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On the Carbon-13 Chemical Shifts of Saturated Hydrocarbons

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A molecular orbital interpretation of the carbon-13 chemical shifts of saturated hydrocarbons is presented. The shielding constant of the carbon atom is shown to be roughly proportional to the excess charge densities of 2p electrons, which is in accordance with experiments. The so-called β- and γ-effects in the carbon-13 chemical shifts are explained on the basis of an MO theory.

Recently carbon-13 nuclear magnetic resonance studies of various compounds have been carried out systematically.1) In a series of aromatic compounds, many workers have observed a direct relationship between the cabron-13 chemical shift and the π-electron charge density; a theoretical basis for this relation has been given by Karplus and Pople.2) However, there have been few theoretical interpretations3) of carbon-13 chemical shifts of saturated hydrocarbons. Carbon-13 chemical shifts of linear and some branched alkanes with a range of about 40 p.p.m. have been found to conform with a simple additivity law.4) This empirical linear expression, of the type given by Eq. 1

$$\delta^{13}\mathrm{C}(j) = \delta^{13}\mathrm{C}(\mathrm{CH_4}) + \sum_i N_{ij}\delta_i \tag{1}$$

has yet to be interpreted theoretically. The chemical shift for methane is $\delta^{13}\mathrm{C}(\mathrm{CH_4})$, and the substituent parameters, δ_i, reflect the effect of a carbon atom in the ith position upon the carbon-13 being investigated, where i denotes the α, β, γ, δ and ε carbon atoms. N_{ij} is the number of ith carbon atoms relative to the jth carbon. In the present paper, an attempt is made to give a molecular orbital interpretation of the carbon-13 chemical shift of these compounds.

Theoretical

The nuclear magnetic shielding constant, σ, may be conveniently expressed as a sum of diamagnetic and paramagnetic terms:5)

$$\sigma = \sigma_\mathrm{d} + \sigma_\mathrm{p} \tag{2}$$

where:

$$\sigma_\mathrm{d} = (e^2/3mc^2)\sum_i \langle\psi_0|r_i^{-1}|\psi_0\rangle$$

$$\sigma_\mathrm{p} = (\sigma_\mathrm{pxx} + \sigma_\mathrm{pyy} + \sigma_\mathrm{pzz})/3 \tag{3}$$

$$\begin{aligned}\sigma_\mathrm{pzz} = &-(e^2/2m^2c^2)\sum_{n\neq0}(E_n-E_0)^{-1}\\ &\times[\langle\psi_0|\sum_i l_z^{(i)}|\psi_n\rangle\langle\psi_n|\sum_j l_z^{(j)}r_j^{-3}|\psi_0\rangle\\ &+\langle\psi_0|\sum_j l_z^{(j)}r_j^{-3}|\psi_n\rangle\langle\psi_n|\sum_i l_z^{(i)}|\psi_0\rangle]\end{aligned} \tag{4}$$

where $l_z^{(i)}$ is the Z-component of the orbital angular momentum of the ith electron, r_i distant from the nucleus in question, and where ψ_0 and ψ_n are the wave functions of the ground and the n-th excited states, with the energies E_0 and E_n respectively. The approximate values of σ_d can be calculated with the Slater atomic orbitals for the carbon sp^3 hybridized atomic orbital. The diamagnetic shielding constant, σ'_d, per 2s or 2p electron becomes:

$$\sigma'_\mathrm{d}(\text{2s or 2p electron}) = 4.45\,Z^* \text{ (p.p.m.)} \tag{5}$$

where Z^* is the "effective nuclear charge" estimated according to Slater's rules. Since these yield a Z^* value of 3.25 for a neutral carbon atom, by taking into account a screening per 2s or 2p electron of 0.35 we can write Z^* for a carbon atom, A, in a molecule as:

$$Z^* = 3.25 - 0.35(q^\mathrm{A}-4) \tag{6}$$

where q^A is the σ-electron density on the atom. Since σ_d is due to four valence electrons of a carbon atom, we obtain

$$\sigma'_\mathrm{d} = 4.45\,Z^* q^\mathrm{A} \tag{7}^\dagger$$

where q^A is the electron density around the carbon atom A and where, for a neutral carbon ($q^\mathrm{A}=4$), σ'_d is 57.2. The increase in σ'_d if a 2s or a 2p electron is added is 16 p. p. m., about 50% of

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1) Cf., e. g., J. B. Stothers, *Quart. Rev.*, **19**, 144 (1965).

2) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963); J. A. Pople, *Mol. Phys.*, **7**, 301 (1964).

3) Recently, a valence bond interpretation of ^{13}C chemical shifts of saturated hydrocarbons was presented by D. M. Grant at the Interantional Symposium on NMR, Tokyo (1965).

4) E. G. Paul and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1701 (1963).

5) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

† σ_d is associated with all electrons, whereas σ'_d is associated only with valence electrons.

the observed effect. However, the change in the calculated σ-electron density in this study is at most 0.3, while the effect due to the diamagnetic term is calculated to be about 4.8 p. p. m. Thus, the diamagnetic shielding, σ'_d, cannot make a principal contribution in the σ-frame carbon compounds. An approximate formula for σ_p may be obtained[2,3,6] by treating $E_n - E_0$ as a constant ΔE in Eq. 4 and by using the LCAO molecular orbital, where each molecular orbital is expressed as a linear combination of valence-shell atomic orbitals:

$$\sigma_p{}^A = -[2e^2h^2/3m^2c^2(\Delta E)]\langle r^{-3}\rangle_{2p}(P_1 - P_2 - P_3) \quad (8)$$

where:

$$P_1 = (P_{xx} + P_{yy} + P_{zz})_{AA}$$
$$P_2 = (P_{xx}P_{yy} + P_{yy}P_{zz} + P_{zz}P_{xx})_{AA}/2$$
$$P_3 = \sum_{B(\neq)A}(P_{xx}P_{yy} + P_{yy}P_{zz} + P_{zz}P_{xx})_{AB}/2$$

In this formulation, $(P_{xx})_{AB}$, for example, designates:

$$(P_{xx})_{AB} = 2\sum_i^{occ} C_{xA}{}^i C_{xB}{}^i \quad (9)$$

where $C_{xA}{}^i$ is the coefficient of the $2P_x$ atomic orbital of the carbon, A, in the ith molecular orbitals. It corresponds to the electron desnity $(A=B)$ of the $2P_x$ AO or bond order matrix $(A \neq B)$ between two $2P_x$ orbitals of the A and B atoms. P_1 is the 2P electron density on the carbon A and has a value of 3 in the neutral carbon. The $\langle r^{-3}\rangle_{2P}$ factor, which is the mean inverse cube radius for carbon 2P orbitals, depends on the local electron desity on the carbon atom.[2] For a Slater 2P orbital, $\langle r^{-3}\rangle_{2P}$ is found to be:

$$\langle r^{-3}\rangle_{2P} = \frac{1}{24a_0{}^3}[3.25 - 0.35(P_1 - 3)]^3 \quad (10)$$

where a_0 is the Bohr radius and $(P_1 - 3)$ is the excess charge density of the 2P electron.

For the calculation of P_1 and P_2, we use a simple LCAO MO theory for the σ-electron developed by Fukui, Kato and Yonezawa.[7] A molecular orbital, φ, is expressed as a linear combination of the sp³ hybridized orbital of the carbon atom, $\chi_{C,,i}$ and the ls orbital of the hydrogen atom, $\chi_{H,l}$, as is shown by the expression:

$$\varphi = \sum_i^n C_i\chi_{C,i} + \sum_l^n C_l\chi_{H,l}$$

The coulomb and resonance integrals are given by the following:

$$\langle\chi_{C,i}|H|\chi_{C,i}\rangle = \alpha$$
$$\langle\chi_{H,l}|H|\chi_{H,l}\rangle = \alpha + a\beta$$
$$\langle\chi_{C,i}|H|\chi_{C,i+1}\rangle = \beta$$

between two sp³ orbitals of two adjacent carbon atoms:

$$\langle\chi_{C,i}|H|\chi_{C,i} + 1\rangle = m\beta$$

between two sp³ orbitals to one and the same carbon atom:

$$\langle\chi_{C,j}|H|\chi_{H,j+1}\rangle = b\beta$$

where a is taken as -0.2; m, as 0.34, and b, as 1.1[7]. In solving the secular equation, we neglected the overlap integrals. Then the electron density, q_r, of the rth atomic orbital is defined by:

$$q_r = 2\sum_i^{ooc} C_{ir}{}^2$$

The x, y, z, components of the charge density and the bond order matrix (Eq. 9) can be represented in terms of electron densities, q_r, as follows if we take x, y and z axes to be as shown in Fig. 1:

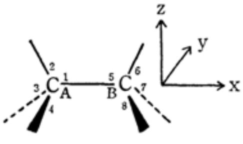

Fig 1.

$$P_{xx} = (3/4)q_1 + (1/12)(q_2 + q_3 + q_4)$$
$$P_{yy} = (1/6)(q_2 + q_4) + (2/3)q_3$$
$$P_{zz} = (1/2)(q_2 + q_4)$$

$$(P_{yy})_{AB} = 2\sum_i^{occ}[-1/\sqrt{6}(C_{i2} + C_{i3}) + \sqrt{2/3}C_{i4}]$$
$$\times[-1/\sqrt{6}(C_{i6} + C_{i7}) + \sqrt{2/3}C_{i8}]$$

The calculated values of P_1, P_2, P_3, $\langle r^{-3}\rangle_{2p}$ and σ_p, together with the observed[3] δ ¹³C and calculated δ¹³C values, are summarized in Table I for several compounds.

When we take ΔE as 10 eV. for Eq. 8, we have:

$$\sigma_p = (44.8Q_{2p\sigma} - 138.1)(P_1 - P_2 - P_3) \quad (11)$$

where $Q_{2p\sigma}$ designates $(P_1 - 3)$. The values of $(P_1 - P_2 - P_3)$ is almost constnat $(P_1 - P_2 - P_3 = 1.498)$. Therefore, if we take $(P_1 - P_2 - P_3)$ as 1.498 for Eq. 11, the total shielding constant, $\sigma(=\sigma'_d + \sigma_p)$, due to the valence electrons of the carbon atom A in a saturated hydrocarbon is, from Eq. 7 and Eq. 11:

$$\sigma = 87.8Q_{2p\sigma} - 1.6Q_{2p\sigma}{}^2 - 207.2 \text{ (p.p.m.)} \quad (12)$$

In order to test the validity of Eq. 12, which was derived theoretically, we plot in Fig. 3 the observed carbon-13 chemical shift against the excess charge density of 2p electrons for several compounds. We thus find an approximate proportionality between $Q_{2p\sigma}$ and δ¹³C.

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6) J. A. Pople, *Proc. Roy. Soc.*, **A239**, 550 (1957); M. Karplus and T. P. Das, *J. Chem. Phys.*, **34**, 1683 (1961).

7) K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **34**, 442, 1111 (1961).

TABLE I. THE CALCULATED VALUES OF ^{13}C CHEMICAL SHIFT FOR SOME SATURATED HYDROCARBONS

Molecule	P_1	P_2	P_3	$(P_1$-P_2-$P_3)$	$\langle r^{-3}\rangle_{2p}$ a.u.	$-\sigma_p$(calcd.) p.p.m.	δ^{13}C(calcd.) p.p.m.	δ^{13}C(obs.)[a] p.p.m.
CH_4	3.2241	1.7295	0	1.4946	1.326	191.4	—	—
C*-C	3.1707	1.6752	0	1.4955	1.351	195.4	−4.0	−8.0
C*-C-C	3.1691	1.6734	0	1.4957	1.352	195.5	−4.1	−17.0
C-C*-C	3.1209	1.6231	0	1.4978	1.374	198.8	−7.4	−18.0
C-$\overset{C}{C}$*-C	3.0706	1.5713	0	1.4993	1.397	202.3	−10.9	−27.3
C*-$\overset{C}{C}$-C	3.1689	1.6731	0	1.4958	1.352	196.0	−4.6	−26.4

a) Chemical shift is referred to methane. (Ref. 4.)

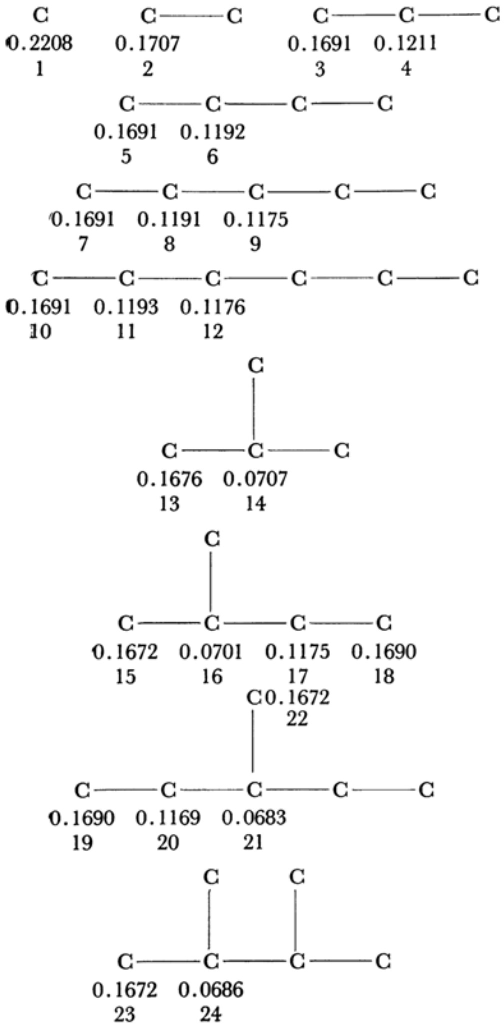

Fig. 2. Excess charge density of 2P electrons ($Q_{2p\sigma}$) of carbon atoms for linear and branched hydrocarbons.

Discussion

Theoretical considerations predict the same simple linear relationship between the excess charge density and the carbon-13 chemical shifts for saturated hydrocarbons as has been exhibited in the aromatic compounds. However, Fig. 3 shows a fairly large scattering.

This is mainly due to the failure of the theoretical interpretation of the anomalous β-effect suggested by Paul and Grant,[4)] which gives an unexpectedly large down-field contribution than the α-effect. The β-effect may be interpreted in terms of the change in the mean excitation energy, ΔE, or the change of the effective nuclear charge, Z^*, due to the influence of the β-methyl group on the radial part of the 2p atomic orbital.[8)] In

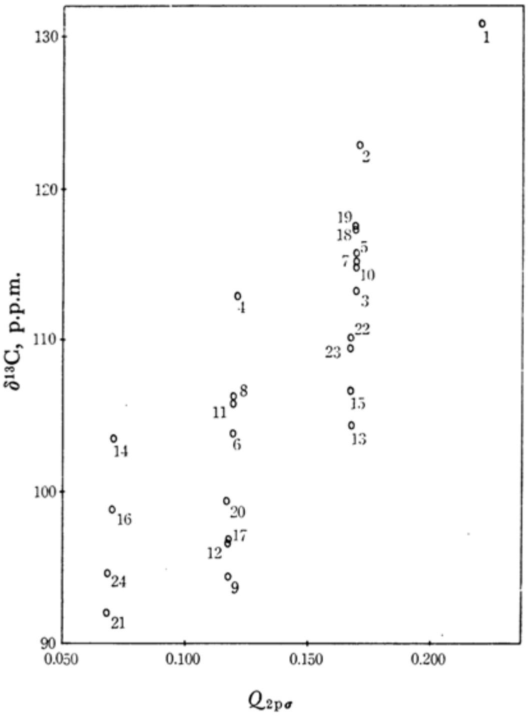

Fig. 3. A plot of the excess charge density of 2P electron ($Q_{2p\sigma}$) versus observed ^{13}C chemical shift (δ^{13}C). The values of $Q_{2p\sigma}$ are summarized in Fig. 2 and the values of ^{13}C chemical shift (δ^{13}C) are given in p.p.m. from CS_2 (Ref. 4).

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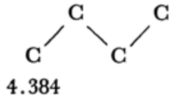
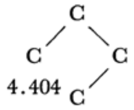
8) This was suggested by D. M. Grant at the International Symposium on NMR, Tokyo (1965).

fact, the diminution of ΔE may be expected in a branched alkane with reference to the value of the ionization potential.(9) The increase in Z^* and the decrease in ΔE may be considered to cause the paramagnetic shift. Another anomalous γ-effect which makes a positive contribution to the carbon-13 chemical shifts can be partly interpreted in terms the electronic effects. The γ-carbon relative to the carbon atom can occupy both a gauche and a trans position relative to the carbon atom under study. For example, consider a trans butane (I) and a gauche butane (II):



trans
(I)



gauche
(II)

We calculated the atom population of the terminal carbon atom by an extended Hückel molecular orbital theory,(10) which is useful in discussing the conformational change of the electronic sturcture by taking account of the resonance integral between non-bonded atoms. The terminal carbon for the gauche form with a larger charge density is more shielded than that for the trans form. Using Eq. 12 this effect was evaluated to be about 1.5 p. p. m. Hence the contribution of the gauche form causes a diamagnetic shift to the terminal carbon of normal butane. Recently, Grant presented(8) a theoretical interpretation of this effect by the valence bond method and also showed experimentally that *trans*-1, 4-carbon-carbon interactions should have a negative effect, while *cis*-1, 4-carbon-carbon interactions has a positive effect. Table I and Fig. 3 also show that the calculated values of $\delta^{13}C$ are fairly small, this may be attributed to a small difference in the calculated excess charge densities. This difficulty may be overcome by the improvement of the parametrization of the coulomb and resonance integrals. However, it may be stressed that the general trends of the carbon-13 chemical shifts of saturated compounds, with the exception of a large βth carbon effect, can be qualitatively interpreted by simple molecular orbital calculations. Our treatment is also applicable to other saturated systems, haloalkanes, for example, but the anomalous upfield tendency of the ^{13}C chemical shifts of the multisubstituted bromo and iodo methane cannot be interpreted by the electronic effect only.

The calculations were carried out partly on the digital compouter KDC-I of Kyoto University and partly on the IBM 7090 at the Japan IBM CO. with the permission of the UNICON Committee, whose help we hereby acknowledge.

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9) The ionization potential (Ip) might be a measure of the mean excitation energy, ΔE. The Ip values of ethane, propane, n-butane and isobutane are 11.76, 11.21, 10.86 and 10.40 eV. respectively.

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