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A THEORETICAL ANALYSIS OF HAMMETT'S σ

THE EVALUATION OF THE SUBSTITUENT CONSTANTS BY THE CALCULATED PHYSICAL CONSTANTS

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Abstract—We have evaluated substituent constants using the two calculated physical constants for the monosubstituted phenylacetic and naphthoic acids systems. The degree of the inductive and resonance effects in the substituent constant, the correspondence of the parameters between in the present study and in the FM method, an ionic character of the ϕ - X bond, and a method of parameter evaluation are also discussed.

WE HAVE obtained good correlations between the substituent constants and various physical constants in the preceding paper in this series. There it was confirmed that correlations exist having the correlation coefficient 0·92 between σ_I and A (charge of a substituent) and between σ_R^0 and E_c (charge-transfer energy) and so on. The method of evaluation of A and E_c were described.

Here, the values of the substituent constants will be evaluated by the use of A and E_c and a vector potential (A/r^2) of a substituent and E_c. The comparison of the calculated values of σ_{ij} are shown in the discussion. One is evaluated with the above method by us and another by the FM method calculated by Dewar *et al.*[1]

RESULTS

The evaluation of Taft's σ_p^0 *by the use of* A *and* $|E_c|$.[2] A is the charge of a substituent and also the degree of migration of an electron between the substituent and the aromatic ring. We may assume that the field effect of the substituent on the reaction center is given approximately by **a**A, **a** being a measure of the effect in the phenylacetic and the naphthoic acids systems. $|E_c|$ represents the degree of resonance between the substituent and the benzene and the naphthalene rings. It may be assumed that the resonance effect of the substituent on the reaction center is given approximately by $\mathbf{b}|E_c|$ in the systems. **b** is a measure of the resonance effect. σ^0 is given by

$$\sigma^0 = \mathbf{a}A + \mathbf{b}|E_c| \tag{1}$$

The values of **a** and **b** were evaluated by the method of least-squares for the given substituents. The obtained equation is

$$\sigma_p^0 = 0{\cdot}255A - 0{\cdot}066|E_c| + 0{\cdot}029 \tag{2}$$

The signs + and − are taken for the acceptor and the donor groups, respectively. The correlation between the obtained and the calculated values for σ_p^0 is shown in Fig 1.

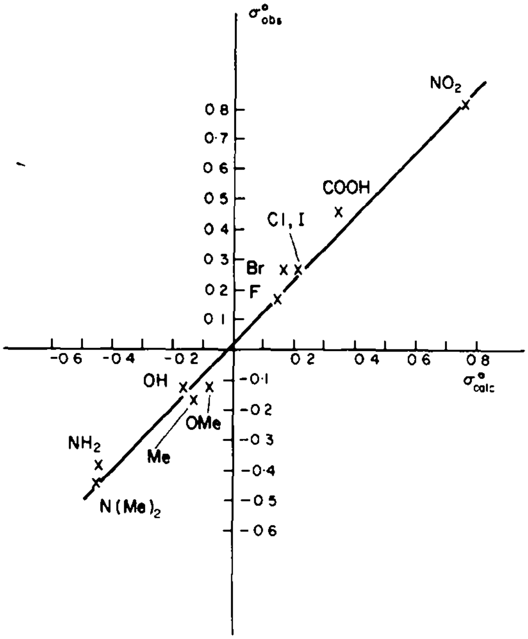

FIG 1. The plot of σ^0 (obs) vs σ^0 (calc) by using A and $|E_c|$

The evaluation of the σ_p^0-values by the use of A *and* μ *(mes).* It was confirmed in the preceding paper that there are good correlations between Yukawa's σ_π^{+}[3] and the mesomeric moment μ (mes). μ (mes) represents the degree of the resonance between a substituent and the benzene ring. We may assume that the resonance effect of the substituent on the reaction center is given approximately by **b**μ (mes). σ_p^0 is given by

$$\sigma_p^0 = \mathbf{a}A + \mathbf{b}\mu\,(\text{mes})$$

The obtained equation is

$$\sigma_p^0 = 0{\cdot}217A + 0{\cdot}354\mu\,(\text{mes}) + 0{\cdot}128 \tag{3}$$

The calculated values of σ_p^0 by the use of Eq 3 are shown in Table 1 and Fig 2.

If A is the charge of a substituent, then, A/r_{kl}^2 is the vector potential which affects the reaction center. k and l are the centers of gravity of the charges for the COOH group and of the substituent, respectively. r_{kl} is the distance between the two centers k and l. $\mathbf{a}A/r_{kl}^2$ represents the field effect more accurately than **a**A. We evaluate the σ^0-, σ_{ij}- and Δpk_{ij}-values using $\mathbf{a}A/r_{kl}^2$ as the field effect and $\mathbf{b}\,|E_c|$ as the resonance effect for the monosubstituted phenylacetic and naphthoic acids systems. **a** is a measure of the field effect and **b** is a measure of the resonance effect. The minus sign of **b** applies to the substituent as a donor for the π-electron system. i and j of σ_{ij} and Δpk_{ij} are the position-numbers of the aromatic C atoms attached to a substituent and to the COOH group, respectively. The values of (A/r_{kl}^2) and E_c were evaluated for substituents at the *para*- and the *meta*-positions in monosubstituted benzoic acids. The evaluation was also

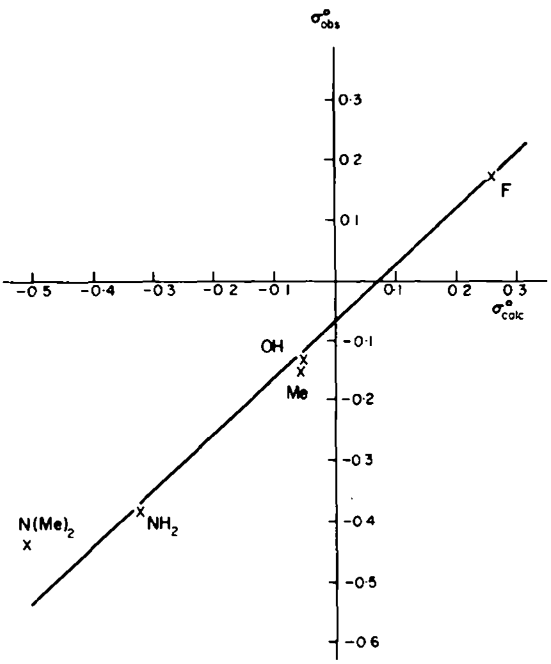

FIG 2. The correlation of the values between the observed and the calculated σ^0

TABLE 1. THE CALCULATED σ^0_p-VALUES AND THE COMPARISON OF THESE VALUES WITH EXPERIMENTAL VALUES[2]

Group	σ^0_p	Group	σ^0_p
N(Me)$_2$	−0·511(−0·44)	OH	−0·05 (−0·13)
NH$_2$	−0·325(−0·38)	F	0·233(0·17)
Me	−0·06 (−0·15)		

made on substituents at all positions except the peri-positions for the COOH group in monosubstituted naphthoic acids. The value of E_c was evaluated by the simple method discussed in previous papers.[4] Then, σ^0, σ_{ij} and Δpk_{ij} are given

$$\sigma^0 = \mathbf{a}(A/r^2_{kl}) - \mathbf{b}|E_c| \text{ (for monosubstituted phenylacetic acids)} \tag{4}$$

$$\sigma_{ij} = \mathbf{a}(A/r^2_{kl}) - \mathbf{b}|E_c| \tag{5}$$

$$\Delta pk_{ij} = \rho\sigma_{ij} = \rho\{\mathbf{c}(A/r^2_{kl}) - \mathbf{d}|E_c|\} = c'(A/r^2_{kl}) - \mathbf{d}'|E_c| \tag{6}$$

Eqs 5 and 6 are applied to the monosubstituted naphthoic acids. In order to simplify the calculation, we took the monosubstituted benzoic acids as the molecular model corresponding to the monosubstituted phenylacetic acids in the evaluation of the σ^0-values. The coefficients in the above equations were evaluated graphically as follows. (1) Evaluate the values of (A/r^2_{kl}) and $|E_c|$ for various substituents at the different positions. The method of evaluation of the values of A and E_c are described in the preceding paper. (2) Substitute these values into Eqs 4, 5 and 6. (3) We have the simultaneous equations for the coefficients **a**, **b**, **c**′ and **d**′ as unknown functions. (4) Draw straight lines for the equations on different substituents as shown in Fig 3.

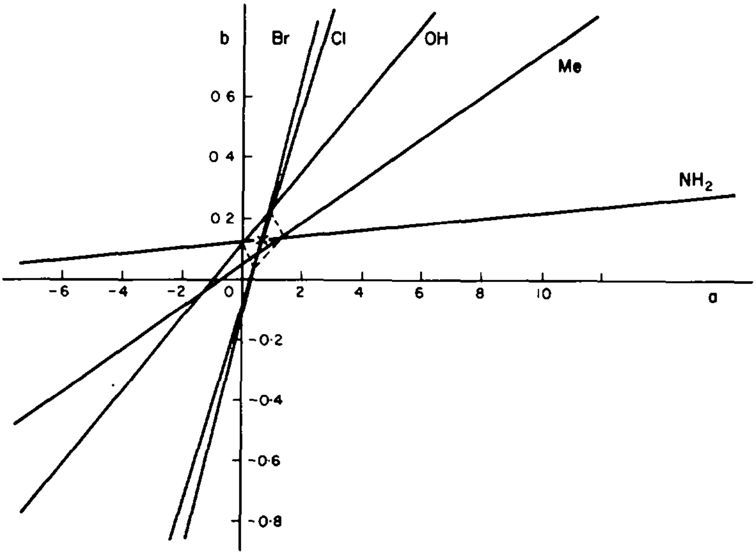

FIG 3. The straight line for Eq. 5

(5) Combine the intersections of the straight lines, then, we have a quadrilateral (in general a polygon) as shown in Fig 3. However, except the intersections a long distance from the quadrilateral in the combining points. (6) Obtain the coordinate of the center of the quadrilateral on the **a** and **b** axes. These values are the approximate mean value for solutions of the simultaneous equations for Eq 5. (7) The values of **a** and **b** for substituents are determined by the coordinate of the intersection passing through the most lines around the center.

Monosubstituted phenylacetic acid system. The σ^0-values were evaluated at the *para*- and *meta*-positions. 16-substituents treated by the evaluation were at the *para*-position and 14 at the *meta*-position. The coefficients **a**, **b** were obtained by solving the simultaneous equations algebraically for several substituents. These substituents have the intersections a long distance from the quadrilateral in Fig 3. The values in parentheses are the experimental values in Tables 2–5.

(1) p-*Substituted phenylacetic acid system.* The obtained values of **a** and **b** are as follows. COOH, COMe and NO_2 (**a** = 0·18, **b** = 0·05), NH_2, $N(Me)_2$, OH and MeO (**a** = 0·01, **b** = −0·08) etc., and all the other substituents (**a** = 0·11, **b** = +0·02). Table 2 shows the calculated σ_p^0-values by the use of obtained **a** and **b**.

TABLE 2. THE CALCULATED σ_p^0-VALUES IN THE *p*-SUBSTITUTED PHENYLACETIC ACID SYSTEM AND THE COMPARISON OF THESE VALUES WITH THE EXPERIMENTAL VALUES[2]

Substituent	σ_p^0	Substituent	σ_p^0
NO_2	0·858(0·82)	SH	0·049(0·15)
CN	0·417(0·69)	$N(Me)_2$	−0·439(−0·44)
COMe	0·445(0·46)	NH_2	−0·424(−0·38)
NO	0·322(0·37)	Me	−0·100(−0·15)
Cl	0·243(0·27)	OH	−0·120(−0·13)
I	0·214(0·27)	MeO	−0·285(−0·12)
Br	0·244(0·26)	$HC{=}CH_2$	−0·083(−0·03)
COH	0·290(0·22)		
F	0·237(0·17)		

TABLE 3. THE CALCULATED σ_m^0-VALUES IN THE *m*-SUBSTITUTED PHENYLACETIC ACID SYSTEM AND THE COMPARISON OF THESE VALUES WITH THE EXPERIMENTAL VALUES[2]

Substituent	σ_m^0	Substituent	σ_m^0
NO_2	0·655(0·71)	COMe	0·293(0·34)
CN	0·502(0·56)	SH	0·185(0·25)
Br	0·372(0·38)	MeO	0·109(0·13)
Cl	0·368(0·37)	OH	0·116(0·12)
COOH	0·337(0·37)	$N(Me)_2$	−0·125(0·15)
COH	0·374(0·35)	Me	−0·097(0·07)
I	0·339(0·35)	$HC{=}CH_2$	−0·030(0·03)

TABLE 4. THE CALCULATED σ_{ij}- AND Δpk_{ij}-VALUES IN THE α-SUBSTITUTED NAPHTHOIC ACID SYSTEM AND THE COMPARISON OF THESE VALUES WITH THE EXPERIMENTAL VALUES[1, 5]

Substituent	σ_{41}	σ_{51}	σ_{61}	σ_{71}	Δpk_{31}
NO_2	0·910(0·86)	0·572(0·54)	0·407(0·41)	0·369(0·36)	0·963(0·93)
CN	0·709(−)	0·510(0·46)	0·333(0·34)	0·338(0·31)	0·851(0·90)
Br	0·301(0·30)	0·329(0·30)	0·183(0·18)	0·059(0·07)	0·507(0·52)
Cl	− (−)	0·236(0·29)	0·176(0·17)	− (−)	0·526(0·46)
NH_2	−0·688(−0·72)	−0·185(−0·13)	− (−)	− (−)	− (−)
OH	−0·481(−0·52)	−0·086(−0·06)	− (−)	−0·064(−0·10)	0·100(0·09)
OMe	−0·352(−0·36)	0·020(−0·01)	−0·079(−0·06)	−0·010(−0·08)	− (−)
Me	−0·176(−0·14)	0·098(0·01)	−0·052(−0·05)	0·067(−0·07)	−0·085(−0·08)

(2) m-*Monosubstituted phenylacetic acid system.* The obtained values of **a** and **b** are as follows. CN(**a** = 0·14, **b** = 0·04), F(**a** = 0·09, **b** = −0·20), $HC{=}CH_2$ (**a** = 0·12, **b** = −0·02) and all the other substituents (**a** = 0·12, **b** = +0·08). Table 3 shows the calculated σ_m^0-values.

(3) *Monosubstituted α- and β-naphthoic acids systems.* The values of Dewar's σ_{ij}[1] were taken for the evaluation on the substituents in monosubstituted α-naphthoic acids. The values of Wells's Δpk_{ij}[5] were taken for the substituents at the C_3-position in monosubstituted α-naphthoic acids, because there are no data on σ_{ij} at this position.

Table 5. The calculated Δpk_{ij}-values in the β-substituted naphthoic acid system and the comparison of these values with the experimental values[5]

Substituent	Δpk_{42}	Δpk_{52}	Δpk_{62}	Δpk_{72}	Δpk_{82}
NO_2	0·723(0·92)	0·602(0·61)	0·640(0·68)	0·578(0·56)	0·413(0·42)
CN	0·897(0·86)	0·587(0·56)	0·553(0·54)	0·512(0·54)	0·359(0·37)
Cl	0·388(0·40)	− (−)	0·239(0·24)	0·260(0·27)	0·25(0·09)
Br	0·318(0·38)	0·245(0·27)	0·227(0·26)	0·262(0·29)	0·010(0·09)
I	0·255(0·34)	− (−)	0·228(0·23)	0·251(0·27)	0·025(0·07)
F	− (−)	− (−)	0·112(0·11)	0·218(0·22)	0·115(0·12)
$N(Me)_2$	− (−)	− (−)	−0·419(−0·44)	−0·184(−0·2)	− (−)
Me	−0·081(−0·13)	− (−)	−0·079(−0·08)	−0·074(−0·07)	−0·023(−0·11)
NH_2	−0·119(−0·13)	− (−)	− (−)	−0·177(−0·23)	−0·046(−0·01)
OH	−0·049(−0·01)	−0·047(−0·04)	− (−)	−0·126(−0·14)	−0·238(−0·22)
OMe	−0·059(−0·02)	−0·040(−0·01)	−0·177(−0·16)	−0·024(−0·01)	−0·176(−0·23)

Wells's values were taken for all the substituents in monosubstituted β-naphthoic acids. The evaluation was made on the substituents at all the positions (except peri) for the COOH group. Some values of **a** and **b** are as follows. All substituents (**a** = 0·14, **b** = ±0·05) for σ_{51}. OH,MeO (**a** = 0·08, **b** = −0·18), Me (**a** = 0·04, **b** = −0·04), NO_2 (**a** = 0·12, **b** = 0·12), Br, Cl (**a** = 0·10, **b** = −0·07) and the other substituents (**a** = 0·08, **b** = ±0·12) for σ_{61}. The calculated values of σ_{ij} and Δpk_{ij} are shown in Tables 4 and 5. Table 6 shows the comparison of the calculated σ_{ij}-values with the calculated Dewar values.

Table 6. The comparison between the two calculated substituent constants by us and by Dewar[1]

Substituent	σ_{41}	σ_{51}	σ_{61}	σ_{71}	$\Delta pk_{31}(\sigma_{31})$
NO_2	0·910(0·84)	0·572(0·52)	0·407(0·41)	0·369(0·53)	0·963(0·71)
CN	0·709(0·73)	0·510(0·43)	0·333(0·32)	0·338(0·43)	0·851(0·56)
Br	0·301(0·19)	0·329(0·22)	0·183(0·23)	0·059(0·21)	0·507(0·39)
Cl	0·294(0·19)	0·236(0·21)	0·176(0·23)	− (−)	0·526(−)
Me	−0·176(−0·21)	−0·098(−0·07)	−0·052(−0·04)	−0·067(−0·08)	−0·085(−)
MeO	−0·352(−0·42)	0·02(−0·05)	−0·079(0·07)	−0·064(−0·08)	− (−)
OH	−0·481(−0·57)	−0·086(−0·09)	−0·07(0·07)	-0·064(−0·08)	0·100(0·12)
NH_2	−0·688(−0·87)	−0·185(−0·29)	− (−)	− (−)	− (−)

The values in parentheses are Dewar's values.

DISCUSSION

The comparison of the method in the present study with the FM method

(a) *Evaluation of parameters.* Dewar *et al.*[1] assumed the field effect by F/r_{ij} and the resonance effect by Mq_{ij} and $M'\pi_{ij}$ in the FM method. **r** is the distance between the aromatic carbon atoms i and j attached to the reaction center and the substituent, respectively. q_{ij} is the formal charge at position j produced by attaching the group $—CH_2^-$ at position i. π_{ij} is the atom–atom polarizability of atoms between i and j.

F is a measure of the field effect on the reaction center, M and M′ are measures of the resonance effects at *meta*- and *para*-positions in benzene, respectively.

In the present study, the field effect was evaluated by $\mathbf{a}A/r_{ij}^2$. $1/r_{ij}$ in the FM method is approximately equal to e/r_{ij}. e is the unit charge of an electron. **r** in the present study is the distance between the centers of gravity of the charges of a substituent and the reaction center. A is the charge of the substituent, then A/r_{ij}^2 is equal to e/r_{ij}^2. This form represents more accurately the electric field of the charge than $1/r_{ij}$ on the reaction center. For the resonance effect, we evaluated directly the resonance energy (charge transfer energy E_c) between the substituent and the aromatic ring. $|E_c|$ represents more accurately the resonance effect of the substituent than π_{ij} in the FM method.

(b) *The correspondence of the parameters between the present study and the FM method.* F/r_{ij} and $Mq_{ij}, M'\pi_{ij}$ may be correlated to A/r_{ij}^2 and $|E_c|$, respectively. We obtained the relation between these parameters. F/r_{ij} and A/r_{ij}^2 are represented by the use of e as follows.

$$F(\text{or } F')/r_{ij} \simeq F(\text{or } F')(e/r_{ij}) \tag{7}$$

$$\mathbf{a}A/r_{ij}^2 = \mathbf{a}(e/r_{ij}^2) \tag{8}$$

r in Eq 7 is different from **r** in Eq 8. We may obtain approximately the following relation multiplying **r** to Eq 8.

$$\begin{aligned} F(\text{or } F')(e/r_{ij}) &\simeq \mathbf{ar}(e/r_{ij}^2) \\ &= \mathbf{a}(e/r_{ij}) \end{aligned} \tag{9}$$

F must correspond to **ar** in Eq 9. However, for the values of **a** obtained by Eq 4, there are only qualitative relations. For example, the value of F for NO_2 is larger than that of F for SH. The same tendency can be seen for the values of **ar**. The order of the magnitudes of F agrees with the order of **ar**.

Dewar[6] has evaluated the molecular orbital energies of the system RS using a perturbation method. These have been evaulated by separating the system into the mesomeric systems R,S. Both R and S are alternant hydrocarbons. The mutual polarizability of atoms s,t is shown approximately in Ref 6 by

$$\pi_{s,t} = \pi_{t,s} = \partial q_t/\partial \alpha_s \simeq a_{0t}^2/2a_{0r}\beta_{rs} \tag{10}$$

s is attached to atom r in R, t is an atom in R. q_t, α_s and β_{rs} are the electron density on atom t, the coulomb integral for atom s in S, and the resonance integral between atoms r and s, respectively. a_{0t}, a_{0r} are the non-perturbed coefficients of atomic orbitals for atoms t and r. Applying Eq 10 into the monosubstituted benzoic and naphthoic acids systems treated in the present study, we can represent E_c using Eq 10. R is taken as a donor molecule (D), and S as an acceptor molecule (A). The interaction energy between the COOH group and the aromatic ring is omitted, because the interaction energy may be common in the systems. The mutual polarizability of atoms d in D and a in A may be given by

$$\pi_{d'a} = C_d^2/2C_{d'}\beta_{d'a} \tag{11}$$

d′ is the atom attached to the acceptor. C_d, $C_{d'}$ are the coefficients of the atomic orbitals for atoms d, d′. E_c taken in the present study may be abbreviated as follows.

$$\begin{aligned} E_c &= \{(H_D - V_A) + \{(H_D - V_A)^2 + (2C_{d'}C_a\beta_{d'a})^2\}^{\frac{1}{2}}\} \\ &\simeq \{(H_D - V_A) + (H_D - V_A + 2C_{d'}C_a\beta_{d'a})\} \\ &= 2(H_D - V_A) + 2C_{d'}C_a\beta_{d'a} \end{aligned} \tag{12}$$

H_D, V_A are the highest occupied energy level of D and the lowest vacant energy level of A, respectively. We can obtain the equation.

$$|E_c| \simeq |2(H_D - V_A) + C_d^2/\pi_{d,a}C_a| \tag{13}$$

i and j of π_{ij} in the FM method may be $\pi_{d,d'}$ by the use of Eq 11. $M'\pi_{ij}$ in the FM method corresponds approximately to $\mathbf{b}|E_c|$ in the present study as follows.

$$M'\pi_{d,d'} \simeq \mathbf{b}|2(H_D - V_A) + C_d^2/\pi_{d,a}C_a| \tag{14}$$

Ionic character of the ϕ—X *bond.* The ionic character of the ϕ—X (ϕ is the benzene ring, X a substituent) bond can be evaluated from the value of A. The charge of a substituent e has the following dimension by the use of dipole moment

$$e = \mu/l[10^{-18}/(10^{-8} \times 4{\cdot}803)\,\text{e.s.u.}] \tag{15}$$

e shows what percentage of unit charge is on the substituent. A was taken as described in the preceding paper.

$$A = \mu/l \times 10^{-10}\,(\text{e.s.u.}) \tag{16}$$

Therefore, the ionic character of a substituent can be obtained by dividing the value of A by 4·803. This ionic character is shown in Table 7 by per cent for substituents.

TABLE 7. THE IONIC CHARACTER OF THE ϕ-X BOND

Substituent	i	Substituent	i
CN	25·4	COOH	11·6
NO_2	24·5	COMe	7·9
F	24·5	SH	4·7
Cl	18·9	OH	3·0
Br	16·4	$N(Me)_2$	−4·9
NO	14·5	$CH{=}CH_2$	−5·4
I	12·9	CH_3	−5·8
CHO	12·9	NH_2	−8·7

i is the ionic character. The signs plus and minus indicate direction of electron migration. Signs are the same as for the calculated dipole moments.

These per cents show the degree of transformation of an electron between the benzene ring and the X groups.

The magnitude of the coefficients **a**, **b**. The relative magnitude of **a** and **b** can be qualitatively assigned a significance. The relative magnitude shows that the contribution of the inductive effect into the σ_p^0-values is greater than that of the resonance effect for the COOH, COMe and NO_2 groups in the phenylacetic acid system. The contribution of the resonance effect is a little greater than that of the inductive effect for the NH_2, OH, MeO and $N(Me)_2$ groups in the system. The order of magnitude of **a** and **b** almost agrees with that of the σ_I- and σ_R^0-values, respectively, for the *meta*- and *para*-substituted systems. This agreement is better than that between the F,M (or F′,M′) and the σ_I- and σ_R-values, therefore, the values of **a** and **b** can be respectively taken as a measure of the inductive and resonance effects. The contribution of these effects with the A- and $|E_c|$-values into the Δpk_{72}-values is shown in Table 8. The value of r_{ij}^2 is omitted from the consideration of the contribution, because it is nearly the same for the different substituents. For the Me group, both the values of A and E_c are small, and the sum of these small values gives rise to the small Δpk-value. For the NH_2 and $N(Me)_2$ groups, the large Δpk-value is caused by the large value of E_c directing to the benzene ring. For the OMe group, the values of middle A and middle E_c cancel each other. The small Δpk-value is caused by both the small values of A and E_c having the same direction for the Me group. Table 8 may be explained from this point of view on the basis of the data on A and E_c. The substituent effect can be evaluated quantitatively by separating the two effects with A and E_c.

TABLE 8. THE CONTRIBUTION OF THE INDUCTIVE AND THE RESONANCE EFFECTS IN THE Δpk_{72}-VALUES

Substituent	A	**a**	E_c	**b**	Δpk_{72}
(donor)					
Me	small(−)	middle	small	middle(−)	small(−)
NH_2 $N(Me)_2$	small(−)	middle	large	middle(−)	large(−)
OH,SH	middle(+)	large	middle	small(−)	middle(−)
OMe	middle(+)	middle	middle	middle(−)	small(−)
(acceptor)					
F	large(+)	middle	small	middle(−)	middle(+)
Cl,I,Br	large(+)	a little large	small	middle(−)	middle(−)
NO_2	large(+)	a little large	large	middle(+)	large(+)

The signs in parentheses show the direction of the transfer of an electron between a substituent and the naphthalene ring. The plus sign is applied for the C → X direction. C is the aromatic carbon and X the substituent.

Evaluation of A. The value of A was obtained by the use of the value of the dipole moment for a unit bond. Eq. 4 suggested that the σ_p^0-value may be evaluated by the use of the data on the dipole moment only. A was used as the unit of the inductive effect of a substituent against the benzene ring which can be evaluated exactly by the LCAO MO method.[7,8] The dipole moment of a molecule can also be evaluated exactly by the general MO method. Therefore, the σ_p^0-value may be evaluated more exactly by the MO method, such as the CNDO and the INDO approaches, for the π- and the σ-electron systems in molecules.

The correlation between the calculated and the experimental σ-values. Figs 4–7 are the graphical expressions of the correlations between the calculated and the

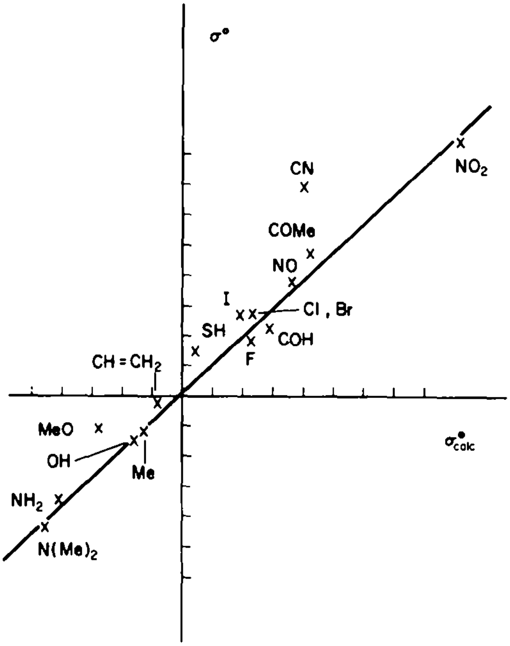

FIG 4. The comparison of the two σ_p^0-values in the monosubstituted phenylacetic acid system

experimental σ_p^0-values in Tables 2–5. Fig 8 expresses the good correlation between the calculated and Dewar's σ_{ij}-values.

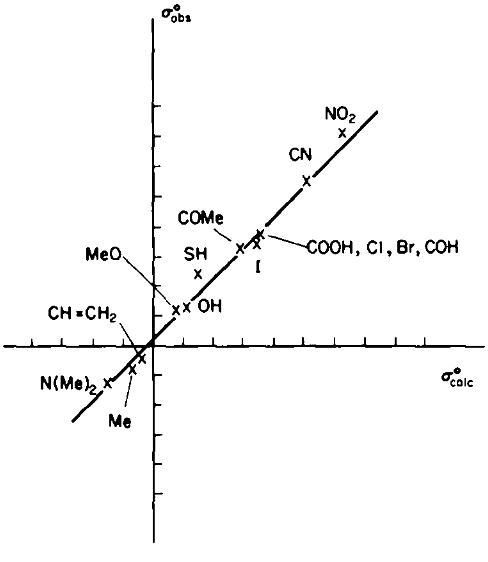

FIG 5. The comparison of the two σ_m^0-values in the monosubstituted phenylacetic acid system

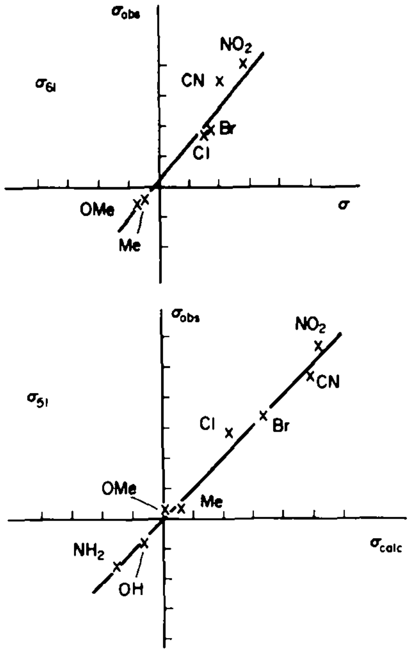

FIG 6. The comparison of the two substituent constants values for σ_{6I} and σ_{5I} in the monosubstituted naphthoic acid system

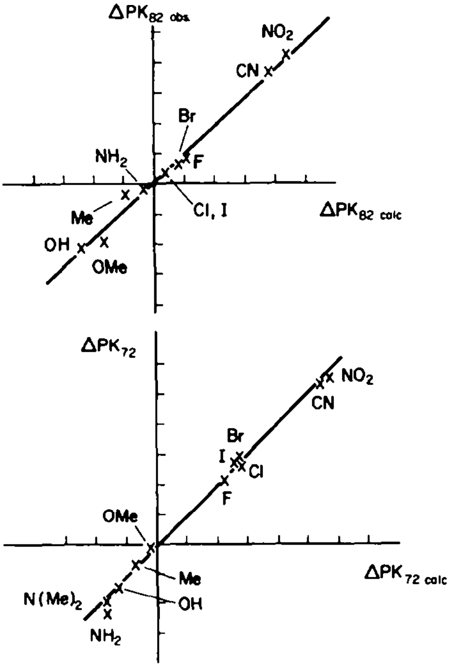

FIG 7. The comparison between the calculated and the experimental values of Δpk_{72} and Δpk_{82} in the monosubstituted naphthoic acid system

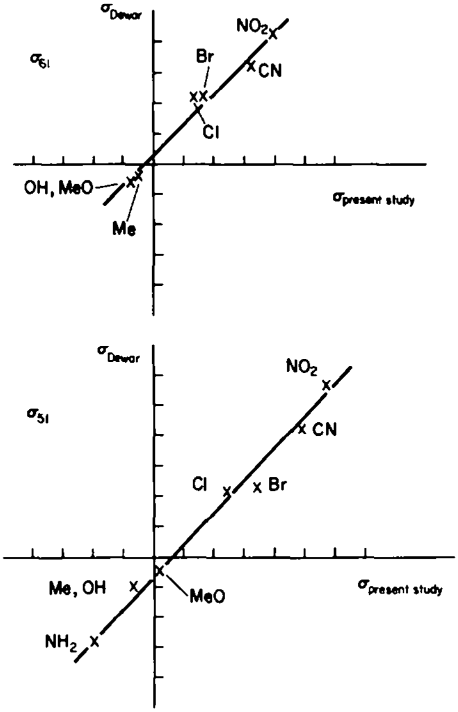

FIG 8. The comparison between the σ_{ij}-values calculated by us and by Dewar[1]

Quantitative analysis of the twisting effect of a substituent on the σ-value. No quantitative analysis of the twisting effect of a substituent has made on the σ-values. The quantitative correlations between an angle of twist of a substituent and E_c have been obtained for the α- and β-isomers of nitronaphthalene, naphthylamine and naphthol in a previous paper.[4] For example, the equation is

$$E_c = -0{\cdot}477\cos\phi + 12{\cdot}244\cos^2\phi + 2{\cdot}036\cos^3\phi - 24{\cdot}03\cos^4\phi + 16{\cdot}632\cos^5\phi \quad \text{(for } \alpha\text{- and } \beta\text{-nitronaphthalenes)}, \qquad (17)$$

where ϕ is the angle of twist of a substituent. We can analyse the σ_{ij}- and Δpk_{ij}-values quantitatively considering the twisting effect of a substituent by using Eq 17.

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REFERENCES

[1] M. J. S. Dewar *et al., J. Am. Chem. Soc.* **84**, 3546 (1962)
[2] R. W. Taft Jr., *J. Phys. Chem.* **64**, 1805 (1960)
[3] Y. Yukawa and Y. Tsuno, *J. Chem. Soc. Japan* **86**, 873 (1965)
[4] K. Sekigawa, *Tetrahedron* **26**, 5395 (1970); K. Sekigawa, *Zh. Struk. Khim.* **12**, No. 3, 526 (1971), *Ibid.*, No. 4, 703 (1971)
[5] R. P. Wells and W. Adcock, *Aust. J. Chem.* **18**, 1365 (1965)
[6] M. J. S. Dewar, *J. Am. Chem. Soc.* **74**, 3350 (1952)
[7] J. M. Cahill and C. R. Mueller, *J. Chem. Phys.* **24**, 513 (1965)
[8] S. Ehrenson, *J. Am. Chem. Soc.* **84**, 2681 (1962)