## Communications to the Editor

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# New Approach for the Elucidation of the *Ipso*- and $\alpha$-$^{13}$C Substituent induced Chemical Shifts by the Linear Combination of the Empirical Parameters

$^{13}$C substituent chemical shift (S.C.S.) of the aromatic *ipso*- and aliphatic $\alpha$- positions can be expressed by the linear combination of the substituent constants $\sigma_i$, $\sigma_\pi$ and the standard entropy difference $\Delta S^{\circ}$.

$$\mathrm{S.C.S.}_{ipso} = 63.9\sigma_i - 3.9\sigma_\pi + 0.6\Delta S^{\circ}_{+} - 0.4\Delta S^{\circ}_{-} + 3.8$$
$$(r = 0.972,\ \mathrm{s.d.} = 2.4,\ n = 13)$$
$$\mathrm{S.C.S.}\alpha = 162.1\ \sigma_i - 10.1\sigma_\pi + 1.2\ \Delta S^{\circ}_{+} - 0.3\ \Delta S^{\circ}_{-} + 2.3$$
$$(r = 0.976,\ \mathrm{s.d.} = 4.9,\ n = 13)$$

$\Delta S^{\circ}_{+}$ and $\Delta S^{\circ}_{-}$ denote the standard entropy difference of the electron donating and electron attracting substituent groups.

**Keywords**——$^{13}$C NMR; substituent effect; standard entropy; linear substituent free energy relationship; *ipso* $^{13}$C substituent chemical shift; $\alpha$ $^{13}$C substituent chemical shift

Numerous approaches[1] have been extended for the nonempirical and empirical elucidation of the $^{13}$C substituent induced chemical shifts (S.C.S.) of organic compounds. The former is characterized by the approximate quantum chemical treatment of the $^{13}$C chemical shifts, whereas the latter evaluates the observed shifts by the empirical parameters, such as Hammett type substituent constants, electronegativity scale, *etc.* Unfortunately, above two kinds of approaches are fruitless for the analyses of the S.C.S. of *ipso*-carbons of monosubstituted benzenes ($\mathrm{S.C.S.}_{ipso}$) or those of $\alpha$-carbons of substituted methanes ($\mathrm{S.C.S.}_{\alpha}$), as compared with the success confirmed for the S.C.S. of *para* carbon. Namely, the $\mathrm{S.C.S.}_{ipso}$ and $\mathrm{S.C.S.}_{\alpha}$ have little correlation with total charge density,[2] the substituent constants $\sigma_i$ and $\sigma_\pi$,[3] or their linear combinations (for instance, *cf.* Eq. 1).

$$\mathrm{S.C.S.}_{ipso} = 13.6\cdot\sigma_i - 32.4\cdot\sigma_\pi + 7.8$$
$$(r = 0.549,\ \mathrm{s.d.} = 11.3,\ n = 14) \qquad (1)$$

In this communication, $\mathrm{S.C.S.}_{ipso}$ and $\mathrm{S.C.S.}_{\alpha}$ were tried to express by the linear combination of the empirical parameters $\sigma_i$, $\sigma_\pi$, and the third one. As the substituent constant does not include the contribution of the entropy term, so the third parameter requires a character of this term. For this purpose, a third parameters, $\Delta S^{\circ}$, defined by the difference of the standard entropy S°[4] of the substituted derivative and the parent one, was proposed.

The result of three-parameter analysis (Eq. 2) is no better than that of Eq. 1.

$$\mathrm{S.C.S.}_{ipso} = 41.9\cdot\sigma_i - 30.2\cdot\sigma_\pi + 0.1\cdot\Delta S^{\circ} + 7.7$$
$$(r = 0.794,\ \mathrm{s.d.} = 6.3,\ n = 13) \qquad (2)$$

Again, a correlation between $\mathrm{S.C.S.}_{ipso}$ and $\sigma_i$ (*cf.* Fig. 1) is re-examined. In the case of larger substituent, the plots are located far apart from a line connecting both plots of smaller substituents H and F, and moreover the plots of electron-donating and -attracting substituent

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1) G.L. Maciel, "Topics in Carbon-13 NMR Spectroscopy," ed. by G.C. Levy, Vol. 1 Chapter 2, John-Wiley and Sons, New York, 1972, and references cited therein.

2) *a*) G.C. Levy, G.L. Nelson, and J.D. Cargioli, *Chem. Comm.*, **1971**, 506; *idem*, *J. Am. Chem. Soc.*, **94**, 3089 (1972); *b*) H. Takai, A. Odani, and Y. Sasaki, *Chem. Pharm. Bull.* **27**, 1780 (1979).

3) Y. Yukawa and Y. Tsuno, *Nippon Kagaku Zasshi*, **86**, 873 (1965).

4) S.W. Benson, "Thermochemical Kinetics," John-Wiley and Sons, New York, 1968; S.W. Benson, F.R. Cruickshank, D.M. Golden, R.G. Haugen, E.E. O'Neal, A.S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

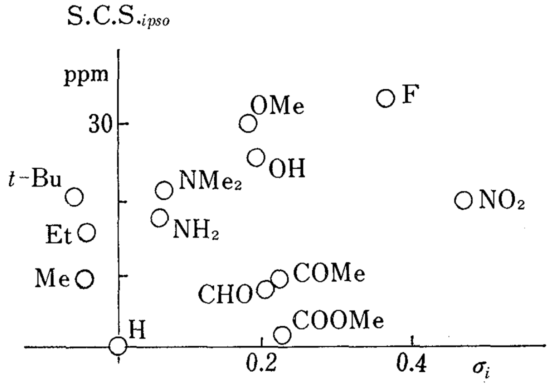

Fig. 1. Plot of $\text{S.C.S.}_{ipso}$ *vs.* $\sigma_i$

group stand at the opposite site of the line. From these observation, it is assumed that contributions of each $\Delta S^\circ$ to S.C.S. differ in direction in accordance with the character of the substituent. This means that $\Delta S^\circ$ of electron-donating and -attracting substituent might be treated separately as $\Delta S^\circ_+$ and $\Delta S^\circ_-$. The subscripts + and − denote electron-donating and -attracting substituents, respectively.

The multiparameter analyses afforded much improved results as shown in Eq. 3 and 4 (*cf.* Fig. 2 and 3).

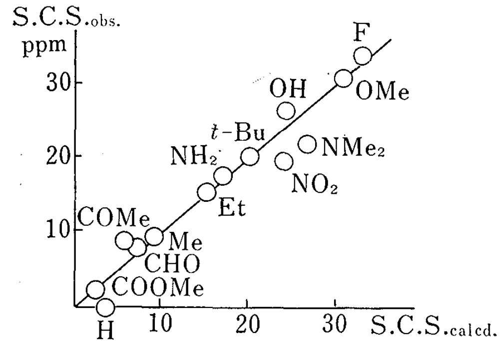

Fig. 2. Correlation between Observed and Calculated $\text{S.C.S.}_{ipso}$

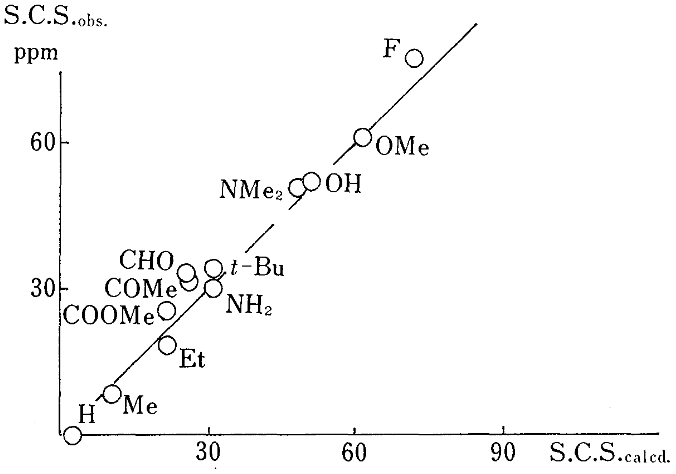

Fig. 3. Correlation between Observed and Calculated $\text{S.C.S.}_{\alpha}$

$$\text{S.C.S.}_{ispo} = 63.9\cdot\sigma_i - 3\cdot 9\cdot\sigma_\pi + 0.6\cdot\Delta S_+^\circ - 0.4\cdot\Delta S_-^\circ + 3.8$$
$$(r=0.972,\ \text{s.d.}=2.4,\ n=13) \qquad (3)$$

$$\text{S.C.S.}_{\alpha} = 162.1\cdot\sigma_i - 10.1\cdot\sigma_\pi + 1.2\cdot\Delta S_+^\circ - 0.3\cdot\Delta S_-^\circ + 2.3$$
$$(r=0.976,\ \text{s.d.}=4.9,\ n=13) \qquad (4)$$

This treatment is also applicable for the analogous positions of other substituted aromatics and heteroaromatics, because their S.C.S. at *ipso* positions correspond well with the $\text{S.C.S.}_{ipso}$.[2b)]

The result summarized above provides a reasonable and clear chemical meaning for the origin of $\text{S.C.S.}_{ipso}$ and $\text{S.C.S}_{\alpha}$.

The detail of our treatment will be published in due time.

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