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Elucidation of the Origin of Substituent Effects. Theoretical Investigation of Field Effect in Aliphatic Systems by *ab initio* Molecular Orbital Calculation Using Simple Models

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The electronic substituent effect in the aliphatic systems was investigated using *ab initio* calculation at STO-3G and 4-31G levels. The relative energy changes, $\delta\Delta E$, in isodesmic reaction of the 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids were compared with those for 1-substituted bicyclo[2.2.2]octanes(XC_8H_{13}), CH_3X, and H–X molecules perturbed with isolated pure point charges. The interaction energies between isolated dipole and point charge system, F–H···(±), were proportional to the reciprocal square of the distance between the center of dipole and the charge. Isodesmic reaction energies for the present systems at the distance longer than 5 Å can be practically explained by charge-dipole interaction. From the comparison of $\delta\Delta E$ in $XCH_3\cdots(\pm)$, $XC_8H_{13}\cdots(\pm)$, and $XC_6H_5\cdots(\pm)$ systems with those for X–H···(±), it was concluded that the pure field parameters for various substituents should be determined on the basis of the isodesmic reaction energy for X–H···(±) system. Correlations between $\delta\Delta E$ in X–H···(±) system and the field parameters recently proposed, σ_F and σ_I(gas), were generally better in the cases calculated at 4-31G level than those at STO-3G level.

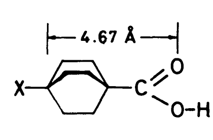
The effect of a partial structural change on the chemical reactivities in organic compounds is one of long standing problems in physical organic chemistry.[1] Recently, some attempts to simplify complicated interactions in the systems have been made in order to make the physical meaning of substituent effect clear. Analyses of acidities and basicities in gas phase[2] free of solvent effect and *ab initio* molecular orbital (MO) calculations[3] of energy changes in isodesmic reactions[4] for isolated molecule systems[5] where only through-space effect is operative have deepened the understanding on the origin and mechanism of transmission of substituent effect.[1c–f]

Usually, the interactions between substituent and reaction (or probe) center have been explained in terms of four effects, namely, field effect (through-space effect),[1c,1f,6] σ-inductive effect (electronegativity or through-bonds effect),[7] resonance and hyperconjugation effects (charge transfer effect),[1,8] and polarization effect,[3a,8] although other effects have also been suggested.[1e]

We reported evidence for σ-inductive effect on spectral data at the adjacent position to substituent,[9] and established a reliable method to calculate inductive substituent parameters (ι; Gk., iota) as a measure of σ-inductive effect.[10] Reynolds, Taft, and Topsom[7] have reported that the charge densities at the hydrogen atom in the H–X molecules (at 6-31G* level) were well correlated with the group electronegativities of the substituents, because of the absence of the hyperconjugative interaction, and soon after, we also showed a similar relationship with our revised electronegativities.[11]

On the other hand, Streitwieser *et al.*[12] reported the results of *ab initio* MO calculations for the monosubstituted benzenes perturbed with positive and negative unit charges as a simple model of substituent effect, and suggested that the highly or weakly polarizable groups should not be included in the Hammett relationship on the basis same as normal substituents.

Recently, the scales of field effect (T_F,[13] σ_I(STO-3G),[1f] $F°$,[8] and σ_F[7]) have been proposed on the basis of *ab initio* calculations of appropriate model systems at the STO-3G and 4-31G levels. However, usefulness of these scales is not so clear. Then we expected that a satisfactory interpretation for substituent effect might be obtained from a comparison of the energy changes in isodesmic reaction of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids (**1**) with those of 1-substituted bicyclo[2.2.2]octane perturbed with positive and negative point charges (**2**) as a simple model, though the acidities of **1** in gas phase have not been reported.



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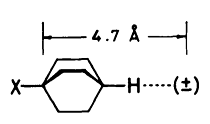

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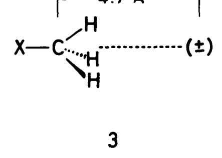

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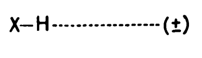

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Systematic *ab initio* MO calculations for the through-space field effect in σ-bond systems **2**—**4** were also carried out using perturbation with pure point charges to model nonbonded reaction center.

Calculation Methods

Calculations were performed on the *ab initio* STO-3G[14a)] or/and 4-31G[14b)] levels using the Gaussian-70[14c)] and 80[14d)] series of computer program, and the molecular geometries were taken from experimentally determined values.[15)] The geometry of the carboxylate moiety in **1** was obtained to be $r_{\text{C-O}}=1.27$ Å and ∠OCO=130.4° from the optimized geometry of formate ion at the STO-3G level, and assumed to be constant for all substituted derivatives (**1**). The geometry of a pure dipole "substituent" having positive and negative point charges is the same as that used by Streitwieser *et al.*[12)]

In other systems (**2**—**4**), perturbation of the systems was induced by both positive and negative point charges. The point charge was located at 1 Å from the 4-hydrogen atom in **2**, and at 4.7 Å from the methyl carbon and hydrogen atoms in **3** and **4**, respectively, along the X-C bond. Thus, the distances (4.7 Å) between *ipso*-carbon atom (hydrogen atom in **4**) and point charge in **2**—**4** are almost equal to that (4.67 Å) between C_4 atom and reaction center in **1**.

The following isodesmic reaction (Eq. 1) was used to evaluate the substituent effect on the above perturbed systems:

$$\underset{\textbf{A}}{\text{X-R}} + \underset{\textbf{B}}{\text{H-R}\cdots(\pm)} \rightleftharpoons \underset{\textbf{C}}{\text{H-R}} + \underset{\textbf{D}}{\text{X-R}\cdots(\pm)} \qquad (1)$$

where X represents substituent and R-H is parent compound. The relative energy change ($\delta\Delta E$) in the above isodesmic reaction was obtained using Eq. 2.

$$\begin{aligned}\delta\Delta E &= (E_{\text{C}}+E_{\text{D}}) - (E_{\text{A}}+E_{\text{B}}) = (E_{\text{D}}-E_{\text{A}}) - (E_{\text{B}}-E_{\text{C}}) \\ &= \Delta E_{\text{X}} - \Delta E_{\text{H}} \qquad (2)\end{aligned}$$

A negative value in $\delta\Delta E$ corresponds to a stabilizing effect compared with that of parent compound. All calculations were carried out on a FACOM M-382 computer at the Nagoya University Computation Center.

Results and Discussion

The total energies of the carboxylic acids (**1**) and the corresponding carboxylate ions, the relative energy changes ($\delta\Delta E$) in the isodesmic reaction (Eq. 3) of the series **1**,

$$\begin{aligned}&\text{XC}_8\text{H}_{12}\text{CO}_2\text{H} + \text{C}_8\text{H}_{13}\text{CO}_2^- \rightleftharpoons \\ &\qquad \text{C}_8\text{H}_{13}\text{CO}_2\text{H} + \text{XC}_8\text{H}_{12}\text{CO}_2^- \qquad (3)\end{aligned}$$

and the relative charge densities (Δq_{H}) at the carboxyl hydrogen atom in **1** are given in Table 1.

The linear relationships between $\delta\Delta E$ and charge densities at a particular atom have been shown in the alkyl chlorides (STO-3G),[16)] substituted phenols and benzoic acids (INDO[17)] and STO-3G[18)]), aliphatic aldehydes (STO-3G),[19)] substituted anilines and toluenes (STO-3G),[20)] and several isolated molecule systems.[6,13)]

Correlation between the relative energy changes in the isodesmic reaction ($\delta\Delta E_{(1)}$) and Δq_{H} in the series **1** is as follows:

$$\delta\Delta E_{(1)} = 2135\Delta q_{\text{H}} - 0.056$$
$$(r=0.9985,\ n=9,\ f=0.045)$$

Analogous correlation of $\delta\Delta E_{(1)}$ with $\Delta\sum q_{\text{O}}(\text{COOH})$ or $\Delta\sum q_{\text{O}}(\text{COO}^-)$, which is the sum of the relative charges on the both oxygen atoms in the carboxyl group of the series **1** or those in the corresponding carboxylate, respectively (see Table 1), shows that $\Delta\sum q_{\text{O}}(\text{COO}^-)$ can be used as a measure of $\delta\Delta E_{(1)}$ similarly to Δq_{H}, as shown in the following equations.

TABLE 1. TOTAL ENERGIES OF CARBOXYLIC ACIDS **1** AND THEIR ANIONS, RELATIVE ENERGY FOR ISODESMIC REACTION, AND Δq_{H} AND Δq_{O} OF THE CARBOXYL GROUP

Substituent X	$\text{XC}_8\text{H}_{12}\text{COO}^-$ / au	$\text{XC}_8\text{H}_{12}\text{COOH}$ / au	$\delta\Delta E$ / kcal mol^{-1} a)	$\Delta q(\text{H}) \times 10^3$ (COO$\underline{\text{H}}$)	$\Delta\sum q(\text{O})$ b) $\times 10^3$ (C$\underline{\text{OO}}$H)	$\Delta\sum q(\text{O})$ b) $\times 10^3$ (C$\underline{\text{OO}}^-$)
-CH_3	−530.37663	−531.12401	0.1	0.141	−0.156	0.170
-H	−491.80476	−492.55205	0.0	0.000	0.000	0.000
-NH_2	−546.11313	−546.85836	−1.3	−0.471	1.367	1.826
-OH	−565.63481	−566.37823	−2.4	−1.184	1.369	2.665
-CHO	−603.02569	−603.76839	−2.9	−1.317	1.815	3.226
-F	−589.26526	−590.00699	−3.5	−1.796	3.313	3.852
-CN	−582.36213	−583.09772	−7.3	−3.451	3.018	7.422
-NO_2	—692.51268	−693.24612	−8.7	−4.003	6.431	9.577
Dipole	−492.54771	−493.28027	−9.2	−4.229	6.788	9.262

a) 1 kcal mol^{-1}=4.184 kJ mol^{-1}. b) See the text.

$$\delta\Delta E_{(1)} = -1352\Delta\Sigma q_{\mathrm{O}}(\mathrm{COOH}) - 0.327 \quad (r=0.943,\ n=9)$$

$$\delta\Delta E_{(1)} = -982\Delta\Sigma q_{\mathrm{O}}(\mathrm{COO^-}) + 0.220 \quad (r=0.997,\ n=9)$$

In the case of the substituted phenols,[21] it has been found that the electron-donating groups deviate considerably from the correlation between the corresponding $\delta\Delta E$ values and the relative charges on the oxygen atom in the substituted phenoxides, because of conjugation of the oxide group with the π-electrons system.

The total energies of 1-substituted bicyclo[2.2.2]octanes, monosubstituted methanes, and H-X molecules at the STO-3G and 4-31G levels are given in Table 2. Table 3 shows $\delta\Delta E$ in the series **2**—**4** at both basis sets.

It was shown for the $CH_4\cdots(-)$ system as an example that the effect of slight change in bond length on $\delta\Delta E$ can be ignored in the case of the relative energy due to substituent effect as shown below. In Table 2, the C-H bond length of 1.10 Å was used. If the length is extend to 1.11 Å, the total energies of methane itself and methane perturbed with negative point charge were calculated to be −39.72450 and −39.72448 au, respectively. Thus the difference in $\delta\Delta E$ is 1×10^{-5} au (*ca.* 0.006 kcal mol^{-1} (1 cal=4.184 J)).

The electrostatic energy due to the interaction between dipole and point charge is calculated as the sum of the energies due to charge-permanent dipole interaction,[10] W_{p} (Eq. 4), and those due to charge-induced dipole interaction (polarizability effect),[10] W_α (Eq. 5):

$$W_{\mathrm{p}} = -ep\cos\theta/(Dr^2) \tag{4}$$

$$W_\alpha = -e^2\alpha/(2Dr^4) \tag{5}$$

where e is the unit electric charge, p permanent dipole moment of substituent, θ the angle between the axis of dipole and the line joining the center of dipole and point charge, r the distance between the center of dipole and point charge, α group polarizability, and D dielectric constant of medium.

Recently, Yoder *et al.*[22] have evaluated the substituent effects on the energies of proton-transfer equilibria in gas phase using classical electrostatic model. Therefore, it is of interest to examine whether the electrostatic model can quantitatively account for the isodesmic reaction energies calculated by *ab initio* MO method in the cases of the systems **2**—**4**.

In order to test if Eq. 4 can be applied sufficiently to our models **2**—**4**, the perturbed energy changes at various distances between F-H, in which a contribution of polarizability effect is small because of a lower polarizability, and point charges were calculated at

TABLE 2. TOTAL ENERGIES (AU) OF H-X, CH_3X, AND 1-SUBSTITUTED BICYCLO[2.2.2]OCTANES (XC_8H_{13})

Substituent X	H-X STO-3G	H-X 4-31G	CH_3-X STO-3G	CH_3-X 4-31G	XC_8H_{13} STO-3G
$-CH_3$	−39.72450	−40.13881	−78.30453	−74.11386	−346.05538
-H	−1.11676	−1.12676	−39.72591	−40.13881	−307.48345
$-NH_2$	−55.45339	−56.10364	−94.02601	−95.06490	−361.78996
-OH	−74.96454	−75.90681	−113.54451	−114.86937	−381.30980
-CHO	−112.35368	−113.69108	−150.94233	−152.68335	−418.70004
-F	−98.57077	−99.88726	−137.16877	−138.85696	−404.93877
-CN	−91.67519	−92.73132	−130.27080	−131.72657	−398.03009
$-NO_2$	−201.83118	−204.27805	−240.41178	−243.27215	−508.17817
Dipole	−1.83562	−1.84658	−40.44939	−40.86365	−308.21249

TABLE 3. RELATIVE ENERGIES ($\delta\Delta E$) OF ISODESMIC REACTIONS (kcal mol^{-1})

Substituent X	X-H$\cdots$(±) (**4**)				X-$CH_3\cdots$(±) (**3**)				X-$C_8H_{13}\cdots$(±) (**2**)	
	STO-3G		4-31G		STO-3G		4-31G		STO-3G	
	(+)	(−)	(+)	(−)	(+)	(−)	(+)	(−)	(+)	(−)
$-CH_3$	−0.2	0.0	−0.2	0.0	−0.3	0.1	−0.5	0.0	−0.5	0.0
-H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$-NH_2$	1.3	−1.4	1.8	−1.9	0.7	−0.9	1.2	−1.5	1.0	−1.4
-OH	2.4	−2.5	4.0	−3.9	1.7	−1.8	3.4	−3.6	2.3	−2.6
-CHO	1.4	−1.7	3.0	−3.3	1.9	−2.3	—	−4.4	2.5	−3.1
-F	3.2	−3.2	5.9	−5.7	2.6	−2.7	6.0	−5.9	3.5	−3.6
-CN	4.4	−4.7	6.2	−6.5	5.1	−5.5	7.1	−7.7	6.9	−7.6
$-NO_2$	5.5	−5.7	8.2	−8.3	6.0	−6.5	—	−9.8	8.4	−9.1
Dipole	7.0	−7.0	8.0	−8.0	7.0	−7.0	8.5	−8.6	9.7	−9.3

the 4-31G level. The results are shown in Table 4. A plot of log|$\delta\Delta E$| against −log r using the values (r=3.0—13.0 Å) listed in Table 4 showed a straight line having slope of nearly 2 (*i.e.*, 1.90 and 1.85 for negative and positive charges, respectively), as expected from Eq. 4.

It has been found that the polarization of the π-electron of ethylene[23] by $\overset{+}{N}H_4$ species approximately follows Eq. 4.

The effect of change of r on electrostatic field energies expressed by Eqs. 4 and 5 was also examined using the dipole moment of p=2.95 D[24] (1 D=3.333×10^{-30} C m) in gas phase and the longitudinal bond polarizability of α=31.3×10^{-25} cm^3[25] for hydrogen cyanide perturbed with both positive and negative point charges as an example. As seen in Fig. 1, the W_p values in the cases of negative and positive charges are mutually reverse in the sign, but the W_α values always correspond to stabilization for both charges. The contribution of W_α at very close distance (within r=2 Å) amounts to above 40% of W_p, but that at longer distances than 5 Å decreases up to below a few percents of W_p. Therefore, the magnitude of electrostatic field effects at such a longer distance can be approximately evaluated using only Eq. 4.

Table 5 summarizes the values p, θ, α, W_p, and W_α in the series **2**, where (4.7+0.5$r_{C\text{-}X}$) Å is used as r, and p and θ are the values calculated at the STO-3G level. Group polarizabilities of substituents (α)[26] were calculated from the values of bond refractivity (R_D) for the D line. The correlation between $\delta\Delta E_{(2)\cdots(\pm)}$ (Table 3) and W_p or (W_p+W_α) for both point charges in the series **2** are as follows:

$$\delta\Delta E_{(2)\cdots(-)} \left[\begin{array}{l} = 0.994W_p^{(-)} - 0.153 \quad (r=0.993,\ n=8) \\ = 0.968(W_p+W_\alpha)^{(-)} + 0.057 \\ \qquad\qquad (r=0.992,\ n=8) \end{array} \right.$$

$$\delta\Delta E_{(2)\cdots(+)} \left[\begin{array}{l} = 0.946W_p^{(+)} - 0.093 \quad (r=0.989,\ n=8) \\ = 0.971(W_p+W_\alpha)^{(+)} + 0.121 \\ \qquad\qquad (r=0.991,\ n=8) \end{array} \right.$$

Thus, it is clear again that $\delta\Delta E$ in the series **2** (at r=5.5 Å as a mean) can be nearly interpreted using only Eq. 4.

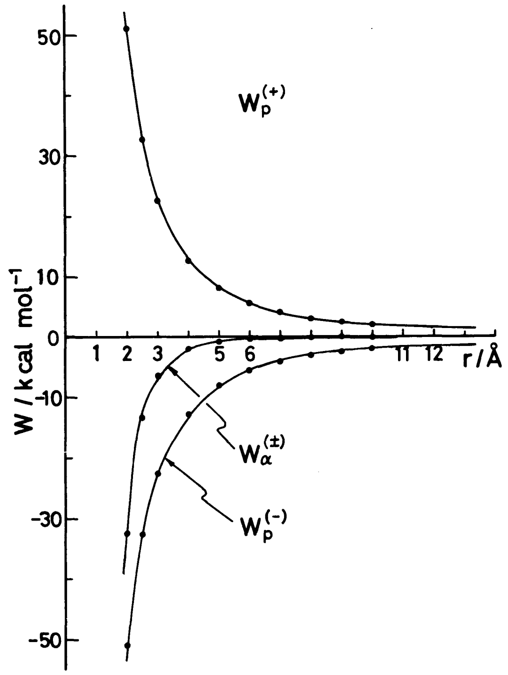

Fig. 1. Plots of electrostatic field energies (W_p and W_α) of hydrogen cyanide perturbed with both positive and negative point charges *vs.* the distances between the center of C–H bond and the point charges.

Table 4. $\delta\Delta E$ values[a] at various distances between F–H and point charges (4-31G level)

r/Å	1.0	3.0	4.7	7.0	10.0	13.0
$\delta\Delta E^{(-)}$/kcal mol^{-1}	−104.10	−14.29	−6.19	−2.91	−1.47	−0.89
$\delta\Delta E^{(+)}$/kcal mol^{-1}	61.17	12.98	5.92	2.84	1.44	0.87

a) The standard is the value in infinite distance.

Table 5. The values p, θ, α, W_p, and W_α in series **2**

Substituent X	p[a] / Debye[b]	θ[a] / degree	$\alpha\times10^{25}$ / cm^3	$\lvert W_p\rvert$ / kcal mol^{-1}	W_α / kcal mol^{-1}
-CH$_3$	0.00	0.00	22.408	0.000	−0.417
-H	0.00	0.00	4.075	0.000	−0.089
-NH$_2$	1.43	70.4	17.592	1.123	−0.335
-OH	1.56	51.6	10.092	2.290	−0.196
-CHO	1.76	43.3	22.313	2.980	−0.419
-F	1.37	0.00	3.2108	3.259	−0.063
-CN	3.49	0.00	21.639	8.195	−0.414
-NO$_2$	3.59	0.00	26.610	8.383	−0.504

a) Calculated at the STO-3G level. b) 1 D=3.333×10^{-30} C m.

In order to clarify whether the substituent effect on the acid dissociation energy in vacuum can be explained by the interaction with the carboxylate group, we examined the correlation between the dissociation energies of **1** ($\delta\Delta E_{(1)}$, Table 1) and the perturbation energies of **2** ($\delta\Delta E_{(2)\cdot\cdot(-)}$, Table 3) with negative charge. In the both cases, the distance (r) is almost same. The following linear relationship having a slope of nearly 1 was obtained, indicating that σ-inductive effect is unimportant in the systems **1**.

$$\delta\Delta E_{(1)} = 0.988\delta\Delta E_{(2)\cdot\cdot(-)} + 0.078$$
$$(r=0.9999,\ n=8,\ f=0.019)$$

We now discuss the polarizability effect on $\delta\Delta E$ from a slightly different point of view. Figure 2 (A) shows a substantially linear plot of $\delta\Delta E$ for the series **4** perturbed with positive charge *vs.* those perturbed with a negative one. Figures 2 (B) and (C) are also similar plots for the series **3** and **2**, respectively, two separate lines being obtained as expected from the result of monosubstituted benzenes perturbed with point charges.[12]

These plots indicate that the substituent effects are not independent of the nature of probe charge and molecular system. Most substituents having relatively large polarizability fall below the dotted line drawn through hydrogen, fluorine atoms, and dipole substituent having rather small polarizability. In comparison of these series, the series **4** showed the least deviation among them, while, the extent of the deviation in the series **3** and **2** becomes larger as the size of substrate increases. Hence, the deviation is probably attributed to the difference in the polarizability of the whole molecule. Thus the substituent parameters defined from data of relatively large molecules are considered to result in broadly scattered values for both negative and positive reaction probes, even in the absence of any specific solvent effects.

The charges at the hydrogen atom in the H-X molecules are free from hyperconjugative interaction,[7] while σ- and π-interactions between substituent and methyl group in monosubstituted methanes occur in the same fashion as in monosubstituted benzenes.[27] Then, it is interesting to compare the $\delta\Delta E$ values in some series having π-character with the $\delta\Delta E$ values in the series **1**.

Figure 3 shows the plots of the $\delta\Delta E$ values in the series **3**, **2**, and monosubstituted benzenes *vs.* those in the series **4** using a negative point charge perturbation, respectively. The lines shown in Fig. 3 are those drawn through dipole substituent and hydrogen atom.

As pointed out by Streitwieser *et al.*,[12] the dipole substituent is a substituent having only "field effect," and the substituents which deviate from the line may be accompanied by some additional effects such as polarization and resonance effects. Since the direct resonance interaction with perturbing negative charge is impossible in the systems **2**—**4**, the deviation from

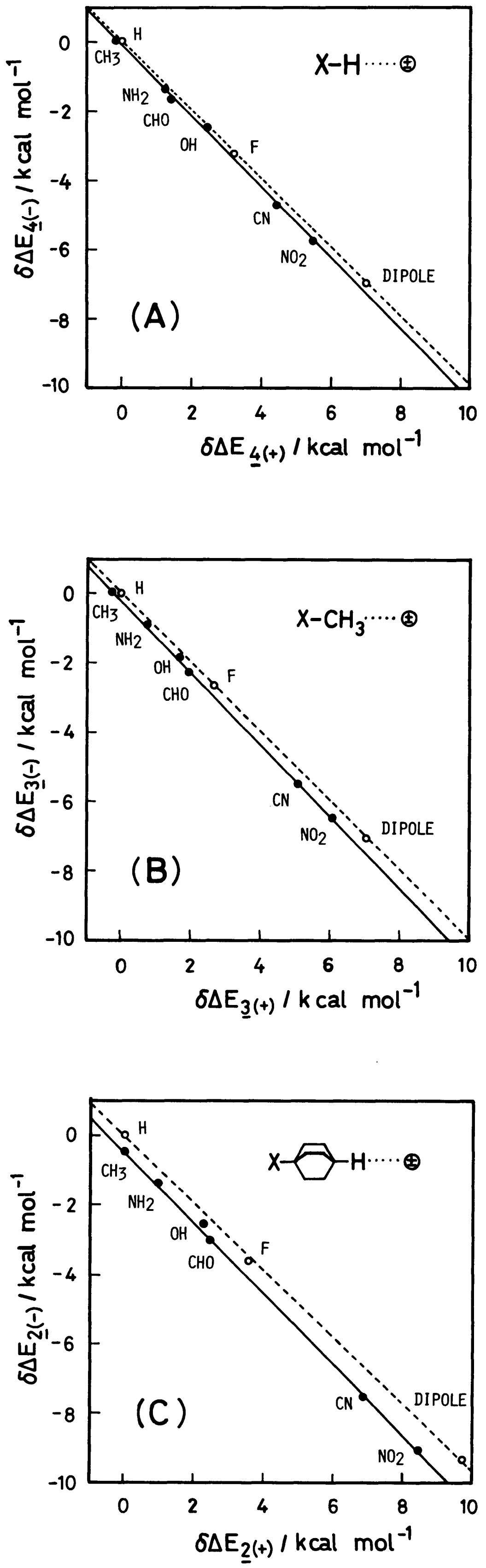

Fig. 2. Plots of isodesmic reaction energies ($\delta\Delta E$) for the aliphatic series perturbed with the point charges, (A) in the series **4**, (B) in the series **3**, and (C) in the series **2**.

Table 6. Comparison between $\delta\Delta E$ and W_p or σ_F and σ_I(gas)

Basis set	Model system	W_p^a)		σ_F^b)		σ_I(gas)^c)	
		Slope	r	Slope	r	Slope	r
STO-3G	**4**(−)	0.849	0.989	−8.61	0.976	−7.65	0.966
4-31G	**4**(−)	0.873	0.991	−12.68	0.994	−11.34	0.990
STO-3G	**4**(+)	0.822	0.984	8.41	0.980	7.44	0.966
4-31G	**4**(+)	0.845	0.983	12.77	0.997	11.35	0.988
STO-3G	**3**(−)	0.835	0.991	−9.42	0.926	−8.63	0.949
4-31G	**3**(−)	0.873	0.990	−14.72	0.973	−13.41	0.989
STO-3G	**3**(+)	0.790	0.986	9.08	0.939	8.28	0.958
4-31G	**3**(+)	0.807	0.976	14.54	0.981	12.12	0.999_9
STO-3G	**2**(−)	0.994	0.993	−13.01	0.926	−11.85	0.944
STO-3G	**2**(+)	0.946	0.989	12.62	0.940	11.45	0.953

a) $W_p = -ae(p\cos\theta/r^2)$, where a is slope. b) Refs. 1d and 6b. c) Ref. 1f.

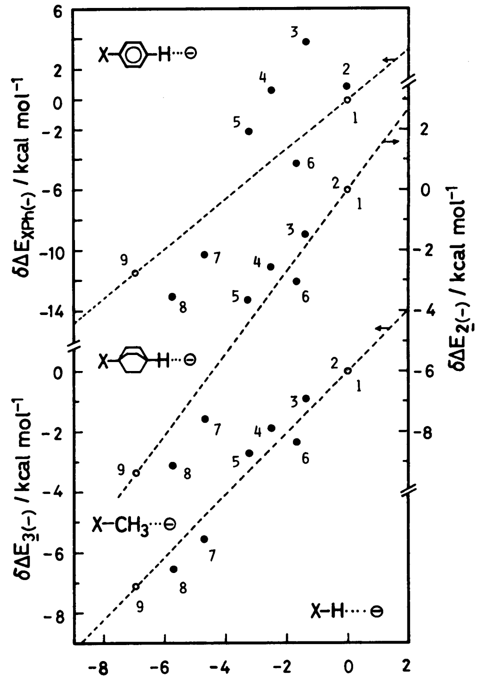

Fig. 3. Plots of the $\delta\Delta E$ in the series **3**, **2**, and monosubstituted benzenes *vs*. those in the series **4** using a negative point charge. 1: H, 2: CH_3, 3: NH_2, 4: OH, 5: F, 6: CHO, 7: CN, 8: NO_2, 9: Dipole.

the line shown in Fig. 3 must be attributed to the interaction of pseudo π-orbital of the methyl in the series **3** or alkyl group in the series **2** with appropriate orbital on the substituents.

Strong π-interaction is observed in the monosubstituted benzenes. For this negative point charge perturbation with substituted benzenes, the π-electron-donating groups such as fluoro, hydroxyl, amino, and methyl groups show a remarkable resonance destabilization, whereas the π-electron-withdrawing groups such as nitro, cyano, and formyl groups exhibit resonance stabilization.

However, deviation of electron-donating substituents from the line exhibits a different trend in aliphatic and aromatic series. From these analyses, it is concluded that pure field parameters for various substituents should reasonably be determined from the energy changes for the series of X–H··(±) system. Detailed analyses are in progress.

Finally, the correlation coefficients and slopes of the correlations between isodesmic energy changes ($\delta\Delta E$) and electrostatic energies (W_p) or various field parameters are summarized in Table 6. The σ_I(gas) values are those determined from acidities of phenols in gas phase.[2]

It is seen from Table 6 that the correlation coefficients using calculated electrostatic field energies (W_p) are generally quite good for all isodesmic energy changes. Correlations between $\delta\Delta E$ and σ_F or σ_I(gas) are generally better in the cases calculated at the 4-31G level than those calculated at the STO-3G level.

By the application of *ab initio* MO calculation, it was concluded that the field parameters, σ_I(gas), which were obtained from gas-phase acidities, can accurately be reproduced by $\delta\Delta E$ calculated at the 4-31G basis set. Thus, σ_I(gas) is a good measure of field effect in gas phase and *ab initio* calculation at the 4-31G basis set is the most suitable to examination of substituent effect, although the calculation is limited to rather small molecules for the present.

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