

Carbon-13 Magnetic Resonance. VIII.^{1a} The Theory of Carbon-13 Chemical Shifts Applied to Saturated Hydrocarbons^{1b}

B. Vernon Cheney and David M. Grant

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received February 20, 1967

Abstract: A valence-bond derivation of the chemical shift expression is presented and the major factors affecting carbon-13 shifts are discussed. Polarization effects are considered in terms of their effect upon the average radial distribution of the carbon electrons. Electron delocalization or deviation from the classical bond structure alters the admixture of paramagnetic terms, and these effects are considered in the normal valence-bond framework. Application of the theoretical formulation to simple alkane molecules indicates that all the trends and shift magnitudes can be rationalized with the theoretical results given in this paper.

The general theory of magnetic shielding developed by Ramsey² has been employed by several workers to calculate chemical shifts in specific systems. Saika and Slichter³ suggested that the screening expression could be subdivided into three contributions: (i) $\sigma^{(d)}$, a diamagnetic term arising from electron circulation induced by the magnetic field on the atom in question; (ii) $\sigma^{(p)}$, a paramagnetic term which has its origin in the intrinsic angular momentum of nonspherical orbitals centered on the same atom; and (iii) $\sigma^{(n)}$, a term which includes screening contributions from all other atoms in the molecule. Using this general approach, they discussed the fluorine-19 chemical shifts in F₂ and HF on the basis of variations in the paramagnetic term arising from a change in the local ionic charge density. Karplus and Pople⁴ obtained an expression for carbon-13 shifts in conjugated and aromatic molecules by a detailed LCAO-MO treatment. They predicted a significant dependence upon the π -electron density which agrees in sign and order of magnitude with the experimentally established relationships.^{5,6} Contributions from two-electron terms of the same form as the mobile bond order were also shown to be important in unsaturated systems. Alger, Grant, and Paul⁷ used a modification of this MO approach in their study of the alternant aromatic hydrocarbons and extended the concept of a variable effective nuclear charge to account for charge polarization effects. Using a simple "atom in a molecule" theoretical model Schneider and Buckingham⁸ correlated shifts of mercury-199, thallium-205, and lead-207 in both covalently bonded and ionic compounds. In these systems variation of the paramagnetic shielding term was also found to dominate the chemical shift parameter.

Jameson and Gutowsky⁹ obtained expressions for $\sigma^{(p)}$ in the valence bond (VB) and LCAO-MO frame-

(1) (a) Previous paper in this series: D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89**, 5315 (1967). (b) Taken in part from the Ph.D. dissertation of B. V. Cheney, University of Utah, June 1966.

(2) (a) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); (b) *ibid.*, **86**, 243 (1952).

(3) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

(4) M. Karplus and J. A. Pople, *ibid.*, **38**, 2803 (1963).

(5) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838, 1846 (1961).

(6) H. Spiesscke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961).

(7) T. D. Alger, D. M. Grant, and E. G. Paul, *J. Am. Chem. Soc.*, **88**, 5397 (1966).

(8) W. G. Schneider and A. D. Buckingham, *Discussions Faraday Soc.*, **34**, 147 (1962).

(9) C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, **40**, 1714 (1964).

work including d as well as p orbitals on the atom in question. In the VB formulation, they considered only the perfect-pairing structure and used a separated electron-pair wave function which incorporated ionic terms. The range of chemical shift values for various nuclei was correlated with their atomic number. In this formulation the paramagnetic term depends upon $\langle 1/r^3 \rangle$, which is a function of the atomic number.

Contributions to the chemical shift arising from neighboring atoms, $\sigma^{(n)}$, result from anisotropy in the magnetic susceptibility of these remote groups.¹⁰ As this remote anisotropic term describes a field effect, protons and heavier nuclei will be affected alike when they are positioned in an equivalent spatial configuration. Thus, the upper bounds in the magnitude of the $\sigma^{(n)}$ term for any nucleus cannot exceed some part, probably relatively small, of the total chemical shift range observed for the proton. As such a value will constitute only a few per cent at most of the total chemical shift range of many heavier nuclei, it is reasonable to conclude that anisotropic effects are relatively unimportant in discussing sizable shifts and that variation in the local electronic structure is the major factor in determining the chemical shift of atoms other than hydrogen. From the works cited above this conclusion would appear to be especially true when the paramagnetic term, $\sigma^{(p)}$, is not reduced to zero by symmetry considerations. Therefore, we proceed in this paper upon the supposition that all sizable substituent effects, both proximate and remote, must follow from some variation induced in the immediate electronic environment of the carbon atom under observation.

Theoretical Considerations

A. General Formulation of the Shielding Expression. The magnetic shielding tensor due to local electronic currents may be written²

$$\vec{\sigma} = \vec{\sigma}^{(d)} + \vec{\sigma}^{(p)} \quad (1)$$

where $\vec{\sigma}^{(d)}$ is a diamagnetic term

$$\vec{\sigma}^{(d)} = (e^2/2mc^2a_0)\langle \Psi_0 | \sum_j (r_j^2 \vec{1} - \vec{r}_j \vec{r}_j) / r_j^3 | \Psi_0 \rangle \quad (2)$$

and $\vec{\sigma}^{(p)}$ is a second-order paramagnetic contribution

(10) J. A. Pople, *Discussions Faraday Soc.*, **34**, 7 (1962).

$$\vec{\sigma}^{(p)} = -(e^2/2m^2c^2a_0^3) \sum_{n \neq 0} (E_n - E_0)^{-1} \times \\ (\langle \Psi_0 | \sum_j \vec{L}_j/r_j^3 | \Psi_n \rangle \langle \Psi_n | \sum_k \vec{L}_k | \Psi_0 \rangle + \\ \langle \Psi_0 | \sum_k \vec{L}_k | \Psi_n \rangle \langle \Psi_n | \sum_j \vec{L}_j/r_j^3 | \Psi_0 \rangle) \quad (3)$$

In these equations $\vec{1}$ is the unit dyadic, \vec{r}_j is the position vector of the j th electron in units of Bohr radii ($a_0 = 0.5292$ A), Ψ_0 is the ground-state wave function with energy E_0 , Ψ_n is an excited state with energy E_n , and the angular momentum operator is $\vec{L}_j = -i\hbar \vec{r}_j \times \nabla_j$.

By assuming an average excitation energy Δ , which may then be removed from the summation, simplification of the expression is possible using the quantum mechanical closure rule, $\sum_{n \neq 0} \Psi_n \langle \Psi_n = 1$, to obtain

$$\vec{\sigma}^{(p)} = -(e^2\hbar^2/m^2c^2a_0^3\Delta) \langle \Psi_0 | \sum_{j,k} \vec{L}_j \cdot \vec{L}_k / r_j^3 | \Psi_0 \rangle \quad (4)$$

where $\vec{L}_j = i\vec{r}_j \times \nabla_j$. Because of the constant tumbling motion of molecules in a liquid, it is necessary to average the nuclear shielding contributions over all orientations of the molecule. Since all directions are equivalent in this system, the average along the magnetic field is given by one-third of the trace of $\vec{\sigma}$ and the total shielding may be expressed as

$$\sigma = \langle \vec{\sigma} \rangle = \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) = \\ (e^2/3mc^2a_0) \langle \Psi_0 | 1/r_j | \Psi_0 \rangle - \\ (e^2\hbar^2/3m^2c^2a_0^3\Delta) \langle \Psi_0 | \sum_{j,k} \vec{L}_j \cdot \vec{L}_k / r_j^3 | \Psi_0 \rangle \quad (5)$$

For a system containing $2n$ electrons, the ground-state wave function may be written

$$\Psi_0 = \sum_{\nu} C_{\nu} \chi_{\nu} \quad (6)$$

where the independent valence-bond structures are

$$\chi_{\nu} = \\ 2^{-n/2} \sum_R (-1)^R R [(2n)!]^{-1/2} \sum_P (-1)^P P a(1)\beta(1)w(2)\alpha(2) \dots \quad (7)$$

in which α represents a positive spin and β a negative spin, P scans the $(2n)!$ permutations of the electrons among the orbitals and their associated spins, and R represents the 2^n interchanges of α and β for the pairs of orbitals which are bonded together in the structure. The orbitals a, b, \dots are considered to be located on the nucleus of interest while w, x, \dots are centered elsewhere in the molecule. A normalized linear combination of Slater s and p functions is used to approximate the atomic orbitals a, b, \dots , etc. as follows

$$a = c_s^a s^a + c_x^a p_x^a + c_y^a p_y^a + c_z^a p_z^a \quad (8)$$

where the Slater functions are given by

$$s^a = R_a/2 \\ p_x^a = R_a^{(3/2)} \sin \theta \cos \phi \\ p_y^a = R_a^{(3/2)} \sin \theta \sin \phi \\ p_z^a = R_a^{(3/2)} \cos \theta \quad (9)$$

The radial function $R_a = R_a(\xi_a, r)$ depends on the radial

component of the electron and the orbital effective nuclear charge ξ_a . In this treatment, the effective nuclear charges of s and p orbitals are assumed equal.

Rumer-Pauling^{11,12} diagrams permit rapid determination of the set of independent canonical structures for the singlet wave functions. A graphical method using superposition diagrams of the structures is then used to calculate the coefficients of the Coulomb and exchange integrals in the various matrix elements of the secular equation. Solution of the secular equation provides the ground-state energy and the corresponding coefficients C_{ν} in the wave function Ψ_0 .

Substitution for the ground-state wave function in (5) yields

$$\sigma = \sum_{\mu, \nu} C_{\mu} C_{\nu} \langle \chi_{\mu} | A \sum_j 1/r_j - \frac{B}{2} \sum_{j,k} \vec{L}_j \cdot \vec{L}_k / r_j^3 | \chi_{\nu} \rangle \quad (10)$$

where

$$A = e^2/3mc^2a_0 = 17.75 \times 10^{-6}$$

and

$$B = 2e^2\hbar^2/3m^2c^2a_0^3\Delta = 965.4 \times 10^{-6}/\Delta$$

The term χ_{μ} contains $(2n)!$ permutations of electrons which yield identical terms in (10). Since this cancels the coefficient $[(2n)!]^{-1}$, the equation becomes

$$\sigma = \sum_{\mu, \nu} C_{\mu} C_{\nu} 2^{-n} \times \\ \sum_{R', R} (-1)^{R'+R} \langle R' a(1)\beta(1)w(2)\alpha(2) \dots | A \sum_j 1/r_j - \\ \frac{B}{2} \sum_{j,k} \vec{L}_j \cdot \vec{L}_k / r_j^3 | R \sum_P (-1)^P P a(1)\beta(1)w(2)\alpha(2) \dots \rangle \quad (11)$$

A procedure for evaluating the integrals in (11) corresponding to Pauling's graphical method may be developed. If the orbitals a, w, \dots are assumed orthogonal and normalized, there are three types of integrals to be computed, eq 12-14. The terms I_1 and I_2 are

$$I_1 = 2^{-n} \frac{A}{2} \sum_{R', R} (-1)^{R'+R} \langle R' a(1)\beta(1)w(2)\alpha(2) \dots \\ | \sum_j 1/r_j | R a(1)\beta(1)w(2)\alpha(2) \dots \rangle \quad (12)$$

$$I_2 = -2^{-n} \frac{B}{2} \sum_{R', R} (-1)^{R'+R} \langle R' a(1)\beta(1)w(2)\alpha(2) \dots \\ | \sum_j \vec{L}_j \cdot \vec{L}_j / r_j^3 | R a(1)\beta(1)w(2)\alpha(2) \dots \rangle \quad (13)$$

$$I_3 = -2^{-n} \frac{B}{2} \sum_{R', R} (-1)^{R'+R} \langle R' a(1)\beta(1)w(2)\alpha(2) \dots \\ | \sum_{j,k>j} \vec{L}_j \cdot \vec{L}_k / r_j | R \sum_P (-1)^P P a(1)\beta(1)w(2)\alpha(2) \dots \rangle \quad (14)$$

similar to Coulomb integrals. Because of the orthogonality of the orbitals and spin functions, only identical permutations yield nonzero contributions. If the superposition diagrams of the canonical structures χ_{μ} and χ_{ν} contain $i_{\mu\nu}$ islands, the spin combinations, R and R' , yield

$$I_1 = 2^{-n+i_{\mu\nu}} A \sum_{\alpha} \langle a(j) | 1/r_j | a(j) \rangle \quad (15)$$

and

$$I_2 = -2^{-n+i_{\mu\nu}} \frac{B}{2} \sum_{\alpha} \langle a(j) | \vec{L}_j \cdot \vec{L}_j / r_j | a(j) \rangle \quad (16)$$

(11) G. Rumer, *Nachr. Ges. Wiss. Göttingen, Gesch. Mitt. Math.-Physik. Klasse*, 337 (1932).

(12) L. Pauling, *J. Chem. Phys.*, 1, 280 (1933).

where summation is taken over orbitals on the atom of interest. Since the integrals are dependent upon $1/r_j$ or $1/r_j^3$, only local electronic contributions are considered important. Therefore, no terms containing the orbitals w, x, \dots are retained. The integral I_3 contains both Coulomb and exchange-type expressions. It may be written

$$I_3 = -2^{-n+i_{\mu\nu}} \frac{B}{2} \sum_{a,b>a} [\langle a(j)b(k) | \vec{l}_j \cdot \vec{l}_k / r_j^3 + \vec{l}_k \cdot \vec{l}_j / r_k^3 | a(j)b(k) \rangle + f_{\mu\nu}(p_{a,b}) \langle a(j)b(k) | \vec{l}_j \cdot \vec{l}_k / r_j^3 + \vec{l}_k \cdot \vec{l}_j / r_k^3 | a(j)b(k) \rangle] \quad (17)$$

where $f_{\mu\nu}(p_{a,b})$ is a function of the number of bonds $p_{a,b}$ in the superposition pattern of the two canonical structures along the path between a and b , the orbitals which are involved in the electron exchange. The values of the term given by Pauling¹² are $-1/2$ for $p_{a,b} = 0$; $+1$ for $p_{a,b} = 1, 3, 5, \dots$; and -2 for $p_{a,b} = 2, 4, 6, \dots$

Using (9) for the atomic orbitals it is possible to evaluate further I_1, I_2 , and I_3 . The integral I_1 becomes

$$I_1 = 2^{-n+i_{\mu\nu}} A \sum \langle 1/r \rangle_a \quad (18)$$

where

$$\langle 1/r \rangle_a = \langle R_a(r_j) | 1/r_j | R_a(r_j) \rangle$$

It is necessary to employ the angular momentum operator

$$l = l_x \vec{i} + l_y \vec{j} + l_z \vec{k}$$

with components

$$l_x = i \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right)$$

$$l_y = i \left(-\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right)$$

and

$$l_z = -i \frac{\partial}{\partial \phi}$$

in order to obtain the following values for terms appearing in I_2 and I_3 .

$$\langle a(j) | \vec{l}_j \cdot \vec{l}_j / r_j^3 | a(j) \rangle = 2 \langle 1/r^3 \rangle_a [(c_x^a)^2 + (c_y^a)^2 + (c_z^a)^2]$$

$$\langle a(j)b(k) | \vec{l}_j \cdot \vec{l}_k / r_j^3 | a(j)b(k) \rangle = 0$$

$$\langle a(j)b(k) | \vec{l}_j \cdot \vec{l}_k / r_j^3 | a(k)b(j) \rangle = \langle 1/r^3 \rangle_{ab} [(c_x^a c_y^b - c_y^a c_x^b)^2 + (c_x^a c_z^b - c_z^a c_x^b)^2 + (c_y^a c_z^b - c_z^a c_y^b)^2]$$

The expressions $\langle 1/r^3 \rangle_a$ and $\langle 1/r^3 \rangle_{ab}$ are given by

$$\langle 1/r^3 \rangle_a = \langle R_a(r_j) | 1/r_j^3 | R_a(r_j) \rangle$$

and

$$\langle 1/r^3 \rangle_{ab} = \langle R_a(r_j) | 1/r_j^3 | R_b(r_j) \rangle \langle R_a(r_k) | R_b(r_k) \rangle$$

With these equations, I_2 and I_3 become

$$I_2 = -2^{-n+i_{\mu\nu}} B \sum_a \langle 1/r^3 \rangle_a P^a \quad (19)$$

and

$$I_3 = -2^{-n+i_{\mu\nu}} B \sum_{a,b>a} f_{\mu\nu}(p_{a,b}) \langle 1/r^3 \rangle_{ab} P^{ab} \quad (20)$$

where

$$P^a = \sum_{i=x,y,z} (c_i^a)^2$$

and

$$P^{ab} = (c_x^a c_y^b - c_y^a c_x^b)^2 + (c_x^a c_z^b - c_z^a c_x^b)^2 + (c_y^a c_z^b - c_z^a c_y^b)^2$$

If the results of eq 18–20 are substituted into eq 11, the shielding expression may be written

$$\sigma = \sum_{\mu,\nu} C_\mu C_\nu 2^{-n+i_{\mu\nu}} \sigma_{\mu\nu} \quad (21)$$

where

$$\sigma_{\mu\nu} = A \sum_a \langle 1/r \rangle_a - B [\sum_a \langle 1/r^3 \rangle_a P^a + \sum_{a,b>a} f_{\mu\nu}(p_{a,b}) \langle 1/r^3 \rangle_{ab} P^{ab}] \quad (22)$$

It is noted that σ involves both the diamagnetic and paramagnetic contributions to the shielding from electrons in the valence orbitals of the atom of interest. Since the inner-shell orbitals are relatively unaffected by bonding, their contribution to the magnetic shielding is considered to be a constant factor which cancels in computing chemical shift differences. Hence, they are not included in the calculation.

It is of interest to compare this formulation with the VB equation for the paramagnetic term obtained by Jameson and Gutowsky.⁹ If the system is adequately described in terms of the perfect-pairing scheme, χ_1 , the paramagnetic portion of (22) becomes, upon substituting for B

$$\sigma^{(p)} \cong \sigma_{11}^{(p)} = -\frac{2e^2 \hbar^2}{3m^2 c^2 \Delta a_0^3} \left(\sum_a \langle 1/r^3 \rangle_a P^a - \sum_{a,b>a} \frac{1}{2} \langle 1/r^3 \rangle_{ab} P^{ab} \right) \quad (23)$$

as $f_{11}(p_{a,b}) = -1/2$ for all orbitals centered on the same atom since they are in different islands of the Rumer superposition diagram. Equation 23 is essentially the same as the Jameson and Gutowsky expression when d orbitals and ionic coefficients are omitted from consideration. The two equations differ only in the treatment of the term $\langle 1/r^3 \rangle_a$ which is withdrawn from the summation by Jameson and Gutowsky. By preserving the shielding expression in the above form, provision is made for possible variation of orbital dimensions within the same atom.

In view of the success enjoyed by several workers⁴⁻⁸ in correlating chemical shifts with local charge density, it is necessary to introduce the features of charge polarization in the chemical shift expression. One way of achieving this is to include ionic structures in the wave equation,⁹ but this method yields an expression which predicts that a small shift to lower fields will accompany an increase in local electronic charge, contrary to experimental results.^{5,6} A major contribution of the correct form resulting from variations in the ionic charge density is exhibited by the $\langle 1/r^3 \rangle_a$ term if the expected expansion of the valence orbitals is considered as electrons are added to the atom. The magnitude of $\sigma^{(p)}$ diminishes with an increasing value of r^3 and produces the observed upfield shift in the resonance signal with increasing electron density. This effect is readily incorporated in the shielding equations of the present

study (see Theoretical Considerations, section C), and the neglect of polar structures in the wave function is felt to be justified as a simplifying assumption for the compounds considered in this work.

B. Electron Delocalization and the Effect of Hund Pairing of Electrons. The effect of electron delocalization on the chemical shift can be analyzed by taking the difference between σ and the shielding parameter, σ_{11} , of the perfect-pairing structure as

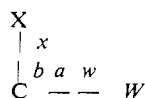
$$\sigma^{(\text{del})} = \sigma - \sigma_{11} = -B \sum_{a,b > a} \langle 1/r^3 \rangle_{ab} P^{ab} \sum_{\mu,\nu} C_\mu C_\nu 2^{-n+i_{\mu\nu}-1} [2f_{\mu\nu}(p_{a,b}) + 1] \quad (24)$$

The unique feature of (24) is found in the term

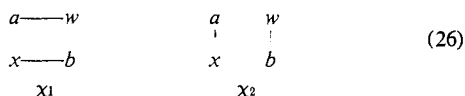
$$\sum_{\mu,\nu} C_\mu C_\nu 2^{-n+i_{\mu\nu}-1} [2f_{\mu\nu}(p_{a,b}) + 1] \quad (25)$$

which can assume both positive and negative values depending upon the nature of electron-spin correlation between the orbitals a and b . Since P^{ab} , $\langle 1/r^3 \rangle_{ab}$, and B do not vary in sign, (25) determines the sign of $\sigma^{(\text{del})}$. If the exchange integrals used in the secular equation to obtain the wave function coefficients, C_μ , favor¹³ an antiparallel spin orientation at a and b , then (25) will be positive, $\sigma^{(\text{del})}$ will be negative, and the resonance will appear at lower fields. Conversely, an upfield shift is predicted if the parallel-spin arrangement at a and b is preferred from energy considerations.

It is instructive to consider the four-electron molecular fragment



with orbitals a and b on the carbon of interest bonded to orbitals w and x , respectively. The two canonical structures for this system are



If the negative, principal bond exchange integrals, K_{aw} and K_{bx} , are very large compared to all other interactions, the following approximate relations for the wave function coefficients may be obtained.

$$C_1 \cong 1 \\ C_2 \cong \frac{K_{ax} + K_{bw} - K_{ab} - K_{wx}}{2(K_{aw} + K_{bx})} \quad (27)$$

In cases where K_{ab} (the positive intraatomic Hund exchange integral) dominates the terms in the numerator of (27), C_2 will be a small positive number for a positive C_1 . Hence, it is possible to determine the sign of (25) by employing the values $f_{11}(p_{a,b}) = f_{22}(p_{a,b}) = -1/2$ and $f_{12}(p_{a,b}) = -2$ to give the reduced expression

$$\sum_{\mu,\nu} C_\mu C_\nu 2^{-n+i_{\mu\nu}-1} [2f_{\mu\nu}(p_{a,b}) + 1] = -\frac{3}{2} C_1 C_2$$

Since the term is negative, a parallel-spin orientation of the electrons in orbitals a and b is favored in accordance with Hund's rule. Thus (24) predicts an upfield shift

(13) M. Barfield and D. M. Grant, *Advan. Magnetic Resonance*, **1** 149 (1965), discuss the relationship between exchange energy and spin correlation in terms of the Dirac Van Vleck vector model.

for electron delocalization which is dominated by the repulsive Hund interaction energy.¹⁴⁻¹⁶ It may be helpful to note that an interchange of orbitals b and x in (26) to give an equivalent set of canonical structures (differing only in the implicit spin assignment) will change not only the sign of $[2f_{\mu\nu}(p_{a,b}) + 1]$ but also the sign in the numerator of (27). In this manner the sign and magnitude of (25) is left invariant, and as expected the choice of the canonical set does not influence the conclusions regarding the nature of spin correlation along with its effect upon the chemical shift parameter.

C. Effective Nuclear Charge and Orbital Dimensions. The Slater radial function for electrons in the L shell is

$$R_a = (\xi_a^5/48)^{1/2} r \exp(-\xi_a r/2) \quad (28)$$

Hence, substitution into the integrals of (22) yields the following values in terms of the orbital effective nuclear charges.

$$\langle 1/r \rangle_a = \xi_a/4 \quad (29)$$

$$\langle 1/r^3 \rangle_a = \xi_a^3/24 \quad (30)$$

$$\langle 1/r^3 \rangle_{ab} = (\xi_a \xi_b)^{3/2}/6(\xi_a + \xi_b)^2 \quad (31)$$

It is seen that slight changes in the values of the effective nuclear charges can cause even greater variations in the integrals $\langle 1/r^3 \rangle_a$ and $\langle 1/r^3 \rangle_{ab}$. The term $\langle 1/r \rangle_a$ also varies, but the relative difference is much less. Since the coefficient, B , of the integrals $\langle 1/r^3 \rangle_a$ and $\langle 1/r^3 \rangle_{ab}$ in the paramagnetic term is much greater than the constant, A , which appears in the diamagnetic term, a slight change in the orbital effective nuclear charge causes a more significant variation in $\sigma^{(p)}$ than in $\sigma^{(d)}$. Thus, some workers have neglected the diamagnetic term in calculating chemical shifts.

In order to account for the expansion or contraction of the atomic orbitals with addition or removal of ionic charge, Karplus and Pople⁴ proposed the relation

$$\xi_A = 3.25 - 0.35(\rho_A - 1)$$

for aromatic compounds with π electron density ρ_A on carbon A. This is a simple extension of Slater's rules for atomic screening to include ionic charges in molecules. Following a similar approach the effective nuclear charge in orbital a may be written^{7,17}

$$\xi_a = \xi_0 \beta' - S \sum_{b \neq a} q_b \quad (32)$$

where ξ_0 is the atomic effective nuclear charge obtained by direct application of Slater's rules, β' is a parameter accounting for changes in the effective nuclear charge due to bond formation, S is the Slater screening factor, and q_b is the ionic charge in orbital b . It is assumed that the usual factor, $S = 0.35$ for 2s and 2p electrons, may be used to determine the effects of small polarization charges on ξ_a . Using a relation similar to (32), Grant and Litchman¹⁷ were able to correlate a number of directly bonded C¹³-H nmr coupling constants with changes in the C¹³ effective nuclear charge as substituents on the carbon are varied.

(14) See ref 13, 15, and 16 for a discussion of the importance of this interaction on geminal and other long-range spin-spin coupling constants.

(15) S. Alexander, *J. Chem. Phys.*, **34**, 106 (1961).

(16) S. Koide and E. Duval, *ibid.*, **41**, 315 (1964).

(17) D. M. Grant and W. M. Litchman, *J. Am. Chem. Soc.*, **87**, 3994 (1965), used slightly different values of β' and q_{CH} from those in the present paper.

In a variational calculation on molecular hydrogen, Wang¹⁸ first determined that the presence of two attractive centers results in contraction of the electronic charge cloud about the hydrogen nuclei. Such an effect is described by an increase in the orbital exponent compared with that of the isolated atom. Coulson¹⁹ suggested that bonding in methane gives rise to an effective nuclear charge, $\xi_c = 3.25\beta$, in the orbitals of the carbon atom where $\beta = 1.1-1.2$. The β parameter employed by Coulson includes all factors in the molecular environment which influence the orbital effective nuclear charge, while β' defined in (32) excludes the effect of shielding by electrons transferred onto the atom as a result of charge polarization in the bonds. Although the parameters are therefore not entirely equivalent they should be very similar in magnitude. Thus, the magnitude of β' used in the present work also should fall within the range given by Coulson, since shielding due to ionic charge is expected to be small in the compounds under consideration. The value $\beta' = 1.15$ is used in this study to predict the general magnitude of carbon orbital contraction with bond formation.

The magnitude and direction of the charge transfer, q_i , have generally been estimated from differences in electronegativity between the two atoms forming a bond²⁰ or from consideration of the bond dipole moment.^{19,21} Depending upon the assumptions made in the calculations, these methods yield values ranging from 0.04 to 0.33 electron for the polarization charge on the carbon atom of a CH bond. The large range in theoretical values makes it difficult to select a value for the polarity in the CH bond. Since polarization charges in the range 0.1-0.2 have been used successfully by other workers^{7,17,22,23} to calculate C¹³ chemical shifts and C¹³-H coupling constants, it is felt that $q_{CH} = 0.15$ is a reasonable intermediate value to employ. Charge transfer in the CC bonds of the hydrocarbon molecules under study has been taken as zero. Although a slight variation in ionic character of a particular carbon-carbon bond is expected from compound to compound, the inclusion at present of such terms in the calculations is not associated with an improvement which warrants the additional computational difficulties.

Results and Discussion

A. Application to the Alkanes. Experimental carbon-13 chemical shift data have been obtained for a few of the simpler alkanes by Spiesecke and Schneider,²⁴ while Grant and Paul²⁵ have determined the chemical shifts of a large number of more complex linear and branched compounds. The latter authors discovered that the shifts obey an additive relationship based upon the number of α , β , γ , δ , and ϵ carbon atoms present in the molecule. The empirical equation has the form

$$\delta_c(k) = B + \sum_l A_l n_{kl} \quad (33)$$

where $\delta_c(k)$ is the chemical shift of the k th carbon, B is a constant which is equal within experimental error to the methane chemical shift, n_{kl} is the number of carbon atoms in the l th position relative to the k th carbon, and A_l is the additive chemical shift term assigned to the l th carbon atom. The major effects can be described by three substituent parameters: $A_\alpha = -9.09 \pm 0.11$ ppm, $A_\beta = -9.40 \pm 0.11$ ppm, and $A_\gamma = +2.49 \pm 0.07$ ppm, where the subscripts indicate the α , β , and γ carbon atoms, respectively. Deviations from simple additivity were noted in highly branched systems, and empirical corrective factors for these cases were reported.

Certain simplifying assumptions are possible in calculating the magnetic shielding for saturated alkanes. The wave function coefficients in these systems generally obey the condition $C_1 \gg |C_\mu|$ indicating that deviations from perfect pairing are minor. In this case, only cross terms between χ_1 and χ_μ need be considered since all other terms will be small. Hence, the shielding parameter may be determined using the relation

$$\sigma \cong \sigma_{11} + \sum_{\mu \neq 1} \sigma_\mu^{(\text{del})} \quad (34)$$

where the contribution, $\sigma_\mu^{(\text{del})}$, from structure χ_μ is given by

$$\sigma_\mu^{(\text{del})} = -BC_1 C_\mu 2^{-n+i_1\mu} \sum_{a,b>a} \langle 1/r^3 \rangle_{ab} P^{ab} [2f_{1\mu}(p_{a,b}) + 1] \quad (35)$$

A simple additive effect on the magnetic shielding is predicted by the linear form of (34) for the delocalized interactions in saturated compounds. Changes in σ_{11} , however, are expected to give rise to the major variations in the chemical shift parameter since delocalized structures make a minor contribution to the ground-state wave function.

B. Charge Polarization Effects. Removal of electronic charge from the carbon under consideration by substituting a methyl group for a hydrogen atom creates a small increase, refer to (32), in the effective nuclear charges of the remaining orbitals. The resultant contraction of the orbitals is manifested by enlarged values for the terms $\langle 1/r \rangle_a$, $\langle 1/r^3 \rangle_a$, and $\langle 1/r^3 \rangle_{ab}$ calculated by eq 29-31, respectively. As shown in Table I, the effect of methyl substitution on the contribution from the perfect-pairing structure is to shift, on the average, the resonance position -9.9 ppm to lower fields. This variation per methyl group is due primarily to the approximately -10.6 ppm contribution arising from the paramagnetic term, whereas the diamagnetic term varies by only $+0.7$ ppm. The relative importance of these two terms in the chemical shift expression is indicated by these two values which differ by more than an order of magnitude. Based on this model, the main source of the α -carbon effect, A_α , therefore can be explained by an increase in $\sigma_{11}^{(p)}$ brought about by removal of negative electronic charge from the atom.

With the assumption of constant bond polarity used in this paper, no change in the electronic charge on an atom occurs when remote substituents are added. Hence, the β and γ carbons do not exert any influence within this approximation on the value of σ_{11} . If an inductive transfer of charge through the CC bonds is calculated using a method similar to that of Smith,

(18) S. C. Wang, *Phys. Rev.*, **31**, 579 (1928).

(19) C. A. Coulson, *Trans. Faraday Soc.*, **38**, 433 (1942).

(20) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 97.

(21) C. A. Coulson, "Valence," 2nd ed, Oxford University Press, London, 1961, p 134.

(22) M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci. U. S.*, **45**, 1269 (1959).

(23) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), also obtained similar values for the C-H polarity from his extended MO treatment in a number of compounds.

(24) H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 722 (1961).

(25) D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964).

Table I. Bond Effective Nuclear Charges and Contributions of the Perfect-Pairing Structure to the Magnetic Shielding^a

Position	ξ_{CC}	ξ_{CH}	$\sigma_{11}^{(d)}$	$\sigma_{11}^{(p)}$	σ_{11}
(a) Addition of α -Methyl Groups					
Methane	...	3.5800	63.545	-307.605	-244.060
Ethane	3.5800	3.6325	64.244	-317.950	-253.706
Propane, C-2	3.6325	3.6850	64.943	-328.467	-263.524
Isobutane, C-2	3.6850	3.7375	65.642	-339.156	-273.514
Neopentane, C-2	3.7375	...	66.340	-350.016	-283.676
(b) Addition of β - and γ -Methyl Groups					
Ethane, propane, <i>n</i> -butane, isobutane, and neopentane, C-1	3.5800	3.6325	64.244	-317.950	-253.706

^a The shielding values in ppm are calculated with the assumption of pure tetrahedral bonding so that $P^a = 0.75$ and $P^{ab} = 0.5$. The average excitation energy is assumed to be 9 eV.

et al.,²⁶ for a molecule containing a β -methyl group, the change in σ_{11} to lower fields is estimated²⁷ to be less than -2 ppm. A shift to lower field in the γ carbon resulting from induction along the carbon chain has also been estimated to be -0.5 ppm. Since the inductive effect is relatively small in these compounds except for groups in the α position and since this effect attenuates rapidly for remote substituent groups, induction along the carbon chain would appear to be unimportant as an explanation of the major parts of the β - and γ -methyl substituent parameters.

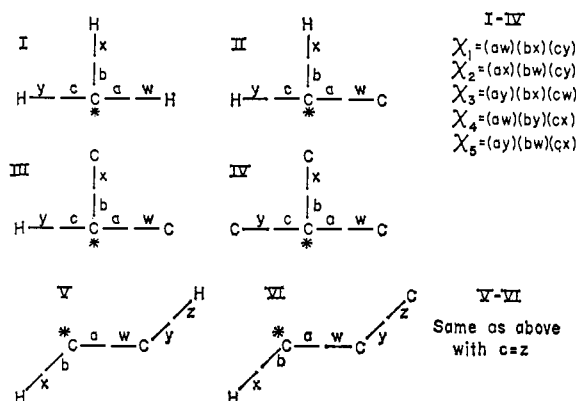


Figure 1. Molecular fragments and the corresponding sets of canonical structures used to calculate the coefficients of the VB wave function. A set of parentheses enclosing two orbitals in a particular χ_μ indicates that those orbitals are spin paired in the canonical structure. The carbon-13 atom is starred.

It is well to emphasize that the simple inductive model predicts a small downfield shift for γ -methyl groups in opposition to the positive empirical value found for the parameter A_γ . Field effects due to magnetic anisotropy in remote CC and CH bonds can be excluded from consideration as these terms cannot account for the effect of the γ -methyl group without assuming impossibly large values for the anisotropy in the magnetic susceptibility of these bonds.²⁵

C. Delocalization Effects. In securing molecular wave functions to determine the chemical shift contribution arising from delocalized structures, several simplifications are employed. When deviations from perfect pairing are minimal it has been noted^{13,28} that the wave function coefficient C_μ for a given structure varies only

(26) R. P. Smith, T. Ree, J. L. Magee, and H. Eyring, *J. Am. Chem. Soc.*, **73**, 2263 (1951).

(27) B. V. Cheney, Ph.D. Thesis, University of Utah, June 1966.

(28) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

slightly if orbitals which do not take part in the unconventional pairing are omitted from the calculation. Thus, it is possible to approximate the contribution of a given type of delocalization by considering only those molecular fragments with the minimum number of orbitals necessary to faithfully portray the essential features of the various deviations from the principal bond structure. Since the contribution of structures containing more than three, and sometimes two, "broken bonds" is negligible in Ψ_0 , the molecules may be treated in this study with the six-electron systems illustrated in Figure 1 which collectively contain all of the significant delocalized interactions in the molecules under consideration.

The exchange integrals used in the secular equations are listed in Table II. Integrals between directly bonded

Table II. Values (eV) of the Exchange Integrals Used to Calculate Wave-Function Coefficients

$K_{ab} = -3.637$	$K_{ai} = +0.250$	$K_{bj} = +0.020$
$K_{ac} = -0.037$	$K_{aj} = -0.040$	$K_{cj} = +0.060$
$K_{ad} = -0.991$	$K_{bc} = +1.235$	$K_{dh} = -0.087$
$K_{af} = -0.630$	$K_{bf} = +0.332$	$K_{dj} = -0.100$
$K_{ag} = -0.010$	$K_{bg} = +0.155$	$K_{ef} = -2.922$
$K_{ah} = -0.263$	$K_{bi} = +0.126$	$K_{ej} = -0.050$

orbitals were obtained by taking 85% of the empirical CC or CH bond energies.²⁹ The integrals between two hydrogen atoms were determined using 85% of the Morse curve energy for the hydrogen molecule at the appropriate internuclear separation. Exchange interactions involving nonbonded carbon orbitals on adjacent atoms were resolved into integrals between s , p_σ , p_π , and $p_{\pi'}$ atomic orbitals with orientation parallel or perpendicular to the internuclear axis. By means of an approximate two-electron Hamiltonian operator, these integrals were cast into the form

(29) E. A. Moelyn-Hughes, "Physical Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1961, p 1042.

Table III. Coefficients of the Various Canonical Structures for the Molecular Fragments Shown in Figure 1

Molecular fragment	Wave-function coefficients				
	C ₁	C ₂	C ₃	C ₄	C ₅
I	0.9664	0.0220	0.0220	0.0220	0.0000
II	0.9666	0.0219	0.0219	0.0220	0.0000
III	0.9574	0.0389	0.0222	0.0222	0.0000
IV	0.9384	0.0399	0.0399	0.0399	0.0000
V (<i>trans</i>)	0.9618	0.0220	0.0220	0.0308	0.0002
V (<i>gauche</i>)	0.9733	0.0232	0.0232	0.0077	-0.0029
VI (<i>trans</i>)	0.9599	0.0407	0.0237	0.0158	-0.0034
VI (<i>gauche</i>)	0.9667	0.0412	0.0240	0.0024	-0.0048

Table IV. Relative Contribution of the Specific Delocalized Structures Which Affect the Chemical Shift for C₁ ≈ 1

χ _A = (C _a [*] , H _z)(C _b [*] , H _w)	C _A = 0.0220
χ _B = (C _a [*] , C _z)(C _b [*] , H _w)	C _B = 0.0228
χ _C = (C _a [*] , C _z)(C _b [*] , C _w)	C _C = 0.0402
χ _D = (C _a [*] , C _y)(C _b [*] , C _w)(H _z , H _z) (<i>trans</i>)	C _D = 0.0002
χ _E = (C _a [*] , C _y)(C _b [*] , C _w)(H _z , H _z) (<i>gauche</i>)	C _E = -0.0029
χ _F = (C _a [*] , C _y)(C _b [*] , C _w)(H _z , C _z) (<i>trans</i>)	C _F = -0.0034
χ _G = (C _a [*] , C _y)(C _b [*] , C _w)(H _z , C _z) (<i>gauche</i>)	C _G = -0.0048

tures with the same unconventional pairing in different fragments show an average variation of less than 10% in the magnitude of the corresponding eigenvector. Due to the form of the spin-correlation function in (35), the only pairing schemes that alter the chemical shift are those in which two or more orbitals centered on the atom of interest are involved in "broken" bonds. Hence, the seven delocalized structures given in Table IV are the only types which need be considered. The coefficients given in Table IV are taken as mean values of the corresponding coefficients reported in Table III for the several structures. In this way approximate orders of magnitude are established for these coefficients which are then used to estimate the magnitude of various chemical shift terms. The notation used for the orbitals in these terms corresponds to that of Figure 1. Results of calculations taking the pairing schemes of Table IV into account are listed in Table V along with the experimental chemical shifts with respect to benzene.

Figure 2 shows the theoretical plots of σ and σ_{11} for the α -carbon effect adjusted to the same scale as the ex-

Table V. Shielding Contributions from Delocalized Structures, Total Magnetic Shielding, and Experimental Chemical Shift Values^a

Position	n _A	σ _A ^(de1)	n _B	σ _B ^(de1)	n _C	σ _C ^(de1)	n _D	σ _D ^(de1)	n _E	σ _E ^(de1)	n _F	σ _F ^(de1)	n _G	σ _G ^(de1)	σ _{II} ^b	σ	δ _{exptl} ^c
(a) Addition of α -Methyl Groups																	
Methane	6	3.384	0	...	0	...	0	...	0	...	0	...	0	...	-244.06	-223.76	130.8
Ethane	3	3.535	3	3.584	0	...	3	0.016	6	-0.220	0	...	0	...	-253.71	-233.62	122.8
Propane, C-2	1	3.690	4	3.743	1	6.459	4	0.016	8	-0.230	2	-0.273	4	-0.386	-263.52	-242.27	112.62
Isobutane, C-2	0	...	3	3.906	3	6.743	3	0.017	6	-0.240	6	-0.285	12	-0.403	-273.51	-249.56	103.52
Neopentane, C-2	0	...	0	...	6	7.035	0	...	0	...	12	-0.298	24	-0.420	-283.68	-255.11	100.8
(b) Addition of β -Methyl Groups																	
Ethane	3	3.535	3	3.584	0	...	3	0.016	6	-0.220	0	...	0	...	-253.71	-233.62	122.8
Propane, C-1	3	3.535	3	3.584	0	...	2	0.016	4	-0.220	1	-0.267	2	-0.377	-253.71	-234.22	113.1
Isobutane, C-1	3	3.535	3	3.584	0	...	1	0.016	2	-0.220	2	-0.267	4	-0.377	-253.71	-234.82	104.35
Neopentane, C-1	3	3.535	3	3.584	0	...	0	...	0	...	3	-0.267	6	-0.377	-253.71	-235.42	97.23

^a The number of equivalent delocalized structures in each molecule are listed under the n_i's. ^b Taken from Table I. ^c Shift values relative to benzene.

$$N_{\alpha\beta\gamma\delta} = -\frac{Z}{2}[S_{\alpha\gamma}(J_{\beta\delta} + J_{\delta\beta}) + S_{\beta\delta}(J_{\alpha\gamma} + J_{\gamma\alpha})] + Z^2 S_{\alpha\gamma} S_{\beta\delta} / R + A_{\alpha\beta\gamma\delta} \quad (36)$$

($\alpha, \beta, \gamma, \delta = s, p_\sigma, p_\pi, p_{\pi'}$)

where R is the internuclear distance, Z is the Hamiltonian nuclear charge, and the other symbols correspond to the notation of Kopineck.³⁰ Values for these integrals were then obtained by interpolation from Kopineck's tables using normal Slater orbitals. The Hund CC exchange integral was calculated with the theoretical formulas of Beardsley³¹ assuming Slater effective nuclear charges in the atomic s and p orbitals. No reliable theoretical or empirical values for long-range CH exchange integrals are available. Hence, these integrals were selected so as to be compatible with calculations of the geminal and vicinal proton coupling constants using the simple formula given by Barfield and Grant.¹³

Table III contains the wave function coefficients obtained for each of the fragments illustrated in Figure 1. It is seen that C₁ ≈ 1 in every wave function. Struc-

perimental curve. The experimental and theoretical values for methane are taken as equal in order to establish a reference for the calculated values. The delocalization terms impart a steadily increasing upward shift in the graph of σ relative to that of σ_{11} . Deviations from linearity in the branched systems therefore may be explained semiquantitatively by electron delocalization. The major features of the experimental trends are essentially reproduced in the curve for σ although an exact quantitative fit is not realized. Minor changes in the various parameters employed in the shielding expression could lead to an exact duplication of the experimental results. However, due to the over-parameterization of the problem and the approximate nature of the calculations, any attempt to match exactly the experimental chemical shifts would be of little conceptual value. It is sufficient for this calculation to indicate that charge polarization effects and deviations from perfect pairing can account for the general trends exhibited by the experimental quantities.

The contribution of delocalized structures to the β -carbon effect is also contained in Table V and illustrated in Figure 3 together with the estimated maximum shifts due to charge polarization through the molecular

(30) H. J. Kopineck, *Z. Naturforsch.*, **5a**, 420 (1950); **7a**, 785 (1952).
 (31) N. F. Beardsley, *Phys. Rev.*, **39**, 913 (1932).

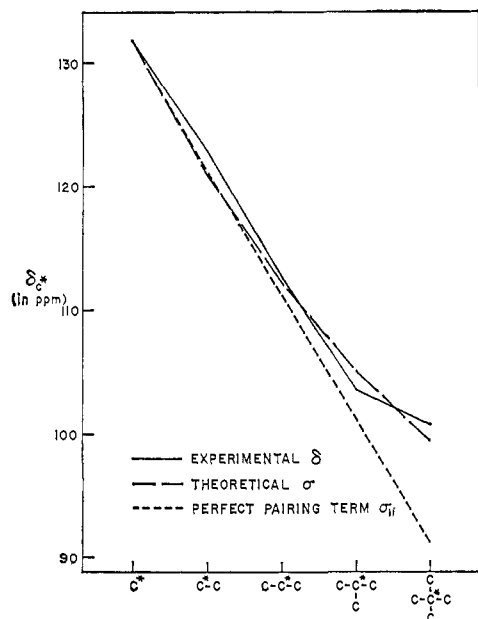


Figure 2. The effect of α -carbon substituents in the alkanes. Theoretical values are scaled to give exact agreement with experimental value for methane.

chain. A combination of these contributions accounts for only a third of the observed magnitude of the A_β parameter, and thus it appears that the simple concepts used to explain the α effect are not satisfactory for rationalizing the β parameter. Two explanations of this failure to predict an adequate A_β parameter are suggested. The first is that the vicinal coefficients (C_D , C_E , C_F , and C_G) given in Table IV are unusually poor and values for $\sigma^{(del)}$ are too small. This possibility suffers from the difficulty that the calculation of vicinal spin-spin coupling constants cannot tolerate any significant increase in the degree of delocalization which is needed to improve the chemical shift calculation. A second possible explanation and one which is preferred is that the downward shift arises from some type of steric interaction with the β -methyl group which causes a slight contraction of the orbitals on the atom of interest. Such an effect may be reflected by an increase in the β' parameter used to calculate the effective nuclear charges. Since a change of $\Delta\beta' = 0.01$ gives a shift to lower field of approximately 6 ppm, only small interactions between remote groups would be required to predict the observed value of A_β . If the whole concept of orbital contraction with bond formation is appropriate, then equally acceptable is the possibility that electron compression will accompany steric crowding by otherwise remote groups. The failure to include such features into our chemical shift model will best explain the present theoretical inadequacies. As no good methods are presently available for estimating possible variations in β' with changes in the steric factors, it is not possible to discuss this proposal quantitatively.

It should be noted that assuming β' to be constant is less damaging for calculation of the α -carbon shifts than for computing the β -carbon effect. When an α -methyl group is added, a possible increase in β' would likely be accompanied by increases in the polarization charges, q_b , of the remaining bonds. Since these factors cannot be separated one from another and tend to cancel each

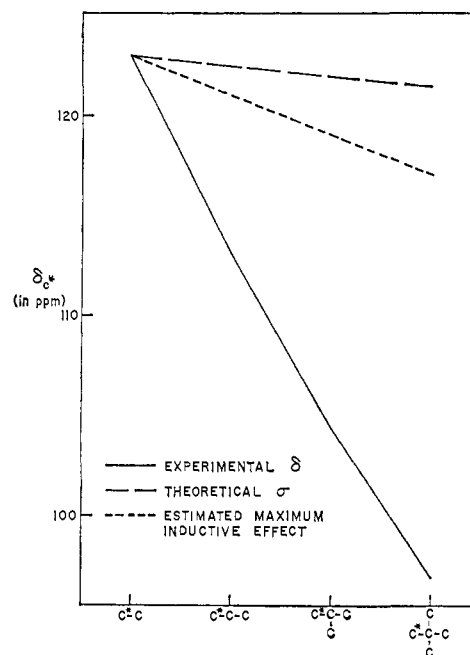


Figure 3. The effect of β -carbon substituents in the alkanes. Theoretical values are scaled to give exact agreement with experimental value for ethane.

other in the orbital effective nuclear charge expression, the values of the ξ_a 's used in this work are assumed to be essentially correct even though they have been obtained for a constant β' value. A consideration of molecular geometry reveals that the distance between the carbon of interest and a γ -methyl group is too large to expect significant changes in β' . Thus, the sterically induced charge polarization model to be discussed in the next section is considered adequate to rationalize the magnitude of the γ parameter.

D. Steric Effects on Carbon-13 Chemical Shifts. To account for the γ -methyl substituent shifts the authors^{1a} have suggested the possible importance of hydrogen-hydrogen nonbonded interactions as a means for explaining upfield shifts for a variety of spatially perturbed methyl groups. The simplified model indicated that the steric shifts can be explained with a slight charge polarization in the HC^{13} bond. This transfer of electron charge is due to the nonbonded repulsion existing between electrons centered on proximate hydrogen atoms. Reproducing eq 7 given in ref 1a as follows

$$\delta_{C^{13}} = +1680 \cos \theta \exp(-2671r) \quad (37)$$

one can estimate a value of +4.8 ppm for the steric shift in *gauche*-butane, shown in Figure 4. The structural parameters used in the calculation are $r = 1.88 \text{ \AA}$ and $\theta = 64.4^\circ$. If one uses a value of 0.8 kcal/mole for the energy difference between *gauche*- and *trans*-butane, the substituent shift parameter for the *gauche* structure combines with a negligible *trans* value to predict a +1.8-ppm value for an equilibrating *n*-butane system. This predicted value for A_γ compared reasonably well with the empirical value²⁵ of +2.49 ppm, thereby lending validity to the suggestion that upfield shifts in γ carbons of "flexible" alkanes arise solely from steric interactions existing when the carbon chain has coiled into the *gauche* configuration.

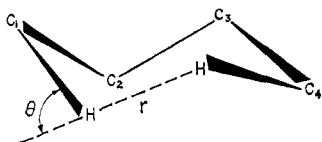


Figure 4. The steric relationship between protons on 1,4-carbon atoms in the *gauche* configuration of *n*-butane. Structural parameters are $r = 1.88 \text{ \AA}$ and $\theta = 64.4^\circ$.

The combined experimental and theoretical trends observed in extending the molecular chain through four carbons are portrayed in Figure 5. Except for the β -carbon shift, which has already been discussed, there is reasonable agreement in the two curves. Figure 5 emphasizes the importance of two types of polarization effects arising from α and γ carbons, respectively, while at the same time displaying the inadequacies of the models presented for the β shifts.

Summary

Carbon-13 chemical shifts have been shown to depend primarily upon changes in the paramagnetic screening term centered on the atom of interest. In this framework, the theory stresses that only changes in the immediate electronic environment of a carbon-13 nucleus can be expected to affect in any significant manner the accompanying chemical shift. Important factors in the carbon-13 chemical shift parameter are summarized as follows.

(1) The availability of low-lying excited states will decrease the average excitation energy, Δ , and thereby shift the resonance to lower fields. Conversely, carbon atoms in molecules with a large excitation energy are expected to have their resonance appear in the high-field range.

(2) Electron polarization affects the $\langle 1/r^3 \rangle$ value in the chemical shift expression through a variation in the effective nuclear charge. Thus, electron withdrawal decreases the distance of the average orbital radius and the resonance position moves downfield. Likewise, opposite upfield shifts can be expected to accompany an increase in electron charge density.

(3) Deviations from classical perfect-pairing bond structures result in either upfield or downfield shifts depending upon the nature of the electron spin correlation accompanying the bond delocalization. Parallel-spin pairing of two electrons centered on the same carbon atom decreases the admixture of high-energy orbitals which enhance the paramagnetic term and the resonance moves upfield. As the positive Hund exchange integral between two orbitals on the same atom favors the parallel-spin configuration, upfield shifts are expected when this integral dominates the spin correlation. Conversely, exchange integrals favoring the antisym-

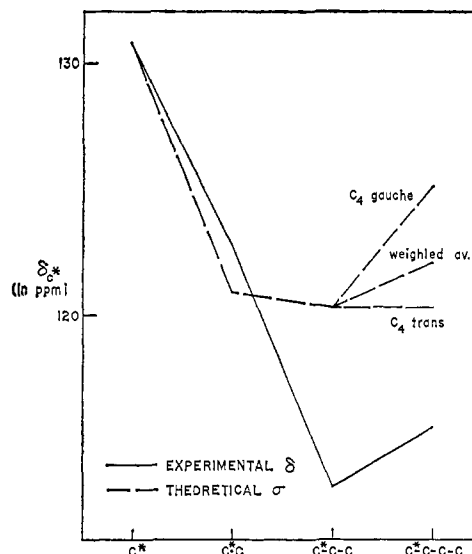


Figure 5. The combined effect of α -, β -, and γ -carbon substituents in the alkanes. Theoretical values are scaled to give exact agreement with experimental value for methane.

metric spin pairing of electrons on the same carbon atom will enhance the paramagnetic term and shift the resonance to lower field positions.

(4) Steric polarization of electrons along an H-C bond accounts for otherwise anomalous remote substituent effects in the γ position. The shift to higher fields with increased charge is compatible with statement 2 above.

(5) Steric crowding in the β position has been observed to give rise to a downfield shift. Enhancement of the paramagnetic term as a result of electron orbital contraction is felt to best explain this phenomenon. Contraction of orbital dimensions is postulated as a means of reducing unfavorable steric interactions.

Just as this article was being submitted for publication the authors became aware of the interesting MO discussions of carbon-13 chemical shifts by Yonezawa, Morishima, and Kato³² and by Sichel and Whitehead.³³ The MO approach stresses the importance of charge-transfer features in a slightly more direct manner, but variation in the spin-pairing schemes is more easily visualized in the VB method.

Acknowledgment. This research was supported in part by the Petroleum Research Fund administered by the American Chemical Society. Helpful discussions with T. D. Alger, W. M. Litchman, and R. J. Pugmire are also acknowledged.

(32) T. Yonezawa, I. Morishima, and H. Kato, *Bull. Chem. Soc. Japan*, **39**, 1398 (1966).

(33) J. M. Sichel and M. A. Whitehead, *Theoret. Chim. Acta*, **5**, 35 (1966).