been proposed as the chemical shift dependence on charge transfer by Spiesecke and Schneider[18] and Lauterbur,[19] respectively. Using the latter value we calculate a value of 0.62×10^5 ppm/dyne for $\mathrm{d}\delta_{\mathrm{C}^{13}}/\mathrm{d}F_l(r)$. In order of magnitude this value compares reasonably well with the 1.30×10^5 ppm/dyne slope found in Figure 3. In spite of the crude approximations embodied in (8), the agreement between the calculated and experimental values suggests that additional theoretical consideration be given to the proposed model that charge transfer may be induced in sterically perturbed chemical bonds.

It is interesting to note that the extended HMO treatment of Hoffmann[20] also predicts small increases in charge densities in sterically perturbed groups. His calculations indicate that the methyl carbon charge is higher in *o*-xylene than in toluene. Similarly, in 2-methylbutane the *gauche*-methyls, which have one pair of proximate hydrogen atoms, do exhibit higher charge densities than is noted for the unperturbed *trans*-methyl. Semiquantitative agreement therefore exists between the two totally unrelated approaches. Future theoretical studies on the importance of angular variations in steric interactions should prove interesting in light of the importance of this term on the carbon-13 shift parameter.

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(13) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

(14) B. V. Cheney and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 5319 (1967).

(15) P. C. Lauterbur, *J. Chem. Phys.*, **43**, 360 (1965).

(16) The authors fully appreciate that $F_l(r)/e$ does not correspond to a homogeneous electrostatic field over the HC^{13} bond for which the polarizability constant α_l is defined. Nevertheless, as a means of initiating an order-of-magnitude calculation, sufficient merit is claimed for eq 8.

(17) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(18) H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961).

(19) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).

(20) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).