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Substituent Effects on the NMR Chemical Shifts of Aromatic Side Chain Protons. I. The Effects of *meta*-Substituents

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The Hammett type treatment of the chemical shift of substituted aromatic side chain protons has not always been successful. The failure might be ascribed to the neglect of magnetic long-range effects. When the corrections were made both for the ring current diminution due to the contribution of polar resonance structure of the introduced substituent and for the substituent magnetic anisotropy effect, an excellent equation was obtained to relate the chemical shifts of *meta*-substituted aromatic side chain protons to the Hammett's constants.

Recent studies on the proton chemical shifts of substituted aromatic system have shown that Hammett type treatment[1a-i] of the substituent effects is not practically successful.[2a-i]

It is well established that the substituent effects on the proton chemical shifts can be divided into

1) a) L. P. Hammett, *J. Amer. Chem. Soc.*, **59**, 96 (1937); b) L. P. Hammett, "Physical Organic Chemistry," McGraw Hill, New York (1940), p. 184; c) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); d) P. R. Wells, *ibid.*, **63**, 171 (1963); e) R. W. Taft, Jr., and I. C. Lewis, *J. Amer. Chem. Soc.*, **80**, 2436 (1958); f) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958); g) Y. Yukawa, Y. Tsuno and M. Sawada, This Bulletin, **39**, 2274 (1966); h) Y. Yukawa and Y. Tsuno, *ibid.*, **32**, 965 (1959); i) Y. Yukawa and Y. Tsuno, *Nippon Kagaku Zasshi*, **86**, 873 (1965).

2) a) P. L. Corio and B. P. Dailey, *J. Amer. Chem. Soc.*, **78**, 3043 (1956); b) A. A. Bothner-By and R. E. Glick, *ibid.*, **78**, 1071 (1956); c) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); d) W. B. Smith and S. Chiranjeevi, *J. Phys. Chem.*, **70**, 3505 (1966); e) A. R. Katritzky, R. E. Reavill and F. J. Swinbourne, *J. Chem. Soc., B*, **1966**, 351; f) R. E. Klinck and J. B. Stothers, *Can. J. Chem.*, **40**, 1071 (1962); g) H. Güsten and M. Salzwedel, *Tetrahedron*, **23**, 173, 187 (1967); h) L. K. Dyall, *Aust. J. Chem.*, **17**, 419 (1964); i) T. Yonemoto, W. F. Reynolds, H. M. Hutton and T. Schäfer, *Can. J. Chem.*, **43**, 2668 (1965).

two main contributions;[3]

(1) Change of the electron density around the resonating proton.

(2) Change of the long range effect arising from the anisotropic magnetic susceptibility of the rest of the molecule.

Since the electron density can be altered by the substituent polar effect, proton chemical shift in aromatic system might be related to the Hammett σ constants[1a,b,f] or its modifications.[1e-i] This expectation will be realized as far as the chemical shifts are mainly determined by the electron density, as may be seen in the cases of the fluorine NMR chemical shifts of substituted fluorobenzenes[4] and ethynyl proton chemical shifts of substituted phenyl acetylenes[5a,b] where the contribution of factor (2) is relatively small.

General failure of the Hammett type treatment might thus be ascribed to the fact that both effects, (1) and (2), are often of equal magnitude and operate in a conflicting way.

The present paper deals mainly with the contribution of factor (2) and an attempt was made to obtain an excellent correlation between the chemical shifts of aromatic side chain protons as well as those of ring protons, and the Hammett's constant of the substituent.

In *para*-substituted aromatic side chain systems, an excess resonance interaction[6,1g,h] between substituent and a side chain can always result in the complication, leading to some difficulty in evaluating the substituent polar effects. For this reason, only the *meta*-substituent effect is considered in this paper and further studies on *para* system, which are now being undertaken, will appear in future.

Experimental

All the materials were purified by fractionation or by recrystallization and identified with their physical constants and elementary analyses.

1,1-Diphenylethylene[7] and most of substituted 1,1-diphenylethylenes were prepared by the dehydration of 1,1-diphenylethanols in 20% H_2SO_4 (Method a)[7] or by the dehydrochlorination of 1,1-diphenylethyl chlorides in pyridine (Method b).[8] The latter method was generally successful for *meta* halogeno derivatives. The 1,1-diphenylethanols were obtained by adding ethereal solution of ethyl acetate (Method A)[7] or of acetophenone (Method B)[9] to the Grignard solution of substituted bromobenzenes, or by adding ethereal solution of substituted benzophenones to the methylmagnesium bromide solution (Method C).[10]

1,1-Bis(cyanophenyl)ethylenes and 1-(cyanophenyl)-1-phenylethylenes were prepared by refluxing the corresponding bromophenylethylenes and cuprous cyanide in dry pyridine for 5—6 hr. (Method D).[10] The cyanides obtained were hydrolysed in alcoholic potassium hydroxide and the resulting carboxylic acids were esterified by dimethyl sulfates in methanolic potassium hydroxide media (Method E).

1,1-Bis(*m*-nitrophenyl)ethylene and 1-(nitrophenyl)-1-phenylethylenes were synthesized from the corresponding nitrobenzophenones through Wittig's reaction (Method F).[11]

1,1-Bis(*p*-nitrophenyl)ethylene was prepared by the dehydrobromination of 1-bromo-1,1-bis(*p*-nitrophenyl)-ethane in pyridine (Method G).[12] The bromide was prepared from 1,1-bis(*p*-nitrophenyl)ethane by bromination in carbon tetrachloride as usual with *N*-bromosuccinimide. In preparing 1,1-bis(*p*-nitrophenyl)ethane, 1,1-diphenylethane was nitrated by fuming nitric acid

TABLE 1-1. CHEMICAL SHIFTS OF METHYL PROTONS OF TOLUENES

Substituent	Observed [mp°C] or (bp°C/mmHg)	$\Delta\delta$/Hz*
p-OCH_3	(95/53,175)	+4.7
p-CH_3	(78.5—79.0/112)	+3.4
m-CH_3	(79.0—79.5/112)	+3.2
p-I	[34.9—35.0]	+2.6
p-Br	(105—106/69)	+2.2
m-I	(101—102/24)	+1.8
m-OCH_3	(108/96)	+1.8
p-F	(114)	+1.3
p-Cl	(87—87.5/70)	+1.2
H	(108.8—109.0)	τ=7.67
m-Br	(84—85/32)	0.0
m-Cl	(157—157.5)	−0.1
m-F	(112—113)	−1.3
m-CN	(118/30)	−4.0
p-Ac	(115—115.5/24)	−4.0
p-$CO_2C_2H_5$	(120—121/20)	−4.0
m-Ac	(108.5—109.5/19)	−4.5
p-CN	(103—103.5/20)	−5.4
p-NO_2	[52.8—53.1]	−8.2
m-NO_2	(108.9—109.2/15.2) [16.8—17.4]	−9.2

* Relative chemical shifts measured in 0.05 mol/*l* carbon tetrachloride solution.

3) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw Hill, New York (1959), p. 175.

4) R. W. Taft, Jr., *J. Phys., Chem.*, **64**, 1805 (1960).

5) a) C. D. Cook and S. S. Danyluk, *Tetrahedron*, **19**, 177 (1963); b) Y. Yukawa and H. Yamada, *Nippon Kagaku Zasshi*, **85**, 501 (1964).

6) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

7) A. H. Blatt, "Organic Syntheses," Coll. Vol I, 226 (1956).

8) See Ref. 12.

9) S. N. Ege and K. W. Sherk, *J. Amer. Chem. Soc.*, **75**, 354 (1953).

10) J. N. Ashley, J. F. Grove and T. Henshnell, *J. Chem. Soc.*, **1948**, 261.

11) G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954).

12) H. H. Szmant and J. F. Deffner, *J. Amer. Chem. Soc.*, **81**, 958 (1959).

Table 1-2. Chemical shifts of methyl protons of anisoles and of acetophenones

Substituent	Anisoles		Acetophenones	
	Observed [mp°C] or (bp°C/mmHg)	$\Delta\delta$/Hz*	Observed [mp°C] or (bp°C/mmHg)	$\Delta\delta$/Hz*
p-OCH_3	[55.5—56]	+3.20	(154/32)	+4.14
p-CH_3	(95/53, 173—4)	+2.44	(115—115.5/24)	+2.47
m-CH_3	(108/96, 173—4)	+1.61	(108.5—109.5/19)	+1.57
m-OCH_3	(101/17.5)	+1.15	(129—130/17)	+1.01
p-Br	(102—102.5/17)	+0.50	[53.5—54.5]	+0.98
p-Cl	(87—87.5/17.5)	+0.30	—	—
H	(84—85/75)	τ=6.24	(118—119/62)	τ=7.47
m-Br	(98.5—99/17)	−1.01	(127.5—128.5/14.5)	−0.30
m-Cl	—	—	(108—109/11)	−0.51
p-CO_2CH_3	[49—50]	−4.16	—	—
p-$CO_2C_2H_5$	(136.5—137.0/12)	−4.27	[56.2—56.7]	−2.66
m-CN	(132—133/26)	−4.43	[97—98.5]	−3.68
p-Ac	(154/32)	−4.89	—	—
m-Ac	(129—130/17)	−4.95	—	—
p-CN	[60.5—61]	−5.24	[59.5—60]	−3.37
p-NO_2	[53.5—54]	−8.16	[80.5—81]	−5.55
m-NO_2	[38.2—38.5]	−8.46	[76—77]	−7.46

* Relative chemical shifts measured in 0.05 mol/*l* carbon tetrachloride solution.

Table 1-3. Chemical shifts of ethylenic protons of 1-(substituted phenyl)-1-phenylethylenes

Substituent	[mp°C] or (bp°C/mmHg)		Method†	$\Delta\delta$/Hz**
	Observed	Reported		
p-OCH_3	[76.5—76.8]	[75][a]	Ca	+7.2, +4.6***
p-CH_3	(121.5—122/6.5)	(90/0.3)[b]	Ca	+3.18
p-F	(112—114/6.2)	(105—110/0.3)[c]	Ca	+1.73
m-CH_3	(129—130/7)	(122—123/0.85)[d]	Ba	+1.84
m-OCH_3	(153.5—155/12.5)	(168/14)[e]	Bb	+0.39
H	(113—114/3.0)	(113/2)[f]	Aa	τ=4.61
p-Cl	(149.5—151/9.5)	(157/12)[g]	Ca	−0.3
p-Br	(167.0—167.4/10.0)[27—29]	(185/10)[25.5—26.0][g]	Ca	−0.5
m-Br	(155.5—156.2/7.2)	*	Bb	−2.18
m-F	(128—130/10.5)	*	Cb	−2.5
m-Cl	(144/7)	(152—153/14)[e]	Cb	−3.0
p-CO_2CH_3	[75—76]	*	E	−5.5
m-CN	(165—167/7)	*	D	−4.3, −7.7***
p-CN	[45.9—46.4]	*	D	−6.3, −8.9***
p-NO_2	[68.3—68.8]	[66—66.5][h]	F	−11.3, −8.8***
m-NO_2	[89.0—89.4]	*	F	−10.01

† Methods of preparation summarized in the experimental part.
* New compound.
** Relative chemical shifts measured in 0.10 mol/*l* carbon tetrachloride solution.
*** Calculated from observed AB-quartet signal in which J=1.0—1.3 Hz. The averaged relative shift, $\frac{1}{2}(\Delta\delta_A+\Delta\delta_B)$, was used for the Hammett type plotting.

a) D. C. Hurd and N. Webb, *J. Amer. Chem. Soc.*, **49** 546 (1927).
b) M.S. Kharasch, A. Fono, W. Nudenberg and C. Poshkus, *J. Org. Chem.*, **15**, 775 (1950).
c) F. Bergmann and J. Szmuszkowicz, *J. Amer. Chem. Soc.*, **70**, 2748 (1948).
d) W.E. McEwen and N.B. Mehta, *ibid.*, **74**, 526 (1952).
e) E. Bergmann and A. Bondi, *Chem. Ber.*, **64B**, 1455 (1931).
f) Ref. 7 in the text.
g) Ref. 22 in the text.
h) Ref. 11 in the text.

TABLE 1-4. CHEMICAL SHIFTS OF ETHYLENIC PROTONS OF 1,1-BIS(SUBSTITUTED PHENYL)ETHYLENES

Substituent	[mp°C] or (bp°C/mmHg) Observed	Reported	Method†	$\Delta\delta$/Hz**
p-OCH_3	[142.0—142.3]	[142—143][a]	Ba	+11.88
p-CH_3	[61.3—61.5]	[61][b]	Ba	+6.32
m-CH_3	(133—134/4.2)	(134—139/5)[c]	Aa	+3.92
p-F	[48.3—48.5]	[46.5—47.0][d]	Aa	+3.42
m-OCH_3	(167—168/9)	(190/10)[e]	Aa	+0.95
p-Cl	[86.3—86.8]	[86.2—86.5][d]	Ca	−0.58
p-Br	[86.9—87.1]	[85.8—86.2][d]	Ca	−1.23
m-Br	(170—175/6)	*	Bb	−4.57
m-F	(104/7)	*	Aa	−4.78
m-Cl	(155.6—156.0/4.0)	*	Aa	−4.85
p-CO_2CH_3	[131.6—131.9]	*	E	−11.04
m-CN	[87.6—87.9]	*	D	−12.42
p-CN	[157.3—158.1]	[158—158.5][f]	D	−14.67
p-NO_2	[174.1—174.6]	[175—176.5][g]	G	−19.6***
m-NO_2	[88.2—88.9]	*	F	−20.25

† Methods of preparation summarized in the experimental part.
* New compound.
** Relative chemical shifts measured in 0.05 mol/*l* carbon tetrachloride solution.
*** Because of the low solubility, the chemical shift was measured with a 0.03 mol/*l* solution at elevated temperatures (80, 67, 61 and 47°C) and these data were extrapolated to 23°C.

a) P. Pfeiffer and R. Wiziner, *Ann. Chem.*, **461**, 132 (1928).
b) R. Anschütz and A. Hilbert, *Chem. Ber.*, **57B**, 1697 (1924).
c) C.S. Marvel and V. E. Nichols, *J. Amer. Chem. Soc.*, **60**, 1455 (1938).
d) Ref. 22 in the text.
e) G. Wittig and W. Gauss, *Chem. Ber.*, **80**, 363 (1947).
f) H.H. Szmant and R. Yonkoskie, *J. Org. Chem.*, **21**, 78 (1956).
g) Ref. 12 in the text.

(d=1.5) at −15°C.[13]

The proton chemical shifts, δx, for the substituted aromatic side chains were measured at 60 MHz in dilute (0.05—0.10 mol/*l*) carbon tetrachloride solution using a JNM-3H-60 spectrometer. Prior to the measurements of the chemical shifts, an NMR sample tube fitted with a thermometer reaching into the liquid paraffin in the tube, was spinned in the probe and the temperatures were directly read on the thermometer scale. Thus, the temperature of the sample under the condition of NMR measurement was estimated to be 20—25°C. The line positions were determined by linear interpolation between known audio frequency side bands of internal TMS or by direct superposition of the side band on the proton signal. The audio frequencies were measured with a frequency counter. The estimated reproducibility of δ_x was ±0.1 Hz. The observed relative chemical shifts, $\Delta\delta=\delta_X-\delta_H$, and the physical constants of the materials are listed in Tables 1-1—1-4.

Results and Discussion

The plots of relative chemical shifts, $\Delta\delta_m$, against Hammett's σ_m[1f] are shown in Figs. 1-1—1-7.

In the case of phenylacetylenes,[5a,b] a satisfactorily linear relationship is observed between the chemical shifts and Hammett constants (Fig. 1.7) as given

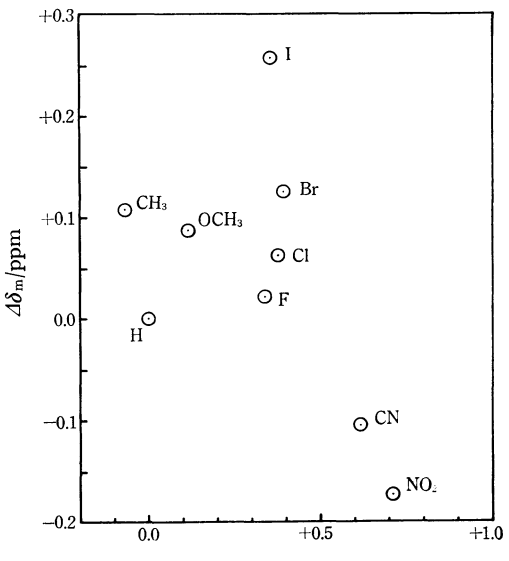


Fig. 1-1. Hammett plot for ring protons[14] *meta* from substituents.

13) I. P. Tsukervanik and M. D. Sokol'nikova, *Zh. Obshch. Khim.*, **24**, 1435 (1954).

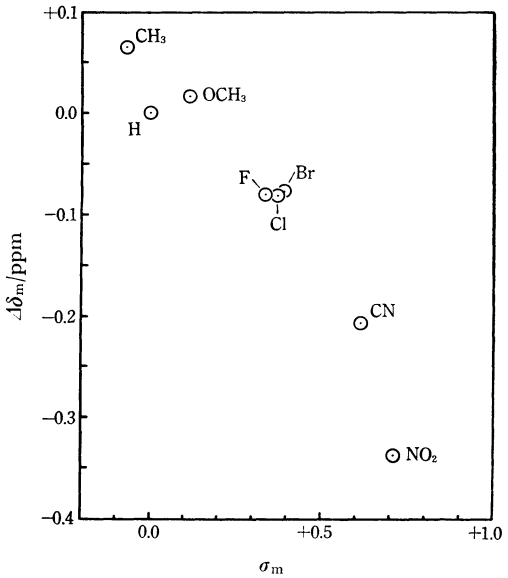


Fig. 1-2. Hammett plot for 1,1-di(*meta*-substituted phenyl)ethylenes.

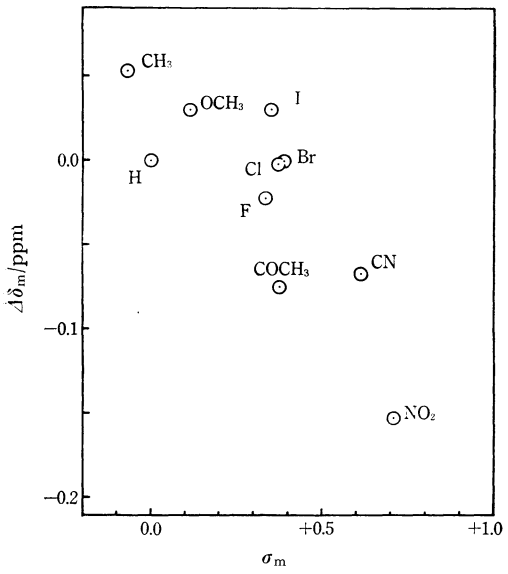


Fig. 1-3. Hammett plot for *meta*-substituted toluenes.

by the equation.

$$\Delta\delta_m = a_m\sigma_m \quad (1)$$

The relationship still roughly holds in the case of diphenylethylenes (Figs. 1-2 and 1-6). The ring protons[14] *meta* to the substituents, however, give no such correlation (Fig. 1-1), the points being scattered seriously. It is noted that the protons located far from the substituent generally give

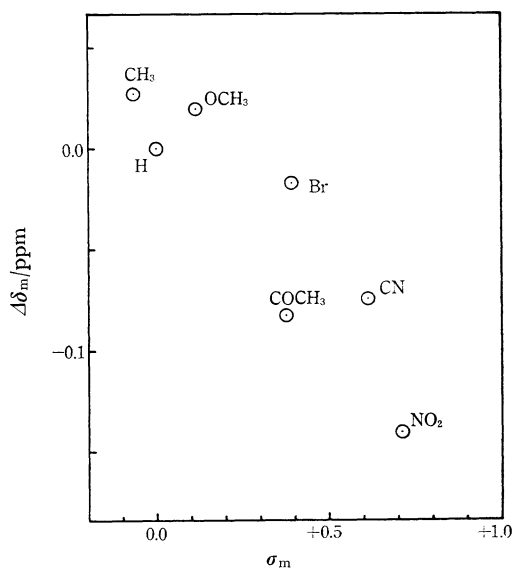


Fig. 1-4. Hammett plot for *meta*-substituted anisoles.

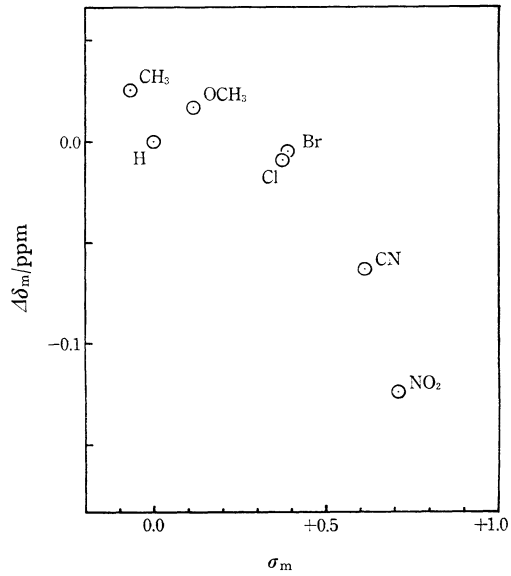


Fig. 1-5. Hammett plot for *meta*-substituted acetophenones.

better correlations.[15] Thus, the failure of correlation (1) could be mainly attributed to the long range effects of substituent magnetic anisotropy.[3,15]

Halogens and cyano group are known to have a large negative (shielding) magnetic anisotropy, $\Delta\chi$, along C-substituent axis.[3,16a-d] In fact, the

14) F. Langenbucher, E. D. Schmidt and R. Mecke, *J. Chem. Phys.*, **39**, 1901 (1963).

15) Y. Yukawa and Y. Tsuno, "Kagaku no Ryoiki," Nankodo, sp. ed. No. 85, Spectrochem. '**68B** (1969), Chap. 4, p. 87.

16) a) J. A. Pople, *Proc. Roy. Soc.*, **A239**, 549, 557 (1957); b) J. A. Pople, *J. Chem. Phys.*, **37**, 60 (1962); c) T. J. Flautt and W. F. Erman, *J. Amer. Chem. Soc.*, **85**, 3243 (1963); d) W. Zeil and H. Buchert, *Z. Phys. Chem.*, **38**, 47 (1963).

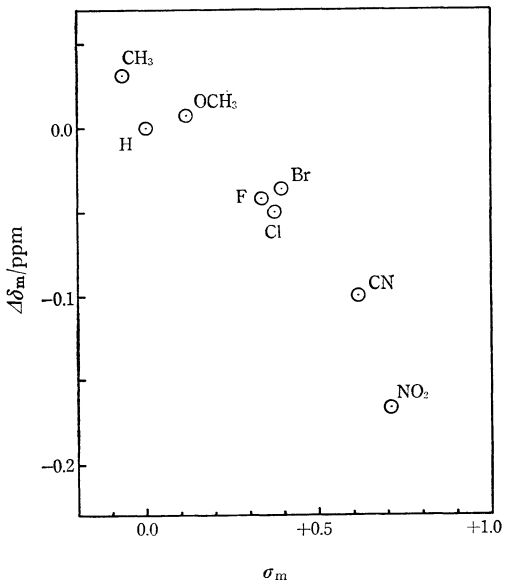


Fig. 1-6. Hammett plot for 1-phenyl-1-*meta*-substituted phenylethylenes.

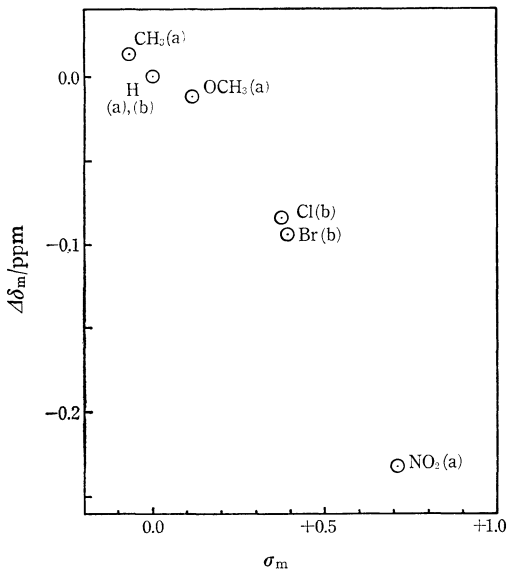


Fig. 1-7. Hammett plot for *meta*-substituted phenylacetylenes. (a) Ref. 5a, (b) Ref. 5b

remarkable deviations to the high field side are observed for these substituents (Figs. 1-1, 1-3, and 1-4). Methoxy, methyl, and nitro groups, on the other hand, show an interesting feature. Examination of Figs. 1-1—1-7 with these substituents indicates that each of the correlation line along the points of the three substituents does not pass through the origin of the coordinate but deviates remarkably to the high field side, in other words, the effect of electron attracting nitro group seems to be abnormally decreased, whereas the effect of electron releasing methyl and methoxy group, to be abnormally increased. It is important, however, to note that no significant anomaly has generally been observed in the Hammett type plotting of the aliphatic compounds[17a,b] with these three substituents as well as the hydrogen (unsubstituted compound). If we consider this observation as evidence suggesting the zero or negligibly small anisotropy of these four groups (hereafter referred to as the selected substituent), the high field deviations observed in the present experiments should not be ascribed to the substituent magnetic anisotropy effect. This suggestion is supported strongly by both theoretical and experimental evaluation of the anisotropy of the selected substituents as discussed below.

For methyl group anisotropy,[18a-d] even though there may still be many arguments about its magnitude (the positive $\Delta\chi$ along the C–CH_3 axis which should give a deshielding effect on the proton under discussion), an isotropic magnetic susceptibility ($\Delta\chi=0$) was proposed by Pople.[16b] Thus the high field deviation of methyl group can never be reduced but rather enlarged by the correction for the anisotropy effect. For hydrogen, such anisotropy can not be predicted theoretically.[16b] In methoxy group, magnitude and direction were calculated theoretically by Pople.[16b] By the use of Pople's $\Delta\chi$, it can be shown that the methoxy group exerts a shielding effect on the proton under investigation,*1 but the effects are negligibly small at the side chains. There has been no quantitative evaluation of nitro group anisotropy, but a negative $\Delta\chi$ could be supposed to exist along the axis perpendicular to O–N–O plane. This anisotropy, however, should give a low field shift of the protons. The situation for nitro group is therefore the same as for methyl group; the correction would result in the increased high field deviation.

In view of these facts, it can be concluded that the high field deviations observed for the three substituents (CH_3O, CH_3, NO_2) should be ascribed to the contribution of an unknown factor other than the substituent magnetic anisotropy effect.

One possible explanation for the high field deviation may be given by the different way of being

17) a) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961); b) H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 722 (1961).

18) a) R. F. Zürcher, *Discuss. Faraday Soc.*, **34**, 66 (1962); b) R. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, **31**, 1302 (1959); c) J. Guy and J. Tillieu, *ibid.*, **24**, 1117 (1956); d) J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders and W. B. Whalley, *Tetrahedron*, **23**, 2339 (1967).

*1 The correction for the anisotropy effect would move the point of methoxy group somewhat downwards (−0.018 ppm in benzene series, −0.009 ppm on toluene series), but the improvement is clearly insufficient.

affected by the polar substituent between the chemical shift and chemical reactivity. According to Buckingham's theory,[19] the polar effect on the proton chemical shift can be given (neglecting the second order term) in terms of the electric field components along the C–H bond as shown in the equation

$$E_z = k_E \sum_i (q_i \cos\theta_i / \varepsilon r_i^2) \qquad (2)$$

where r_i denotes the distance between the resonating proton and the atom i carrying a point charge q_i, and θ_i is the angle between r_i and the C–H bond.

On the other hand, Hammett's σ_m constant, determined from a reactivity measurement, should approximately be related to a potential energy[20] arising from an interaction between the point charge induced at the reaction center and point charges, q_i, which are distributed over the rest of the molecule. Hammett's σ_m constant could thus be related to the term

$$\sum_i (q_i/\varepsilon R_i)$$

where R_i is the distance between the reaction center and the location of charges on the reacting molecule in transition or product state.

It is convenient to divide the electric field effect into two classes:

(a) An effect attributable to the charge distribution brought about in the side chain by a polar effect of substituted phenyl group.

(b) An effect attributable to the charge distribution arising from the C(phenyl)-substituent polarization and to the π-electron distribution affected by the polar resonance of the substituent.

Effect (a) on the chemical shift will be the same in character as that on the potential energy change. Then the effects may be expressed, in both cases, in terms of Hammett's σ_m. For effect (b), however, a somewhat larger contribution of the π-electronic charge in the case of chemical shift could be expected since the distance between the resonating proton and the π-electronic charge, r_π or R_π, will be generally shorter than that between the resonating proton and the charges distributed in the C(phenyl)-substituent dipole, r_μ or R_μ:

We have $r_\pi \ll r_\mu$ and $R_\pi \ll R_\mu$ as cited above and if $\cos\theta_\pi \fallingdotseq \cos\theta_\mu$ as might be expected in the molecule having a long side chain, then

$$\frac{\cos\theta_\pi / r_\pi^2}{\cos\theta_\mu / r_\mu^2} > \frac{1/R_\pi}{1/R_\mu}$$

If this is true, the polar effect on the chemical shift could be expressed in the following form by allowing the additional contribution of π-electronic effect, $k\sigma_\pi$,

$$\Delta\delta_m = a_m\sigma_m + k\sigma_\pi \qquad (3)$$

in which the σ_π is Yukawa-Tsuno's parameter[11] measuring the resonance ability[4] of the substituent.*2

Another possible cause for high field deviation is a variation in the magnetic anisotropy of benzene ring due to π-electronic perturbation in the ring system brought about by the polar resonance of the substituent. There are two different aspects to interpret the effect of π-electronic perturbation. First of which predicts a decrease on the ring current by +R substituent[4] leading to a high field shift of the protons or an increase in the ring current by −R substituent[4] leading to a low field shift of the protons. If it is assumed that the variation of the π-electronic density on the benzene ring is proportional to the resonance ability, σ_π, of an introduced substituent, the correction for the ring current effect may be given in the same expression as (3).*3

By the use of Eq. (3), the deviations are somewhat reduced than before. However, the improvement is still not quite satisfactory, as may be seen in the case of ring protons and toluenes (Fig. 2). Failure of the additional π-electron contribution model is further verified by the fact that the evaluations of the geometric factors for the side chain systems under investigation show that the relative contributions of π-electronic effect in the chemical shift are generally equal to those in the reactivity and also that the contributions are independent of the nature of side chains at *meta* position.*4

$$\frac{\sum_i (\cos\theta_i/r_i^2)_\pi}{\sum_i (\cos\theta_i/r_i^2)_\mu} \fallingdotseq \frac{\sum_i (1/R_i)_\pi}{\sum_i (1/R_i)_\mu} \fallingdotseq \text{const.} \qquad (4)$$

It is well known that the olefinic protons of

19) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).
20) T. Ri and H. Eyring, *J. Chem. Phys.*, **8**, 433 (1940).

*2 Yukawa and Tsuno separated the substituent effect into the sigma-inductive effect, σ_i, and pi-electronic effect, σ_π, and demonstrated the generality and utility of this separation.[11] The success of this separation in explaining the polar effects justifies the use of σ_π here.

*3 Equation (3) is similar in form to the equation proposed by Taft

$$\Delta\delta_m = \alpha\sigma_I + \beta\sigma_R^0 = \alpha\sigma_m + (\beta-\alpha)\sigma_R^0$$

or to the equation[15]

$$\Delta\delta_m = \alpha\sigma_p^0 \fallingdotseq \alpha\sigma_m + \beta'\sigma_R^0$$

Although both these equations gave better correlations than in the simple Hammett relation, no detailed discussion was made about the correction term, $(\beta-\alpha)\sigma_R^0$ or $\beta'\sigma_R^0$.

*4 An exception for the generality (4) is noted in the case of ring protons at *para* position for which a large excess contribution of π-electronic effect to the chemical shift can be calculated from the examination of the geometric functions and this is consistent with the observation that the *para* ring protons[2c] are satisfactorily correlated to the σ_π constants[11] rather than to the σ_P^0 constants.[4]

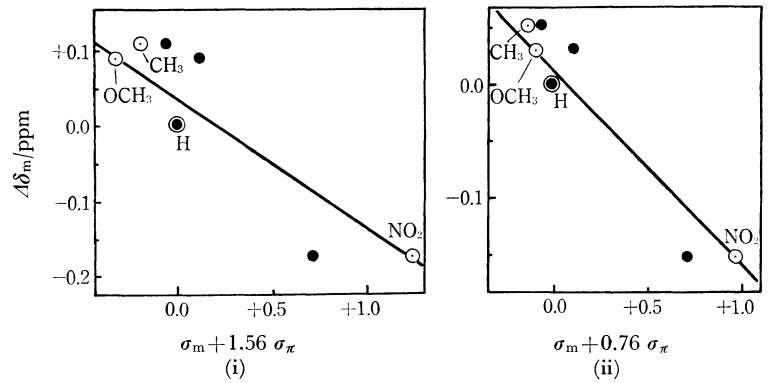


Fig. 2. Failure of the Eq. (3).
(i) Ring protons. (ii) Toluenes. Closed circle shows the original σ_m plot.

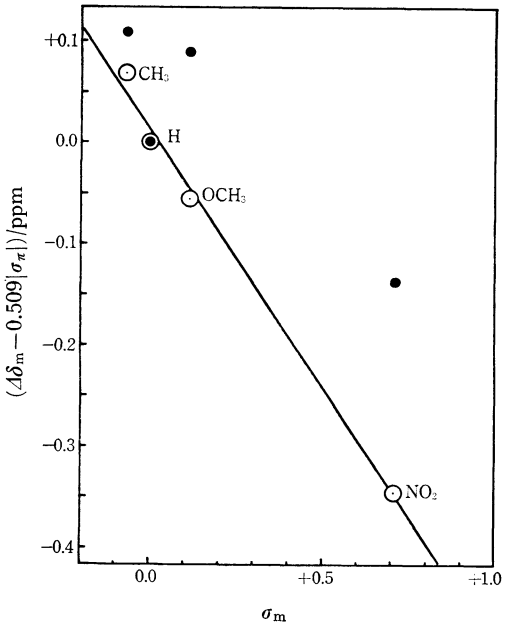


Fig. 3-1. Application of the Eq. (5) to ring protons *meta* from substituents.
Closed circle denotes the observed relative shift, $\Delta\delta_m$.

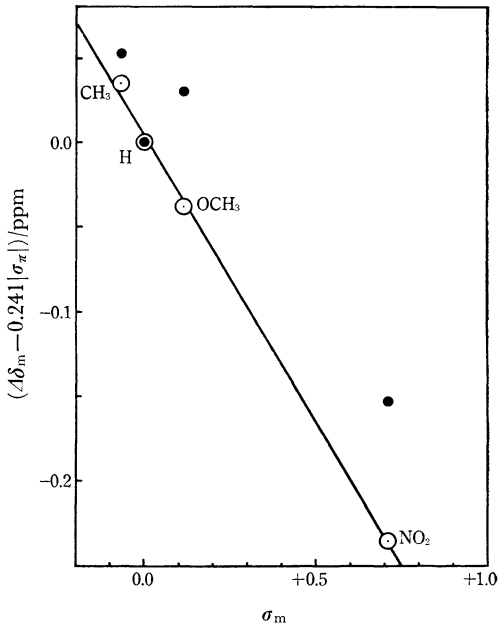


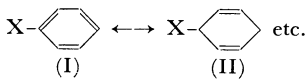
Fig. 3-2. Application of the Eq. (5) to *meta*-substituted toluenes.

TABLE 2. APPLICATION OF EQ. (5) AND JOHNSON-BOVEY'S RING CURRENT SHIFTS

Side chain system	Application of Eq. (5)				Ring current shift
	$-a_m$/ppm	K/ppm	r_c*	s/ppm**	$-f(\rho,z)$/ppm
X-$C_6H_4\underline{H}$	0.511	0.509	0.993	0.026	1.50
(X-$C_6H_4)_2C{=}C\underline{H}_2$	0.623	0.312	1.000	0.002	0.70
X-$C_6H_4C\underline{H}_3$	0.339	0.241	0.999	0.009	0.57
X-$C_6H_4O\underline{CH}_3$	0.283	0.187	0.999	0.006	0.40
X-$C_6H_4COC\underline{H}_3$	0.251	0.164	1.000	0.003	0.34
X-C_6H_4,$C_6H_5C{=}C\underline{H}_2$	0.305	0.149	1.000	0.002	0.35
X-$C_6H_4C{\equiv}C\underline{H}$	0.367	0.116	0.997	0.017	0.21

* Correlation coefficient.
** Standard deviation.

cycloolefin having localized double bonds show somewhat higher chemical shifts as compared with the normal aromatic ring protons. The feature has generally been explained in terms of the lack of ring current in those cyclic molecules.[21a,b] This suggests another possibility to interpret the effect of π-electronic perturbation due to introduced substituent. The introduction of substituent will result in an additional contribution of quinoidal structure (II) in the resonance hybrid and hence



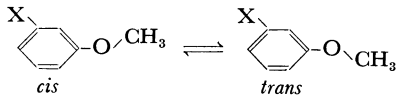
(I) (II)

lead to some decrease of the ring current. The extent of the contribution of structure (II), depending only on the resonating ability of the substituent but not on the direction of electronic displacement, could be estimated by the term, $|\sigma_\pi|$. Correcting for this term, we can express $\Delta\delta_m$ for the selected substituents at *meta* position as

$$\Delta\delta_m = a_m\sigma_m + K|\sigma_\pi| \quad (5)$$

where K is a proportionality constant describing susceptibility to the contribution of quinoidal structure (II). Figures 3-1 and 3-2 show two examples of the plots of the relative chemical shifts corrected for the quinoidal effect, $\Delta\delta_m - K|\sigma_\pi|$, against Hammett's σ_m constants. The parameters, a_m and K, were determined using least squares method and are summarized in the first four columns of Table 2 where correlation coefficients, r_c and standard deviations, s, also are included. It is clear that the employment of treatment (5) for the given series yields significant improvements in the correlations. Additional evidence for the contribution of decreased ring current term, $K|\sigma_\pi|$, is provided by an examination of the variation of parameter K. Since K is a susceptibility coefficient to the diminution of ring current effect, it should depend only on the geometric relation between the resonating protons and the benzene ring. In order to testify this suggestion, the Johnson and Bovey's ring current shifts[21a] in ppm, $f(\rho,z)$, were utilized as a measure of the geometric factors for the resonating protons located at the usual cylindrical coordinates ρ and z.

In the last column of Table 2, the calculations of $f(\rho,z)$ were performed by averaging over all the reasonable orientations of the side chains; for the methyl protons, $f(\rho,z)$'s were calculated by assuming free rotation of the methyl group. In anisoles and acetophenones, the calculations were based on the planar *cis*- and *trans*-model of equal



cis *trans*

21) a) G. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958); b) J. S. Waugh and R. W. Fessenden, *J. Amer. Chem. Soc.*, **79**, 846 (1957).

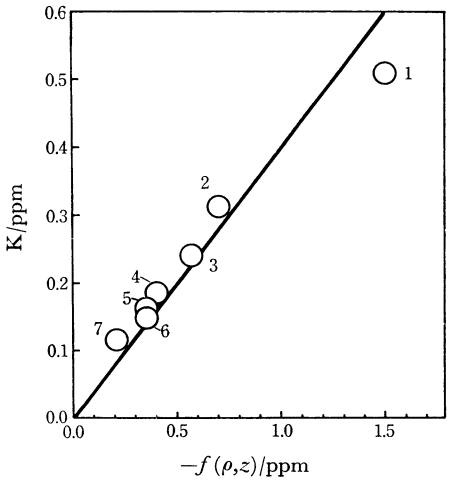


Fig. 4. Dependence of K in Eq. (5) on the Johnson-Bovey's ring current effect.
1. X-$C_6H_4\underline{H}$, 2. $(X\text{-}C_6H_4)_2C{=}C\underline{H}_2$, 3. X-$C_6H_4$-$C\underline{H}_3$, 4. X-$C_6H_4O\underline{CH}_3$, 5. X-$C_6H_4C\underline{OCH}_3$, 6. X-$C_6H_4$,$C_6H_5C{=}C\underline{H}_2$, 7. X-$C_6H_4C{\equiv}C\underline{H}$

populations. In diphenylethylenes, two benzene rings were twisted 30° out of $C{=}CH_2$ plane[22] and the equal populations of *cis*- and *trans*-form were assumed.

The result of closer examination of the relationship between K and $f(\rho,z)$ is shown in Fig. 4. A linear dependence of K on $f(\rho,z)$,

$$K = -0.4f(\rho, z) \quad (6)$$

is consistent with the expectation that the effect of the ring current depression on the chemical shift will be nearly proportional to the strength of the ring current field to which the resonating proton is exposed. Using relation (6), we obtain, from (5),

$$\Delta\delta_m + 0.4f(\rho, z)|\sigma_\pi| = a_m\sigma_m \quad (7)$$

which involves only one parameter, a_m. In applying Eq. (7) to the given side-chain systems, the agreement was quite satisfactory and no essential differ-

Table 3. Substituent constants in Eq. (10)

Substituent	σ_m	-10^{23}A/(cm^{3}ppm)	$\lvert\sigma_\pi\rvert$[11i]
OCH_3	+0.115	0.0	0.281
CH_3	−0.069	0.0	0.078
H	0.000	0.0	0.000
F	+0.337	1.1	0.118
Cl	+0.373	1.7	0.070
Br	+0.391	2.0	0.054
I	+0.352	~2.3	0.056
CN	+0.615	1.3	0.25
NO_2	+0.710	0.0	0.34

22) G. E. Cootes and L. E. Sutton, *J. Chem. Soc.*, **1942**, 567.

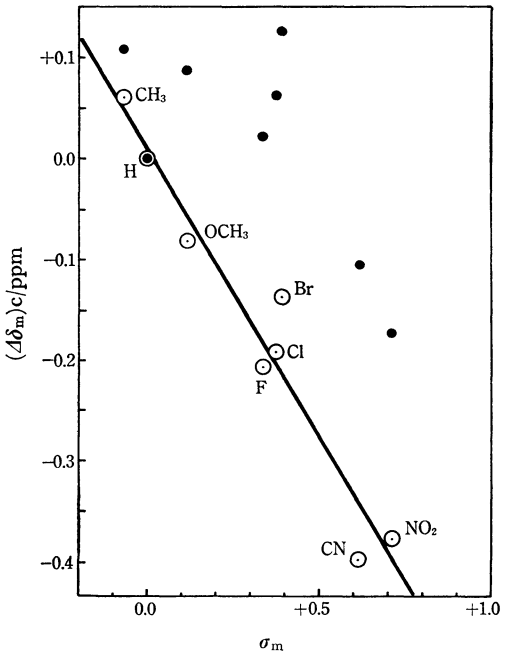


Fig. 5-1. Application of the Eq. (10) to ring protons *meta* from substituents.
Closed circle denotes the observed relative shift, $\Delta\delta_m$.

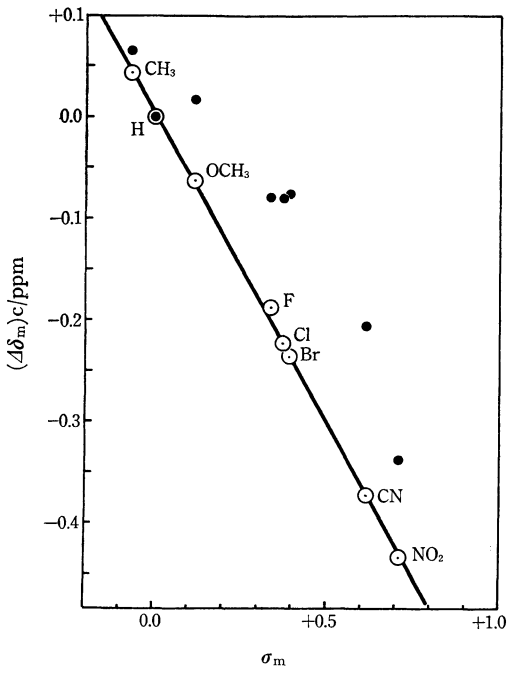


Fig. 5-2. Application of the Eq. (10) to 1,1-di (*meta*-substituted phenyl)ethylenes.

ence in results was noted as compared with the use of Eq. (5). While the present report was being written,[23a] Figeys and Flammang calculated theoretically the variation of ring current effect for the

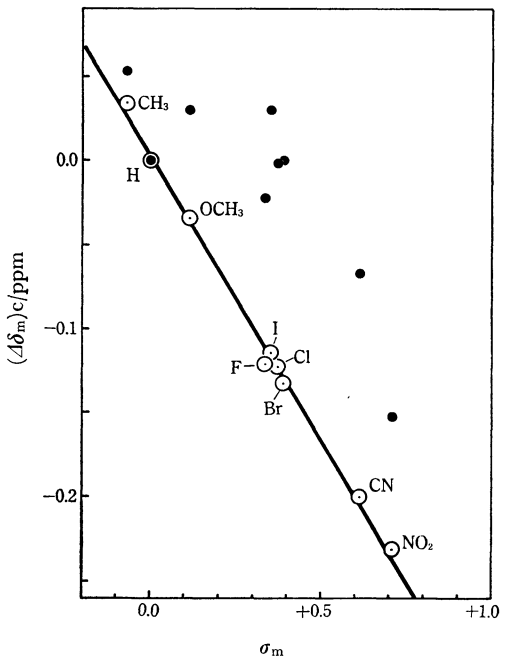


Fig. 5-3. Application of the Eq. (10) to *meta* substituted toluenes.

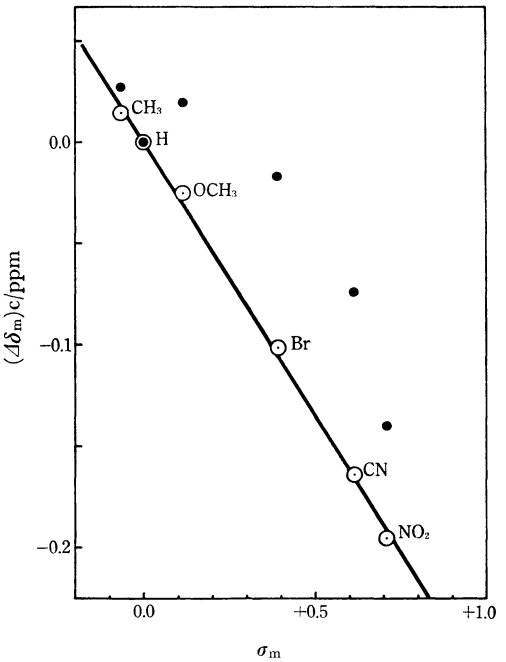


Fig. 5-4. Application of the Eq. (10) to *meta*-substituted anisoles.

ring protons at *para* position of mono-substituted benzenes.[23b] The calculated decreases of ring

23) a) H. Yamada, Dr. thesis, Osaka University (1968); b) H. P. Figeys and R. Flammang, *Mol. Phys.*, **12**, 581 (1967).

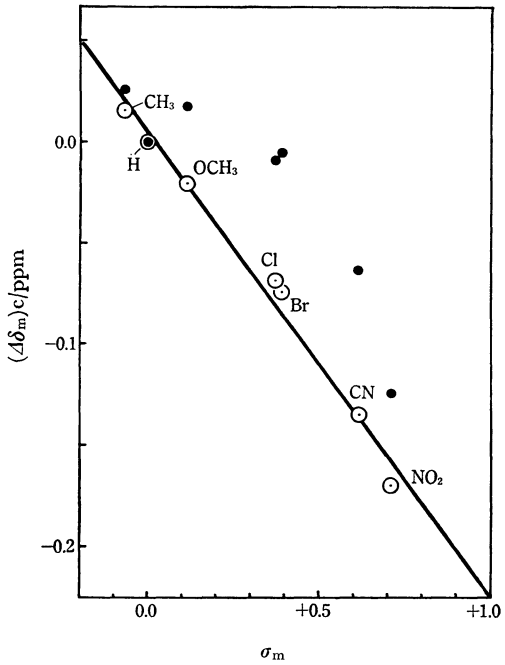


Fig. 5-5. Application of the Eq. (10) to *meta*-substituted acetophenones.

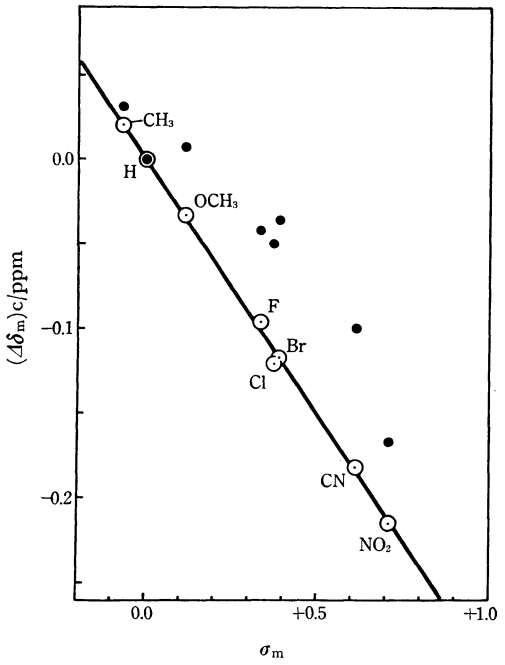


Fig. 5-6. Application of the Eq. (10) to 1-phenyl-1-*meta*-substituted phenylethylenes.

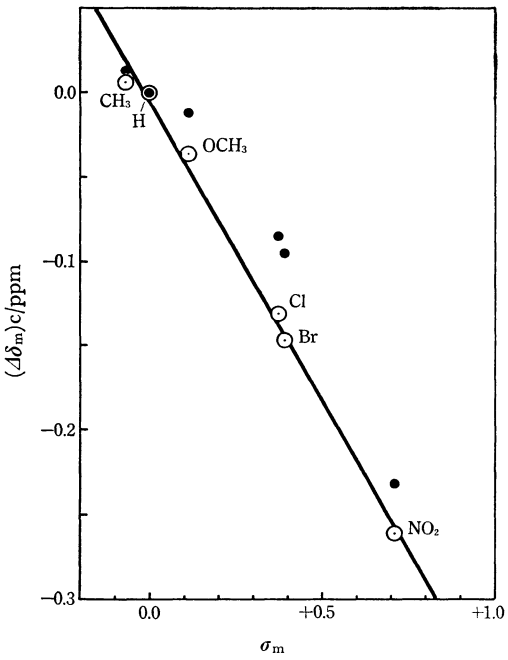


Fig. 5-7. Application of the Eq. (10) to *meta*-substituted phenylacetylenes.

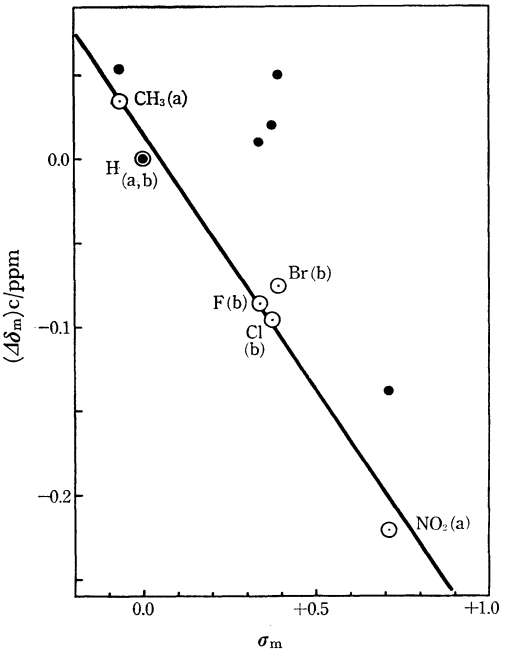


Fig. 5-8. Application of the Eq. (10) to *meta*-substituted benzaldehydes.
(a) T. Kinugasa, H. Yamada and S. Hamano, unpublished data. (b) Ref. 2f.

current effect were 0.15 ppm for NH_2, 0.08 ppm for OCH_3 and 0.06 ppm for $C\equiv N$. The values are in qualitative agreement with our estimations based on the term, $-0.4f(\rho,z)|\sigma_\pi|$ in Eq. (7). This fact, in addition to the success of correlation (6), suggests strongly that the observed high field deviations result from the decreased ring current due to introduced substituent.

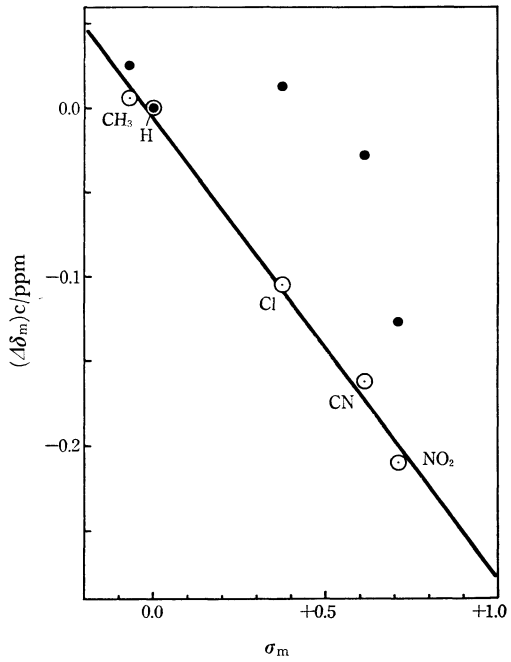


Fig. 5-9. Application of the Eq. (10) to α-protons of *meta*-substituted *trans*-cinnamic acids.[24]

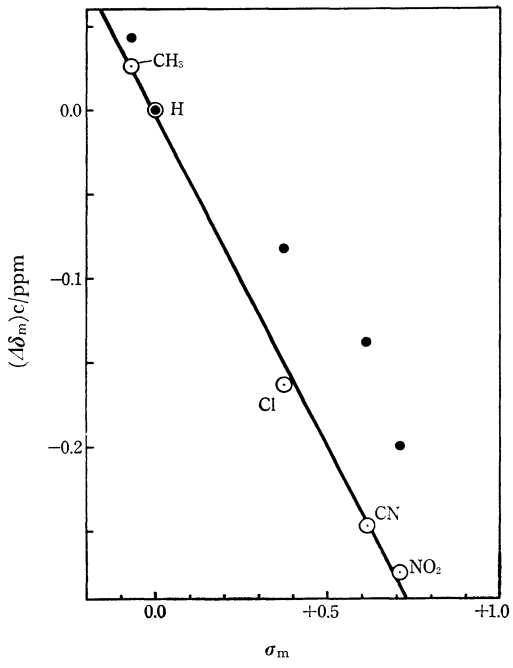


Fig. 5-10. Application of the Eq. (10) to β-protons of *meta*-substituted *trans*-cinnamic acids.[24]

The plot of the anisotropic substituents, however, still shows considerable deviations from the line required by Eq. (7). We may now consider the effect of the anisotropic substituents. If it is assumed that the observed deviation, Δ, is mainly ascribed

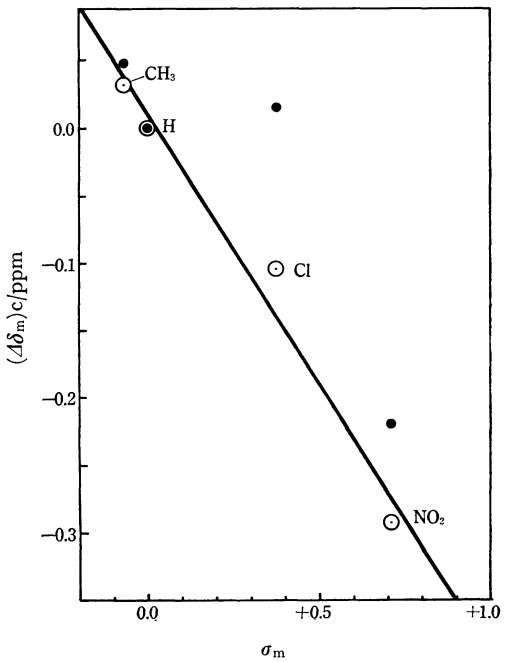


Fig. 5-11. Application of the Eq. (10) to α-protons of *meta*-substituted *cis*-cinnamic acids.[24]
The calculations of the geometric terms were based on the model in which the benzene ring was twisted 90° out of CH=CH plane.

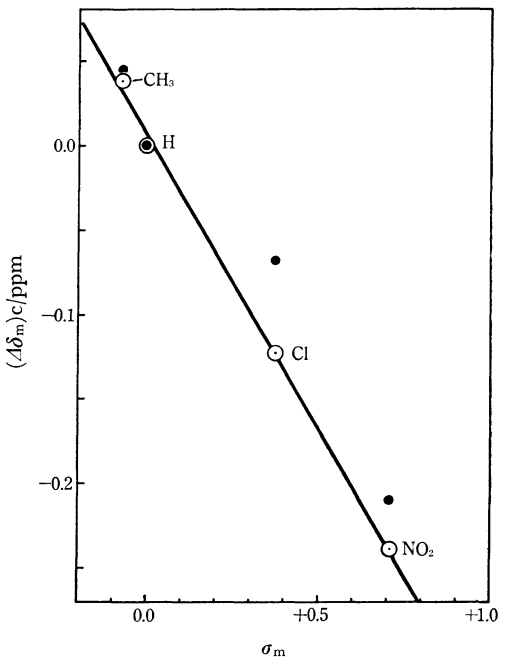


Fig. 5-12. Application of the Eq. (10) to β-protons of *meta*-substituted *cis*-cinnamic acids.[24]
The calculations of the geometric terms were based on the model in which the benzene ring was twisted 90° out of CH=CH plane.

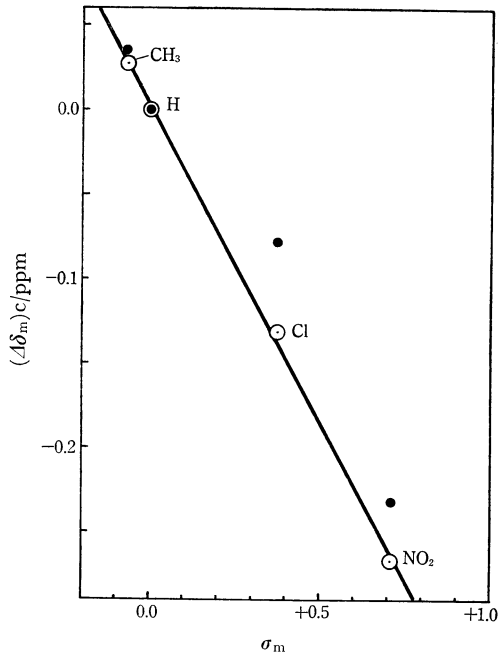


Fig. 5-13. Application of the Eq. (10) to *trans* protons of *meta*-substituted styrenes.[24]

to the anisotropy effect of the substituent, and also that the point dipole approximation[3] is applicable, the relative magnitude of the anisotropy effect between series A and B is given by

$$\frac{\Delta_B}{\Delta_A} = \frac{\Delta\chi(3\cos^2\theta_B - 1)3NR_A^3}{\Delta\chi(3\cos^2\theta_A - 1)3NR_B^3} = \frac{(3\cos^2\theta_B - 1)R_A^3}{(3\cos^2\theta_A - 1)R_B^3} \quad (8)$$

Equation (8) indicates that a magnetic anisotropy effect, Δ, in any side chain system can be calculated experimentally from Δ_A for a specified system A and geometric factors of the respective systems, even if the anisotropy of the substituent $\Delta\chi$ is not known:

$$\Delta = \Delta_A\frac{(3\cos^2\theta - 1)R_A^3}{(3\cos^2\theta_A - 1)R^3} \equiv \mathbf{A}\cdot\frac{3\cos^2\theta - 1}{R^3} \quad (9)$$

where **A** is a substituent anisotropy effect per unit geometric factor

$$\mathbf{A} = \Delta_A\frac{R_A^3}{3\cos^2\theta - 1},$$

and this can be calculated from a particular side chain system taken as the standard. In this study the values of **A** were evaluated by averaging two calculations based on toluenes and bis-(substituted phenyl)ethylenes (Table 3). For each of the halogen substituents, a magnetic point dipole μ_M, was assumed to be along the C(phenyl)-halogen bond, and located at the position of the halogen nucleus. For cyano group, the μ_M directed to the C≡N bond was located at the center of the bond. All the calculations were made on the basis of the same molecular model as that used in the estimation of ring current effect, $f(\rho,z)$.

Table 4. Application of Eq. (10)

Side chain system	$-a_m$/ppm	r_c*	s/ppm**
X-$C_6H_4\underline{H}$[a]	0.571	0.971	0.042
(X-$C_6H_4)_2C{=}C\underline{H}_2$	0.610	0.999	0.006
X-$C_6H_4C\underline{H}_3$	0.337	0.998	0.006
X-$C_6H_4OC\underline{H}_3$	0.270	0.999	0.004
X-$C_6H_4COC\underline{H}_3$	0.229	0.992	0.010
X-C_6H_4,$C_6H_5C{=}CH_2$	0.301	0.999	0.004
X-$C_6H_4C{\equiv}C\underline{H}$	0.355	0.997	0.009

a) $\Delta\delta_m$ for iodobenzene was omitted from the least squares calculation.
* Correlation coefficient.
** Standard deviation.

Introduction of the substituent anisotropy term (9) into Eq. (7) gives

$$\Delta\delta_m + 0.4f(\rho,z)|\sigma_\pi| + \mathbf{A}\cdot\frac{3\cos^2\theta - 1}{R_3} = a_m\sigma_m \quad (10)$$

which should be applicable to all the substituents including magnetically anisotropic ones. The left hand side of Eq. (10) represents the observed relative shifts corrected for the ring current variation and for the substituent magnetic anisotropy. This corrected value is regarded as an observable relative shift which depends only on the polar effects of the substituent. In Figs. 5-1—5-7, the corrected relative shifts, $(\Delta\delta_m)_c$, are plotted against Hammett's σ_m constants and the results are summarized in Table 4. The agreement is quite satisfactory. The applicability of Eq. (10) was further tested using data reported in literature.[2f,24] The successful results (Figs. 5-8—5-13) are collected in Table 5.

In view of the above results it may be concluded that Eq. (10) is fairly general in spite of the approximate nature of the derivation and useful, because of its simplicity, for estimating substituent chemical shifts and for examining the rotational conformation of the side chains.

It is pointed out that the variation of the susceptibility parameter to the polar effects, a_m, exhibits the same trend as that of ρ for the dissociation constants of corresponding carboxylic acid in a given solvent.[25] The lack of strict linear correlation between a_m and ρ might be attributed to the difference in the geometric functions for the chemical

24) T. A. Wittstruck and E. N. Trachtenberg, *J. Amer. Chem. Soc.*, **89**, 3803 (1967).
25) R. W. Taft, Jr., and I. C. Lewis, *ibid.*, **81**, 5343 (1959).

TABLE 5. APPLICATION OF EQ. (10) TO DATA OBTAINABLE FROM LITERATURE

Side chain system		$-f(\rho,z)$/ppm	$-a_m$/ppm	r_c*	s/ppm**	Ref.
X-C_6H_4C$\underline{H}$O		0.61	0.305	0.982	0.019	2f
X-C_6H_4 $\underline{H}_B$ >=< $\underline{H}_A$ CO_2H	A	0.62	0.272	0.995	0.011	24
	B	0.56	0.394	0.999	0.009	24
X-C_6H_4 CO_2H >=< $\underline{H}_A$ $\underline{H}_C$	A†	0.54	0.400	0.986	0.030	24
	C†	0.21	0.348	0.999	0.007	24
X-C_6H_4 H >=< H $\underline{H}$		0.26	0.374	0.999	0.005	24

* Correlation coefficient.
** Standard deviation.
† The calculations of the geometric terms were based on a model in which the benzene ring was twisted 90° out of CH=CH plane.

shift and for the reactivity. The quantitative explanation for this situation will require a precise knowledge of electronic distribution on the side chain.

Exceptions to the applicability of Eq. (10) are the iodo- and bromo-substituted benzene system. This might be partly due to the incorrect estimation of anisotropy effects for these substituents. The point dipole approximation may be no more valid in bromo- and iodobenzenes where the dimension of the anisotropic substituent seems to be too large as compared with the distance R. Nakagawa *et al.* suggested the importance of the spin polarization effects[26] particularly in the molecule possessing heavy atoms such as iodine and bromine. Such effects may also contribute to the relative chemical shifts of ring protons *meta* to the substituent since the transmittance of the spin coupling will be considerably larger than in other side chain systems in which the resonating protons are separated from the spin polarizable substituent by more than three atoms. An investigation of this possibility, in addition to the study on *para* systems, must be the subject of future research.

The authors wish to express their gratitude to Professor Toshio Kinugasa of Kobe University for his constant advice and encouragement and for making facilities available for carrying out the NMR measurements.

26) N. Nakagawa, M. Shinada and T. Ô-hinata, Preliminary Report of the 6th NMR Symp., Kyoto, p. 8 (1967).