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SUBSTITUENT EFFECTS ON C-13 CHEMICAL SHIFTS IN ALIPHATIC AND AROMATIC SERIES. PROPOSAL OF NEW INDUCTIVE SUBSTITUTENT PARAMETER (ι; IOTA) AND THE APPLICATION

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In the previous papers,[1-3] we reported that the relative substituent C-13 chemical shifts (^{13}C-SCS) of aliphatic and aromatic carbons are mainly controlled by group electronegativity (χ_x) showing periodical dependence and to a small extent by resonance-like effect. We now propose a new inductive substituent parameter which is determined based on the atomic properties, in order to interpret ^{13}C-SCS universally.

Modifying the electronegativity defined by Gordy,[4] we examined empirically to evaluate an inductive parameter for the atom directly bonded to ring or chain as a function of the effective nuclear charge in the valence shell (Z_{eff}) and the effective principal quantum number (n_{eff}), which are given by Slater rule. We define the inductive parameter of atoms, ι_{atom} (iota in Greek letter), by the following equation, in order to avoid the periodical dependence.[2]

$$\iota_{atom} = (Z_{eff} + 1)/n_{eff}$$

For the second period group substituents, the Z_{eff} values were calculated using the charge obtained from bond dipole moment,[5] and the inductive substituent parameters (ι) were estimated using the equation ($\iota = 0.64\chi_x + 0.53$), which was obtained from the plot of the calculated ι_{atom} and ι against χ_x. For the other period substitutents, the ι_{atom} values were used as it stands. The ι values obtained for various atoms and groups are given in Table.

To test the applicability of the new ι parameter, a number of selected data[1-3] on ^{13}C-SCS in aliphatic and aromatic series were examined.[6] Plot of C_α-SCS in monosubstituted methanes and ethanes against ι is shown in Fig. 1. With exception of the groups such as cyano- and iodine-groups the points fall closely along a straight line (C_α-SCS = -54.90ι + 96.37, r = 0.940. n = 18). The deviation of those groups may arise from their anisotropy[7] and further for iodine may be attributed to its large spin-orbit interaction (LS) shift.[8]

Figs. 2, 3 and 4 show the correlation between C_{ipso}-, C_o- and C_m-SCS in monosubstituted benzenes and the ι, respectively. In the case of C_{ipso}-SCS, the plot showed two lines having positive or negative slope depending on the lower or higher electronegativity of the group, respectively. Similar behavior

Table The ι parameter for various substituents (X)

X	ι	X	ι	X	ι	X	ι
Li	1.15	PPh_2	1.93	COCl	2.27	NHCOMe	2.61
MgBr	1.28	$AsPh_2$	1.97	COMe	2.29	C≡CH	2.64
ZnMe	1.45	H	2.00	CHO	2.32	CF_3	2.66
$PbMe_3$	1.50	Bu^t	2.12	Br	2.32	NH_2	2.71
$GaMe_2$	1.62	I	2.15	COOH	2.35	NO_2	2.74
$SnMe_3$	1.66	Pr^i	2.15	Cl	2.37	OAc	2.78
$SiMe_3$	1.72	SMe	2.15	$CH=CH_2$	2.50	OMe	2.83
$BiPh_2$	1.74	Et	2.18	Ph	2.53	OEt	2.94
$GeMe_3$	1.80	Me	2.21	CN	2.56	OH	3.02
$SbPh_2$	1.83	COPh	2.26	NMe_2	2.58	F	3.05

was also observed in the case of C_α-SCS for monosubstituted ethylenes. Comparison of Figs. 1 and 2 suggests that the less electronegative groups directly bonded to unsaturated systems interact markedly with π-electron on C_{ipso}-(C_i) or C_α-atom.

On the contrary, C_o-SCS showed a good linear relationship with ι as shown in Fig. 3, indicating that C_o-SCS are approximately controlled by inductive effect. Deviation of NH_2 and OMe groups having lone pair electrons may be attributed to a contribution of π-inductive effect.[9]

The nearly linear relationship between the C_m-SCS and ι is observed as shown in Fig. 4, though several substituents deviate because of some interaction with π-electron.

In the case of C_p-SCS, it seems reasonable to assume that the line drawn through H- and NO_2-groups in the plot of C_p-SCS against ι is regarded as that controlled only by inductive effect, because the σ_R values for H- and NO_2-groups are zero.[10] Plot of the deviation (ΔC_p-SCS) from the above line against the resonance substituent constant σ_R which was used tentatively gave a satisfactory linear relationship as shown in Fig. 5. Thus, the C_p-SCS are well explained by a new type of formula (C_p-SCS = $-6.01(\iota + 2.87\sigma_R) + 11.56$, r = 0.861, n = 31). The C_β-SCS of monosubstituted ethylenes are similar to those of the C_p-SCS.

Similar dual parameter equations are also applied to C_α- and C_β-SCS of side chain in 3- and 4-substituted benzene derivatives. The typical examples are as follows.

	C-SCS	r	n	ref.
$4\text{-}XC_6H_4\underline{C}H_3$[11]	$-0.35(\iota + 4.53\sigma_R) + 0.71$	0.904	16	1
$4\text{-}XC_6H_4\underline{C}OOH$	$1.86(\iota + 1.18\sigma_R) - 3.91$	0.931	7	3
$3\text{-}XC_6H_4\underline{C}OOH$	$2.85(\iota + 1.09\sigma_R) - 6.01$	0.910	6	3
$4\text{-}XC_6H_4\underline{C}\equiv N$	$3.07(\iota + 1.24\sigma_R) - 6.41$	0.965	13	3
$3\text{-}XC6H4\underline{C}\equiv N$	$3.35(\iota + 0.83\sigma_R) - 7.00$	0.901	11	3
$4\text{-}XC_6H_4CH_2\underline{C}H_3$	$0.82(\iota + 1.16\sigma_R) - 1.78$	0.870	10	12
$4\text{-}XC_6H_4C(Me)=\underline{C}H_2$	$-3.86(\iota + 1.50\sigma_R) + 7.75$	0.844	10	13

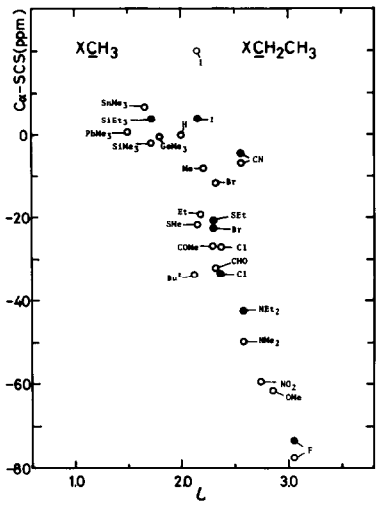

Fig. 1. C_α-SCS vs. ι for substituted methanes (o) and ethanes (●).

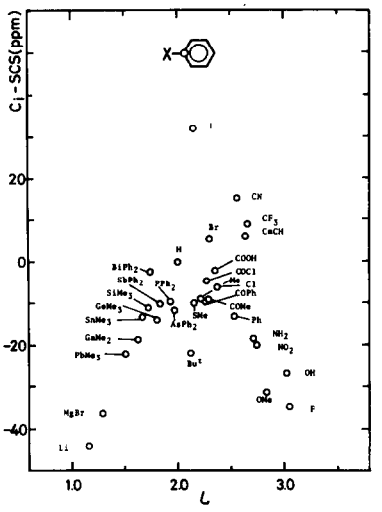

Fig. 2. C_i-SCS vs. ι for monosubstituted benzenes (C_6H_5X).

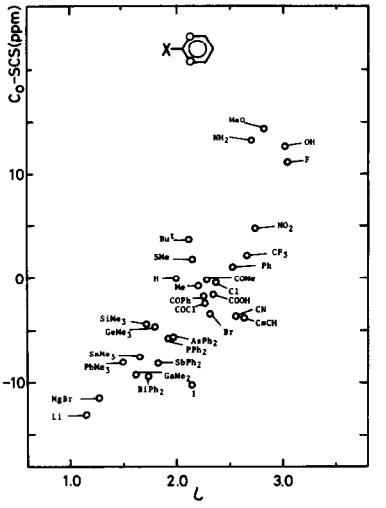

Fig. 3. C_o-SCS vs. ι for C_6H_5X.

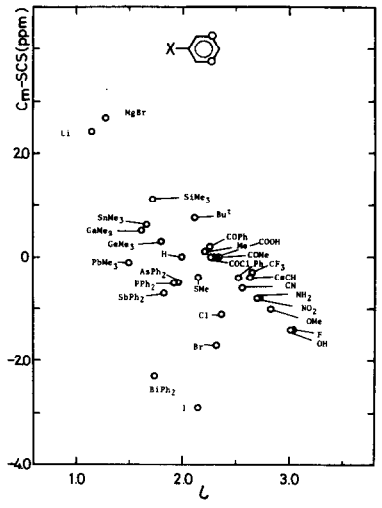

Fig. 4. C_m-SCS vs. ι for C_6H_5X.

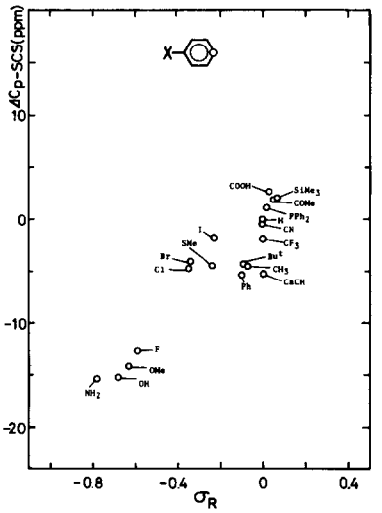

Fig. 5. ΔC_p-SCS vs. σ_R (see text).

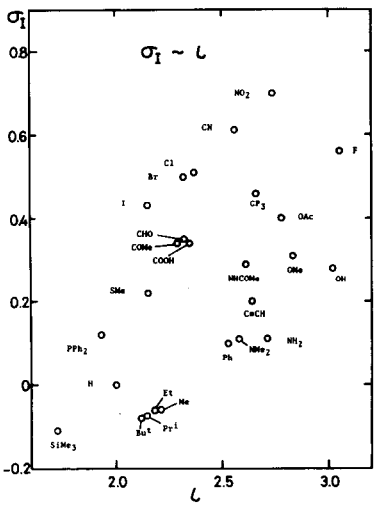

Fig. 6. σ_I vs. ι

Usually, ^{13}C-SCS have been explained by dual parameter equations containing σ_I and σ_R.[9] The plot of inductive substituent constant σ_I[10] against ι is shown in Fig. 6, but the plot appears to show two separate lines due to the electron-withdrawing or the higher period substituents and the electron-donating or the second period substituents with lone pair electrons, respectively.

The significant merit of ι parameter is the point that the values for the most substituents are calculated very easily from χ_x[14] without any experimental results.

In conclusion, the above results strongly suggest that the ι parameter contains undoubtedly only inductive effect, and the ^{13}C-SCS in aliphatic and aromatic series are satisfactory interpreted by the equation, $a(\iota + b\sigma_R) + c$, using the widely applicable ι parameter, which would be useful for other linear free energy relationships. Moreover, the plot against ι is considered to be very helpful to find out any interaction with substituent, and to clarify the transmission mechanism of substituent effect.

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