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AN IMPROVED CNDO APPROACH TO THE ^{1}H CHEMICAL SHIFTS OF OLEFINIC COMPOUNDS

Okitsugu KAJIMOTO and Takayuki FUENO
Department of Chemistry, Faculty of Engineering Science, Osaka University,
Toyonaka, Osaka

A theoretical expression has been derived for the magnetic shielding constant of aliphatic hydrogens, without using the customary point dipole approximation. The expression, combined with CNDO/2 electron densities, has correctly reproduced the ^{1}H chemical shifts observed for various substituted ethylenes and butadienes. It is concluded that the diamagnetic shielding from the neighboring carbon constitutes an important contribution to the shifts.

It has recently been shown by Kato that the proton nuclei in hydrocarbons should be in a sizable extent of diamagnetic shielding from neighboring atoms.1) We wish to show herewith a dominant importance of this shielding to proper understanding of the effects of polar substituents on proton chemical shifts of olefinic compounds.

Pople2) derived an LCAO MO expression for the ^{1}H shielding constant σ on three major assumptions: (1) zero-differential atomic integral, (2) average excitation energy approximation, and (3) point magnetic dipole approximation. However, agreement between the theoretical σ values thus obtained and the observed is generally unsatisfactory, primarily because of the inadequacy of the point dipole approximation3); the diamagnetic contribution of the neighboring atom is calculated to be too small under this approximation.

We here transform the famous Ramsey formula4) for σ into an LCAO MO expression, persisting to Pople's first two assumptions but without invoking the point dipole approximation. The expression derived for a proton A in aliphatic compounds is as follows:

$$\sigma^{A} = \frac{e^{2}}{3mc^{2}} P_{1s,1s}{}^{A} \left\langle \phi_{1s}{}^{A} \middle| 1/r_{A} \middle| \phi_{1s}{}^{A} \right\rangle + \frac{e^{2}}{3mc^{2}} \sum_{i} P_{ii}{}^{B} \left\langle \phi_{i}{}^{B} \middle| 1/r_{A} \middle| \phi_{i}{}^{B} \right\rangle - \frac{e^{2}\hbar^{2}}{6m^{2}c^{2}\Delta E} \left\langle \phi_{z}{}^{B} \middle| 1/r_{A}{}^{3} \middle| \phi_{z}{}^{B} \right\rangle (Q_{xx}{}^{B} + Q_{yy}{}^{B})/2 \qquad (1)$$

with

$$Q_{xx}^{B} = 2[P_{yy}^{B} + P_{zz}^{B} - P_{yy}^{B}P_{zz}^{B} + (P_{yz}^{B})^{2}] \qquad (2)$$

where the summation covers over the valence-shell atomic orbitals of the neighboring carbon atom B, P's are the electron density—bond order matrix elements and ΔE is the average excitation energy of the molecule being considered. The z-axis is so taken as to coincide with the A-B bond of interest. The first term of Eq.(1) represents the diamagnetic shielding by a 1s electron of the hydrogen atom A in question. The second and third terms respectively denote the diamagnetic and paramagnetic shieldings caused by the directly bonded atom B. Contributions from atoms more distant than B may be ignored to a first approximation.

The Coulomb-type integrals can easily be evaluated from Roothaan's formula$^{5)}$ on the basis of the Slater atomic orbitals. For the 1s orbital of hydrogen, Slater's effective nuclear charge is modified as $Z_{eff} = 1.2 - 0.3(q_H - 1)$.$^{6)}$ The integral $\langle\phi|1/r^3|\phi\rangle$ appearing in the third term can be evaluated by numerical integration, as has already been practiced by Kato.$^{1)}$ If we take the C-H bond length to be 1.08 Å and assume ΔE = 10 eV as a typical value, Eq.(1) is reduced to

$$\begin{aligned}\sigma^{A} &= 17.75 \times 10^{-6}(-0.3q_H^{2} + 1.5q_H)\\ &+ 10^{-6}\{8.362q_{2s}^{B} + 10.073q_{2pz}^{B} + 7.564(q_{2px}^{B} + q_{2py}^{B})\}\\ &- 15.03 \times 10^{-6}(Q_{xx}^{B} + Q_{yy}^{B})\end{aligned} \qquad (3)$$

where q's are the electron densities on the atomic orbitals specified.

In evaluating each term of Eq.(3), we have used the CNDO/2 formalism. The results have shown that the last term remains almost constant for olefinic protons and that the second term can well be approximated to the total electron density q_C of carbon atom multiplied by the average coefficient of 8.39, in place of contributions from the four atomic orbitals.

The chemical shift of a given proton, defined as $\delta(\text{ppm}) = (\sigma - \sigma_{st}) \times 10^{6}$, can then be expressed as

$$\delta = 16.0\Delta q_H + 8.39\Delta q_C \qquad (4)$$

where Δq_H and Δq_C are the respective increments in electron density on the hydrogen atom of interest and its bonded carbon atom, relative to the densities in ethylene as a standard. This equation essentially differs from Pople's original formulation in that the δ value largely depends on Δq_C.

Importance of the second term of Eq.(4), a diamagnetic contribution from the bonded carbon atom, can be clearly seen in Table 1, in which the chemical shifts calculated for the β-protons of various monosubstituted ethylenes are compared with the experimental values.$^{7)}$ For this family of compounds,

Δq_C is larger than Δq_H, so that the former quantity forms a more important contribution to δ. Pople's equation, in which this important contribution has apparently been left out of account, fails to reproduce the observed shifts. Clearly, this indicates inadequacy of the use of the dipole approximation for the prediction of chemical shifts.

Table 1. Chemical Shifts of the β-Protons in Monosubstituted Ethylenes[a)]

Substituent	β-Proton	Δq_H	Δq_C	δ_{calc}[b)]	δ_{obs}[7)]	δ_{Pople}[c)]
OCH_3	_cis_	-0.0107	0.0993	0.66	1.35	0.35
	trans	-0.0030	0.0993	0.78	1.50	0.47
CH_3	_cis_	0.0033	0.0254	0.36	0.38	0.51
	trans	0.0098	0.0254	0.37	0.47	0.62
$CH=CH_2$	_cis_	0.0019	0.0111	0.12	0.19	0.51
	trans	0.0090	0.0111	0.23	0.29	0.62
Cl	_cis_	-0.0190	-0.0163	-0.44	-0.17	0.31
	trans	-0.0128	-0.0163	-0.34	-0.09	0.41
CN	_cis_	-0.0091	-0.0167	-0.29	-0.44	0.31
	trans	-0.0009	-0.0167	-0.15	-0.62	0.45
COOH	_cis_	-0.0144	-0.0463	-0.62	-1.03	0.18
	trans	-0.0006	-0.0463	-0.40	-0.47	0.40
NO_2	_cis_	-0.0425	-0.0457	-1.06	-1.30	-0.21
	trans	-0.0269	-0.0457	-0.81	-0.66	0.04

a) All values listed are relative to ethylene, in which $q_H = 0.9844$, $q_C = 4.0312$ and $\delta_{obs} = 4.27$. b) Calculated from Eq.(4). c) Calculated by the method of Ref. 1.

Figure 1 shows plots of the ^1H chemical shifts calculated for some _trans_-1-substituted butadienes against the observed values.[8)] It is seen in Fig. 1 that the theory correctly predicts the positional differences in the δ values for the β, γ, δ_{cis} and δ_{trans} protons. This suggests applicability of Eq.(4) to the assignment of the observed peaks. For the α protons, however, the plotted points are greatly scattered, perhaps because of inadequacy of the neglect of contributions from atoms other than the bonded carbon.

Equation (4) also sheds light on the origin of the Hammett ρσ relationships reported for various series of compounds bearing a substituted phenyl group.[9] The observed relationships could be taken as an indication of the Hammett-type dependences of both q_H and q_C on substituents. The situation will be fully discussed elsewhere in connection with the ^1H and ^{13}C chemical shifts of substituted phenyl vinyl ethers and sulfides.

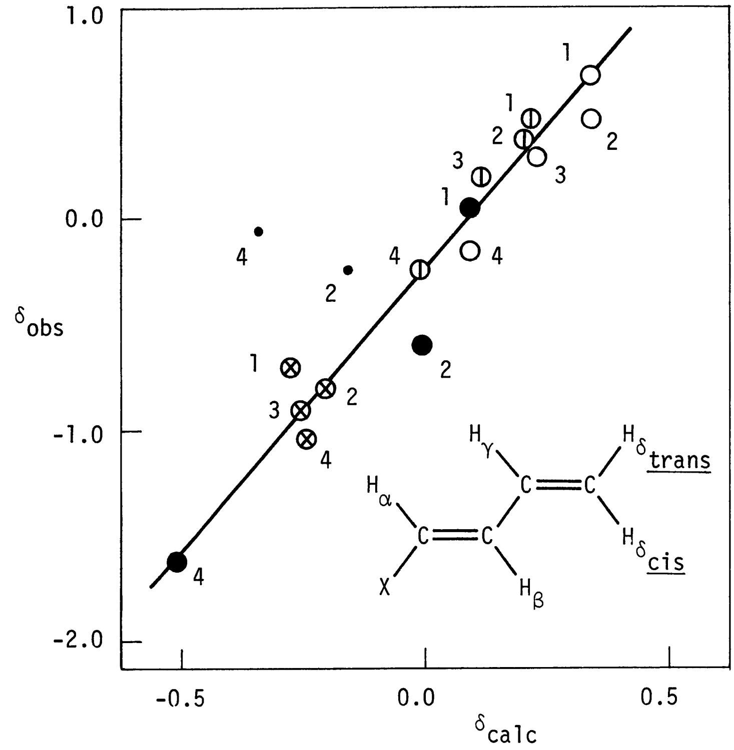

Fig.1. Plots of δ_{calc} vs. δ_{obs} for trans-1-substituted butadienes.
1 OCH_3, 2 CH_3, 3 H, 4 CN. ○ δ_{trans}, ⦶ δ_{cis}, ⊗ γ, ● β, • α.

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