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# RELATIONSHIP BETWEEN SUBSTITUENT ELECTRONEGATIVITY AND FIELD PARAMETER IN THE ALIPHATIC SERIES. INTRODUCTION OF CHARGE SEPARATION PARAMETER ($\lambda$)

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**The problem of non-proportionality between the substituent field parameter ($\sigma_F$) and substituent electronegativity ($\Delta\iota$ or $\sigma_\chi$) was clarified by the introduction of the 'charge-separation parameter' ($\lambda$), which is the component for the direction of the H—X axis of the distance between positive and negative poles of the dipole in the H—X molecule. Thus $\sigma_F$ was correlated with $\Delta\iota$ or $\sigma_\chi$ by the equation $\sigma_F = a\Delta\iota\lambda$ (or $\sigma_F = a'\sigma_\chi\lambda$). The above proposal was further supported by performing an energy decomposition analysis for the isodesmic reaction in the isolated molecule system (X—H···H$\overset{+}{N}$H$_3$ or X—H···HCO$_2^-$) at shorter distances (2·0–4·5 Å). It was further shown that field parameters such as $\sigma_i$, F and $\sigma_{F(theor)}$, and the p$K_a$ values in the series of aliphatic acids, and spectral data (UPS and $^{13}$C-SCS) were also well correlated with $\Delta\iota\lambda$ or $\sigma_\chi\lambda$. It is concluded that $\lambda$ and $\Delta\iota$ or $\sigma_\chi$ are essential parameters for interpreting the electrostatic field effect in aliphatic substituent effects, and that the transmission due to the $\sigma$-inductive effect is considered to be not as significant as the field effect after a few bonds away from the substituent.**

## INTRODUCTION

The concept of the inductive effect was first introduced as the through-$\sigma$-bond effect (i.e. the $\sigma$-inductive effect) by Robinson[1a] and Ingold.[1b] Currently, however, the polar substituent effect in aliphatic systems is described as the sum of through-$\sigma$-bond and field effects, and that in aromatic systems as the sum of field, resonance[2,3] and $\pi$ polarization effects.[4,5]

The $\sigma$-inductive effect originates from bond polarization due to the difference in electronegativities between the substituent and the adjacent atom, and is transmitted through progressive but diminishing $\sigma$-bond polarization.[6,7] On the other hand, the field mechanism for transmission of substituent effects is mainly attributed to the Coulombic field interaction between the dipole of the substituent and the charge of the probe centre (dipole–charge interaction).[8] The transmission due to the $\sigma$-inductive effect has been considered to be less significant than the field effect after two bonds away from the substituent.[9]

Recently, non-linearity in the plot of the field parameters ($\sigma_F$ or $\sigma_I$) of the dipole moments ($p_{MeX}$) of CH$_3$X against the group electronegativities ($\chi_X$) or the inductive substituent parameters ($\iota$) has been reported by several workers.[3b,10,11] Further, it has not been explained why the field effect is dominant for the $\Delta$p$K_a$ values[12] of XCH$_2$CO$_2$H, while the electronegativity of a substituent correlates linearly with the proton chemical shift parameter ($\delta_{CH_2} - \delta_{CH_3}$) in an apparently similar system, XCH$_2$CH$_3$.[13]

These facts led us to examine the reason for the non-proportionality between the field parameter and electronegativity. Then we attempted to obtain information regarding the interaction between the point charge of the probe centre and the pure dipole 'substituent'[14,15] using the isodesmic reaction (1), and applied energy decomposition analysis[16] to the isodesmic reaction (1) for the molecular pair **1**, composed of the pure dipole 'substituent,' H—H, and point charge as the probe centre, where the field effect would be dominant.

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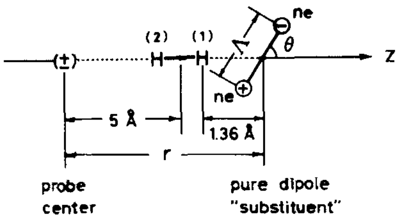
$$\underset{(A)}{H{-}H(+\,-,\theta)} + \underset{(B)}{(\pm)\cdots H{-}H} \longrightarrow \underset{(C)}{H{-}H} + \underset{(D)}{(\pm)\cdots H{-}H(+\,-,\theta)} \quad (1)$$



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In **1**, *ne* represents the charge on the pure dipole 'substituent,' Λ the distance between positive and negative charges in the pure dipole 'substituent' and θ the angle between the dipole and the *z*-axis. From the result thus obtained, a linear relationship between the electrostatic field energy (*ES*) and the *z*-component of the dipole moment ($p_z = ne\Lambda\cos\theta$; see **1**) was observed, but there was no similar relationship between *ES* and the charge (*ne*) on the dipole 'substituent.' Consequently, the major reason for the non-proportionality[10,11] between the field parameters ($\sigma_F, \sigma_I$ and $p_{MeX}$) and the electronegativity or inductive substituent parameter ($\sigma_\chi, \Delta_\iota = \iota_X - \iota_H$) may be clarified by means of this analysis.

A theoretical scale of the field parameter [$\sigma_{F(theor)}$][17] has recently been derived from MO calculation (at the 4-31G level) for the proton transfer reaction (2) in the molecular pair (**2**), where $r' = 4{\cdot}5$ Å and above;[18] $r'$ is the distance between the hydrogen atom of the H—X molecule and the nitrogen or carbon atom of $NH_4^+$ (**2**) or $HCO_2^-$ (**3**). However, the studies concerned were made under the assumption that the electrostatic interaction is dominant at such longer distances.

Strictly, in the interaction between the substituent and probe centre, different types of interactions contribute to the total interaction energy ($\Delta E$),[16] i.e.

$$\Delta E = ES + PL + CT + EX + MIX$$

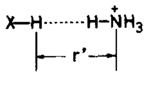
where *ES* is electrostatic energy, *PL* polarization energy, *CT* charge-transfer energy, *EX* electron-exchange repulsion energy and *MIX* the higher order terms. The components of such interactions are often complicated at shorter distances. Therefore, we also performed energy decomposition analysis[16] for the proton transfer isodesmic reactions (2) and (3) in molecular pairs **2** and **3** at several distances.

$$(X{-}H\cdots NH_3) + (H{-}H\cdots H\overset{+}{N}H_3) \longrightarrow (H{-}H\cdots NH_3) + (X{-}H\cdots H\overset{+}{N}H_3) \quad (2)$$

$$(X{-}H\cdots HCO_2H) + (H{-}H\cdots HCO_2^-) \longrightarrow (H{-}H\cdots HCO_2H) + (X{-}H\cdots HCO_2^-) \quad (3)$$

$X = H, NH_2, F, CN, NO_2$

$r' = 2{\cdot}0, 2{\cdot}25, 2{\cdot}5, 3{\cdot}5, 4{\cdot}5$ Å



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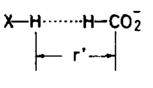

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The result of the analyses shows that the electrostatic energy terms (*ES*) in reactions (2) and (3) are correlated, even at a short distance ($r' = 2{\cdot}5$ Å), with the dipole parameter $\Delta\iota\lambda$,[19] where λ is the *z*-component of the distance (Λ) between the positive and negative poles in the H—X molecule (i.e. $\lambda = \Lambda\cos\theta$; cf. **1**), namely the charge separation parameter.

In order to ascertain whether the charge separation parameter (λ)[19] is independent of the systems or not, we also examined the utility of the parameter, $\Delta\iota\lambda$ or $\sigma_\chi\lambda$,[19] for the observed data such as relative p$K_a$ values ($\Delta pK_a$) in substituted aliphatic acids,[20,21] UPS data[22] and carbon-13 substituent chemical shifts ($^{13}$C-SCS) in aliphatic derivatives.[23]

## CALCULATIONS AND RESULTS

MO calculations were performed by the *ab initio* method at 4-31G and 6-31G basis levels using the GAUSSIAN-80[24a] and IMSPAC[24b] program series. Molecular geometries were taken from observed values.[25] All calculations were carried out with a FACOM M-382 computer at the Nagoya University Computation Center.

The pure dipole 'substituent' having only positive and negative point charges was taken to be the same as that used in previous papers.[14,15] The probe centre and the centre of the pure dipole 'substituent' were located on the H—H molecular axis as shown in **1**. In the hypothetical system **1**, the total energy of interaction is composed of electrostatic (*ES*) and polarization (*PL*) energies. We chose 5·0 Å as the distance between the probe centre and the centre of the H—H bond (see **1**). The centre of the dipole was always fixed at 1·36 Å away from the hydrogen atom H(1) on the *z*-axis, as used by Vorpazel *et al.*[15] When $\Lambda = 0{\cdot}72$ Å and $ne = 1{\cdot}0$, the dipole moment of the pure dipole 'substituent' nearly corresponds to that of nitromethane. We used $\Lambda = 0{\cdot}72$, 1·0 and 1·5 Å, $ne = 1{\cdot}0$, 0·5 and 0·3 units and $\theta = 0°$, 30°, 60° and 90° (see **1**).

Table 1 summarizes the results calculated at the 4-31G level for reaction (1) in the case of the negative point charge in **1**. The energies for the isodesmic reaction (1) (i.e. $E_A$, $E_B$, $E_C$ and $E_D$), the electrostatic interaction energies ($ES_D$ and $ES_B$) and the relative energy components ($\delta\Delta E$, $\delta ES$ and $\delta PL$) for the energy decomposi-

Table 1. Energy decomposition analysis for the isodesmic reaction (at the 4-31G level)

$$\underset{(A)}{\text{H—H}(+\,-,\theta)} + \underset{(B)}{(-)\cdots\text{H—H}} \rightarrow \underset{(C)}{\text{H—H}} + \underset{(D)}{(-)\cdots\text{H—H}(+\,-,\theta)}$$

| | | | | | | | Relative energy component/kcal mol$^{-1e}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| No. | $ne^a$ | $\Lambda^a$/Å | $\theta^a$/° | $E_A{}^b$/a.u. | $E_D{}^c$/a.u. | $ES_D{}^d$/a.u. | $\delta\Delta E$ | $\delta ES$ | $\delta PL$ | $ne\ \lambda\cos\theta = ne\ \lambda$/debye (D) |
| 1 | —$^f$ | —$^f$ | —$^f$ | −1·12676$^g$ | −1·12754$^h$ | −1·12713$^i$ | 0·00<br>(−0·49)$^j$ | 0·00<br>(−0·23)$^k$ | 0·00<br>(−0·26)$^l$ | 0·00 |
| 2 | 1·0 | 0·72 | 0 | −1·84658 | −1·86041 | −1·86004 | −8·19 | −8·21 | 0·02 | 3·46 |
| 3 | 1·0 | 0·72 | 30 | −1·84939 | −1·86131 | −1·86093 | −7·02 | −7·04 | 0·02 | 3·00 |
| 4 | 1·0 | 0·72 | 60 | −1·85452 | −1·86164 | −1·86124 | −3·98 | −3·99 | 0·01 | 1·73 |
| 5 | 1·0 | 0·72 | 90 | −1·86171 | −1·86250 | −1·86209 | −0·01 | −0·01 | 0·00 | 0·00 |
| 6 | 1·0 | 1·00 | 60 | −1·64814 | −1·65749 | −1·65711 | −5·35 | −5·37 | 0·02 | 2·40 |
| 7 | 1·0 | 1·50 | 60 | −1·47292 | −1·48559 | −1·48520 | −7·46 | −7·48 | 0·02 | 3·60 |
| 8 | 0·5 | 0·60 | 60 | −1·34338 | −1·34684 | −1·34643 | −1·68 | −1·68 | 0·00 | 0·72 |
| 9 | 0·5 | 1·00 | 30 | −1·24595 | −1·25444 | −1·25405 | −4·84 | −4·85 | 0·01 | 2·08 |
| 10 | 0·3 | 0·60 | 60 | −1·20368 | −1·20607 | −1·20566 | −1·01 | −1·01 | 0·00 | 0·43 |
| 11 | 0·3 | 1·00 | 30 | −1·16533 | −1·17074 | −1·17035 | −2·90 | −2·92 | 0·02 | 1·25 |

[a] Cf. 1.
[b] Total energy for system A.
[c] Total energy for system D perturbed with negative point charge.
[d] Electrostatic energy for system D perturbed with negative point charge.
[e] $\delta\Delta E = (E_D - E_A) - (E_B - E_C) = \Delta E_{\text{subst}} - \Delta E_H$; $\delta ES = ES_{\text{subst}} - ES_H$, $ES_{\text{subst}} = ES_D - E_A$, $ES_H = ES_B - E_C$; $\delta PL = \delta\Delta E - \delta ES$.
[f] Unsubstituted system.
[g] $E_C$.
[h] $E_B$.
[i] $ES_B$.
[j] $\Delta E_H = E_B - E_C$.
[k] $ES_H = ES_B - E_C$.
[l] $PL_H = \Delta E_H - ES_H$.

tion analysis are also shown in Table 1. The last column in Table 1 lists values of $ne\,\Lambda\cos\theta$ ($= p_z$). A linear relationship between the relative interaction energies ($-\delta\Delta E$) and $p_z$ ($= ne\,\Lambda\cos\theta$) for **1** is shown in Figure 1. On the other hand, no linear relationship between $-\delta\Delta E$ and $ne$ is observed.

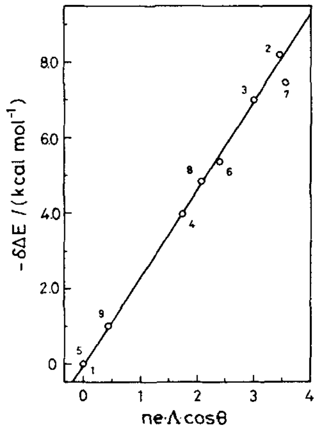


Figure 1. Linear relationship between the relative isodesmic reaction energies ($\delta\Delta E$) in reaction (1) and $ne\,\Lambda\cos\theta$ ($= p_z$) in **1**

Table 2 gives the charge density ($1 - q_H$) on the hydrogen atom, $p_z$ ($= p\cos\theta$) calculated for the H−X

Table 2. The charge on hydrogen ($1 - q_H$), z-component of dipole moment ($p_z$) and charge separation parameter ($\lambda$) in H−X molecule

| | 4-31G | | | 6-31G | | |
|---|---|---|---|---|---|---|
| X | ($1 - q_H$) | $p_z$/D | $\lambda$/Å | ($1 - q_H$) | $p_z$/D | $\lambda$/Å |
| $CH_3$ | 0·1522 | 0·00 | 0·000 | 0·1549 | 0·00 | 0·000 |
| $NH_2$ | 0·3042 | 0·73 | 0·500 | 0·3096 | 0·73 | 0·495 |
| $OCH_3$ | 0·3967 | 1·24 | 0·651 | 0·3977 | 1·24 | 0·649 |
| OH | 0·3936 | 1·60 | 0·846 | 0·4257 | 1·62 | 0·796 |
| CHO | 0·1541 | 1·57 | 2·121 | 0·1484 | 1·58 | 2·221 |
| F | 0·4786 | 2·28 | 0·992 | 0·4820 | 2·30 | 0·992 |
| $CF_3$ | 0·2104 | 2·17 | 2·147 | 0·1972 | 2·20 | 2·320 |
| $COCH_3$ | 0·1559 | 1·20 | 1·603 | 0·1498 | 1·21 | 1·682 |
| $CO_2H$ | 0·2158 | 1·34 | 1·289 | 0·2093 | 1·36 | 1·351 |
| $CO_2CH_3$ | 0·2125 | 1·72 | 1·684 | 0·2076 | 1·75 | 1·750 |
| CN | 0·3308 | 3·25 | 2·046 | 0·3336 | 3·27 | 2·039 |
| $NO_2$ | 0·4320 | 3·51 | 1·692 | 0·4247 | 3·53 | 1·733 |

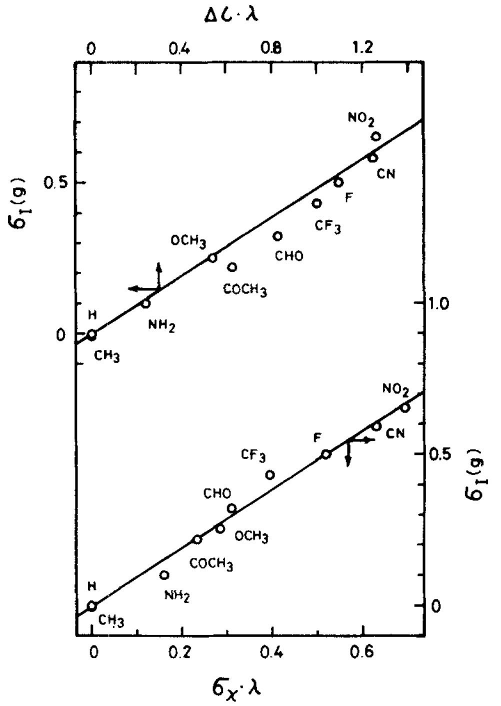


Figure 2. Relationship between field parameter, $\sigma_I(g)$, and $\Delta_\ell\lambda$ or $\sigma_X\lambda$

molecule and the charge separation parameter ($\lambda$), which was obtained from the equation $\lambda = p\cos\theta/[e(1-q_H)]$, where $p$ represents the dipole moment of the H—X molecule in place of the group dipole moment of X.

Figure 2 shows the relationship between the field parameter $[\sigma_I(g) = \sigma_F]^{26}$ and dipole parameter ($\Delta_\ell\lambda$ or $\sigma_X\lambda$).

Tables 3 and 4 give the interaction energies ($\Delta E$) and the component terms (i.e. *ES*, *PL*, *CT*, *EX* and *MIX*) calculated at several distances (2·0–4·5 Å) for **2** (X = $NO_2$) and **3** (X = F) using the 4-31G basis set. The corresponding results of the energy decomposition analyses for the neutral molecule system (i.e. X—H···H—$NH_2$ and X—H···H—$CO_2H$) at $r'$ = 2·5 and 4·5 Å are shown in parentheses.

Figure 3 shows the distance dependence of the interaction energy ($\Delta E$) and the component energies for **3** (X = F). The interaction energies ($\Delta E$) and their component terms for the isodesmic proton transfer reactions [(2) and (3)], together with the corresponding relative interaction energies $[\delta\Delta E = (\Delta E_X - \Delta E_H)]$ and their relative component terms $[\delta ES = (ES_X - ES_H)$, $\delta PL = (PL_X - PL_H)$, $\delta CT = (CT_X - CT_H)$, etc.] at $r'$ = 4·5 Å, and the corresponding values at $r'$ = 2·5 Å are given in Tables 5 and 6, respectively.

Table 3. Energy decomposition analysis for **2** (X=$NO_2$) (at the 4-31G level)

| | Energy/kcal mol$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| $r'$/Å | $\Delta E$ | *ES* | *PL* | *CT* | *EX* | *MIX* |
| 4·5 | 9·78 | 10·24 | −0·43 | −0·03 | 0·00 | 0·00 |
| 4·5 | (0·87)[a] | (0·95) | (−0·05) | (−0·03) | (0·00) | (0·00) |
| 3·5 | 14·62 | 16·19 | −1·15 | −0·58 | 0·05 | 0·11 |
| 2·5 | 27·10 | 30·55 | −5·47 | −3·62 | 3·51 | 2·13 |
| 2·5 | (6·07)[a] | (5·65) | (−2·14) | (−2·84) | (4·79) | (0·61) |
| 2·25 | 36·10 | 37·70 | −9·87 | −6·49 | 9·43 | 5·33 |
| 2·0 | 54·72 | 49·02 | −20·06 | −20·06 | 24·67 | 21·15 |

[a] The results for the neutral molecule system (X—H···H—$NO_2$) are given in parentheses.

Table 4. Energy decomposition analysis for **3** (X=F) (at the 4-31G level)

| | Energy/kcal mol$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| $r'$/Å | $\Delta E$ | *ES* | *PL* | *CT* | *EX* | *MIX* |
| 4·5 | −4·79 | −4·54 | −0·13 | −0·13 | 0·00 | 0·01 |
| 4·5 | (1·10)[a] | (1·16) | (−0·04) | (−0·02) | (0·00) | (0·00) |
| 3·5 | −7·53 | −6·53 | −0·46 | −0·82 | 0·25 | 0·03 |
| 2·5 | −7·52 | −11·02 | −4·21 | −4·13 | 10·05 | 1·79 |
| 2·5 | (8·79)[a] | (7·78) | (−2·29) | (−3·12) | (5·48) | (0·94) |
| 2·25 | −1·36 | −12·97 | −8·80 | −8·60 | 23·38 | 5·63 |
| 2·0 | 17·09 | −13·18 | −19·23 | −22·20 | 53·05 | 18·65 |

[a] The results for the neutral molecule system (X—H···$HCO_2H$) are given in parentheses.

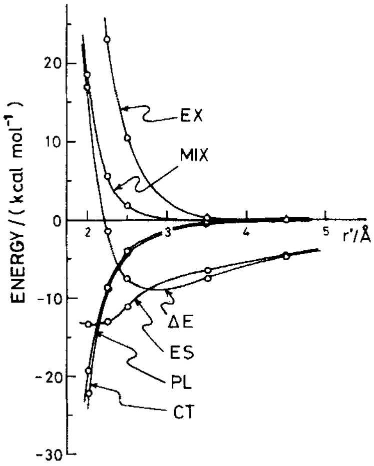


Figure 3. Distance dependence of each of the energy components of the intermolecular interaction energy in the F—H···$HCO_2^-$ system

Table 5. Energy decomposition analysis for the isodesmic reaction (2) (at the 4-31G level)

| $r'$/Å | X | Energy (kcal mol$^{-1}$)<br>$\delta\Delta E$ | $\delta ES$ | $\delta PL$ | $\delta CT$ | $\delta EX$ | $\delta MIX$ |
|---|---|---|---|---|---|---|---|
| 4·5 | H | 0·00<br>(−0·09)[a] | 0·00<br>(0·24) | 0·00<br>(−0·32) | 0·00<br>(−0·01) | 0·00<br>(−0·01) | 0·00<br>(0·01) |
| | F | 6·09 | 5·92 | 0·16 | 0·02 | 0·01 | −0·02 |
| | $NO_2$ | 9·00 | 9·05 | −0·06 | 0·01 | 0·01 | −0·01 |
| | $NH_2$ | 1·60 | 1·62 | −0·02 | 0·01 | 0·00 | −0·01 |
| | CN | 6·28 | 6·42 | −0·16 | 0·02 | 0·00 | 0·00 |
| 2·5 | H | 0·00<br>(−2·16)[a] | 0·00<br>(2·23) | 0·00<br>(−3·91) | 0·00<br>(−0·87) | 0·00<br>(−1·33) | 0·00<br>(1·72) |
| | F | 17·55 | 15·96 | 2·46 | −0·27 | 0·18 | −0·78 |
| | $NO_2$ | 23·19 | 22·67 | 0·58 | 0·09 | 0·05 | −0·20 |
| | $NH_2$ | 3·96 | 4·33 | −0·02 | −0·73 | −0·03 | 0·41 |
| | CN | 15·12 | 15·29 | 0·18 | 0·18 | −0·19 | −0·34 |

[a] Values in parentheses are energy values of each term when X = H.

Table 6. Energy decomposition analysis for the isodesmic reaction (3) (at the 4-31G level)

| $r'$/Å | X | Energy/kcal mol$^{-1}$<br>$\delta\Delta E$ | $\delta ES$ | $\delta PL$ | $\delta CT$ | $\delta EX$ | $\delta MIX$ |
|---|---|---|---|---|---|---|---|
| 4·5 | H | 0·00<br>(−0·41)[a] | 0·00<br>(−0·22) | 0·00<br>(−0·14) | 0·00<br>(−0·06) | 0·00<br>(0·01) | 0·00<br>(0·00) |
| | F | −5·48 | −5·48 | 0·05 | −0·05 | −0·01 | 0·01 |
| | $NO_2$ | −8·49 | −8·26 | −0·12 | −0·17 | −0·06 | 0·12 |
| | $NH_2$ | −1·85 | −1·80 | 0·00 | −0·04 | 0·00 | −0·01 |
| | CN | −6·15 | −5·93 | −0·10 | −0·10 | 0·00 | −0·02 |
| 2·5 | H | 0·00<br>(−0·17)[a] | 0·00<br>(−4·22) | 0·00<br>(0·17) | 0·00<br>(−2·58) | 0·00<br>(5·79) | 0·00<br>(0·67) |
| | F | −16·14 | −14·58 | −2·09 | 1·57 | −1·22 | 0·18 |
| | $NO_2$ | −22·69 | −20·51 | −3·30 | 0·70 | −0·44 | 0·86 |
| | $NH_2$ | −5·02 | −4·69 | −0·75 | 1·30 | −0·32 | −0·56 |
| | CN | −14·73 | −14·01 | −2·24 | 0·74 | 0·26 | 0·52 |

[a] Values in parentheses are energy values of each term when X = H.

Table 7 summarizes the results of statistical analyses for the relative p$K_a$ values ($\Delta$p$K_a$) of various series of substituted aliphatic carboxylic acids and ammonium salts,[20,21] ionization potentials (*IP*) or relative rate of methylation of 4-substituted quinuclidines,[22,31] $^{13}$C-SCS in the phenyl *p*-carbon of 4-substituted 1-phenylbicyclo[2.2.2]octanes[23] and others[29] and relative rate of esterification of substituted acetic acids[30] using the dipole parameter ($\Delta\iota\lambda$ or $\sigma_\chi\lambda$).

## DISCUSSION

The field parameter ($\sigma_F$ or $\sigma_I$) depends essentially on the group dipole moment of the substituent ($p_X$) which is correlated with $\Delta\iota\lambda$, whereas the $\sigma$-inductive effect is related directly to the group electronegativity ($\chi_X$, $\sigma_\chi$ or $\Delta\iota$). Therefore, there is no relationship between $\sigma_F$ (or $\sigma_I$) and $\sigma_\chi$ (or $\Delta\iota$).[10,11]

A decisive answer concerning this non-proportionality was obtained from the following consideration using the results in Table 1. According to the energy decomposition analysis for the case of a negative probe charge, the field energies ($\Delta E$) in the system **1** are almost entirely composed of the electrostatic energy (*ES*) as shown in Table 1, and the contribution of the polarization energy (*PL*) can be ignored. It was previously pointed out[14] that the logarithm of the interaction energy (log $\Delta E$) between molecules X—H and point charge [i.e. ($\pm$)···H—X) is well correlated with $-\log r$ having a slope of nearly 2 at various distances ($r$) between the hydrogen atom of X–H and point charge as expected from equation (4). Hence the interaction

Table 7. Statistical results for $\Delta pK_a$, ionization potential ($IP$), $^{13}$C-SCS and relative rate [log($k/k_0$)] vs $\Delta\iota\lambda$ (first value listed) or $\sigma_\chi\lambda$ (second value listed)

| Parameter | System | Slope | | $r^a$ | | $f^b$ | | $n^c$ | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| | | $\alpha$ | $\beta$ | | | | | | |
| $\Delta pK_a$ | X—G—$CO_2H$: | | | | | | | | |
| | G = $CH_2$ | 2·09 | 4·15 | 0·963 | 0·975 | 0·17 | 0·14 | 10 | 20·21 |
| | $(CH_2)_2$ | 0·74 | 1·46 | 0·960 | 0·970 | 0·18 | 0·16 | 10 | 27 |
| | $(CH_2)_3$ | 0·33 | 0·67 | 0·983 | 0·962 | 0·16 | 0·22 | 7 | 27 |
| | $(CH_2)_4$ | 0·32 | 0·69 | 0·922 | 0·961 | 0·32 | 0·23 | 6 | 27 |
| | $CH_2C_6H_4$-*p* | 0·39 | 0·76 | 0·947 | 0·935 | 0·23 | 0·28 | 5 | 20[d] |
| | **5** | 1·57 | 3·02 | 0·984 | 0·960 | 0·15 | 0·23 | 6 | 28 |
| | **6** | 0·35 | 0·64 | 0·987 | 0·996 | 0·16 | 0·08 | 6 | 20[d] |
| | **7** | 0·52 | 1·03 | 0·978 | 0·983 | 0·15 | 0·17 | 5 | 20 |
| | **8** | 0·72 | 1·30 | 0·990 | 0·991 | 0·09 | 0·09 | 6 | 20 |
| | **9** | 0·75 | 1·49 | 0·960 | 0·976 | 0·19 | 0·15 | 8 | 20 |
| | **10** | 0·79 | 1·65 | 0·980 | 0·980 | 0·15 | 0·15 | 7 | 20[d] |
| | **11** | 0·58 | 1·13 | 0·973 | 0·990 | 0·22 | 0·15 | 5 | 20 |
| | X—G—$\overset{+}{N}H_3$: | | | | | | | | |
| | G = $CH_2$ | 4·35 | 8·52 | 0·997 | 0·997 | 0·073 | 0·076 | 5 | 20[d] |
| | **12** | 2·41 | 4·68 | 0·984 | 0·984 | 0·12 | 0·13 | 11 | 20[d] |
| | **13** | 1·09 | 2·14 | 0·927 | 0·927 | 0·42 | 0·42 | 5 | 20 |
| *IP* | **14** | 0·57 | 1·08 | 0·995 | 0·997 | 0·09 | 0·07 | 6 | 22 |
| $^{13}$C-SCS | **4** (C-4) | 0·63 | 1·27 | 0·974 | 0·976 | 0·15 | 0·15 | 9 | 23 |
| | **15**(C-4′) | −0·97 | −1·90 | 0·991 | 0·990 | 0·12 | 0·13 | 5 | 29 |
| Log($k/k_0$) | $XCH_2CO_2H + Ph_2CN_2$ | 1·17 | 2·31 | 0·989 | 0·991 | 0·17 | 0·16 | 6 | 20, 30[e] |
| | $XCH_2CO_2H + Ph_2CN_2$ | 1·81 | 3·56 | 0·994 | 0·995 | 0·12 | 0·11 | 6 | 20, 30[f] |
| | **14** + MeI | −0·54 | −1·05 | 0·969 | 0·981 | 0·19 | 0·15 | 10 | 20, 31[d,g] |

[a] Correlation coefficient.
[b] Goodness of fit (= SD/RMS, where SD = standard deviation and RMS = root mean square of the data).
[c] Number of data points.
[d] The λ value for the $CONH_2$ group was estimated from equation (10) as 1·968 Å.
[e] In EtOH at 25 °C.
[f] In $Me_2SO$ at 30 °C.
[g] In MeOH at 10 °C.

energies ($\Delta E$) in **1** can be approximately calculated by

$$\Delta E = -(ep \cos \theta)/r^2 \qquad (4)$$

and

$$\Delta E = -e\,(ne\,\Lambda)\cos \theta/r^2 \qquad (5)$$

where *e* represents the probe point charge. Accordingly, if the distance ($r$) between the probe charge and the centre of the pure dipole 'substituent' is kept constant (for example, $r = 6{\cdot}73$ Å in **1**), a linear relationship between $\Delta E$ and $p_z (= ne\,\Lambda \cos \theta)$ will be expected from equation (5). In fact, the relative interaction energies ($\delta\Delta E$) and $p_z$ ($= ne\,\Lambda \cos\theta = ne\,\lambda$, cited in Table 1) can be well connected by equation (6) with an excellent correlation coefficient. Since $\delta\Delta E$ is nearly same as $\delta ES$ as shown in Table 1, equation (7) is also given with a comparable precision to that of equation (6) (see also Fig. 1);

$$\delta\Delta E = -2{\cdot}23\ ne\,\Lambda \cos\theta - 0{\cdot}067 \qquad (6)$$
$$(r_c = 0{\cdot}996, f = 0{\cdot}058, n = 11)$$

$$\delta ES = -2{\cdot}24\ ne\,\Lambda \cos\theta - 0{\cdot}067 \qquad (7)$$
$$(r_c = 0{\cdot}996, f = 0{\cdot}058, n = 11)$$

In contrast, there is no linear relationship between $\delta\Delta E$ and the charges ($ne$) on the pure dipole 'substituent' as shown in Table 1. Hence it is necessary to explain why $\sigma_F$ (or $\sigma_I$) is not linearly correlated with the substituent electronegativity, $\sigma_\chi$ (or $\Delta\iota$), because a linear relationship between fractional charge and electronegativity has been indicated[32] and further the $\sigma_\chi$ values have been evaluated from the charge densities on the hydrogen atom $(1 - q_H)$ in compounds X—H,[10b] and the inductive substituent parameter ($\iota$)[11] are related to $(1 - q_H)$.[33]

### Charge separation parameter (λ)

The λ parameter of each substituent listed in Table 2 was obtained from the *z*-component of the dipole moment, $p_z$ ($= p \cos\theta$), for the molecule H—X and the charge density, $(1 - q_H)$, on the hydrogen atom in the molecule H—X by an *ab initio* molecular orbital calculation at the 4-31G or 6-31G level.

The $p_z$ values listed in Table 2 are expected to show a linear relationship with field parameters, $\sigma_I(g)$, which were derived recently from the acidities of the substituted phenols in the gas phase.[26] The results are $\sigma_I(g) = 0{\cdot}191p_z$ ($r_c = 0{\cdot}991$, $f = 0{\cdot}088$, $n = 10$ at the 4-31G level) and $\sigma_I(g) = 0{\cdot}189p_z$ ($r_c = 0{\cdot}991$, $f = 0{\cdot}087$, $n = 10$ at the 6-31G level), indicating almost the same correlation coefficient ($r_c$), goodness of fit ($f$) and slope. The types of substituent groups used in the statistical analysis are H, $CH_3$, $NH_2$, $OCH_3$, CHO, F, $CF_3$, $COCH_3$, CN and $NO_2$. Owing to the lack of evaluation of $\sigma_I(g)$ for the $CH_3$ group, the $\sigma_I$ value given by Charton[20] was used, but the substituent $CO_2CH_3$ is eliminated from this statistical analysis, because the inclusion of this group leads to a significant deviation from the regression lines ($r_c = 0{\cdot}969$, $n = 11$ at the 4-31G and 6-31G levels). The reason for this deviation can probably be attributed to an imperfection in the separation of the $\sigma_I(g)$ value into the $\sigma_I$ and $\sigma_R$ components, because the correlations with $\sigma_i$[34] and the other data in solution are excellent or fairly good even when the $CO_2CH_3$ group is included, as mentioned later.

On the other hand, we reported previously[33] a good correlation between the relative inductive substituent parameter ($\Delta\iota$) and $(1 - q_H)$ in H—X molecules.[10b] According to equation (6), it is expected that the product of the $\lambda$ value and $\Delta\iota$[11,33] or $\sigma_\chi$[10b] probably bears a linear relationship to the field parameter ($\sigma_I$ or $\sigma_F$),[26] because the $\sigma_{F(\text{theor})}$ (or $\sigma_F$) values have recently been evaluated using an interaction energy of isolated molecule systems.[17] In fact, it was found that the $p_z$ values were correlated with $\Delta\iota\lambda$ ($r_c = 0{\cdot}968$, $n = 13$ at the 4-31G level; $r_c = 0{\cdot}962$, $n = 13$ at the 6-31G level) and with $\sigma_\chi\lambda$ ($r_c = 0{\cdot}986$, $n = 13$ at the 4-31G level; $r_c = 0{\cdot}992$, $n = 13$ at the 6-31G level).

Figure 2 shows plots of $\sigma_I(g)$ values against $\Delta\iota\lambda$ or $\sigma_\chi\lambda$, and the following relationships were obtained with a good correlation coefficient for the 10 substituents mentioned above:

$$\sigma_I(g) = 0{\cdot}479\Delta\iota\lambda_{4\text{-}31G} - 0{\cdot}023 \qquad (r_c = 0{\cdot}987, f = 0{\cdot}11) \tag{8a}$$

$$\sigma_I(g) = 0{\cdot}465\Delta\iota\lambda_{6\text{-}31G} - 0{\cdot}021 \qquad (r_c = 0{\cdot}982, f = 0{\cdot}13) \tag{8b}$$

$$\sigma_I(g) = 0{\cdot}975\sigma_\chi\lambda_{4\text{-}31G} - 0{\cdot}004 \qquad (r_c = 0{\cdot}987, f = 0{\cdot}11) \tag{9a}$$

$$\sigma_I(g) = 0{\cdot}968\sigma_\chi\lambda_{6\text{-}31G} - 0{\cdot}009 \qquad (r_c = 0{\cdot}992, f = 0{\cdot}08) \tag{9b}$$

As can be seen in Figure 2, the plot of $\sigma_I(g)$ against $\Delta\iota\lambda$ is slightly more scattered than that against $\sigma_\chi\lambda$. The reason may be attributed to the incomplete evaluation of $\sigma_I(g)$, because $\Delta\iota\lambda$ correlates excellently with $\sigma_i$, as shown later. According to the results expressed by equations (8a) and (8b) and (9a) and (9b), it is obvious that the evaluation of $\lambda$ on the basis of approximation at the 4-31G level is favourable with respect to the field parameter, $\Delta\iota\lambda$, but that based on approximation at the 6-31G level is better for the field parameter $\sigma_\chi\lambda$.

The reasoning could be an accidental result due to the following data in the range of the limited substituents. The $\Delta\iota$ values correlated with the $(1 - q_H)$ values of H—X molecules calculated at the 4-31G level slightly better than those at the 6-31G level ($r_c = 0{\cdot}950$ vs $0{\cdot}946$), and the $\sigma_\chi$ values correlated with those at the 6-31G level slightly better than those at the 4-31G level ($r_c = 0{\cdot}989$ vs $0{\cdot}983$), because the $\sigma_\chi$ values were obtained based on the $(1 - q_H)$ values calculated at the 6-31G* level.

Hence it seemed that the introduction of a new parameter, namely the charge separation parameter, $\lambda$,[19] is necessary in order to identify the reason for the non-linear relationship between the field effect and the substituent electronegativity parameter.[3b,10,11]

The validity of the charge separation parameter ($\lambda$) becomes clear by comparing Figure 2 with Figure 5 in Ref. 10b [extremely scattered plot of $\sigma_F$ (or $\sigma_I$) against $\sigma_\chi$], because of a remarkable improvement in the non-linear relationship between $\sigma_F$ (or $\sigma_I$) and electronegativity.

A linear relationship between $\Delta\iota\lambda$ or $\sigma_\chi\lambda$ and the field parameter, $\sigma_i$,[34] was found with high precision as follows:

$$\begin{aligned} &\sigma_i = 0{\cdot}356\Delta\iota\lambda_{4\text{-}31G} - 0{\cdot}013 \qquad (r_c = 0{\cdot}991, f = 0{\cdot}087)\\ &\text{and}\\ &\sigma_i = 0{\cdot}702\sigma_\chi\lambda_{6\text{-}31G} - 0{\cdot}006 \qquad (r_c = 0{\cdot}977, f = 0{\cdot}14) \end{aligned} \tag{10}$$

Individual substituents used in the statistical analysis were H, $CH_3$, $NH_2$, $OCH_3$, OH, F, $CF_3$, $COCH_3$, $CO_2CH_3$, CN and $NO_2$. A similar treatment was also applied to other field parameters, $F$[35] and $\sigma_{F(\text{theor})}$,[17] and the following linear relationships having a slightly less precise linearity were obtained; $F = 0{\cdot}669\Delta\iota\lambda_{4\text{-}31G} + 0{\cdot}073$ ($r_c = 0{\cdot}963$, $f = 0{\cdot}17$, $n = 12$); $F = 1{\cdot}355\sigma_\chi\lambda_{6\text{-}31G} + 0{\cdot}073$ ($r_c = 0{\cdot}974$, $f = 0{\cdot}145$, $n = 12$); $\sigma_{F(\text{theor})} = 0{\cdot}414\Delta\iota\lambda_{4\text{-}31G} + 0{\cdot}007$ ($r_c = 0{\cdot}930$, $f = 0{\cdot}22$, $n = 13$); $\sigma_{F(\text{theor})} = 0{\cdot}861\sigma_\chi\lambda_{6\text{-}31G} + 0{\cdot}006$ ($r_c = 0{\cdot}961$, $f = 0{\cdot}16$, $n = 13$).

In the plot of $\sigma_i$ against $\sigma_\chi\lambda_{6\text{-}31G}$, substituent groups such as $CF_3$, $COCH_3$ and OH deviated from the regression line. On the other hand, in the plot of $F$ against $\Delta\iota\lambda_{4\text{-}31G}$, $OCH_3$, $NH_2$, $CO_2H$ and $NO_2$ groups deviated considerably from the regression line. In the relationship between $\sigma_{F(\text{theor})}$ and $\Delta\iota\lambda_{4\text{-}31G}$, a larger deviation from the regression line was observed for CHO and $NO_2$ groups.

## Energy decomposition analysis for isodesmic reaction

It is generally observed from the results in Tables 4 and 5 that the $\Delta E$ value consists mainly of an electrostatic ($ES$) term at longer distances ($r' = 4\cdot5$ Å or above), but the other energy terms such as $PL, CT, EX$ and $MIX$ contribute to the $\Delta E$ value to various extents at shorter distances ($r' = 2\cdot0$–$3\cdot5$ Å) in both series **2** and **3**. In the case of **3** (X = F) (see Figure 3), the $\Delta E$ value changed from stabilization (negative value at $r' = 3$ Å or above) to destabilization (positive value at $r' = 2\cdot0$–$2\cdot5$ Å) with a decrease in the distance between two species (HF and $HCO_2^-$). This result is ascribed to the sum of both stabilization due to an increase in $ES$, $CT$ and $PL$ terms and destabilization caused by an increase in $EX$ and $MIX$ terms.

The relative component energies (i.e. $\delta PL, \delta CT, \delta EX$ and $\delta MIX$) in reactions (2) and (3) at a longer distance ($r' = 4\cdot5$ Å) play only a minor role compared with the electrostatic energy term ($\delta ES$), as shown in Tables 5 and 6. The point to be noted is that the electrostatic term ($\delta ES$) is also dominant at a shorter distance ($r' = 2\cdot5$ Å), although other terms such as $\delta PL, \delta CT, \delta EX$ and $\delta MIX$ show a considerably greater contribution than those at longer distances.

In general, the relationship between the relative electrostatic energy, $\delta ES$ (see Tables 5 and 6), and $\sigma_F$[26] shows excellent linearity as follows: $r_c = 0\cdot984$ at $r' = 4\cdot5$ Å and $r_c = 0\cdot978$ at $r' = 2\cdot5$ Å for reaction (2), and $r_c = 0\cdot982$ at $r' = 4\cdot5$ Å and $r_c = 0\cdot976$ at $r' = 2\cdot5$ Å for reaction (3).

As shown in Figure 4, the $\delta ES$ value is nearly correlated with $\Delta_\iota\lambda$ at a closer distance (at $r' = 2\cdot5$ Å in **2** and **3**). This trend was also generally observed in the isodesmic reactions at a longer distance ($r' = 4\cdot5$ Å).

The magnitude of the energy ($\Delta E = 9\cdot78$ kcal mol$^{-1}$) in the charge–dipole interaction (in the case of $O_2N{-}H\cdots H{-}\overset{+}{N}H_3$ at $r' = 4\cdot5$ Å listed in Table 3) is more than ten times of that of the relative energy ($\Delta E = 0\cdot87$ kcal mol$^{-1}$ at $r' = 4\cdot5$ Å, as shown in Table 3) in the case of the dipole–dipole interaction ($O_2N{-}H\cdots H{-}NH_2$). Consequently, the field effect due to charge–dipole interaction becomes more important than that due to dipole–dipole interaction. As mentioned in the Introduction, the reason why the field effect for $\Delta pK_a$ is dominant in the charged molecules, $XCH_2CO_2^-$, but the electronegativity of the substituent correlates linearly with the chemical shift parameter ($\delta_{CH_2} - \delta_{CH_3}$) in the neutral molecules ($XCH_2CH_3$) may be attributed to the fact mentioned above.

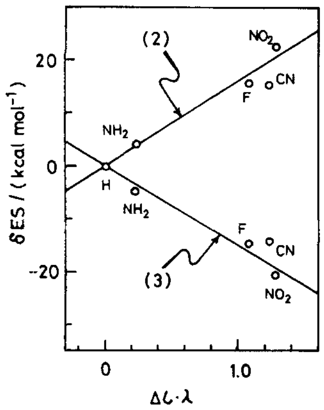


Figure 4. Relationship between $\delta ES$ and $\Delta_\iota\lambda$ in reactions (2) and (3) at $r' = 2\cdot5$ Å

## Application of $\Delta_\iota\lambda$ or $\sigma_\chi\lambda$ to $\Delta pK_a$ and some physical data

The relative $pK_a$ values ($\Delta pK_a$) of a wide variety of aliphatic acids[20,21,27,28] were analysed with high precision using $\Delta_\iota\lambda$ or $\sigma_\chi\lambda$ as shown in Table 7.

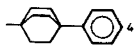
$$\Delta pK_a = \alpha\Delta_\iota\lambda_{4\text{-}31G} + c \qquad \text{or} \qquad \beta\sigma_\chi\lambda_{6\text{-}31G} + c' \tag{11}$$

These results support the validity and generality of the $\lambda$ parameter. The ionization energies of the lone pair on the nitrogen atom in 4-substituted quinuclidines (**14**)[22] were also precisely related with $\Delta_\iota\lambda$ or $\sigma_\chi\lambda$ (see Table 7).

From the analysis with equation (11) it was confirmed in the aliphatic systems that the electrostatic dipolar field effect on the reaction centre is much more important than the through-$\sigma$-bond effect.

Recently, Adcock and co-workers[23] reported that $^{13}C$-SCS of the C-4 atom for 4′-substituted bicyclo[2.2.2]octylbenzenes (**4**) are proportional to $\sigma_F$, even though the atoms are contained in the unsaturated probe linkage. In this case, the C-4 SCS are also well correlated with $\Delta_\iota\lambda$ or $\sigma_\chi\lambda$, as shown in Table 7.

Hence the validity of introduction of the charge separation parameter ($\lambda$) into the relationship between the field parameter and the electronegativity or inductive substituent parameter was best judged by comparing physical and chemical data such as $\Delta pK_a$,[20,21,27,28] $IP$,[20,22] $^{13}C$-SCS[23,29] and $\log(k/k_0)$[20,30,31] with the parameter $\Delta_\iota\lambda$ or $\delta_\chi\lambda$ as shown in Table 7.

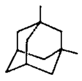


**4**

**5**

**6**

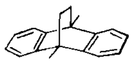
**7**



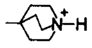
**8**

**9**

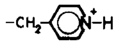
**10**



**11**



**12**



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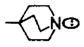
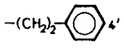


**14**



**15**

The $\alpha$ ($=0\cdot58$) [or $\beta$ ($=1\cdot13$)] value of the slope for **11** in Table 7 is considerably smaller than those for **9** ($\alpha=0\cdot75$ or $\beta=1\cdot49$) and **10** ($\alpha=0\cdot79$ or $\beta=1\cdot65$), although the geometrical relationships between the substituent and COOH group are nearly same. However, it is known that the substituent effect for **11** is almost same as those for **9** and **10**, when the H atom and $CH_3$ group are omitted.[36] Therefore, the difference in slopes may be attributed to a deviation of H and $CH_3$ in **11**.

It is concluded that both the charge separation parameter ($\lambda$) and substituent electronegativity are essential parameters for interpreting the electrostatic field effect. Our approach on the basis of the inductive substituent parameter ($\iota$) and the charge separation parameter ($\lambda$) will be very useful as a means of predicting the field parameter ($\sigma_F$). Hence these results should cast a new light on an interpretation of the electronic substituent field effect in aliphatic series.

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