The Ab Initio Modeling of Hammett-Type Correlations. The Separation of Inductive Effects from Mesomeric Effects in Aromatic Systems

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Substituent effects have been modeled using both substituted hydrogens and substituted benzenes perturbed with point charges in order to separate the inductive (field) effect from the mesomeric effect with the use of ab initio techniques. Several pure dipole 'substituents' have been introduced to derive the scale of inductive effects common to both aliphatic and aromatic systems. In the above systems the interaction energies have been estimated by dividing into electrostatic interaction and polarization. Calculations with the use of 4-31G basis set show satisfactory correlations with the experimentally determined substituent constants. The propriety of the present approach has also been examined for the gas-phase acidities of phenols.

Recently substituent effects in Hammett correlations have been investigated by Streitwieser et al. with the use of STO-3G basis set ab initio techniques,[1] where substituted benzenes are perturbed with pure point charges in order to model the nonbonded reaction center. They have concluded that most substituents have essentially the same polarizability and that they are, therefore, independent of the reaction-center-charge type.

They have, however, made no explicit estimate of the electrostatic interaction (ES) and polarization (PL) between substituent and probe. Comparison with experimentally determined substituent constants has also shown serious discrepancies in the substituents, such as Cl, CF_3, CHO, and $COCH_3$.

On the other hand, years of analyses of Hammett-type correlations have led to a separation of the inductive (field) effects from the mesomeric (resonance) effects in aromatic systems.[2] It has a priori been based on an implicit consensus that the inductive effect of a substituent is uniformly transmitted to the reaction center independently of any structure variation in the parent compounds throughout aliphatic and aromatic systems, while the mesomeric effect varies greatly depending on the extent to which the reaction center interacts with the substituent.

Several experimental and theoretical attempts have been made to derive the standard scale of the inductive effect inherent in each substituent itself.[2,3] Inconsistencies between the scales appear to be a consequence of how well the interactions other than the electrostatic interaction between substituent and reaction center or probe (namely, such effects as resonance, hyperconjugation, and polarization) are eliminated in the aliphatic systems adopted to derive the scale.

One of the major problems remaining in separating the inductive effects from mesomeric effects is to clarify theoretically whether or not such a standard scale of inductive effect inherent in each substituent can be derived. In order to settle this problem using ab initio techniques, we have chosen isodesmic reactions for the systems of substituted hydrogens, HX, and substituted benzenes, C_6H_5X, perturbed with point charges (+)/and(−)···HX (**1**) and (+)/and(−)····C_6H_5X (**2**), respectively, where point charges are located on the molecular axis in the former and in the para-direction in the latter.

The advantage of Systems **1** and **2** as the reference systems is that the HX molecules in System **1** contain no mesomeric interactions and that no mesomeric effects can be due to direct mesomerc interactions with the perturbing site in System **2**.

In the above systems, several pure dipole 'substituents' carrying different charges have been introduced in order to model pure 'inductive' (field) effect substituents and to make a standard scale of the inductive effect, one common to both aliphatic and aromatic systems. The electronic interactions between substituent and probe have been estimated by dividing into electrostatic interaction (ES) and polarization (PL) by utilizing the energy decomposition analysis.[4]

Furthermore, in order to ascertain the propriety of our approach we have attempted to separate the inductive effect from the mesomeric effect in the gas-phase acidities of phenols,[5] in which there exist strong direct mesomeric interactions between the substituent and the reaction center.

Calculation Methods

Calculations were performed using the IMSPAK series[6] of the computer program at the 4-31G basis level, in which the procedure of energy-decomposition analysis[4] was included. The procedure may be briefly described as follows. We express the Hartree–Fock (HF) wave function for the isolated molecule as ψ^0 and its energy as E_0. If we denote the HF wave function of the molecule perturbed with a point charge and its energy as ψ^1 and E_1 respectively, the HF total interaction energy, ΔE_{SCF}, is given by:

$$\Delta E_{SCF} = E_1 - E_0$$

The electrostatic interaction (ES) is the interaction

between the undistorted electron distribution of the molecule and the point charge. In our scheme, ES is calculated as the difference between E_2 and E_0, E_2 being the energy associated with the wave function ψ^0:

$$ES = E_2 - E_0$$

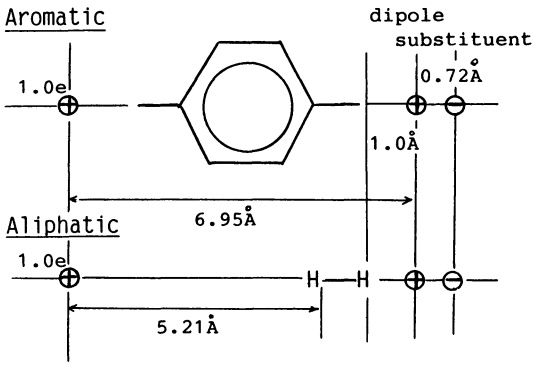
The polarization (PL) is the effect of the distortion of the electron distribution of the molecule by the point charge. Then the difference E_1-E_2 corresponds to the energy change due to the polarization by the point charge:

$$PL = E_1 - E_2$$

The geometries of the benzenoid rings were maintained constant for each substituent; r_{C-C}=1.39 Å r_{C-H}=1.083 Å, and all angles=120°. The geometries of the substituent groups were taken from the experimentally determined values.[7] In the geometry of a pure dipole 'substituent', we have taken the same geometry as Streitwieser et al.[1] used; that is, a positive pole carrying a charge (1.0e) was located at 1 Å from the hydrogen atom of the parent compound, and the distance between positive and negative poles was taken to be 0.72 Å so as to coincide with the dipole moment experimentally determined for nitromethane (3.5 D). The other dipole substituents were set up to carry 0.3e and 0.5e respectively.

The unit point charge of the probe was located at 1 Å from the hydrogen atom along the C–H bond in the para-position in C_6H_5X and at 5.21 Å in HX molecules so as to make their values equal to the distance from the positive pole of the dipole substituent in System **2** (see the Scheme 1 below).

As the means of evaluating the substituent effects on the above perturbed molecules, the following isodesmic reaction was used:



Scheme 1.

$$\underset{A}{RX} + (\pm)\cdots\underset{B}{RH} \rightarrow \underset{C}{RH} + (\pm)\cdots\underset{D}{RX} \quad (1)$$

where X represents a substituent, and RH, a parent compound. The total change in the energy($\delta\Delta E_{SCF}$) for the isodesmic reaction was obtained using Eq. 2. It corresponds to a substituent effect for the perturbed system:

$$\delta\Delta E_{SCF}=(E_C + E_D) - (E_A + E_B)=(E_D - E_A) - (E_B - E_C)=\Delta E_{subst} - \Delta E_H \quad (2)$$

A negative value in $\delta\Delta E_{SCF}$ corresponds to the energy which is stabilized compared with that of the parent compound.

Results and Discussion

The total energies, E_0, E_1, and E_2, are summarized in Tables 1 and 4. The respective energy changes, $\Delta E_{SCF}(\Delta E_{subst})$, are summarized in Tables 2 and 5, where they are also shown divided into electrostatic interactions (ES) and polarization (PL). As may clearly be seen from the tables, the contributions of PL

Table 1. Total Energies of Substituted Hydrogens (HX) and Those Perturbed with Point Charges (hartree)

Substituent	HX	Point charge (+)		Point charge (−)	
	E_0	E_1	E_2	E_1	E_2
1. CH_3	−40.13758	−40.13785	−40.13742	−40.13815	−40.13774
2. H	−1.12676	−1.12675	−1.12649	−1.12729	−1.12703
3. NH_2	−56.10365	−56.10128	−56.10098	−56.10659	−56.10631
4. OCH_3	−114.86845	−114.86403	−114.86365	−114.87362	−114.87325
5. CHO	−113.69106	−113.68696	−113.68651	−113.69606	−113.69562
6. $COCH_3$	−152.68400	−152.68115	−152.68058	−152.68796	−152.68742
7. CF_3	−336.33417	−336.32708	−336.32675	−336.34190	−336.34159
8. F	−99.88727	−99.87943	−99.87928	−99.89539	−99.89525
9. Cl	−459.56313	−459.55712	−459.55671	−459.56994	−459.56954
10. CN	−92.73133	−92.72297	−92.72252	−92.74058	−92.74015
11. NO_2	−204.27804	−204.26709	−204.26674	−204.28966	−204.28933
12. Dipole(1.0e)	−1.84658	−1.83566	−1.83543	−1.85798	−1.85775
13. Dipole(0.5e)	−1.29906	−1.29357	−1.29331	−1.30506	−1.30481
14. Dipole(0.3e)	−1.18511	−1.18181	−1.18155	−1.18893	−1.18868

Table 2. Energies of Electrostatic Interactions (ES) and Polarizations (PL) of Substituted Hydrogens (HX) Perturbed with Point Charges (kcal mol^{-1})

Substituent	Point charge (+)			Point charge (−)		
	ΔE_{SCF}[a)]	ES[a)]	PL[a)]	ΔE_{SCF}[a)]	ES[a)]	PL[a)]
1. CH_3	−0.17	0.10	−0.27	−0.36	0.10	−0.26
2. H	0.01	0.17	−0.16	−0.33	−0.17	−0.16
3. NH_2	1.49	1.68	−0.19	−1.85	−1.67	−0.18
4. OCH_3	2.77	3.01	−0.24	−3.24	−3.01	−0.23
5. CHO	2.57	2.85	−0.28	−3.14	−2.86	−0.28
6. $COCH_3$	1.79	2.15	−0.36	−2.49	−2.15	−0.34
7. CF_3	4.45	4.66	−0.21	−4.85	−4.66	−0.19
8. F	4.92	5.01	−0.09	−5.10	−5.01	−0.09
9. Cl	3.77	4.03	−0.26	−4.27	−4.02	−0.25
10. CN	5.25	5.53	−0.28	−5.81	−5.53	−0.28
11. NO_2	6.87	7.09	−0.22	−7.29	−7.09	−0.20
12. Dipole(1.0e)	6.85	7.00	−0.15	−7.15	−7.01	−0.14
13. Dipole(0.5e)	3.44	3.60	−0.16	−3.77	−3.60	−0.17
14. Dipole(0.3e)	2.07	2.23	−0.16	−2.40	−2.24	−0.16

a) Differences at two places below the decimal points show the limits of the accuracy of the present calculations.

Table 3. Isodemic Energies of Substituted Hydrogens (HX) Perturbed with Point Charges (kcal mol^{-1})

Substituent	Point charge (+)			Point charge (−)		
	$\delta\Delta E_{SCF}$	δES	δPL	$\delta\Delta E_{SCF}$	δES	δPL
1. CH_3	−0.2	−0.1	−0.1	0.0	0.1	−0.1
2. H	0.0	0.0	0.0	0.0	0.0	0.0
3. NH_2	1.5	1.5	0.0	−1.5	−1.5	0.0
4. OCH_3	2.8	2.8	0.0	−2.9	−2.8	−0.1
5. CHO	2.6	2.7	−0.1	−2.8	−2.7	−0.1
6. $COCH_3$	1.8	2.0	−0.2	−2.2	−2.0	−0.2
7. CF_3	4.4	4.5	−0.1	−4.5	−4.5	0.0
8. F	4.9	4.8	0.1	−4.8	−4.8	0.0
9. Cl	3.8	3.9	−0.1	−3.9	−3.9	0.0
10. CN	5.2	5.4	−0.2	−5.5	−5.4	−0.1
11. NO_2	6.9	6.9	0.0	−7.0	−6.9	−0.1
12. Dipole(1.0e)	6.8	6.8	0.0	−6.8	−6.8	0.0
13. Dipole(0.5e)	3.4	3.4	0.0	−3.4	−3.4	0.0
14. Dipole(0.3e)	2.1	2.1	0.0	−2.1	−2.1	0.0

Table 4. Total Energies of Monosubstituted Benzenes (C_6H_5X) and Those Perturbed with Point Charges (hartree)

Substituent	C_6H_5X	Point charge (+)		Point charge (−)	
	E_0	E_1	E_2	E_1	E_2
1. CH_3	−269.35678	−269.41059	−269.31329	−269.46820	−269.40033
2. H	−230.37710	−230.42667	−230.33085	−230.49016	−230.42333
3. NH_2	−285.32524	−285.38428	−285.28645	−285.43214	−285.36402
4. OCH_3	−344.07902	−344.13186	−344.03450	−344.19152	−344.12353
5. CHO	−342.92560	−342.96163	−342.86480	−343.05460	−342.98640
6. $COCH_3$	−381.90433	−381.94435	−381.84706	−382.03006	−381.96160
7. CF_3	−565.56236	−565.59608	−565.50083	−565.69051	−565.62389
8. F	−329.10717	−329.14647	−329.05174	−329.22877	−329.16260
9. Cl	−688.77574	−688.81668	−688.72013	−688.89871	−688.83135
10. CN	−321.96928	−321.99981	−321.90317	−322.10325	−322.03538
11. NO_2	−433.51752	−433.53859	−433.44307	−433.65925	−433.59197
12. Dipole(1.0e)	−231.09762	−231.12420	−231.03003	−231.23117	−231.16520
13. Dipole(0.5e)	−230.54858	−230.58686	−230.49185	−230.67171	−230.60531
14. Dipole(0.3e)	−230.43472	−230.47758	−230.38224	−230.55378	−230.48720

Table 5. Energies of Electrostatic Interactions (ES) and Polarizations (PL) of Substituted Benzenes (C_6H_5X) Perturbed with Point Charges (kcal mol^{-1})

Substituent	Point charge (+)			Point charge (−)		
	ΔE_{SCF}[a]	ES[a]	PL[a]	ΔE_{SCF}[a]	ES[a]	PL[a]
1. CH_3	−33.76	27.29	−61.05	−69.93	−27.33	−42.60
2. H	−31.10	29.02	−60.12	−70.94	−29.01	−41.93
3. NH_2	−37.05	24.34	−61.39	−67.08	−24.33	−42.75
4. OCH_3	−33.15	27.93	−61.08	−70.61	−27.93	−42.68
5. CHO	−22.61	38.15	−60.76	−80.96	−38.16	−42.80
6. $COCH_3$	−25.12	35.94	−61.06	−78.91	−35.94	−42.97
7. CF_3	−21.16	38.61	−59.77	−80.43	−38.62	−41.81
8. F	−24.66	34.78	−59.44	−76.30	−34.78	−41.52
9. Cl	−25.69	34.90	−60.59	−77.18	−34.90	−42.28
10. CN	−19.16	41.48	−60.64	−84.06	−41.48	−42.58
11. NO_2	−13.22	46.71	−59.93	−88.93	−46.71	−42.22
12. Dipole(1.0e)	−16.68	42.41	−59.09	−83.80	−42.40	−41.40
13. Dipole(0.5e)	−24.02	35.60	−59.62	−77.28	−35.60	−41.68
14. Dipole(0.3e)	−26.89	32.93	−59.82	−74.72	−32.94	−41.78

a) Differences at two places below the decimal points show the limits of the accuracy of the present calculations.

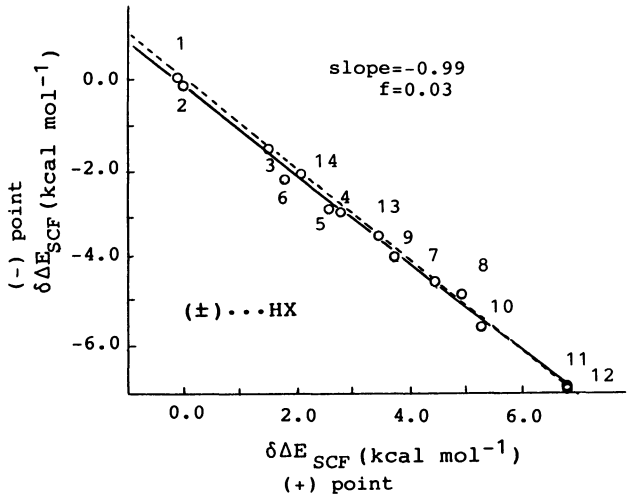
Table 6. Isodesmic Energies of Monosubstituted Benzenes (C_6H_5X) Perturbed with Point Charges (kcal mol^{-1})

Substituent	Point charge (+)			Point charge (−)		
	$\delta\Delta E_{SCF}$	δES	δPL	$\delta\Delta E_{SCF}$	δES	δPL
1. CH_3	−2.7	−1.7	−1.0	1.0	1.7	−0.7
2. H	0.0	0.0	0.0	0.0	0.0	0.0
3. NH_2	−6.0	−4.7	−1.3	3.9	4.7	−0.8
4. OCH_3	−2.1	−1.1	−1.0	0.3	1.1	−0.9
5. CHO	8.5	9.1	−0.6	−10.0	−9.1	−0.9
6. $COCH_3$	6.0	6.9	−0.9	−8.0	−6.9	−1.1
7. CF_3	9.9	9.6	0.3	−9.5	−9.6	0.1
8. F	6.4	5.8	0.6	−5.4	−5.8	0.4
9. Cl	5.4	5.9	−0.5	−6.2	−5.9	−0.3
10. CN	11.9	12.5	−0.6	−13.1	−12.5	−0.6
11. NO_2	17.9	17.7	0.2	−18.0	−17.7	−0.3
12. Dipole(1.0e)	14.4	13.4	1.0	−12.9	−13.4	0.5
13. Dipole(0.5e)	7.1	6.6	0.5	−6.3	−6.6	0.3
14. Dipole(0.3e)	4.2	3.9	0.3	−3.8	−3.9	0.1

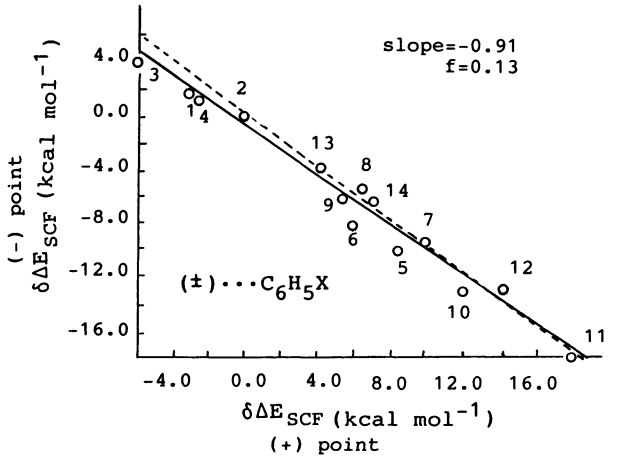
to the total interaction energies, ΔE_{SCF}, are small compared with those of ES, except for X=H and CH_3 in Systerm **1**, while those of PL are much more than those of ES in System **2**. However, the contributions of PL to the isodesmic energies ($\delta\Delta E_{SCF}$) (Tables 3 and 6) are almost the same in magnitude in the two systems; as a whole, their contributions to the substituent effects are small compared with those of ES.

According to the comments of Streitwieser et al.[1] the original assumptions for the Hammett equation were that the susbstituent constants are independent of the nature of the reactions and that a different charge center changes only the sign of the reaction constant. Strictly speaking, these assumptons are valid only in an approximate sense. The latter assumption should be restricted only to the electrostatic interactions because the contributions of PL act as a disturbing factor for the assumption, even in the present model systems, which are perturbed only with point charges.

Figure 1-(a) shows plots of the $\delta\Delta E_{SCF}$ values in System **1** perturbed with positive and negative charges, where the dotted line of a unit slope is drawn through the points for the δ ES values. The deviations from the line show the contributions of PL to the substituent effects. Such contributions can almost be ignored in System **1**. The solid line shows the correlation between the $\delta\Delta E_{SCF}$ values of the systems (the value of slope: −0.99, correlation coefficient: r=0.998, goodness of 'fit':[8] f=0.03). These results practically satisfy the original assumptions for the Hammett equation including the dipole 'substituents'; this means that System **1** can be used as a reference system to derive a standard scale of the inductive effect independent of the charge type of the probe. On the other hand, the contributions of PL to the substituent effects in System **2** are rather too large to ignore (Fig.1-(b)), and those perturbed with positive point chrges are a little larger than those perturbed with negative point charges (r=0.985, f=0.13). These results imply that the standard σ^0 values experimentally derived in cationic



(a)



(b)

Fig. 1. (a) Plots of the isodesmic energy changes ($\delta\Delta E_{SCF}$) for point charge perturbed substituted hydrogens (HX).
(b) Plots of the isodesmic energy changes ($\delta\Delta E_{SCF}$) for point charge perturbed para-substituted benzenes (C_6H_5X). The dotted line connects the point for δES with a slope of −1.00. The regression line shown corresponds to the open circles. The numbering corresponds to that in Tables 3 and 6, respectively.

systems must be somewhat different from those derived in anionic systems. Therefore, in order to derive experimentally the 'inherent' substituent constants, it is necessary to choose the system in which there exists no polarization contribution arising from charged probe centers and in which complicating solvent effects have been eliminated as much as possible. Recently several attempts have been performed to derive 'inherent' substituent constants by utilizing gas-phase reactions.[9] However, all the reactions thus far examined have carried charged probe centers and also contained additive resonance interactions between the substituents and the reaction center.

Therefore, up to the present, the σ_R^0 values redefined

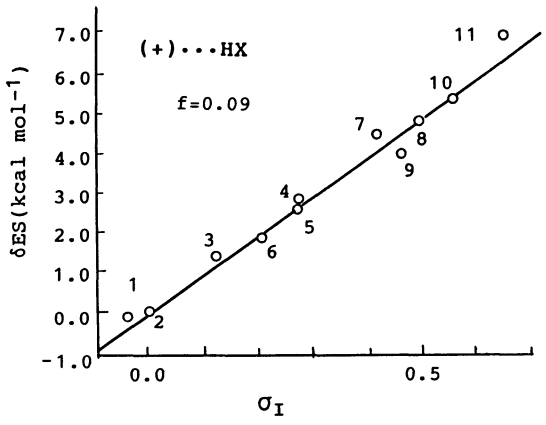


Fig. 2. Plots of δES against σ_I for the positive point charge perturbed substituted hydrogens (HX). The numbering corresponds to that in Table 3.

by Taft et al.[10] appear to be the nearest to the original assumptions for the Hammett equation; they have been determined on the basis of the substituent chemical shift, ^{13}C, at the para-position (C_p-SCS) of monosubstituted benzenes in diluted 'inert' solvents and, therefore, the ^{13}C 'probe' is a part of the 'neutral' aryl ring unperturbed by the charge. In the present analysis we will define the experimental 'inherent' substituent constants σ^0 (inh) using σ_I and σ_R^0 values determined by Taft et at.,[10] that is, $\sigma^0(\text{inh})=\sigma_I+\sigma_R^0$ (Table 2 in Ref. 10).

Figure 2 shows plots of the δ ES in System **1** against the σ_I values determined by Taft et al.,[10] where representative eleven substituents are chosen. The δES values obtained at 4-31G show a 'good' fit (r=0.989, f=0.09), while those at STO-3G show serious discrepancies in the substituents F, Cl, CF_3, CHO, and $COCH_3$.

Theoretical approaches to derive the field-effect parameter (σ_F) have also been performed by several workers, using the isodesmic reactions (NH_4^+/HX), measuring the polarization of a bond produced in an isolated moloecule by the HX molecule (HH/HX), and using the electrostatic potentials ($EP_{(HX)}$) obtained from the interaction of a positive charge at a determined geometry from a HX molecule, and so on.[3b] The third approach is essentially identical with that of Streitwieser et al.[1] The $\sigma_{F(theo)}$ values recommended by Topsom are summarized in Ref. 3b (Table 19 on p. 166). The correlation of δES and $\sigma_{F(theo)}$ values showed a 'good' fit (r=0.988, f=0.10, n=11), while that of δES and $EP_{(HX)}$ was properly excellent (r=0.997, f=0.05, n=9).

Figure 3 shows plots of the δES against values $\sigma^0(\text{inh})=(\sigma_I+\sigma_R^0)$[10] in System **2**. The δES values obtained at 4-31G also show a 'fair' fit for the eleven substituents (r=0.988, f=0.13). In this case, too, values obtained at STO-3G show serious discrepancies for the substituents, CF_3, CHO, $COCH_3$, and Cl. The correla-

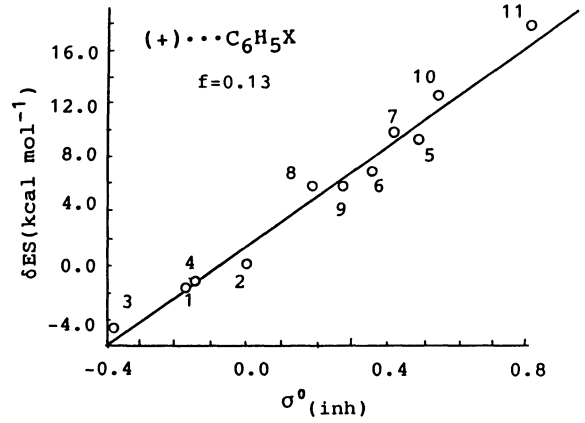


Fig. 3. Plots of δES against σ^0(inh)($=\sigma_I+\sigma_R^0$) for para-substituted benzenes (C_6H_5X). The numbering corresponds to that in Table 6.

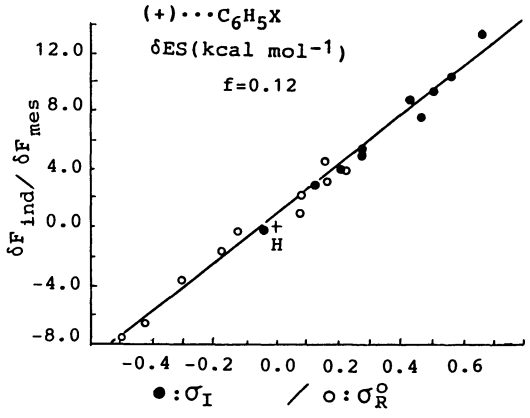


Fig. 5. Correlation between δF_{ind} and δF_{mes} against $\sigma_{I(inh)}$ and σ_R^0, respectively, on the same regression line.

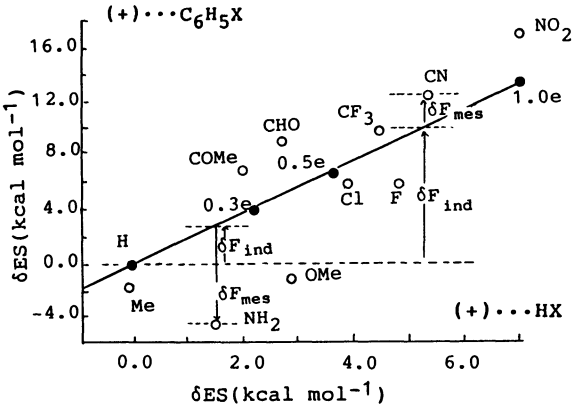


Fig. 4. Separation of inductive effects from mesomeric effects. Plots of δES for the positive point charge perturbed substituted hydrogens (HX) and benzenes (C_6H_5X). A regression line shows the correlation between hydrogen and dipole substituents. The deviations from the line (δF_{ind} and δF_{mes}) correspond to the inductive and mesomeric contributions of substituents in C_6H_5X.

tion between the $\delta\Delta E_{SCF}$ values which contain the contribution of PL and σ^0(inh) also shows a 'fair' fit (r=0.985, f=0.16 and r=0.988, f=0.13 for both systems, perturbed with positive and negative point charges respectively).

Figure 4 shows plots of the δES values in System **2** against those in System **1** perturbed with the positive point charge, where the correlation line is drawn for three 'dipole' substituents and hydrogen to derive the scale of inductive effects in aromatic systems (r=0.999, f=0.03). The intersecting point of a perpendicular line drawn from a substituent with the correlation line corresponds to its inductive effect, because it contains no mesomeric interactions and it is a quantity directly proportional to the inductive effect in System **1**. Points above the line correspond to π-destabilizing groups, while points below the line correspond to π-stabilizing groups. Thus, deviations from the correlation line correspond to the 'mesomeric effects' in the Hammett equations.

There can not be any direct mesomeric interactions between a substituent and a probe in System **2**. Therefore, the mesomeric contribution must be attributed to the field effect caused by the distribution of charges on the molecule, a distribution which stems from a strong interaction between the π-system of the benzene ring and suitable orbitals on the substituent group. Hereafter, we will abbreviate the former effect as δF_{ind}, and the latter, as δF_{mes}. The latter is expected to be proportional to the experimentally determined σ_R^0 values. The values of δF_{ind} and δF_{mes} are summarized in Table 9, while those of σ_I, σ_R^0, and σ_R^- (g)[5] are cited in Table 10.

Figure 5 shows plots of δF_{ind} against σ_I and those of δF_{mes} against σ_R^0. The correlation shows a 'fair' fit (r=0.991, f=0.12) on the same correlation line; no substituents examined show any serious deviations from the correlation line.

The theoretical σ_R^0 values have also been derived by the calculation of the overall π-electron transfer, $\sum q_\pi$, in monosubstituted benzenes and ethylenes.[3b] The correlation of δF_{mes} with the $\sigma_{R(theo)}^0$ values was 'fair' (r=0.986, f=0.18, n=11), while δF_{mes} was well correlated with the experimental σ_R values summarized by Topsom (Table 1 in p. 16 of Ref. 3b) (r=0.992, f=0.13, n=11).

Strictly speaking from the experimental point of view, a common scale of inductive effects exists, of course, only in an approximate sense. In the present approach, a common scale of inductive effects throughout the aliphatic and aromatic systems has been obtained by the introduction of the pure dipole 'substituents'. Our results imply that the hypothetical dipole of the substituent group in the aromatic system which corresponds to that of the aliphatic system can be estimated from the correlation line. Although the pure dipole 'substituents' are undoubtedly not actual,

the existence of the common scale is guaranteed since they are intrinsically of an abstract nature.

The propriety of the present approach has further been investigated for the gas-phase acidities of *p*-substituted phenols.[5] The corresponding isodesmic reaction is:

$$XC_6H_4OH + C_6H_5O^- \rightarrow XC_6H_4O^- + C_6H_5OH \quad (3)$$

where the geometries of the parent compounds, C_6H_5OH and $C_6H_5O^-$, were optimized by means of the energy-gradient method at the 3-21G level,[11] while those of the substituent groups were taken from the experimentally determined values.

The total energies calculated at 4-31G for *p*-substituted phenols and phenoxide ions are summarized in Table 7. The isodesmic energies ($\delta\Delta E_{SCF}$) are summarized in Table 8 and compared with the experimentally obtained values.[12] The calculations considerably overestimated the observed substituent effects ($\delta\Delta G^0$ (g) kcal mol^{-1}). As may clearly be seen from Fig. 6, however, the correlation between observed and calculated values shows almost a 'good' fit (r=0.993, f=0.11) for all the substituents measured.

Table 7. Total Energies of Phenols (XC_6H_4OH) and Phenoxide Ions ($XC_6H_4O^-$) (hartree)

Substituent	XC_6H_4OH	$XC_6H_4O^-$
1. CH_3	−344.06472	−343.46771
2. H	−305.12403	−304.53078
3. NH_2	−360.06859	−359.46623
4. OCH_3	−418.83220	−418.23581
5. OH	−379.86506	−379.27200
6. CHO	−417.67369	−417.10948
7. CF_3	−640.31004	−639.73952
8. F	−403.85238	−403.26757
9. CN	−396.71666	−396.15618
10. NO_2	−508.26620	−507.71714
11. Dipole(1.0e)	−305.84254	−305.27846
12. Dipole(0.5e)	−305.29428	−304.71565
13. Dipole(0.3e)	−305.18086	−304.59638

Table 8. Comparison of Experimental Values with Theoretical Calculations of the Relative Gas-Phase Acidities of Para-Substituted Phenols (kcal mol^{-1})

Substituent	$\delta\Delta G^0$(g)	$\delta\Delta E_{(SCF)}$
1. CH_3	1.1	2.4
2. H	0.0	0.0
3. NH_2	3.3	5.7
4. OCH_3	1.2	2.0
5. OH	1.2	−0.1
6. CHO	−15.8	−18.2
7. CF_3	−11.9	−14.1
8. F	−2.3	−5.3
9. CN	−16.6	−20.6
10. NO_2	−20.9	−27.7
11. Dipole(1.0e)	—	−18.3
12. Dipole(0.5e)	—	−9.2
13. Dipole(0.3e)	—	−5.5

In order to separate the inductive effects from the mesomeric effects in this case, too, the pure dipole 'substituents' have been introduced in the same way as in System **2**. Figure 7 shows the plots of the $\delta\Delta E_{SCF}$ values against the δES values in System **1** perturbed with negative point charge, where the correlation line

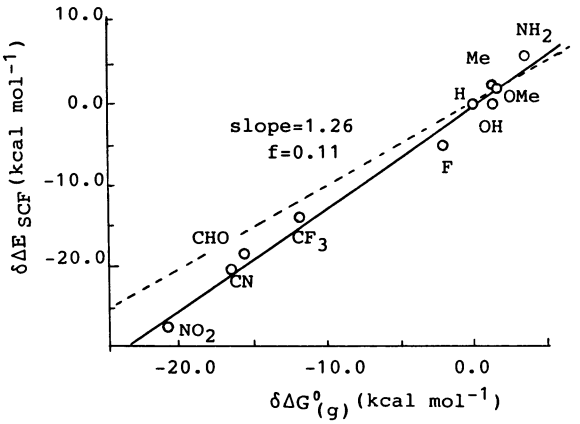


Fig. 6. Correlation of $\delta\Delta E_{SCF}$(calcd) against $\delta\Delta G^0$(g)-(obsd) for the isodesmic reactions for *p*-substituted phenols. The dotted line shows a unit slope.

Table 9. Values of δF_{ind} and δF_{mes} in Monosubstituted Benzenes (C_6H_5X), and Values of Inductive and Mesomeric Components ($\delta\Delta E_{ind}$ and $\delta\Delta E_{mes}$) in Isodesmic Reactions of *p*-Substituted Phenols (kcal mol^{-1})

Substituent	C_6H_5X		XC_6H_4OH	
	δF_{ind}	δF_{mes}	$\delta\Delta E_{ind}$	$\delta\Delta E_{mes}$
1. CH_3	−0.1	−0.3	0.2	2.2
2. H	0.0	0.0	0.0	0.0
3. NH_2	2.9	−7.6	−4.0	9.8
4. OCH_3	5.5	−6.5	−7.6	9.6
5. CHO	5.2	4.0	−7.2	−11.1
6. $COCH_3$	3.8	3.1	—	—
7. CF_3	8.6	1.0	−12.0	−2.1
8. F	9.3	−3.5	−13.0	7.7
9. Cl	7.4	−1.5	—	—
10. CN	10.3	2.2	−14.4	−6.2
11. NO_2	13.3	4.4	−18.6	−9.2

Table 10. Values of σ_I, σ_R^0, and σ_R^-(g)

Substituent	σ_I	σ_R^0	σ_R^-(g)
CH_3	−0.04(—)	−0.13	−0.09
H	0.00(0.00)[a]	0.00	0.00
NH_2	0.12(0.10)	−0.50	−0.24
OCH_3	0.27(0.25)	−0.42	−0.29
CHO	0.27(0.32)	0.22	0.46
$COCH_3$	0.20(0.22)	0.16	0.43
CF_3	0.42(0.43)	0.08	0.15
F	0.50(0.50)	−0.31	−0.38
Cl	0.46(0.46)	−0.18	−0.17
CN	0.56(0.58)	0.08	0.23
NO_2	0.65(0.65)	0.15	0.41

a) Values in parentheses are cited from Ref. 5.

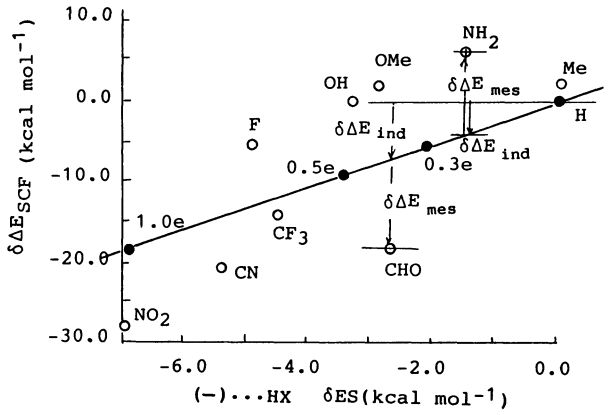


Fig. 7. Separation of inductive effects from mesomeric effects. Plots of the isodesmic energy changes ($\delta\Delta E_{SCF}$) for *p*-substituted phenols against δES for negaitive point charge perturbed hydrogens. A regression line shows the correlation between hydrogen and dipole substituents. The deviations from the line ($\delta\Delta E_{ind}$ and $\delta\Delta E_{mes}$) correspond to the inductive and mesomeric contributions of substituents.

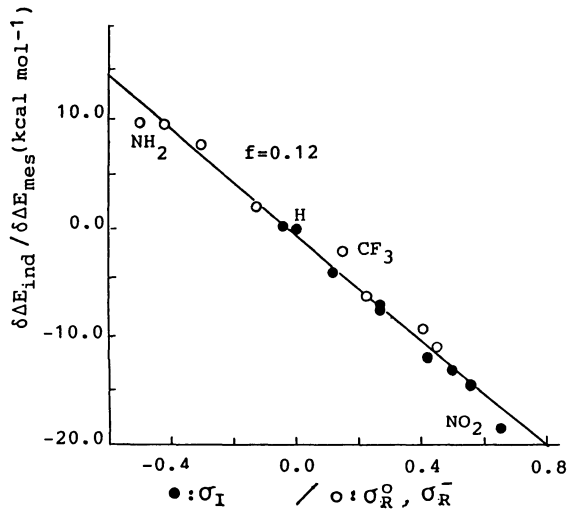


Fig. 8. Correlation between $\delta\Delta E_{ind}$ and $\delta\Delta E_{mes}$ against σ_I and σ_R^0(for EDG)/σ_R^-(g)(for EWG), respectively, on the same correlation line.

is drawn for three dipole 'substituents' and hydrogen. The correlation is very good (r=1.000, f=0.001). By the same procedure as that described in System **2**, the inductive effects ($\delta\Delta E_{ind}$) can be estimated. The points above the line correspond to π-destabilizing groups (electron donating groups; EDG), while the points below the line correspond to π-stabilizing groups (electron withdrawing groups; EWG). Thus, deviations from the correlation line correspond to mesomeric effects ($\delta\Delta E_{mes}$). Therefore, the deviations above the line may be expected to be proportional to the σ_R^0 values, while the downward deviations may be expected to be proportional to the σ_R^- (g) values.

Figure 8 shows plots of $\delta\Delta E_{ind}$ against σ_I and also plots of $\delta\Delta E_{mes}$ against σ_R^0 for EDG and against σ_R^- (g) for EWG. The correlation shows a 'fair' fit (r=0.992, f=0.12) on the same correlation line.[13]

The present approach provides us with theoretical grounds for the separation of the inductive effect from the mesomeric effect in aromatic systems. It can also be applied to gas-phase reactions in which the reaction center carries a positive charge. We will present the results of analyses of these in succeeding papers.

The numerical calculations were carried out on a FACOM M-382 computer at the Nagoya University Computation Center.

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12) Calculations were also performed for some phenoxide ions with 4-31+G, where a diffuse sp function (exponent: 0.068) is taken into account. Althoguh the total energies were improved (for example, X=H; −304.54540, X=NO_2; −507.72919 (hartree)), the isodesmic energy was not so much affected ($\delta\Delta E_{SCF}$ for X=NO_2: −26.1 kcal mol^{-1}).

13) When σ_R^- (g) values were used for the EDG, the correlation partly collapsed for F and NH_2 (r=0.986, f=0.16).