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Studies on the Proton Magnetic Resonance Spectra in Aliphatic Systems. II.[1] On the Inductive and Electric Field Effect of Alkyl Derivatives

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α-^{1}H chemical shift of alkyl derivatives is dependent mainly on the sigma- and π-electronic contributions, and the detailed discussions have proved that the former is conformed to the so-called inductive effect and the latter is substantiated from an electric field effect provided by the substituent group. And, the same result is also reliable in the ^{13}C chemical shift of above series.

Introduction

In the previous paper of this series, the proton magnetic resonance chemical shifts of alkyl derivatives have been analysed with respect to the substituent constant σ_i and σ_π, and it was proved that α-^{1}H chemical shifts were linear with σ_i—0.25 σ_π.

This result indicates that 20% π-electronic together with 80% sigma-electronic-polar effect transmitted through sigma bond-effect takes part in determining α-^{1}H shift. In this work, the semi-quantitative discussions of above two factors have been explored.

Discussion

Inductive and Field Effect

Formerly, it has been defined that an inductive effect[3] is the transmission of polar effect through sigma-bond framework, whereas field effect[4] is that of directly through space.

Recently, Dewar and Grisdale[5] have suggested that an inductive effect bear substantially an analogous meaning with the field effect, but there remains an ambiguity that this field effect is substantiated by the electric field effect in proton magnetic resonance.

Then, in the first place, sigma- and π-electronic contributions on α-^{1}H chemical shift of alkyl series has been examined.

Sigma-Electronic Contribution $\delta\sigma_i$

According to our previous treatment,[1] the sigma- and π-electronic contributions of α-^{1}H chemical shifts in Me–R, Et–R and iso-Pr–R series have been estimated in Table I, correcting the shifts of R=CN in all three series, R=NO_2 in iso-Pr–R series, R=Cl, Br in Me–R and Et–R series due to the positive magnetic anisotropy effect, respectively. (*cf.* Table I).

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[1] Part I: Y. Sasaki, S. Ozaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **16**, 2120 (1968).

[2] Location: *Toneyama 6–5, Toyonaka, Osaka.*

[3] G.E.K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice Hall, New York, N. Y., 1941, p. 192, 258.

[4] J.G. Kirkwood and F.H. Westheimer, *J. Chem. Phys.*, **6**, 506,513 (1938); F.H. Westheimer and M.W. Shookhoff, *J. Am. Chem. Soc.*, **61**, 555 (1939).

[5] M.J.S. Dewar and P.J. Grisdale, *J. Am. Chem. Soc.*, **85**, 3539 (1962); *ibid.*, **84**, 3548 (1962).

Table I. σ_i and σ_π Fraction of α-^{1}H Chemical Shifts of Me–R, Et–R and iso-Pr–R Series from CH_4 Reference (ppm)

R	Me-		Et-		iso-Pr-	
	$\delta\sigma_i$	$\delta\sigma_\pi$	$\delta\sigma_i$	$\delta\sigma_\pi$	$\delta\sigma_i$	$\delta\sigma_\pi$
NO_2	−3.26	−0.82	−3.32	−0.83	−3.44	−0.86
COMe	1.56	0.39	1.78	0.45	1.74	0.44
CO_2Me	1.48	0.37	1.70	0.43	1.86	0.47
CN	2.88	0.72	2.96	0.74	3.20	0.80
F	3.24	0.81	3.38	0.85		
Cl	2.96	0.74	3.04	0.76	3.14	0.79
Br	2.88	0.72	2.96	0.74	3.18	0.80
Me	0.55	0.14	0.90	0.22		
OMe	2.42	0.61	2.52	0.63	2.66	0.67
OH	2.54	0.64	2.70	0.68	2.96	0.74
NH_2	1.78	0.45	2.02	0.51	2.28	0.57
NMe_2	1.62	0.41				
H	0	0	0.54	0.14	0.90	0.23

Generally speaking, δ_α-^{1}H of Me–R series is expressed as below.

$$\delta_\alpha\text{-}^1\mathrm{H}=\delta\sigma_i\text{-}\alpha\text{-}^1\mathrm{H}+\delta\sigma_\pi\text{-}\alpha\text{-}^1\mathrm{H}$$

And, in the similar way, δ_β-^{1}H of Et–R series are linear with σ_i.[1]

Then, in the Et–R series,

$$\begin{aligned}\delta_\beta\text{-}^1\mathrm{H}-\delta_\alpha\text{-}^1\mathrm{H}&=\delta\sigma_i\text{-}\beta\text{-}^1\mathrm{H}-(\delta\sigma_i\text{-}\alpha\text{-}^1\mathrm{H}+\delta\sigma_\pi\text{-}\alpha\text{-}^1\mathrm{H})\\&=\delta\sigma_i(\beta\text{-}^1\mathrm{H}-\alpha\text{-}^1\mathrm{H})-\delta\sigma_\pi\text{-}\alpha\text{-}^1\mathrm{H}\end{aligned}$$

where $\delta\sigma_i$ and $\delta\sigma_\pi$ are sigma- and π-electronic contribution of chemical shift.

And, when

1. the transmission of σ_π factor from α- to β-position is neglected.
2. the transmission factor 1/2,8 is tentatively afforded between $\delta\sigma_i$-β-^{1}H and $\delta\sigma_i$-α-^{1}H.

Then,

$$\varDelta=\delta(\beta\text{-}^1\mathrm{H}-\alpha\text{-}^1\mathrm{H})+\delta\sigma_\pi\text{-}\alpha\text{-}^1\mathrm{H}=-0.643\delta\sigma_i\text{-}\alpha\text{-}^1\mathrm{H} \qquad (1)$$

The above result is compatible with data estimated in Et–R series summarised in Table II, and in which the values of the last column are comparable with those of −0.643 $\delta\sigma_i$-α-^{1}H in Me–R series, and this result supports that $\delta\sigma_i$ is the contribution equivalent to the so-called inductive effect by nature.

Table II. ^{1}H Chemical Shift of Et–R Series (ppm)

R	$\delta\alpha$-^{1}H	$\delta\beta$-^{1}H	$\delta\beta$-^{1}H$-\delta\alpha$-^{1}H	$\delta\sigma_\pi\alpha$-^{1}H/Me–R	$\varDelta$
NO_2	−4.15	−1.35	2.80	−0.82	1.98
CO_2H	−2.13	−0.93	1.20	0.37	0.83
CN	−3.90	−1.08	2.82	0.72	2.10
H	−0.75	−0.75	0	0	0
Br	−3.90	−1.47	2.43	0.72	1.71
Cl	−4.00	−1.29	2.71	0.74	1.97
F	−4.23	−1.14	3.09	0.81	2.28
Et	−1.21	−0.81	0.40	0.14	0.26
OEt	−3.30	−1.02	2.28	0.61	1.67
OH	−3.37	−0.95	2.42	0.64	1.78
NH_2	−2.52	−0.87	1.65	0.45	1.20
NEt_2	−2.39	−0.90	1.49	0.41	1.08

π-Electronic Contribution $\delta\sigma_\pi$

Formerly, the several shielding factors have been taken into account in the discussion of aliphatic ^1H chemical shift.
These are in the following:

1. diamagnetic shielding by electron cloud
2. neighbour anisotropic effect
3. intramolecular electric field effect
4. C–C bond shift

Among above conditions, as we have already refered in the preceding section, $\delta\sigma_\pi$-α-^1H must be conformed to an intramolecular electric field effect.

In this work, the character of above electric field effect provided by the substituent group with dipole moment has been examined as below.

In the polar molecule with dipole moment μ, the relation between an electric field E and polarizability α is given by the next equation (2)

$$\mu=\alpha\cdot E \qquad (2)$$

and α is estimated from the following equation (3)

$$P_e+P_a=4\pi N/3\cdot\alpha \qquad (3)$$

where μ=dipole moment[6] in 10^{-8}esu.·cm
α=polarizability cm^3
P_e=electronic polarization[7]
P_a=atomic polarization[7]
N=Avogadro's number $6,023\times10^{23}$

Then, when α is known from equation (3), E is estimated by the following equation (4)

$$E=\mu/\alpha=\mu/(P_e+P_a)\cdot3/4\pi N \qquad (4)$$

And, when an analgous geometrical condition is allowed between α-^1H and substituent R, E afforded by R must be assumed.

In Table III, α and E values of Me–R series have been summarised.

TABLE III. Polarizability $\alpha\times10^{-23}$ cm^3 and $E\times10^5$ esu/cm^2 of Me–R Series

CH_3–R	α	E
CH_4	0.26	0
C_2H_6	0.45	0
CH_3F	0.36	5.10
CH_3Cl	0.54	3.73
CH_3Br	0.61	3.07
CH_3OCH_3	0.52	2.50
CH_3OH	0.40	4.00
CH_3NH_2	0.53	1.89
$(CH_3)_3N$	0.83	0.77
CH_3COCH_3	0.66	4.33
CH_3NO_2	0.72	4.80

Moreover, the calculated E in Table III and $\delta\sigma_\pi$ in Table I are roughly linear as shown in Fig. 1.

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6) McCllelan, "Tables of Experimental Dipole Moments," Freeman San Francisco, 1963.
7) Landolt–Börnstein, "Zahlenwerte und Funktionen," I Band, 3 Teil Springer–Verlag, 1951, p.514.

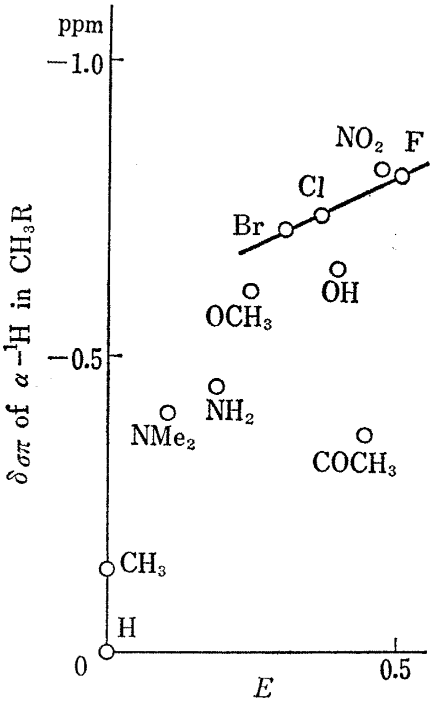

Fig. 1

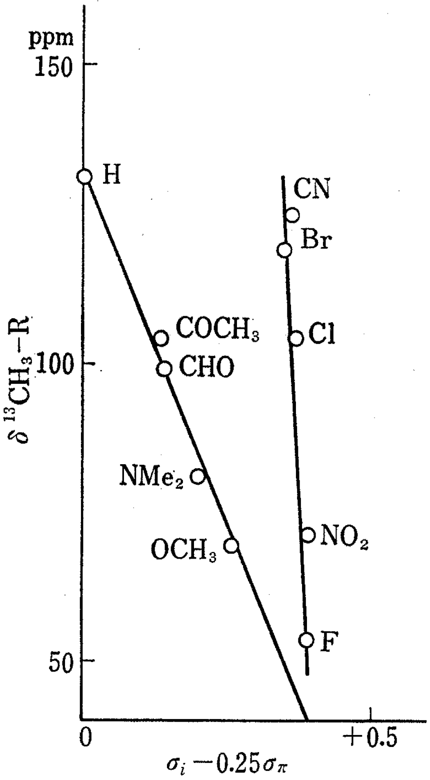

Fig. 2

From above facts, we are obliged to assume that an electric field E provided by substituent R is reconciled to $\delta\sigma_\pi$ fraction.

Consequently, it is concluded that both sigma-electronic or so-called inductive effect transmitted through sigma bond and an electric field effect which is affected directly through space are the dominant factors in determining the α-¹H chemical shift.

^{13}C Chemical Shifts of Me-R Series

In this section, the ^{13}C chemical shifts of $H_3{}^{13}C$–R series[8] have been analysed with respect to the substituent constants, and similar result with those of obtained in ^{1}H shifts[9] has been acknowledged (*cf.* Fig. 2).

Table IV. ^{13}C Chemical Shifts of Me–R (δ in ppm referred to C_6H_6) and It's $\delta\sigma_\pi$(ppm)

	δ	$\delta\sigma_\pi$
CH_4	130.8	26.1
C_2H_6	122.8	24.6
Me_4C	97.1	19.4
MeF	53.3	8.0
MeCl	103.8	9.0
MeBr	119.3	10.0
Me_2O	69.3	13.8
Me_3N	81.2	16.2
$MeNO_2$	71.4	8.0
acetone	104	20.8
MeCN	124	10.0
MeCHO	99.1	19.8

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8) H. Spiesecke and W.G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).
9) Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **16**, 2128 (1968).

And, the $\delta\sigma_\pi$ fractions of ^{13}C chemical shifts of $H_3{}^{13}C$–R series have been summarised in Table IV affording the positive corrections in CN, NO_2, F, Cl and Br groups, respectively (*cf.* Table IV).

These shifts summarised in the above Table IV are also linear with E——the electric field——as shown in Fig. 3.

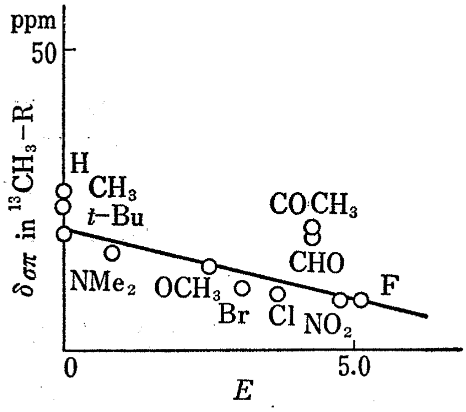

Fig. 3