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CALCULATION OF NEW INDUCTIVE SUBSTITUENT PARAMETER (ι) FOR GROUP AND THE APPLICATION

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The ι values for more than 150 substituents were calculated from group electronegativities obtained by revised method, being in agreement with those obtained from ionicity and bond moment, and were applied to σ-electron densities of $XC_6H_4^+$, C_α-SCS of RCH_2X, J_{HH}^{trans} of vinyl compounds, and various σ values for electron-withdrawing substituents.

We previously proposed new inductive substituent parameter (ι)$^{1)}$ to remove a periodicity of electronegativity, and reported the justification of the definition and the usefulness of ι value for atom.$^{2)}$

The present paper describes on verification of ι values for groups by three different methods and reports ι values for more than 150 substituents. The three methods are as follows:

1) From Group Electronegativity ($^\iota\chi$). In each period in the periodic table, the Gordy's electronegativities $(\chi)^{3)}$ satisfactorily correlated with the ι values of atoms$^{2)}$ as follows:

For the 2nd period, $\iota = 0.639\chi + 0.599$ $(r = 0.999,\ n = 7)$
For the 3rd period, $\iota = 0.616\chi + 0.562$ $(r = 0.997,\ n = 7)$
For the 4th period, $\iota = 0.611\chi + 0.712$ $(r = 0.999,\ n = 7)$
For the 5th period, $\iota = 0.676\chi + 0.572$ $(r = 0.999,\ n = 7)$
For the 6th period, $\iota = 0.684\chi + 0.499$ $(r = 0.999,\ n = 4)$

We established a revised calculation method for group electronegativity in the preceding paper.$^{4)}$ From the above relationships and group electronegativities,$^{4)}$ ι values for every substituents can easily be obtained. The ι values thus calculated are summarized in Table 2.

2) From Ionicity of Single Bond ($^\iota\delta$). Ionicity of single bond A-B is represented by Eq. (1).$^{5)}$

$$\text{Ionicity} = 0.16|\chi_A - \chi_B| + 0.035(\chi_A - \chi_B)^2 \tag{1}$$

The change of electron density on the atom A in the radical -AB can be estimated from Eq. (1). Then the effective nuclear charge $(Z_{eff})^{6)}$ of the central atom A in the radical -AB is corrected by the Grant's method (Eq. (2)),$^{7)}$

$$Z_{eff} = Z_\circ - 0.35\sum_k Q_k \tag{2}$$

where $Z_\circ$ is the effective nuclear charge of the central atom A and Q_k is the electric charge on the central atom A in each single bond, taking a shift of electron pairs to the central atom positive.

Thus the ι values for groups can be obtained by the definition of ι value[1] (Eq. (3)),

$$\iota = (Z_{eff} + 1)/n_{eff} \qquad (3)$$

where n_{eff} is the effective principal quantum number of the central atom A.[6]

3) From Bond or Group Dipole Moment (ι_D). If the bond or group dipole moment of the A-B bond is available, one can obtain the electric charge (Q_k) on the atom A from the moment by Grant's method (Eq. (4)),[7] where we used D_{C-H} = 0.4 (Debye unit) and r_{C-H} = 1.11 (× 10^{-8} cm),

$$Q_k = 0.4995 \times (D_{C-X}/r_{C-X}) \qquad (4)$$

where D_{C-X} is the bond moment of the C-X bond and r_{C-X} is the bond distance of the C-X bond. Similarly to that described in 2), the ι values can be calculated.

Table 1 shows a comparison of a part of ι_X (method 1)), ι_δ(method 2)), and ι_D(method 3)) obtained from these three methods, indicating these satisfactory agreement. These results indicate a justification of revised calculation method for group electronegativity described in the preceding paper.[4]

Table 1. Comparison of ι_X, ι_δ, and ι_D.

Group	ι_X	ι_δ	ι_D	Group	ι_X	ι_δ
Me	2.14	2.09	2.03	BeH	1.51	1.50
CF_3	2.47	2.28	2.40	BH_2	1.83	1.82
CCl_3	2.26	2.17	2.34	CH_2Cl	2.18	2.12
NH_2	2.41	2.39	2.36	$CHCl_2$	2.22	2.14
NMe_2	2.48	2.42	2.42	NHMe	2.50	2.41
OH	2.79	2.73	2.64	NHAc	2.50	2.42
OMe	2.82	2.74	2.73	OAc	2.80	2.76
SH	2.17	2.14	2.12	MgBr	1.36	1.32
SMe	2.16	2.15	2.12	$SiMe_3$	1.79	1.76
CHO	2.39	-	2.26	SiF_3	1.98	1.89
COMe	2.39	-	2.29	PMe_2	1.95	1.94
CO_2H	2.36	-	2.34	ZnMe	1.53	1.47
COCl	2.30	-	2.37	$GeMe_3$	1.90	1.83
CN	2.61	-	2.43	$AsMe_2$	2.01	1.99
NO_2	2.745	-	2.74	$SnMe_3$	1.78	1.71
SOMe	2.31	-	2.24	HgMe	1.35	1.30
SO_2Me	2.41	-	2.39	$PbMe_3$	1.70	1.63

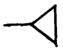
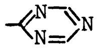
Thus, the ι values (ι_X) calculated from group electronegativities are hereafter used, because the method 1) is applicable to every types of substituents, and the ι values were shown in Table 2.

Some correlations with $\Delta\iota$ values ($\Delta\iota = \iota - \iota_H = \iota - 2.00$) are shown below. For σ-electron densities (q_σ) on the C^+ atom in the singlet state of monosubstituted phenyl cations by ab initio calculation (STO-3G),[8]

o-series: $q_\sigma = 0.346 \cdot \Delta\iota - 0.194$ (r = 0.992, r = 8)

m-series: $q_\sigma = 0.341 \cdot \Delta\iota - 0.184$ (r = 0.993, r = 8)

Table 2. Inductive Substituent Parameters (ι).

Group	ι	Group	ι	Group	ι	Group	ι
-H	2.000	-CF$_3$	2.466	-AlMe$_2$	1.583	-GeMe$_3$	1.899
-Li	1.150	-CCl$_3$	2.262	-SiHMe$_2$	1.774	-GePh$_3$	1.931
-BeH	1.512	-CBr$_3$	2.195	-SiMe$_3$	1.788	-GeF$_3$	2.078
-BH$_2$	1.825	-CHO	2.390	-SiEt$_3$	1.790	-GeCl$_3$	1.961
-B(OH)$_2$	2.010	-COMe	2.389	-SiPhMe$_2$	1.800	-AsMe$_2$	2.006
-CH$_3$	2.138	-COCF$_3$	2.436	-SiPh$_3$	1.823	-AsPh$_2$	2.032
-Et	2.145	-COPh	2.272	-SiF$_3$	1.978	-SeMe	2.162
-n-Pr	2.146	-COCN	2.458	-SiMeCl$_2$	1.832	-SeCF$_3$	2.190
-i-Pr	2.152	-CONH$_2$	2.304	-SiCl$_3$	1.855	-SePh	2.182
-CHMeEt	2.153	-COOH	2.363	-SiBr$_3$	1.811	-SeCN	2.224
-t-Bu	2.157	-COOR	2.369	-PH$_2$	1.911	-Br	2.324
	2.153	-COCl	2.303	-PMe$_2$	1.947	-CdMe	1.414
-CH=CH$_2$	2.339	-CSNH$_2$	2.183	-PPh$_2$	1.977	-InMe$_2$	1.608
-CH=CHMe	2.340	-CN	2.609	-P(CN)$_2$	2.034	-SnMe$_3$	1.784
-CH=CHNO$_2$	2.353	-NH$_2$	2.471	-P(NMe$_2$)$_2$	2.012	-SnEt$_3$	1.785
-Ph	2.295	-NHMe	2.496	-PF$_2$	2.119	-SbMe$_2$	1.873
-C≡CH	2.523	-NHAc	2.498	-PCl$_2$	2.005	-SbPh$_2$	1.897
-C≡CPh	2.527	-NHCOCF$_3$	2.497	-P(O)Me$_2$	2.085	-TeMe	2.012
-CH$_2$CF$_3$	2.180	-NHCOPh	2.491	-P(O)Ph$_2$	2.114	-I	2.150
-CH$_2$Ph	2.161	-NHCONH$_2$	2.496	-PO(OR)$_2$	2.052	-IO$_2$	2.487
-CH$_2$CONH$_2$	2.162	-NHCSNH$_2$	2.497	-POCl$_2$	1.982	-HgMe	1.345
-CH$_2$COOH	2.169	-NHNH$_2$	2.497	-P(S)Ph$_2$	2.039	-HgCF$_3$	1.368
-CH$_2$CN	2.197	-NMe$_2$	2.484	-P(S)Cl$_2$	1.877	-HgCN	1.378
-CH$_2$NH$_2$	2.180	-NEt$_2$	2.483	-SH	2.173	-HgOAc	1.391
-CH$_2$NMe$_2$	2.183	-N=C=O	2.829	-SMe	2.159	-HgCl	1.365
-CH$_2$NO$_2$	2.210	-N=C=S	2.799	-SEt	2.158	-PbMe$_3$	1.697
-CH$_2$OH	2.215	-N=NPh	2.799	-SCF$_3$	2.196	-PbEt$_3$	1.698
-CH$_2$OMe	2.218		2.429	-SPh	2.169	-BiPh$_2$	1.846
-CH$_2$OAc	2.216	-NO	2.841	-SAc	2.182	-COO$^-$	2.334
-CH$_2$F	2.243	-NO$_2$	2.745	-SF$_5$	2.457	-O$^-$	2.600
-CH$_2$SiMe$_3$	2.127	-OH	2.791	-SOMe	2.312	-PO$_3$H$^-$	2.028
-CH$_2$SO$_2$CF$_3$	2.183	-OMe	2.823	-SOPh	2.323	-S$^-$	2.033
-CH$_2$Cl	2.181	-OEt	2.823	-SO$_2$Me	2.409	-SO$_3^-$	2.364
-CH$_2$Br	2.158	-OCF$_3$	2.787	-SO$_2$CF$_3$	2.437	-CH$_2\overset{+}{\mathrm{N}}H_3$	2.230
-CH$_2$SnMe$_3$	2.115	-OPh	2.811	-SO$_2$Ph	2.419	-$\overset{+}{\mathrm{C}}$Me$_2$	2.583
-CH$_2$I	2.141	-OCHO	2.800	-SO$_2$NH$_2$	2.247	-$\overset{+}{\mathrm{N}}$H$_3$	2.930
-CHPh$_2$	2.177	-OAc	2.802	-SO$_3$Et	2.296	-$\overset{+}{\mathrm{N}}$Me$_3$	2.893
-CH(CN)$_2$	2.254	-OSO$_2$Me	2.779	-SO$_2$Cl	2.246	-$\overset{+}{\mathrm{N}}\equiv$N	3.712
-CHF$_2$	2.352	-OSO$_2$Ph	2.777	-Cl	2.367	-$\overset{+}{\mathrm{O}}$Me$_2$	3.320
-CHCl$_2$	2.222	-F	3.100	-ZnMe	1.528	-$\overset{+}{\mathrm{P}}$Me$_3$	2.257
-CHBr$_2$	2.177	-MgBr	1.360	-GaMe$_2$	1.725	-$\overset{+}{\mathrm{S}}$Me$_2$	2.469

p-series: $q_\sigma = 0.335\cdot\Delta\iota - 0.159$ (r = 0.994, n = 8)

For ^{13}C-SCS ($\Delta\delta = \delta_H - \delta_X$) of α-carbon in monosubstituted methanes[9)] and ethanes,[9,10)]

$\underline{C}H_3X$: $\Delta\delta = -62.12\cdot\Delta\iota - 9.40$ (r = 0.970, n = 15)

$CH_3\underline{C}H_2X$: $\Delta\delta = -59.40\cdot\Delta\iota - 7.77$ (r = 0.960, n = 18)

For J_{HH}^{trans} in monosubstituted ethenes,[11)]

$J_{HH}^{trans} = -5.35\cdot\Delta\iota + 18.76$ (r = 0.932, n = 21)[12)]

The ι values thus obtained correlated very well with various σ values[13)] for electron-withdrawing substituents as follows, indicating that these mesomeric effects are in proportion to the ι values, except for σ_p^- values where electron-withdrawing mesomeric effect is considerably larger.

$\sigma_I = 0.879\cdot\Delta\iota + 0.006$ (r = 0.985, n = 10)

$\sigma_m = 0.938\cdot\Delta\iota + 0.005$ (r = 0.997, n = 9)

$\sigma_p = 1.034\cdot\Delta\iota + 0.056$ (r = 0.988, n = 9)

$\sigma_m^\circ = 0.967\cdot\Delta\iota + 0.004$ (r = 0.995, n = 7)

$\sigma_p^\circ = 1.088\cdot\Delta\iota + 0.022$ (r = 0.995, n = 7)

General formula containing mesomeric substituent parameter for whole substituents are under investigation.

Therefore, it is concluded from above results that the ι values of groups are good measures of σ-electron density in saturated systems and σ-inductive effect by through-bond transmission as shown by Reynolds.[14)]

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12) In this case, the following ι values being not shown in Table 2 were used: $-AlR_2$ 1.613, $-AsR_2$ 2.041, $-SnR_3$ 1.818, $-SbR_2$ 1.905, -HgR 1.361, and $-PbR_3$ 1.736, where R is vinyl group.
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