[Chem. Pharm. Bull. 20(12)2522—2527(1972)]

UDC 547.211.03 : 543.422.25

Carbon-13 Chemical Shifts of Aliphatic Systems. II.[1] On the CNDO/2 Calculation and C-13 Chemical Shift of Substituted Methane Series

Yoshio Sasaki and Miyoko Suzuki

Faculty of Pharmaceutical Sciences, Osaka University[2]

(Received Nobember 11, 1971)

The eigenvalues and eigenvectors of the MeR (R=F, OH, NH_2, Me, H, CN, CHO and NO_2) series were presented by the CNDO/2 method. There values were applied to the theoretical treatment of C-13 chemical shift under the three conditions, namely, (a) ΔE= 10 eV, (b) ΔE=the ionization potential, (c) $\Delta E=\varepsilon_i - \varepsilon_j$, and compared with the experimental data. Of the three conditions, the method (a) and (b) afford the perturbation effect of the substituent group.

Introduction

With regard to H-1 and C-13 nuclear magnetic resonance chemical shifts of substituted methyl derivatives, only the correlation of the shifts with the electronegativities of the substituents has so far been examined.[3–6] However, due to recent progress in quantum chemical treatments of the σ-framework, it is now possible to examine the electronic states of substituted aliphatic hydrocarbons. A few years ago, Pople, *et al.*[7–9] presented an approximate method for obtaining self-consistent molecular orbitals of all valence electrons of large molecules. Moreover, in the molecular orbital theory of diamagnetism, they[10,11] established a connection between nuclear magnetic resonance chemical shifts and diamagnetic susceptibilities. From the molecular orbital theory for the C-13 chemical shift, it seems that the local paramagnetic term should be a dominant factor in several terms contributing to the chemical shifts. They applied their idea to saturated and unsaturated hydrocarbon molecules[12–14] with success, but they did not examine the effect of the substituent group on the electronic structure of the molecule, until they developed *ab initio* molecular orbital calculations with limited success.[15] Recently, Yonezawa, *et al.*[16] applied the "Coupled Hartree-Fock perturbation theory,[17]" without the ΔE approximation, in calculating C-13 and N-14 chemical shifts, and found that calculated values agreed well with experimental values. They examined the contribution of each excited state to the C-13 chemical shift in detail and concluded that the chemical shift is not governed by any particular excited state. In this paper, the C-13

1) Part I: G. Miyajima, Y. Sasaki, and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **18**, 1489 (1970).
2) Location: *Toneyama 6-1-1, Toyonaka, Osaka.*
3) B.P. Dailey and J.N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).
4) J.R. Cavanaugh and B.P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).
5) H. Spiesecke and W.G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).
6) P. Bucci, *J. Am. Chem. Soc.*, **90**, 252 (1968).
7) J.A. Pople, D.P. Santry, and G.A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).
8) J.A. Pople and G.A. Segal, *J. Chem. Phys.*, **43**, S136 (1965).
9) J.A. Pople and P.A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).
10) J.A. Pople, *J. Chem. Phys.*, **37**, 53 (1962).
11) J.A. Pople, *J. Chem. Phys.*, **37**, 60 (1962).
12) J.A. Pople and D.P. Santry, *Mol. Phys.*, **7**, 269 (1964).
13) M. Karplus and J.A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).
14) J.A. Pople, *Mol. Phys.*, **7**, 301 (1964).
15) R. Ditchfield, D.P. Millers, and J.A. Pople, *J. Chem. Phys.*, **54**, 4186 (1971).
16) H. Kato, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Japan*, **43**, 1921 (1970).
17) R.A. Hegstrom and W. Lipscomb, *J. Chem. Phys.*, **46**, 1594 (1967).

chemical shift of substituted methane derivatives is calculated by the CNDO/2 method with special consideration of the following items,

1) whether the perturbation effect of the substituent group is appreciable in this calculation of the C-13 chemical shift,

2) how the excitation energy should be estimated.

Method of Calculation

1) CNDO/2 Method——In the CNDO/2 approximation, using the valence s and p functions, the LCAO SCF Hartree-Fock matrix elements are given by the following equations:

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - 1/2P_{\mu\mu})\gamma_{AA} + \sum_{B(\neq A)}(P_{BB}\gamma_{AB} - v_{AB})$$

$$F_{\mu\nu} = \beta^0_{AB}S_{\mu\nu} - 1/2P_{\mu\nu}\gamma_{AB} \quad (\mu \neq \nu)$$

$$P_{\mu\nu} = 2\sum_{i}^{occ.} C_{i\mu}C_{i\nu} \qquad P_{AA} = \sum_{\mu}^{A} P_{\mu\mu}$$

All symbols are defined as in the literatures.[9,10] The calculations were carried out for the ground state of the staggered conformation of MeR (R=NH_2, OH, Me, CHO) and for the ground state of MeR (R=CN, F, NO_2). The inter-atomic distances and bond angles of Me-Me, MeOH and $MeNH_2$ were taken from the literature[10] and for $MeNO_2$, MeCHO, MeCN and MeF, parameters were also adopted from the literature.[18] The calculations were carried out on a FACOM-230-60 Type Electronic Computer at Kyoto University Computer Center, using the QCPE 91 of Quantum Chemistry Program Exchange with minor modification.

2) Calculation of Chemical Shift——The screening constant of the nucleus of an atom A may be written as follows:[19]

$$\sigma^A = \sigma_d^{AA} + \sigma_p^{AA} + \sum_{B(\neq A)} \sigma^{AB} + \sigma^{A,ring}$$

Where $\sigma_d{}^{AA}$ is the contribution to the diamagnetic circulation on an atom A. $\sigma_P{}^{AA}$ is the contribution due to the paramagnetic current on this atom induced from the mixing of the ground and excited electronic states in the magnetic field. $\sum\sigma^{AB}$ is the contribution from the other atoms. The last term, $\sigma^{A,ring}$, is the contribution from the ring current delocalized in the frame work of the aromatic nucleus. For the carbon atom, it is suggested that the perturbation of the local paramagnetic term is the dominant factor for variation in the chemical shift.[13] The paramagnetic component $\sigma_P{}^{AA}$ is divided into three component as follows.

$$\sigma_p^{AA} = \{(\sigma_p^{AA})_{XX} + (\sigma_p^{AA})_{YY} + (\sigma_p^{AA})_{ZZ}\}/3$$

The ZZ-component is given by equation (1).

$$(\sigma_p^{AA})_{ZZ} = -[e^2h^2/2m^2c^2(\Delta E)](r^{-3})_{2p}\{(Q_{AA})_{ZZ} + \sum_{B\neq A}(Q_{AB})_{ZZ}\} \qquad (1)$$

$$(Q_{AA})_{ZZ} = 2 - 2(P_{AXAX} - 1)(P_{AYAY} - 1) + 2P^2_{AXAY}$$

$$(Q_{AB})_{ZZ} = -2P_{AXBX}P_{AYBY} + 2P_{AXBY}P_{AYBX}$$

Where $\sum_{B\neq A}$ is the sum of the contribution from all the atoms other than atom A, $(r^{-3})_{2P}$ is the mean inverse cubic radius of the carbon 2p orbitals and ΔE is the average excitation energy. P_{AUBV} is the element of the charge density and bond order matrix in the molecular orbital treatment of the unperturbed molecule. The suffix AX, BX, AY, BY, AZ and BZ correspond to the various 2p atomic orbitals of the atoms A and B.

The next equation is obtained using the net charge $-q_Ae$ on atom A and the Slater atomic orbitals. $(r^{-3})_{2P} = 34.33\ a_o^{-3}\ (1 - 0.323q_A)/24$ a_0 being the Bohr radius. If B is a neighboring atom and the Y-axis is chosen along the bond in the Q_{AB} term, the cross term $P_{AXBY}P_{AYBX}$ is usually small and the mean value of Q_{AB} can be represented as

$$Q_{AB} = -2/3[P^{\sigma}_{AYBY}(P^{\pi}_{AXBX} + P^{\pi}_{AZBZ}) + P^{\pi}_{AXBX}P^{\pi}_{AZBZ}]$$

P_{AYBY} is the bond-order between two 2p atomic orbitals of the σ-bond and P_{AXBX} & P_{AZBZ} are the π-bond orders, respectively. First, equation (1) was calculated using $\Delta E = 10$ eV for all compounds. Next, the ionization potentials were used. Aliphatic compounds with lone pairs generally have two ultraviolet (UV) absorption bands. The wavelengths affording to the absorption maxima migrate to the same direction as the

18) G.W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., 1955.
19) J.A. Pople, *Disc. Faraday Soc.*, 34, 7 (1962).

ionization potentials of the compounds.[20] Accordingly, the ionization potentials seem to show the excitation energy values which are affected by the substituent. Finally, as a theoretically higher approximation, the energy value of each excited state was used in the following equation (2).

$$(\sigma_p^{AA})_{ZZ} = -2e^2h^2/m^2c^2\langle r^{-3}\rangle_{2p}\sum_{i}^{occ.}\sum_{j}^{unocc.}(\varepsilon_j-\varepsilon_i)^{-1}(C_{iAX}C_{jAY}-C_{iAY}C_{jAX}) \times \sum_{B}(C_{iBX}C_{jBY}-C_{iBY}C_{jBX}) \quad (2)$$

Result and Discussion

The results obtained from the CNDO/2 calculation are summarized in Table I.

Table I. Bond Orders and Charge Densities of the CH_3R Series

R	P_{CURU}	P_{CUCU}	R	P_{CURU}	P_{CUCU}
NH_2	X= 0.1522	X=0.9744	CN	X= 0.2141	X=0.9943
	Y=−0.7474	Y=0.9495		Y=−0.5967	Y=1.0299
	Z= 0.1710	Z=0.9698		Z= 0.2141	Z=0.9943
OH	X= 0.1562	X=0.9745	F	X= 0.1421	X=0.9861
	Y=−0.7737	Y=0.8816		Y=−0.7722	Y=0.7986
	Z= 0.1534	Z=0.9790		Z= 0.1421	Z=0.9861
CH_3	X= 0.1698	X=0.9750	CHO	X= 0.2402	X=0.9912
	Y=−0.7198	Y=1.0360		Y=−0.6501	Y=1.0565
	Z= 0.1698	Z=0.9750		Z= 0.1580	Z=0.9987
H		X, Y, Z: 0.9971	NO_2	X= 0.1908	X=1.0325
				Y=−0.6969	Y=0.9047
				Z= 0.1907	Z=1.0327

X,Y,Z indicate $2p_X$, $2p_Y$, $2p_Z$ orbitals.

Next, σ_p (ΔE=10 eV) was calculated using equation (1) (*cf.* Table II).

Table II. Correlation between Observed and Calculated ^{13}C Chemical Shifts of CH_3R

R	$\langle r^{-3}\rangle_{2p}$ (a.u.)	$Q_{CC}+Q_{CR}$	$-\sigma_p$(calcd.) (ppm)	δ_C(calcd.) (ppm)	δ_C(obsd.) (ppm)
F	1.536	2.1289	236.7	−29.1	−77.5
OH	1.506	2.1398	233.2	−25.7	−49.8[a]
NH_2	1.480	2.1413	229.4	−21.8	−14.8[a]
CH_3	1.436	2.1445	222.9	−15.3	− 8.0
H	1.434	2.0000	207.6	0.0	0.0
CN	1.422	2.1400	220.3	−12.7	− 6.8
CHO	1.409	2.1478	219.0	−11.5	−31.7
NO_2	1.444	2.1290	222.5	−14.9	−26.8

a) C.H. Holm, *J. Chem. Phys.*, **26**, 707 (1957)
others: H. Spiesecke and W.G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961)

In calculation of the Q_{CC} and Q_{CR}, $2P^2_{CUCV}$ and $2P_{CURV}\cdot P_{CVRU}$ were neglected, because the former was almost zero and the latter was only <0.0001. The paramagentic contribution to the carbon atom expressed in equation (1) contains both an intra-atomic term Q_{CC}, depending primary on the carbon atom and an inter-atomic term Q_{CR}, depending on the bond order between the atoms in the substituent groups. The latter is more sensitive to the chemical environment than the former. At this low approximation with the mean electronic excita-

20) C.N. Rao, "Ultra-Violet and Visible Spectroscopy, Chemical Applications," Butterworth & Co., Ltd., London, 1961, p. 22.

tion energy, equation (1) can be expressed in terms of the atomic charge density and the bond order. Table II shows that the calculated and observed shifts are in qualitative agreement and a correlation between these shifts and the electronegativities of the substituents was observed.[5]

In the above treatment, the eigenvalues were not regarded as variables and as a result the effect of the substituent on the excitation energy was neglected. Expecting a better agreement with the observed data, the ionization potential for each compound was used in equation (1), instead of the mean electronic excitation energy (*cf.* Table III).

Table III. Correlation between Observed and Calculated ^{13}C Chemical Shifts of CH_3R

R	ΔE (a.u.)	$(r^{-3})_{2p}$ (a.u.)	$Q_{CC}+Q_{CR}$	$-\sigma_p$(calcd.) (ppm)	δ_C(calcd.) (ppm)	δ_C(obsd.) (ppm)
F	0.474[a]	1.536	2.1289	183.3	−20.0	−77.5
OH	0.397[b]	1.506	2.1398	215.8	−52.8	−49.8
NH_2	0.338[c]	1.480	2.1413	248.9	−85.9	−14.8
CH_3	0.426[d]	1.436	2.1445	191.6	−28.6	− 8.0
H	0.467[d]	1.434	2.0000	163.0	0.0	0.0
CN	0.448[e]	1.422	2.1400	180.0	−17.0	− 6.8
CHO	0.375[b]	1.409	2.1478	214.1	−51.1	−31.7
NO_2	0.412[f]	1.444	2.1290	197.8	−34.8	−26.8

a) D.C. Frost and C.A. McDowell, *Proc. Roy. Soc.* (London), **A241**, 194 (1957)
b) M.J.S. Dewar and S.D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).
c) M.I.Joboury and D.W. Turne, *J. Chem. Soc.*, **1964**, 4434
d) A.D. Baker, C. Baker, C.R. Brundle, and D.W. Turne, *Int. J. Mass. Spectrom. Ion Phys.*, **1**, 285 (1968)
e) Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectry. Radiat. Transfer*, **2**, 369 (1963)
f) M.J.S. Dewar, M. Shanshal, and S.D. Worley, *J. Amer. Chem. Soc.*, **91**, 3590 (1969)

The result gives improvement in the calculated values except for CH_3F and CH_3NH_2, but rather overestimates the effect of the substituent. This is probably because only one Rydberg state was considered. It is necessary to obtain the contribution to the chemical shift of each transition state.

Finally, the paramagnetic shifts were calculated by equation (2) using each excitation energy (*cf.* Table IV).

Table IV. Correlation between Observed and Calculated ^{13}C Chemical Shifts of CH_3R

R	$-\sigma_p$(calcd.) (ppm)	δ_C(calcd.) (ppm)	δ_C(obsd.) (ppm)
F	73.5	+2.8	−77.5
OH	73.9	+2.4	−49.8
NH_2	71.9	+4.4	−14.8
CH_3	73.9	+2.4	− 8.0
H	76.3	0.0	0.0
CN	71.2	+5.1	− 6.8
CHO	73.3	+3.0	−31.7
NO_2	80.4	−4.1	−26.8

This calculation gave the worst results and values did not show an obvious difference corresponding to the effect of the substituent and were also of opposite signs. At this higher approximation, the results obtained are not neccessarily good. But it is evident that the excitation energy has a dominant effect on the chemical shift. Moreover the effect of the substituent on the excitation energy in the MeR series should not be averaged to 10 eV, which was chosen by Pople.[7] This work on substituted compounds provides no theoretical proofs for this value of 10 eV. As shown in the foregoing discussion, the ionization potential does

not seem to be a most suitable approximation of the excitation energy either. A satisfactory value for chemical shift was not obtained, probably due to the inaccuracy of the calculation of excitation energy inherent to the CNDO/2 method, but theoretically the third method seems the most reasonable. So, equation (2) was used to evaluate of which excited states the contribution to the chemical shift is largest and to see whether the mean excitation energy is nearly 10 eV.[11]

Table V. Contribution to ^{13}C Chemical Shifts of CH_3CH_3 at Each Excited State

i→j	$(\sigma_p)_{XX}$ (ppm)	$(\sigma_p)_{YY}$ (ppm)	$(\sigma)_{pZZ}$ (ppm)
3→ 8		− 8.8	
4→ 8		− 7.5	
3→ 9		− 7.5	
4→ 9		− 8.8	
5→12	−35.3		
6→12		−14.0	
7→12		− 5.0	
5→13			−35.3
6→13		− 5.0	
7→13		−14.0	
3→14			−29.2
4→14	−29.2		

As shown in Table V, rather high excited states, including the transition to the highest vacant orbital, give large contribution to the chemical shift and in several states the contribution is of the same order as the largest one. These results exclude the possibility that in general a particular transition, especially the transition to the lowest excited state, governs the magnitude of the chemical shift. For discussion of chemical shifts of the MeR series, the excited states which give the largest contributions to $(\sigma_p)_{XX}$, $(\sigma_p)_{YY}$ and $(\sigma_p)_{ZZ}$ and their excitation energies were collected.

Table VI. Largest Contribution to ^{13}C Chemical Shifts of CH_3R at Certain Excited States

R	X		Y		Z	
	i→j	ΔE (a.u.)	i→j	ΔE (a.u.)	i→j	ΔE (a.u.)
F	4→11	1.219	3→10	1.173	3→11	1.219
OH	3→12	1.219	3→10	1.17	4→12	1.194
NH_2	4→13	1.21	4→ 9	1.117	3→13	1.266
CH_3	5→12	1.036	7→13	0.97	5→13	1.036
H	2→ 8	1.054	2→ 6	1.054	2→ 6	1.054
CN	4→12	1.183	4→13	1.197	3→12	1.183
CHO	6→15	1.163	5→13	1.152	5→15	1.239
NO_2	4→15	1.256	9→17	0.98	4→17	1.27

As shown in Table VI, their excitation energies are much greater than 0.37 a.u. (10 eV). The excitation energy of all substituted compounds are about 20% larger than those of methane and ethane (about 1 a.u.), but there are no clear difference in the effect of different substituents. These results may explain the small and nearly constant values of the eight chemical shifts shown in Table IV.

Conclusion

Values of C-13 chemical shifts were calculated under three conditions.

(a) $\Delta E=10$ eV. It seems that this method is not suitable for substituted compounds, but the obtained values showed the perturbation effect of the substituent group.

(b) $\Delta E=$ionization potential. As the energy values are treated as variables, the effect of the substituent on the excitation energy may be estimated. The result gave improvement in the calculated values, but rather overestimated the perturbation effect of the substituent.

(c) $\varepsilon_i-\varepsilon_j$. Each excitation energy was considered. Theoretically this is the most precise method, but the calculated values showed no obvious difference corresponding to the effect of the substituent and had opposite signs to the observed values. It is well known that the CNDO/2 method is not good for calculation of excitation energy. So Lipscomb's method,[17] which may be higher than Pople's method with respect to the energy calculation in the approximate theory of the chemical shift, was not used in method (c) in the present work. In our laboratory the more precise treatment of C-13 chemical shifts, using Lipscomb's method and the M-CNDO/2 method modified for use in calculation of the excitation energy,[21] is now in progress.

21) A. Tajiri, N. Ohmichi, and T. Nakajima, *Bull. Chem. Soc. Japan*, **44**, 2347 (1971).