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Studies on ^{13}C Magnetic Resonance Spectroscopy. XVI.[1] On the Introduction of the Entropy Term ΔS° for the Elucidation of *Ipso*- and α-^{13}C Substituent-Induced Chemical Shifts by an Empirical Approach

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^{13}C Substituent-induced chemical shifts (SCS) at the *ipso* and α positions of monosubstituted benzenes or methanes can be expressed by a linear combination of three kinds of empirical parameters, σ_i, σ_π, and ΔS°.

ΔS° represents the difference of the entropy (due to the substituent) between the standard entropy S° of the substituted compound and that of the parent one. The following results were obtained.

$$\mathrm{SCS}_{ipso} = 63.9\cdot\sigma_i - 3.9\cdot\sigma_\pi + 0.6\cdot\Delta S^\circ_+ - 0.4\cdot\Delta S^\circ_- + 3.8$$
$$(r=0.972,\ \mathrm{SD}=4.9\ \mathrm{ppm},\ n=13)$$
$$\mathrm{SCS}_{\alpha} = 162.1\cdot\sigma_i - 10.1\cdot\sigma_\pi + 1.2\cdot\Delta S^\circ_+ - 0.3\cdot\Delta S^\circ_- + 2.3$$
$$(r=0.976,\ \mathrm{SD}=4.9\ \mathrm{ppm},\ n=13)$$

where + and − subscripts of ΔS° indicate electron-donating and -attracting groups, respectively.

This treatment is also applicable for elucidation of the ^{13}C SCS of analogous positions of many substituted aromatics and heteroaromatics, including *ortho*-disubstituted benzenes, and provides a reasonable and explicit chemical basis for the origin of the ^{13}C SCS_{ipso} and SCS_α.

The same treatment also provides an explicit chemical basis for Mulliken's electronegativity scale and the steric substituent constant, E_s.

Keywords——^{13}C NMR; standard entropy S°; *ipso* ^{13}C SCS; α ^{13}C SCS; substituent constant; electronegativity; steric substituent constant; *ortho*-disubstituted benzene

Introduction

Many attempts have been made to achieve a nonempirical or empirical understanding of the ^{13}C substituent-induced chemical shifts (SCS) of organic compounds.[3] The former approach is characterized by an approximate quantum chemical treatment of the ^{13}C chemical shifts (*e.g.*, molecular orbital calculation of the total charge density of the carbon atom, and/or calculation of the screening tensor), whereas the latter approach attempts to evaluate the results of statistical analysis in terms of a linear combination of empirical parameters, such as Hammett-type substituent constants, electronegativity scale, *etc.*

Unfortunately, these approaches have been unsuccessful for analysis of the SCS at the *ipso* position of monosubstituted benzenes (SCS_{ipso}) or the α position of monosubstituted methane derivatives (SCS_α). Similar difficulties have been encountered at the same positions of substituted aromatics and heteroaromatics. Namely, SCS_{ipso} and SCS_α could not be cor-

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1) Part XV: T. Tsujimoto, C. Kobayashi, T. Nomura, M. Iifuru, and Y. Sasaki, *Chem. Pharm. Bull.*, **27**, 2105 (1979).

2) Location: *a*) *Yamadakami 133-1, Suita, Osaka 565, Japan*; *b*) *Motoyamakita 4-19-1, Higashinada, Kobe 658, Japan.*

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

related either with the total charge density calculated by the CNDO or MINDO/2 method or with the substituent constants σ_i and σ_π[4] or linear combinations of them.

In the previous communication,[5] we showed that ^{13}C SCS$_{ipso}$ and SCS$_\alpha$ adjacent to the substituent group of monosubstituted benzenes or monosubstituted methanes could be expressed in terms of a linear combination of the substituent constants σ_i, σ_π and an entropy $\Delta S°$, defined as the difference between the standard entropy $S°$[6] of the substituted compound and that of the parent one.

In this report, we present details of the regression analysis with these three parameters. Moreover, in order to confirm the validity of this treatment, we have analyzed ^{13}C SCS$_{ipso}$ of substituted aromatics, heteroaromatics and several *ortho*-disubstituted benzenes by the same procedure.

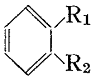
Experimental

^{13}C SCS$_{ipso}$ and SCS$_\alpha$ Data The SCS data were taken from the indicated sources: monosubstituted benzenes;[7,8] monosubstituted methanes;[8] 2-, 3-, and 4-substituted pyridines;[9,10] 2-substituted- and 2-substituted-6-methoxy naphthalenes;[11] 6-substituted quinolines and quinoxalines;[12] *ortho*-substituted toluenes;[7,13,14] *ortho*-substituted fluorobenzenes;[7,13] and *ortho*-substituted anilines.[7,8,13,14]

Table I. ^{13}C SCS$_{ipso}$ (ppm) of *Ortho*-disubstituted Benzenes

	R_1										
R_2	NH_2	OMe	OH	Et	Me	H	F	CHO	COMe	CO_2Me	NO_2
Ia : $R^1=R_2$											
	6.12[a]	20.86[b]	15.26 (143.52)		7.58[c]	0 (128.26)	22.54[d]	8.22 (136.48)		3.76 (132.02)	14.64 (142.90)
Ib : $R_2=NO_2$											
	16.59 (144.85)	24.78 (153.04)	26.93 (155.19)	10.69 (138.95)	5.28 (133.54)	−4.83 (123.43)	27.35 (155.61)	3.15 (131.41)	9.70 (137.96)	−0.65 (127.61)	14.64 (142.90)
Ic : $R_2=NH_2$											
	6.12[a]	19.13 (147.39)		−0.46[e]	−7.33[c]	−13.24[b]	23.94[d]		−9.95 (118.33)		4.02 (132.28)
Id : $R_2=Me$											
	18.05[c]	28.96[c]	27.07[c]		7.58[c]	0.72[b]	33.74[d]	5.98 (134.24)	9.23[c]	0.93[c]	21.14 (149.40)

a) M. Yamazaki, T. Usami, and T. Takeuchi, *Nippon Kagaku Kaishi*, **1973**, 2135; b) Ref. 7; c) Ref. 14; d) Ref. 13; e) Ref. 8.

I 

Observed chemical shifts are given in parentheses (ppm downfield from internal TMS).

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[4] Y. Yukawa and Y. Tsuno, *Nippon Kagaku Zasshi*, **86**, 873 (1965).

[5] Y. Sasaki, H. Takai, and T. Tsujimoto, *Chem. Pharm. Bull.*, **28**, 677 (1980).

[6] 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. Roger, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 297 (1969).

[7] H. Takai, K. So, and Y. Sasaki, *Chem. Pharm. Bull.*, **26**, 1303 (1978).

[8] J.B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press Inc., New York, 1972, Chapter 5; and references cited therein.

[9] G. Miyajima, Y. Sasaki, and M. Suzuki, *Chem. Pharm. Bull.*, **20**, 429 (1972).

[10] H. Takai, T. Tsujimoto, and Y. Sasaki, unpublished work.

[11] H. Takai, A. Odani, and Y. Sasaki, *Chem. Pharm. Bull.*, **26**, 1966 (1978).

[12] H. Takai, A. Odani, and Y. Sasaki, *Chem. Pharm. Bull.*, **26**, 1672 (1978).

[13] W.B. Smith and D.L. Davenport, *J. Magn. Reson.*, **7**, 364 (1972).

[14] M. Mishima, Ph. D. Thesis, Osaka Univ., 1976.

Materials *Ortho*-disubstituted benzenes studied in this work are all commercially available, and the ^{13}C SCS data are summarized in Table I.

Measurement of ^{13}C NMR Spectra The ^{13}C NMR spectra were recorded on a Nichiden-Varian-21 spectrometer in the Fourier transform mode. The measurements were carried out as described in the previous report.[7] Chemical shifts were expressed in ppm from the internal reference, TMS. Samples were dissolved in $CDCl_3$ at 0.5 M concentration.

Difference of the Standard Entropy $\Delta S°$ The difference of the standard entropy $\Delta S°$ of the substituent group was defined as the difference between the standard entropy $S°$ [gibbs/mol][6,15] according to the 3rd law of thermodynamics observed for the substituted compound and that for the parent compound; the values used in this work are summarized in Table II.

Table II. Values of the Difference of Standard Entropy, ΔS^0 [gibbs/mol][6]

Substituent	ΔS^0
NMe_2	26.6[a]
NH_2	12.2
OMe	21.9
OH	10.9
t-Bu	31.7
Et	21.9
Me	12.6
H	0.0
F	7.9
Cl	10.9
Br	13.6
I	15.7
CHO	21.7
COMe	28.1[a]
CO_2Me	38.7[a]
CN	12.6
NO_2	22.7[a]

a) Estimated from $\Delta S°$ of aliphatic compounds.

Table III. Values of Substituent Constants σ_i and σ_π[4]

Substituent	σ_i	σ_π
NMe_2	0.06	−0.54
NH_2	0.06	−0.42
OMe	0.185	−0.281
OH	0.19	−0.34
t-Bu	−0.060	−0.054
Et	−0.045	−0.069
Me	−0.045	−0.078
H	0	0
F	0.363	−0.118
Cl	0.348	−0.070
Br	0.337	−0.054
CHO	0.20[14]	0.34[14]
COMe	0.21	0.29
CO_2Me	0.22	0.23
CN	0.41	0.25
NO_2	0.47	0.34

Method of Statistical Analysis The three parameters $\Delta S°$, σ_i, and σ_π used in this work are shown in Table II and Table III.

Correlation coefficients (r) and standard deviations (SD) were all estimated from the relationship between the experimental chemical shift data and the linear combination of the three empirical parameters.

Results and Discussion

Analysis with Two Parameters

The ^{13}C SCS of aromatic ring carbons of monosubstituted benzenes and those of α-carbons of monosubstituted methanes can be expressed as a linear combination of the substituent constants σ_i and σ_π. The results are as follows:

$$\mathrm{SCS}_{ipso} = 41.5\cdot\sigma_i - 29.2\cdot\sigma_\pi + 9.5\ (r=0.790,\ \mathrm{SD}=6.3,\ n=13) \quad (1)$$

$$\mathrm{SCS}_{ortho} = -26.7\cdot\sigma_i + 24.8\cdot\sigma_\pi - 0.6\ (r=0.977,\ \mathrm{SD}=1.4,\ n=13) \quad (2)$$

$$\mathrm{SCS}_{meta} = 3.9\cdot\sigma_i - 1.6\cdot\sigma_\pi - 0.1\ (r=0.929,\ \mathrm{SD}=0.2,\ n=13) \quad (3)$$

$$\mathrm{SCS}_{para} = -0.2\cdot\sigma_i + 20.9\cdot\sigma_\pi - 1.0\ (r=0.995,\ \mathrm{SD}=0.6,\ n=13) \quad (4)$$

$$\mathrm{SCS}_{\alpha} = 128.3\cdot\sigma_i - 44.1\cdot\sigma_\pi + 16.4\ (r=0.878,\ \mathrm{SD}=10.3,\ n=13) \quad (5)$$

It is clear that analysis with these two parameters works well for the *para*, *meta*, and *ortho* positions but does not for SCS_{ipso} and SCS_{α}.

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15) gibbs/mol = 4.184 *J*/mol·deg

Difference of the Standard Entropy ΔS°

As is generally known, the substituent constants σ_i and σ_π are deduced from the thermodynamics of the hydrolysis of *meta*- and *para*-substituted ethyl benzoate; in other words, they are not affected by the entropy term of the substituent. Namely, the substituent constant represents a scale for the electronic effect due to the substituent, without including the entropy term.

As stated in the previous section, ^{13}C SCS could be expressed in terms of a linear combination of the two parameters σ_i and σ_π, for the *ortho*, *meta*, and *para* positions, where the electronic effect of the substituent is predominant. On the other hand, analyses of the ^{13}C SCS of other positions in this way failed because the contribution of the entropy term could not be disregarded at these positions, adjacent to the substituents. Thus, it is reasonable to introduce an entropy term as a new 3rd term in addition to σ_i and σ_π.

ΔS° was selected for the following reasons. As is well known, the distance r between the *ipso* or α carbon and the center of gravity of the substituent and/or the van der Waals radius closely correlates with the geometry of the substituent. The use of the factor $r^{\pm n}$ ($n=1, 2, 3,\cdots\cdots$) as the 3rd factor results in an improved correlation in regression analyses of SCS$_{ipso}$ and SCS$_\alpha$, where r^{-n} is essentially the electric character, *i.e.*, electric potential when $n=1$, electric field when $n=2$, magnetic field when $n=3$, and dispersion force when $n=6$. These factors should be included in the electronic effect, whereas, on the other hand, r^{+n} relates to the bulk of the substituent. However, as this term varies from case to case, $r^{\pm n}$ does not afford a correct estimate.

Of course, molecular weight (MW) or molar volume (MV) is also valid as a measure of the bulk of the substituent, except in the case of NH$_2$ and OH, which are affected by association in the liquid state (cf. Eq. 6 and 7).

$$\mathrm{SCS}_{ipso} = 63.4\cdot\sigma_i + 0.3\cdot\mathrm{MW}_+ + 0.1\cdot\mathrm{MW}_- - 16.0$$
$$(r=0.943,\ \mathrm{SD}=3.4\ \mathrm{ppm},\ n=13) \tag{6a}$$

$$\mathrm{SCS}_{ipso} = 62.8\cdot\sigma_i - 2.1\cdot\sigma_\pi + 0.3\cdot\mathrm{MW}_+ + 0.1\cdot\mathrm{MW}_- - 15.6$$
$$(r=0.943,\ \mathrm{SD}=3.4\ \mathrm{ppm},\ n=13) \tag{6b}$$

$$\mathrm{SCS}_{ipso} = 71.7\cdot\sigma_i + 0.3\cdot\mathrm{MV}_+ + 0.1\cdot\mathrm{MV}_- - 15.3$$
$$(r=0.926,\ \mathrm{SD}=3.9\ \mathrm{ppm},\ n=13) \tag{7a}$$

$$\mathrm{SCS}_{ipso} = 69.7\cdot\sigma_i - 8.3\cdot\sigma_\pi + 0.3\cdot\mathrm{MV}_+ + 0.1\cdot\mathrm{MV}_- - 15.6$$
$$(r=0.935,\ \mathrm{SD}=3.7\ \mathrm{ppm},\ n=13) \tag{7b}$$

where + and − signs correspond to electron-donating and electron-attracting substituent groups, respectively.

These results suggest, in addition to the electronic factor, the need to take account of the bulk steric factor, or implicitly the entropy term, in the cases of SCS$_{ipso}$ and SCS$_\alpha$, where the contributions of rotation about the bond axis or the neighboring magnetic anisotropy$^{16)}$ of the substituent group cannot be disregarded.

These considerations prompted us to introduce ΔS°, the difference of the standard entropy due to the substituent, as a 3rd term:

$$\Delta S^\circ = S^\circ_{\mathrm{R}} - S^\circ_{\mathrm{H}}$$

where S°_{R} is the standard entropy of monosubstituted benzenes or methanes, and S°_{H} is that of the parent compounds.

The values of ΔS° in the C$_6$H$_5$R and MeR series show a good correspondence (Fig. 1), and data which are not available can be estimated from the regression equation, *e.g.*, R=NMe$_2$,

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16) B.R. Appleman and B.P. Daily, "Advances in Magnetic Resonance," Vol. 7, ed. by J.S. Waugh, Academic Press Inc., New York, 1974, pp. 231—321.

COMe, CO_2Me, and NO_2 of C_6H_5R. The values of ΔS° used in this work are summarized in Table II.

The correlations between ΔS° values and the substituent constants σ_i and σ_π are illustrated in Fig. 2 and 3, which show these three parameters to be independent of each other.

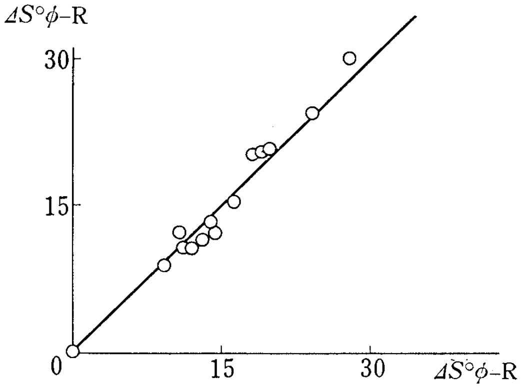

Fig. 1. Correlation between ΔS° Values of Monosubstituted Benzenes and Those of Monosubstituted Methanes

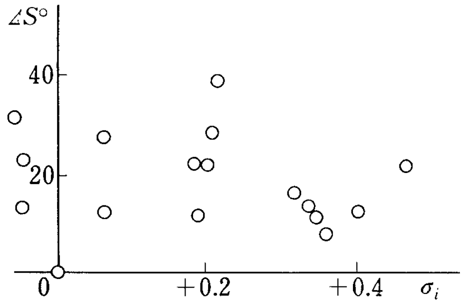

Fig. 2. Plot of ΔS° *vs.* σ_i

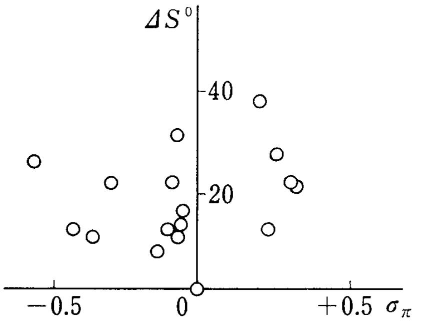

Fig. 3. Plot of ΔS° *vs.* σ_π

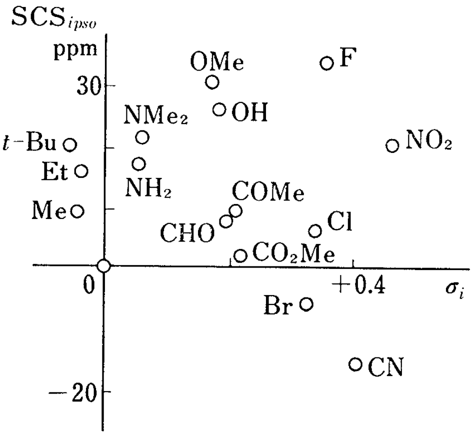

Fig. 4. Plot of SCS_{ipso} *vs.* σ_i

The regression analysis of *ipso* ^{13}C SCS of monosubstituted benzenes with a linear combination of the three parameters σ_i, σ_π, and ΔS°, unexpectedly gave a poor result ($r=0.631$, SD$=6.1$ ppm, $n=13$). However, as illustrated in Fig. 4, the correlation of ^{13}C SCS_{ipso} *vs.* σ_i suggests that electron-donating and electron-attracting groups are located separately in the upper and lower regions of the plots, respectively. In the former groups, the plots appear to be arranged in the order of the bulk of the substituent, and this pattern suggests opposite contributions of the entropy term in the two groups.

Nelson and Levy,17) in their study of the correlation between ^{13}C SCS and total charge density calculated by the CNDO/2 method, pointed out the need to correct for the bond multiplicity at the electron-attracting group site. Their conclusion also suggests that electron-donating and -attracting groups should be treated separately. Thus, we divided ΔS° into two classes ΔS°_+ and ΔS°_- according to electron-donating and -attracting character, respec-

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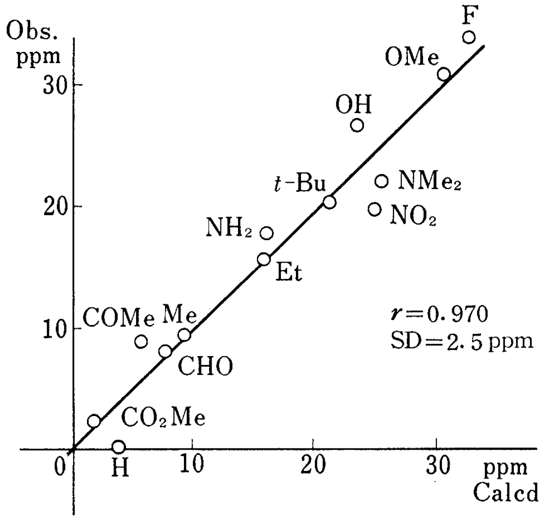
17) G.C. Levy, G.L. Nelson, and J.D. Cargioli, *Chem. Commun.*, **1971**, 506; *idem*, *J. Am. Chem. Soc.*, **94**, 3089 (1972).

tively. The results of regression analysis of SCS_{ipso} and SCS_α of the monosubstituted benzene or methane series are now as follows:

$$SCS_{ipso} = 63.9\cdot\sigma_i - 3.9\cdot\sigma_\pi + 0.6\cdot\Delta S^\circ_+ - 0.4\cdot\Delta S^\circ_- + 3.8$$
$$(r=0.972,\ SD=2.4\ ppm,\ n=13) \qquad (8)$$
$$SCS_\alpha = 162.1\cdot\sigma_i - 10.1\cdot\sigma_\pi + 1.2\cdot\Delta S^\circ_+ - 0.3\cdot\Delta S^\circ_- + 2.3$$
$$(r=0.976,\ SD=4.9\ ppm,\ n=13) \qquad (9)$$

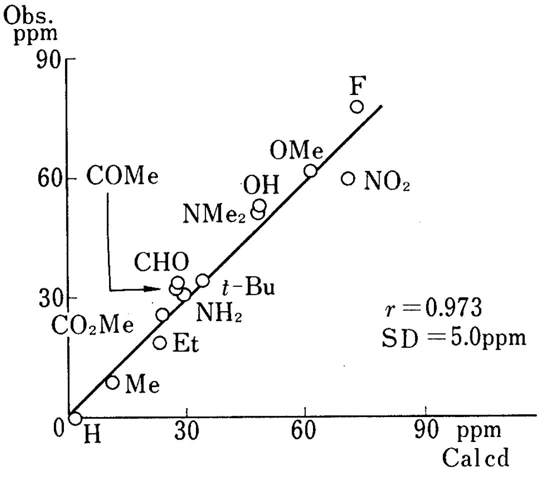
In the above equations, the relative weights of σ_π are negligibly small, and dropping this term does not affect the correlation significantly, as shown by Eqs. 10 and 11 (see Figs. 5 and 6).

$$SCS_{ipso} = 64.5\cdot\sigma_i + 0.7\cdot\Delta S^\circ_+ - 0.4\cdot\Delta S^\circ_- + 3.9$$
$$(r=0.970,\ SD=2.5\ ppm,\ n=13) \qquad (10)$$
$$SCS_\alpha = 163.8\cdot\sigma_i + 1.3\cdot\Delta S^\circ_+ - 0.4\cdot\Delta S^\circ_- + 2.8$$
$$(r=0.973,\ SD=5.0\ ppm,\ n=13) \qquad (11)$$



$SCS^{calcd}_{ipso}=64.5\sigma_i+0.7\Delta S^\circ_+-0.4\Delta S^\circ_-+3.9$

Fig. 5. Correlation between Observed and Calculated SCS_{ipso}.



$SCS^{calcd}_{\alpha}=163.8\sigma_i+1.3\Delta S^\circ_+-0.4\Delta S^\circ_-+2.8$

Fig. 6. Correlation between Observed and Calculated SCS_α

Sign of ΔS°

The standard entropy S°, determined from the temperature dependence of C°_P, is defined as the entropy according to the 3rd law of thermodynamics, and takes a positive sign. And, by the definition, ΔS°_+ and ΔS°_- are also positive. This means that electron-attracting groups displace ^{13}C SCS_{ipso} or SCS_α to high field, whereas electron-donating groups cause a low field shift. To clarify these facts, quantum chemical studies are desirable.

Evaluation of Electronegativity Scale and Steric Substituent Constant

Spieseche and Schneider[18] examined the ^{13}C SCS_{ipso} in terms of a combination of the electronegativity and the magnetic anisotropy effect of the substituent, and since then there have been many studies along this line.[19] Bucci[20] tried to correlate ^{13}C and ^1H chemical shifts of Me_nM and Et_nM type compounds with the electronegativity and the number of lone pairs

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[18] H. Spieseche and W.G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).
[19] L. Phillips and V. Wray, *J. Chem. Soc. Perkin II*, **1972**, 214.
[20] P. Bucci, *J. Am. Chem. Soc.*, **90**, 252 (1968).

on M. Further, Inamoto, *et al.*[21] recently presented a new inductive substituent parameter ι including the electronegativity of the substituent group.

The electronegativities[22] of several types of atoms directly bonded to Me and C_6H_5 were analyzed in terms of linear combination of the three parameters, and the results formulated as Eqs. 12 and 13 were obtained.

$$\Delta\chi_{calcd.} = 4.05\cdot\sigma_i + 0.31\cdot\sigma_\pi + 0.02\cdot\Delta S^\circ_+ - 0.01\cdot\Delta S^\circ_- + 0.24$$
$$(r=0.978,\ \mathrm{SD}=0.09,\ n=13) \tag{12}$$

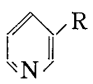
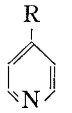
$$\Delta\chi_{calcd.} = 4.10\cdot\sigma_i + 0.02\cdot\Delta S^\circ_+ - 0.01\cdot\Delta S^\circ_- + 0.25$$
$$(r=0.973,\ \mathrm{SD}=0.09,\ n=13) \tag{13}$$

As is generally known, the steric substituent constants *Es*[23] were proposed to express the steric effects of substituents, but in practice it clearly seems necessary to consider both steric and electronic factors. The result of regression analysis with the three parameters was as follows:

TABLE IV. Correlation Coefficients (r) and Standard Deviation (SD) of ^{13}C SCS_{ipso} of Monosubstituted Pyridines as determined by Three Methods of Analysis

	σ_i, σ_π		σ_i, $\Delta S^\circ_\pm$		σ_i, σ_π, $\Delta S^\circ_\pm$	
	r	SD	r	SD	r	SD
II	0.627	4.07	0.961	1.45	0.972	1.23
III	0.815	5.55	0.986	1.58	0.989	1.39
IV	0.426	6.55	0.976	1.62	0.982	1.40

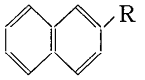
II

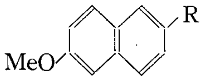
III

IV


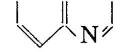
R=variable substituent

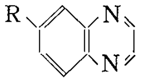
TABLE V. Correlation Coefficints (r) and Standard Deviations (SD) of ^{13}C SCS_{ipso} of Substituted Naphthalenes, Quinolines, and Quinoxalines as determined by Three Methods of Analysis

	σ_i, σ_π		σ_i, $\Delta S^\circ_\pm$		σ_i, σ_π, $\Delta S^\circ_\pm$	
	r	SD	r	SD	r	SD
V	0.864	5.57	0.966	2.86	0.969	2.72
VI	0.881	5.59	0.973	2.70	0.984	2.10
VII	0.885	4.88	0.975	2.32	0.976	2.26
VIII	0.867	5.08	0.968	2.56	0.968	2.25

2-substituted naphthalenes
V


2-substituted-6-methoxynaphthalenes
VI


6-substituted quinolines
VII


6-substituted quinoxalines
VIII


R=variable substituent

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$$Es = 0.39 \cdot \sigma_i - 2.32 \cdot \sigma_\pi - 0.07 \cdot \Delta S^\circ - 0.34$$
$$(r = 0.922,\ \mathrm{SD} = 0.3,\ n = 10) \qquad (14)$$

where the substituent constants σ_i are interchangeable for both aromatic and aliphatic systems, because they are linear with respect to σ'[24] or σ_I^q[25] determined in the 4-substituted bicyclo-[2.2.2]octane-1-carboxylic acids and 4-substituted quinuclidines, respectively.

These results afford an explicit chemical basis for the electronegativity scale and the steric substituent constants.

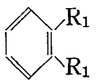
Reliability of Analyses with the Three Empirical Parameters σ_i, σ_π, and ΔS°

In order to evaluate the reliability of the present approach, we analyzed ^{13}C SCS_{ipso} for various substituted aromatic and heteroaromatic compounds, including *ortho*-disubstituted benzenes. The results, summarized in Tables IV, V, and VI, support the validity of this treatment.

Table VI. Correlation Coefficients (r) and Standard Deviations (SD) of ^{13}C SCS_{ipso} of *Ortho*-disubstituted Benzenes as determined by Two Methods of Analysis

		σ_i, σ_π		σ_i, $\Delta S^{\circ}_{\ddagger}$	
		r	SD	r	SD
Ic	$R_2 = NH_2$	0.924	4.78	0.969	3.10
Id	$R_2 = Me$	0.928	3.84	0.965	2.73
Ib	$R_2 = NO_2$	0.897	4.67	0.918	4.19
Ia	$R_1 = R_2$	0.841	4.00	0.960	2.09

I



R_1 = variable substituent

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