

# A THEORETICAL ANALYSIS OF HAMMETT'S $\sigma$ THE CORRELATIONS BETWEEN SUBSTITUENT CONSTANTS AND VARIOUS PHYSICAL CONSTANTS

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(Received in Japan 13 January 1971; Received in the UK for publication 25 July 1971)

**Abstract**—Correlations between substituent constants and physical constants have been obtained. The correlation between Taft's  $\sigma_R^0$  and the charge-transfer energy of a substituent ( $E_c$ ) has been obtained for various substituents. Furthermore, the contribution of the  $\pi$ -bond system to the  $A$ -value and the correlation between Huheey's group electronegativity and  $A$ , are discussed.

## INTRODUCTION

HAMMETT'S  $\sigma$  has theoretically been analysed by many authors<sup>1-3</sup> in recent years. The correlations have been obtained between various substituent constants and calculated physical constants. Jaffe<sup>1</sup> has obtained the correlation between  $\sigma$  and the calculated  $\pi$ -electron density for disubstituted aromatic compounds, pyridine, azo-substituted hydrocarbons and naphthalene and evaluated the  $\rho$ -values. Sixma<sup>2</sup> has obtained the correlation between  $\sigma$  and the calculated localization energy for  $\pi$ -electrons. Peters<sup>3</sup> has analysed the correlation between the substituent constants and the calculated physical constants by a simple perturbation method. Taft<sup>4</sup> has separated  $\sigma$  into  $\sigma_I$  and  $\sigma_R$ .  $\sigma_I$ ,  $\sigma_R$  are caused by the inductive and the resonance effects of a substituent, respectively, in both *m*- and *p*-monosubstituted phenylacetic acids. Dewar *et al.*<sup>5</sup> have evaluated the  $\sigma$ -values separating into two parts (inductive and resonance) by the FM method. The magnitude of the field effect has been evaluated by  $F/r_{ij}$ , and the resonance effect by  $Mq_{ij}$  (or  $M'\pi_{ij}$ ). The meaning and values of these parameters ( $F$ ,  $r$ ,  $M$ ,  $q$ ) are described in Ref. 5.

We consider that the magnitude of the following two substituent effects may be proportional to each other. One is the substituent effect on the reaction center in the *para*-substituted phenylacetic acid system, and another on the ring in the *para*-substituted benzene system. We have obtained the correlations between Taft's  $\sigma_I$ ,  $\sigma_R^0$  caused by the former effect and the calculated physical constants  $A$ ,  $E_c$  caused by the latter effect, and the other correlations. The magnitude of these physical constants may be a measure of the substituent effect in the *para*-substituted benzene system.  $E_c$  is the charge-transfer energy between a substituent and the benzene ring.  $A$  is the calculated charge of a substituent. The method of the evaluation of  $E_c$  and  $A$  will be described later. All the data on the correlations between the substituent constants and the physical constants have been evaluated by the method of least-squares.

## EVALUATION AND RESULTS

*The correlation between Taft's  $\sigma_R^0$  and the charge-transfer energy ( $E_c$ ) of a substituent.* We obtained the correlation of the values between  $\sigma_R^0$ <sup>6</sup> and the calculated charge-transfer energy ( $E_c$ ) of a substituent in the monosubstituted phenylacetic acid system.

$E_c$  between the substituent and the benzene ring was obtained from Kimura's<sup>7</sup> data and taken approximately equal to the stabilization energy of the ground configuration of the benzene molecule. The stabilization energy is caused by the interaction between a substituent and the benzene ring. This approximation is the same as described in previous papers<sup>8</sup> for monosubstituted naphthalenes. Hine's  $\sigma_r^o$ <sup>6</sup> was used for substituents ( $\text{NH}_2$ ,  $\text{NO}_2$ ) there being no data on  $\sigma_r^o$  at the *para*-position in the monosubstituted phenylacetic acids. The sign of  $E_c$  is always minus. We obtained the correlation between the values of  $|E_c|$  and  $\sigma_r^o$ . The obtained correlations are shown in Fig 1 and the following equation can be obtained:

$$\sigma_r^o = -0.095 |E_c| + 0.019 \quad (1)$$

( $r = 0.92$ )

$r$  is the correlation coefficient.

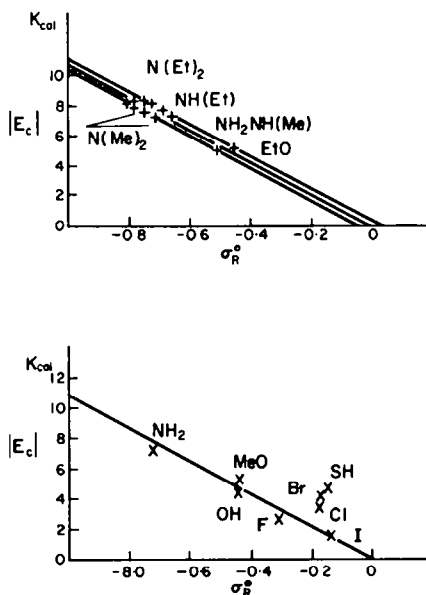


FIG 1. The correlations between  $\sigma_r^o$  and  $|E_c|$  for donor group in the monosubstituted phenylacetic acid system, the  $\sigma_r^o$ -values are estimated from the  $|E_c|$ -values for  $\text{N(Et)}_2$ ,  $\text{NH(Et)}$ ,  $\text{N(Me)}_2$ ,  $\text{NH(Me)}$  and  $\text{EtO}$

The correlation between Taft's  $\sigma_1$  and the charge of a substituent (A). As is well known, the dipole moment ( $\mu$ ) of a molecule is

$$\mu = l e \quad (2)$$

$l$  is a degree of migration of an electron and  $e$  the electronic charge. The relation  $\mu/l$  gives the charge  $e$  from Eq. 2.

In the present study, the charge of a substituent was evaluated by applying the relation  $\mu/l$  for the monosubstituted benzene and naphthalene systems. The charge

of a substituent (A) represents a degree of migration of an electron between a substituent and an aromatic ring:

$$\mu/l \times 10^{-10} = A \text{ (e.s.u.)} \quad (3)$$

$\mu$  was taken as dipole moment of the substituent, and  $l$  taken as the distance between the aromatic C atom attached to the substituent and the center of gravity for the charge of the substituent. The direction from the aromatic atom toward the substituent was taken as plus for the direction of  $\mu$ . The dipole moment of the substituent was evaluated by a vector addition of bond moments for each bond in the substituent.

The method of drawing figures in the evaluation of A is shown in Figs 2 and 3.

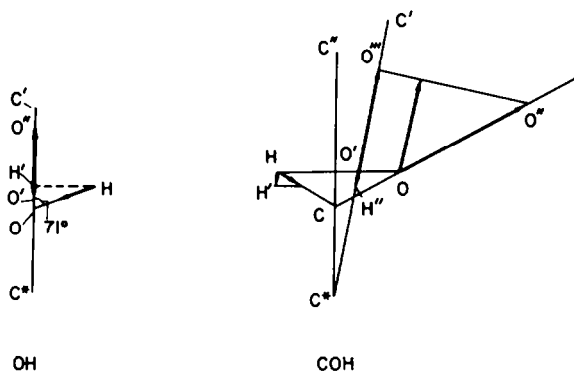


FIG 2. The method of drawing figures in the evaluation of A is shown for the OH and CHO groups. C\* shows the aromatic carbon atom attached to a substituent

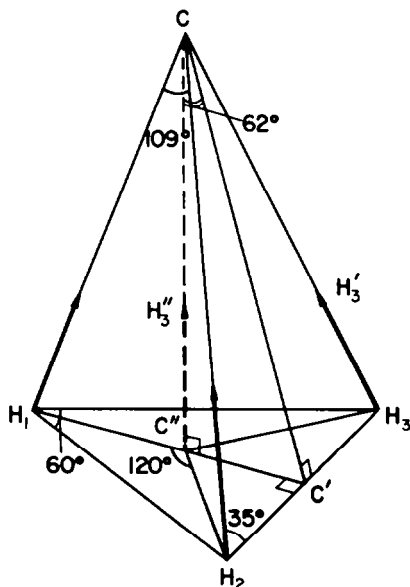


FIG 3. The method of drawing figure of the spatial model used in the evaluation of A of the  $\text{CH}_3$  group

The data on all molecular structures used in the drawing figures for the evaluation of  $A$  were taken from Ref. 9. (*For the OH group*) (1) Draw the points  $C^*$ , O and H analogously to the molecular structure of phenol on a section paper. (2) Draw a straight line  $\overline{C^*C}$  from the point  $C^*$  toward the point O. (3) Draw the vector  $\overline{H'O}$  of the projection of  $\overline{HO}$  (vector of the bond moment HO,  $\mu(\text{HO})$ ) on the line  $\overline{C^*C}$ . The values of all bond moments used in the evaluation were taken from Ref. 10. The  $sp^3$  hybridization was estimated for the orbital structure of the O atom. (4) Draw the vector  $\overline{H'O''}$  (vector of  $\mu(C^*O)$ ) on the line  $\overline{H'C}$ . The magnitudes of the projection of the  $\overline{HO}$  ( $\overline{H'O}$ ), the resultant dipole vector ( $\overline{H'O''} - \overline{H'O}$ ) are obtained graphically on the section paper. These values are 0.492 (D) ( $\overline{H'O}$ ), 0.248 (D) (resultant vector) and  $l = 1.708$  (Å), respectively.  $A$  can be obtained as follows

$$A(\text{OH}) = \mu/l \times 10^{-10} = 0.248/1.708 = 0.145 \text{ (e.s.u.)} \quad (4)$$

(*For the COH group*) (1) Draw the points  $C^*$ , C, O and H analogously to the molecular structure of benzaldehyde. (2) Join two points H and O by a straight line. (3) Draw the center of gravity of a charge ( $O'$ ) between the O and H atoms on the line  $\overline{HO}$ . (4) Draw a straight line  $\overline{C^*C}$  through the point  $O'$  from the point  $C^*$ . (5) Draw the vector  $\overline{O'O''}$  of the projection of the vector  $\overline{OO}$  (vector of  $\mu(C=O)$ ) on the line  $\overline{C^*C}$ . (6) Draw the vector  $\overline{O'H''}$  of the projection of the vector  $\overline{HH}$  (vector of  $\mu(\text{HC})$ ) on the  $\overline{C^*C}$ .

The magnitudes of  $\overline{O'O''}$ ,  $\overline{O'H''}$ , the resultant vector and  $l$  ( $C^*O'$ ) are obtained graphically. The values of the resultant dipole vector and  $l$  are 1.3 (D) and 2.1 (Å), respectively. Then,

$$A(\text{COOH}) = \mu/l \times 10^{-10} = 0.619 \text{ (e.s.u.)} \quad (5)$$

(*For the  $\text{CH}_3$  group*) The method of drawing figure of the  $\text{CH}_3$  group is shown in Fig 3. The point  $C''$  is the center of gravity of  $\Delta H_1H_2H_3$  in Fig 3. The vector  $\overline{C''H_3''}$  is the projection of the vector  $\overline{H_3H_3}$  on the  $\overline{CC''}$ . The resultant vector of  $\text{CH}_3$  is given by three times  $\overline{C''H_3''}$ . The magnitude of  $\overline{C''H_3''}$  and the length of  $\overline{CC''}$  were obtained, respectively, as 0.186 (D) and 0.517 (Å) after the simple calculation. Then, the magnitude of the resultant vector of  $\text{CH}_3$  is  $3 \times 0.186 = 0.559$  (D).

$$A = \mu/l = -0.559/2.027 = -0.276 \text{ (e.s.u.)} \quad (6)$$

(*For the  $\text{COCH}_3$  and  $\text{HC}=\text{CH}_2$  groups*) The method of drawing figures is similar to the one for the OH and CHO groups in Fig 2. The values of the resultant vector and  $A$  for the  $\text{COCH}_3$  and  $\text{HC}=\text{CH}_2$  groups are

$$\mu = 0.871 \text{ (D)}, l = 0.23 \text{ (Å)}, A = 0.379 \text{ (e.s.u.)} \\ \text{(for COMe)}$$

$$\mu = -0.75 \text{ (D)}, l = 2.9 \text{ (Å)}, A = -0.259 \text{ (e.s.u.)} \\ \text{(for HC}=\text{CH}_2\text{)}$$

$A$  was evaluated for the other 11 substituents ( $\text{NO}_2$ , F, Cl, Br, I etc). Fig 4 shows the method of drawing or the  $\text{COCH}_3$  and  $\text{HC}=\text{CH}_2$  groups.

The value of the bond moment of the  $C^*-X$  ( $X$  is a substituent) bond was taken as half of the value for a double bond. This treatment was made on the substituents ( $\text{NO}_2$ , NO,  $\text{NH}_2$  etc) having the large resonance effect on the benzene ring. The reason is that the bond was estimated to be an intermediate state ( $C^*-X$ ) between

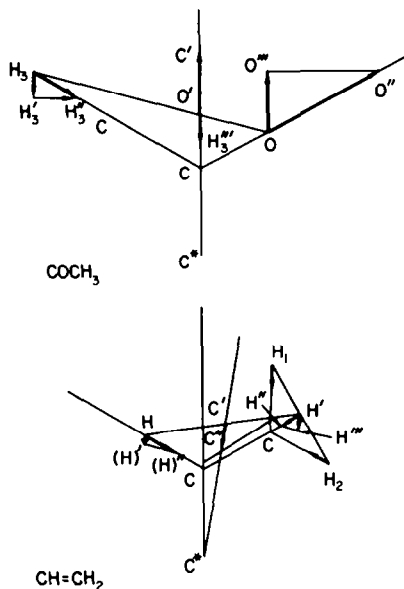


FIG 4. The method of drawing figures for the  $\text{COCH}_3$  and the  $\text{HC}=\text{CH}_2$  groups

single and double bonds. The intermediate state may be given by the resonance between the benzene ring and the substituent. Fig 5 shows the obtained correlation of  $A$  vs  $\sigma_1$  ( $r = 0.94$ ). The intercepts of the lines **a** and **b** are  $-0.28$  and  $-0.50$  in Fig 5, respectively. In order to unify the lines **a** and **b** to one straight line,  $0.28$  and

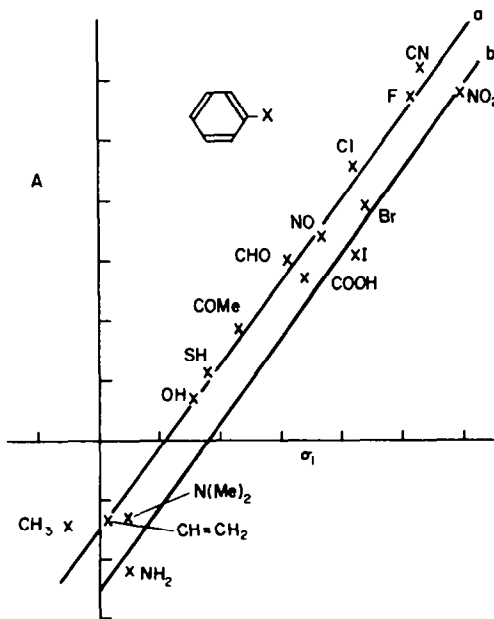


FIG 5. The plot of  $A$  vs  $\sigma_1$  in the monosubstituted phenylacetic acid system

0.50 were added to the values of A for the substituents on the lines **a** and **b**, respectively ( $\text{N}(\text{Me})_2$ ,  $\text{COOH}$  are on the line **b**). The unified line is shown in Fig 6 and the equation is

$$\sigma_1 = 0.368 A + 0.03 \quad (7)$$

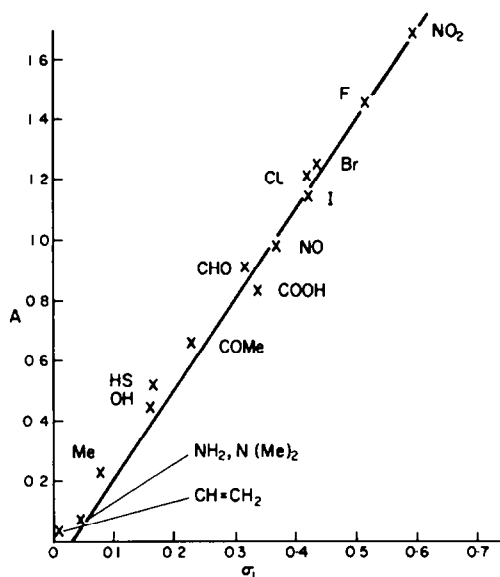


FIG 6. The unified straight line for the lines a and b in Fig 5

The magnitude of the contribution of the resonance effect in the value of A will be discussed later.

The correlation of Yukawa's  $\sigma_{\text{R}}^{\pm}$  vs  $|E_{\text{c}}|$ . Yukawa and Tsuno<sup>11</sup> have evaluated the magnitude of the resonance effect on various  $\sigma$ -values using the  $\Delta\bar{\sigma}_{\text{R}}^{\pm}$  parameter in the following way.

$$\sigma_{\text{p}}^{\circ} = 0.74 \sigma' + 0.41 \Delta\bar{\sigma}_{\text{R}}^{\pm} \quad (8)$$

$$\sigma_{\text{p}}^{\pm} = 0.71 \sigma' + 1.41 \Delta\bar{\sigma}_{\text{R}}^{\pm} \quad (9)$$

$\sigma_{\text{p}}^{\circ}$ ,  $\sigma_{\text{p}}^{\pm}$  and  $\sigma'$  are determined by Taft,<sup>12</sup> Brown<sup>13</sup> and Roberts,<sup>14</sup> respectively. Furthermore, Yukawa and Tsuno<sup>11</sup> unified the above relation at the *para*- and the *meta*-positions by  $\sigma_1$  and  $\sigma_{\pi}$  ( $\sigma_1 = 0.74 \sigma'$ ,  $\sigma_{\pi} = 0.41 \Delta\bar{\sigma}_{\text{R}}^{\pm}$ ).

We obtained the correlation of  $\sigma_{\text{R}}^{\pm}$  vs  $|E_{\text{c}}|$ .  $\sigma_{\text{R}}^{\pm}$  is taken for the substituent that reacts as a donor to the benzene ring. The sign (+) is taken for the donor. Fig. 7 shows the correlation between  $\sigma_{\text{R}}^{\pm}$  and  $|E_{\text{c}}|$ .

The following equation for the correlation in Fig. 7 was obtained.

$$\sigma_{\text{R}}^{\pm} = -0.066 |E_{\text{c}}| + 0.020 \quad (r = 0.98) \quad (10)$$

The agreement of  $|E_{\text{c}}|$  against the parameter of the resonance effect on the  $\sigma$ -value in Eq 10 is better than that in Eq 1. The resonance effect on the  $\sigma$ -value may be suggested more directly with  $\sigma_{\text{R}}^{\pm}$  than with  $\sigma_{\text{R}}^{\circ}$ .

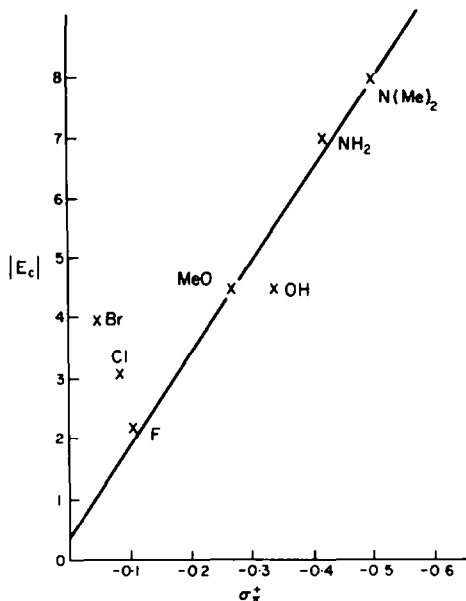


FIG 7. The plot of  $|E_c|$  vs  $\sigma_{\pi}^+$  for the donor groups in the monosubstituted benzene system

The correlation between  $\sigma_{\pi}^+$  and the mesomeric moment  $\mu$  (mes). The mesomeric moment ( $\mu$  (mes)) has been described to evaluate the magnitude of the resonance between a substituent and the benzene ring in Ref 15.  $\mu$ (mes) is given as the difference in the dipole moments  $\mu(\text{Ph-X}) - \mu(\text{Alk-X})$ . Ph and Alk are the phenol and the alkyl molecules, and X is a substituent. The correlation between  $\sigma_{\pi}^+$  and the experimental

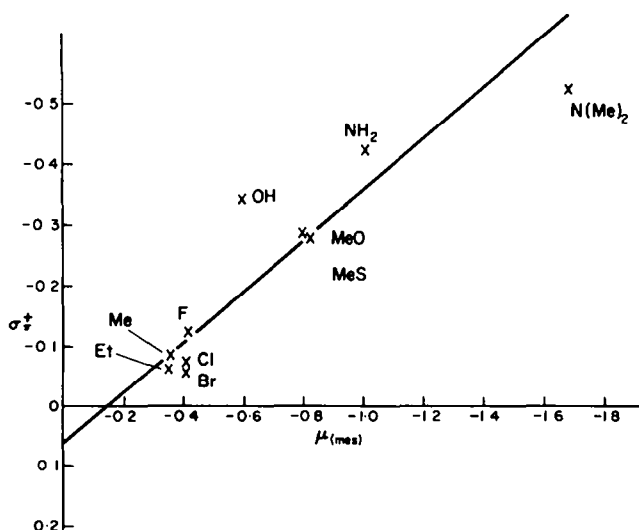


FIG 8. The plot of  $\sigma_{\pi}^+$  vs  $\mu(\text{mes})$  for the donor groups in the monosubstituted benzene system

$\mu(\text{mes})$  was obtained for some substituents in the present study. The obtained correlation is shown in Fig. 8. The following equation was obtained for the straight line.

$$\sigma_{\pi}^{+} = 0.422 \mu(\text{mes}) + 0.059 \quad (r = 0.93) \quad (11)$$

#### DISCUSSION

*Contribution of the  $\pi$ -bond system to the A-value.* A was evaluated for the  $\sigma$ -bond system on the substituents treated in Fig. 5. Fig. 9 shows the comparison of the values of A for the substituents between for the  $\sigma$ -bond system and for the  $\sigma$ - and  $\pi$ -bonds

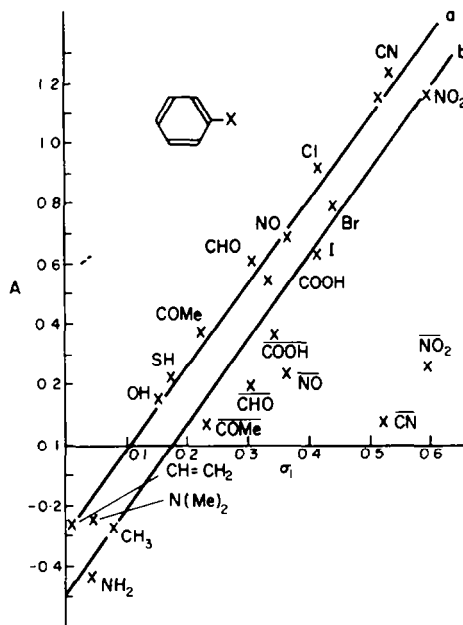


FIG. 9. The comparison of the values of A for the substituents marked with a bar and for the substituents marked with not a bar in the relation of Fig. 5. The former values were calculated for the only  $\sigma$ -bond system, and the latter values were calculated for both the  $\sigma$ - and  $\pi$ -bond system

system. The numbers (percent) in the following parentheses show the contribution of the  $\pi$ -bond system to the value of A. The contributions are CN (94), COMe (80),  $\text{NO}_2$  (78), COH (69), COOH (36). These values suggest that the  $\sigma_1$ -values are affected by the  $\pi$ -bond system for the substituents having the  $\pi$ -bond.

Yukawa<sup>11</sup> has suggested that the  $\sigma_1$ -value includes the  $\pi$ -inductive effect  $0.26 \sigma_1$  at least. The above fact may support Yukawa's suggestion.

*The method of calculation of  $E_c$ .* A more simple method of calculation for  $E_c$  than that treated in this paper was discussed in the previous papers.<sup>8</sup> That is,  $E_c$  may be evaluated by the use of the values of  $H_D$ ,  $H_A$  and  $\beta_{AD}$ . These marks and the method of evaluation are described in the discussion of the previous papers. This method was used to evaluate the values of  $E_c$  for the molecules of monosubstituted phenylacetic and naphthoic acids in another paper of this series.



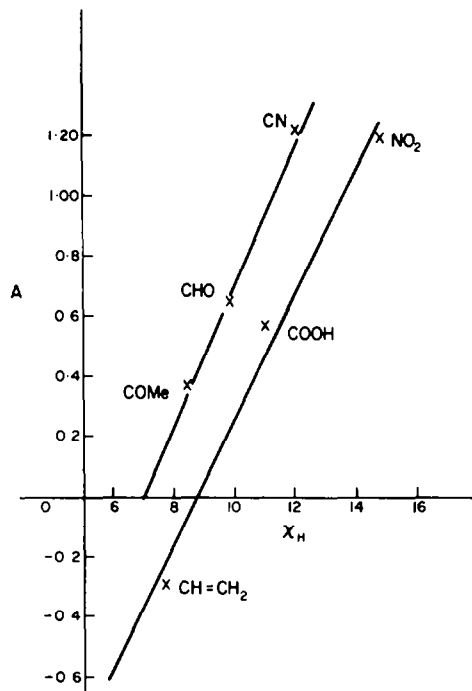


FIG 10. The plot of  $A$  vs Huheey's electronegativity  $\chi_H$  (in Mulliken unit, vol/electron)

The correlation of  $A$  vs the group electronegativity. Huheey<sup>16</sup> has evaluated the electronegativity of multiply bonded groups such as CN, CO, SO<sub>2</sub> and H<sub>2</sub>C=CH. Plot of  $A$  vs  $\chi_H$  (Huheey's electronegativity) is shown in Fig. 10. There are correlations between  $A$  and  $\chi_H$ .

The way of taking  $l$ .  $l$  must be taken as  $l'$  as shown in Fig. 11 (a) originally. We compared the values of  $\sigma_1$  with the relativistic values of  $A$  in the present study.

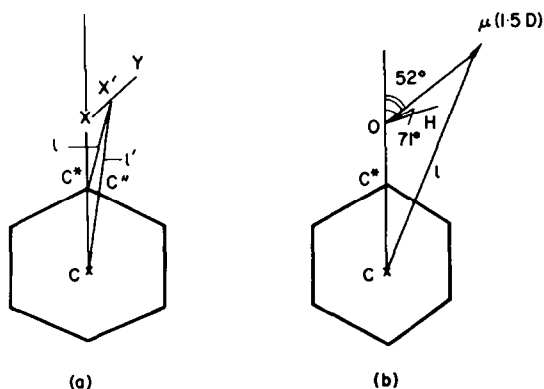


FIG 11. The way of taking of  $l$  and  $l'$  in the monosubstituted benzene system.  $X-Y$  is a substituent, and  $X'$  is the center of gravity of the charge of  $X-Y$ .  $\mu$  (1.5 D) is the dipole moment of the phenol molecule

Therefore, it is enough that we know the relativistic length of  $l'$  for various substituents.  $l$  in Fig. 11 (a) can be taken approximately as the relativistic length of  $l'$ .

When the experimental data on dipole moments are used for the phenol molecule,  $l$  may be taken as shown in Fig. 11 (b). This method for the evaluation of  $l$  must be reasonable. However, we cannot know the dipole moment of a substituent only using the experimental data, because the data show only a resultant moment as a molecule. Furthermore, we cannot know separately the dipole moments for the  $\pi$ -bond system and for the  $\sigma$ -bond system of a molecule using the experimental data. We have not used  $l$  as shown in Fig. 11 (b).

*Acknowledgments* The author wishes to thank Dr. Masuda of the University of Tokyo for his useful suggestions and discussions.

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