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Studies on the Proton Magnetic Resonance Spectra in Aromatic Systems. III.[1] Discussions on the Substituent Shielding Parameter and π-Electron Charge Density

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The revised substituent shielding parameter has been proposed in *ortho* and *meta* ^{1}H shift for estimating the π-electron charge densities in substituted benzene series, and, also the resonance contribution has been proved to be a dominant factor in determining the *meta* ^{1}H shift.

The π-electron charge density calculated from simple sum rule of the revised shielding parameter showed passable agreement with those from HMO treatment.

In the previous communication,[1] the authors examined the correlations among substituent shielding parameter in mono-substituted benzene series *vs.* π-electron charge density and proposed the revised shielding parameter appropriate to obtain π-electron charge density without mathematical treatment. These parameters have been proved reliable for π-electron charge density estimation in poly-substituted benzene series.

In the present study, the authors examined the correlations among revised substituent shielding parameter and π-electron density, *etc.* and estimated the revised shielding parameter for each substituent.

Discussion

1) On the Substituent Shielding Parameter and π-Electron Charge Density

Formerly, Corio and Dailey[3] estimated the aromatic ring ^{1}H chemical shift in *ortho, meta* and *para* positions, and a few years ago, Martin, Dailey,[4] Spiesecke, Schneider,[5] and Diehl[6] obtained more accurate results from their advanced experiments. And, for the physical organic treartment of above parameters, the correlations *vs.* Hammett constants σ_I and σ_R have been investigated from several groups of workers.[6-9]

Recently, Schaefer, *et al.*[10] have estimated from their elegant experiment the magnitude of aromatic ^{1}H chemical shift per one π-electron as below:

$$\delta = 10.7 \pm 0.2\ \mathrm{ppm}/e \cdot \Delta\rho$$

where δ = ^{1}H chemical shift

$\Delta\rho$ = excess charge density

1) Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **15**, 1429 (1967).
2) Location: *Toneyama, Toyonaka, Osaka.*
3) P.L. Corio and B.P. Dailey, *J. Am. Chem. Soc.*, **78**, 3043 (1956).
4) J.S. Martin and B.P. Dailey, *J. Chem. Phys.*, **39**, 1722 (1963).
5) H. Spiesecke and W.G. Schneider, *J. Chem. Phys.*, **37**, 731 (1961).
6) P. Diehl, *Helv. Chim. Acta*, **44**, 829 (1961).
7) Y. Yukawa, *et al.*, Memories of Sci. and Ind. Res. Inst. Osaka University, **17**, 185 (1960).
8) R.W. Taft Jr., *J. Phys. Chem.*, **64**, 1805 (1960).
9) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, **32**, 960 (1963).
10) T. Schaefer and W.G. Schneider, *Can. J. Chem*, **4**, 966 (1963).

And the derived charge density from above equation has been compatible with those from HMO calculation in electron releasing substituent groups——for example, anisole, aniline, *etc.* In our previous treatment[1], the revised shielding parameters have been estimated from following reasons.

i) d_p——The shielding parameter in *para* position——is mainly controled from the resonance factor transmitted by π–electron framework, and in this position the contribution of inductive factor transmitted through 5 σ–bonds could be ignored.[5]

ii) d_m——The magnitude of which is within ± 0.2 ppm——is dependent on inductive, resonance and magnetic anisotropy effects to a certain extent, and in some molecule——for instance, nitrobenzene——the contribution from "electric field effect"[11] shows good coincidence. Consequently, the contribution from π–electron charge in d_m has been neglected in view of ρ_m/ρ_p relation.

iii) d_o——The shielding parameter in *ortho* position——is controled mainly from the resonance effect as well as magnetic anisotropy effect, *etc.* and in this case, the inductive contribution transmitted through 3 σ–bonds remains unsettled.

In conclusion, as the so-called shielding parameter does not always reflect π–electron charge density, we can't correlate both directly.

2) π-Electron Charge Density and Revised Shielding Parameter

Formerly, π–electron charge densities in monosubstituted benzene series have been calculated by HMO method from several groups of workers.[12–19] In the preceding communication,[1] ρ_o/ρ_p[20] and ρ_m/ρ_p relations have been examined and definite correlations have been confirmed. On the other hand, d_o/d_p[21] relation shows nearly the same gradient with ρ_o/ρ_p, especially in electron releasing substituent groups. Consequently, in the above case, we are able to assume d_o/d_p, ρ_o/ρ_p. Nevertheless, in electron attracting substituent group, d_o/d_p relation deviates markedly in the low field site, and the deviations from above extention line have been attributed to sum of factors other than π–electron charge. Moreover, d_m/d_p relation seems to be irregular, but general trend is somewhat interesting. Then, if d_o/d_p, d_m/d_p relations were revised approximately equal to ρ_o/ρ_p, ρ_m/ρ_p the following correlations would be satisfied. Namely,

$$d_o/d_p \doteqdot \rho_o/\rho_p$$

$$d_m/d_p \doteqdot \rho_m/\rho_p$$

According to the above assumption, the substituent shielding parameter for ρ value estimation has been revised in the previous study.[1]

In this work, the correlations among these shielding parameter——d_p and revised d_o——and σ_π[22] have been examined, and a linear relation, comparable with those from several calculated π–electron density ρ_{calcd},[14,19,23] has been observed (*cf.* Fig. 1,2).

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11) A.D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).
12) K. Fukui, T. Yonezawa, C, Nagata, H. Kato, A. Imamura, K. Morokuma, "Introduction to Quantum Chemistry," Kagaku Dojin, Kyoto, 1964, p. 152, 177, 624.
13) R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry," Interscience, 1959, p. 213.
14) H. Baba and H. Suzuki, *J. Chem. Phys.*, 32, 1706 (1960).
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17) A. Azumi, "Quantum Chemistry," Baifukan, Tokyo, 1960, p. 248.
18) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John–Wiley and Sons, 1961, p. 353.
19) T.K. Wu and B.P. Dailey, *J. Chem. Phyz.*, **41**, 2796 (1964).
20) ρ=π–electron charge density; o=*ortho*, m=*meta*, p=*para*, respectively.
21) d=substituent shielding parameter; o=*ortho*, m=*meta*, p=*para*, respectively.
22) Y. Yukawa and Y. Tsuno, *Nippon Kagaku Zasshi*, **86**, 873 (1965).
23) K. Nishimoto, *Theoretica Chimica Acta*, **7**, 207 (1967).

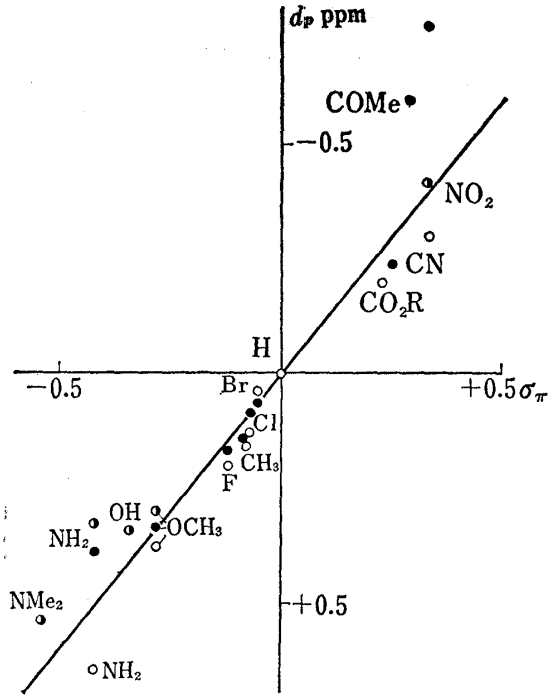

Fig. 1

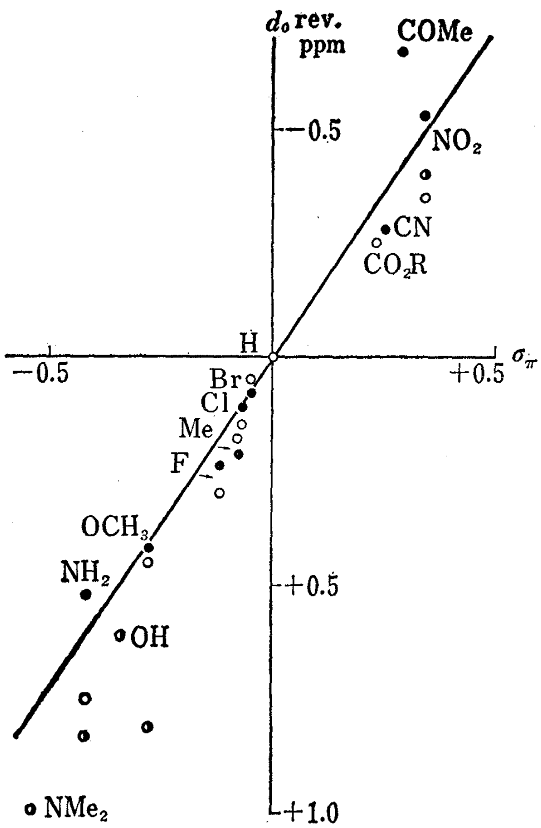

Fig. 2

○: d_p and d_o rev.,[1] respectively ●: T.K. Wu, B.P. Dailey[19]
△: H. Baba, S. Suzuki[14] ◑: K. Nishimoto[23].

All shifts except shielding parameters are calculated by the following equation.

$\delta=10.7\times\Delta\rho$ ppm where $\Delta\rho$=calculated excess charge

The lines from the least square method in d_p and d_o rev.[1] are slided to pass the origin. The deviations from the line in d_p and d_o rev. are corrected, and the shielding parameters in Table I are estimated.

In the next place, d_m/d_p relation shown in the previous communication[1] signifies an interesting evidence——namely, even in *meta* position, the resonance contribution in the opposite direction should be taken into account, contrary to the results of HMO calculation. This conclusion has been confirmed also in *para*-substituted anisole and toluene, 1-substituted 3,4-dimethoxybenzene (*cf.* Fig. 3,4), respectively.

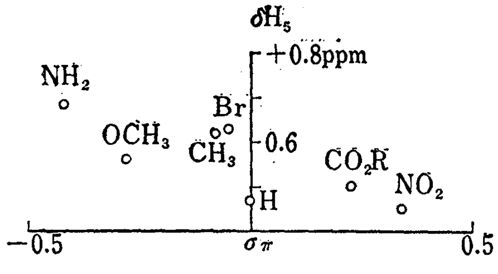

Fig. 3. H-5 Shift in 1-Substituted 3,4-Dimethoxybenzene Series *vs.* σ_π

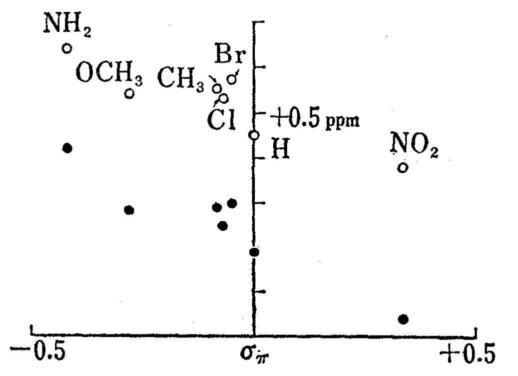

Fig. 4. H-2 and H-6 Shift in *para*-Substituted Anisole (○), Toluene (•) Series *vs.* σ_π

Then we have examined the linear correlation among d_m/d_p and estimated the revised *meta* shielding parameter $d_m$rev. (*cf.* Table I), which is also linear with σ_π(*cf.* Fig. 5).

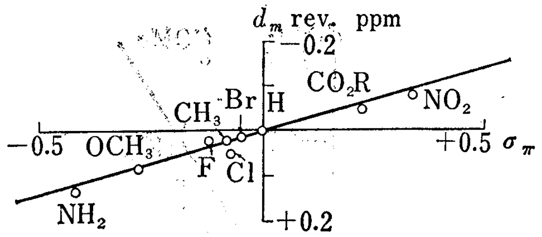

Fig. 5. d_m rev. *vs.* σ_π

Thus, from the correlation among d_p, d_o rev. and d_m rev. *vs.* σ_π, we are able to propose tentatively the revised three parameters for each substituent groups by interpolation as below (*cf.* Table I).

These mutal correlations described above are summarized graphically in the following (*cf.* Fig. 6).

Table I. Revised Shielding Parameter (ppm)

	d_o rev.	d_m rev.	d_p rev.		d_o rev.	d_m rev.	d_p rev.
$N(CH_3)_2$	+0.78	+0.15	+0.65	C_6H_5	+0.13	+0.03	+0.11
NH_2	+0.61	+0.12	+0.50	NO_2	−0.49	−0.09	−0.40
OH	+0.58	+0.09	+0.41	$COCH_3$	−0.42	−0.08	−0.34
OCH_3	+0.43	+0.08	+0.34	SO_2CH_3	−0.40	−0.08	−0.33
CH_3	+0.12	+0.03	+0.10	SO_2NH_2	−0.37	−0.07	−0.31
C_2H_5	+0.11	+0.02	+0.09	CN	−0.36	−0.07	−0.30
t-C_4H_9	+0.08	+0.02	+0.07	CF_3	−0.34	−0.06	−0.29
F	+0.17	+0.04	+0.15	CO_2R	−0.33	−0.06	−0.27
Cl	+0.11	+0.02	+0.09	$SOCH_3$	−0.16	−0.03	−0.13
Br	+0.08	+0.02	+0.07	N^+Me_3	−0.19	−0.03	−0.15

The shielding parameters—d_o rev., d_m rev. and d_p rev. which are not determined from experimental shift, have been estimated by interpolation in Fig. 1, 2 and 5.

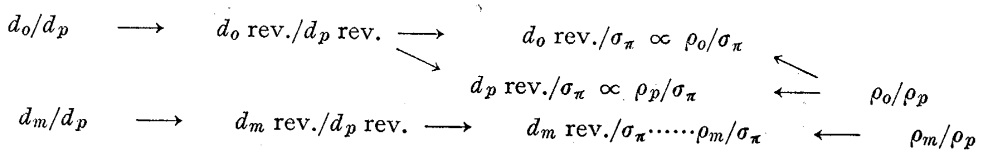

Fig. 6

As illustrated in Fig. 1 and 2, the correspondence among $d_p$rev. and $d_o$rev. in Table I *vs.* shift calculated from excess charge in HMO treatment[14,19,23] has been compared, and apparent discrepancies have been observed in the latter, though the general trends are very similar.

In conclusion, the correlation $d_o$rev./σ_π, $d_p$rev./σ_π are nearly proportional with those of ρ_o/σ_π, ρ_p/σ_π, but it is self-evident that $d_m$rev./σ_π is not with ρ_m/σ_π(*cf.* Fig. 1,2). Namely, in the present step, these discrepancies are somewhat apparent, but will be settled by the more refined calculation in the near future.

3) Simple Sum Rule of Revised Shielding Parameter and π-Electron Charge Density

In the previous papers of this series,[24] the ring ^1H chemical shift in poly-substituted benzene series has been shown by simple sum of substituent shielding parameter. Namely, the perturbation among substituent affects little in estimating ring ^1H chemical shift. From above fact, the following schemes are proposed.

$$d_A = \pi\text{-Factor A} + \text{Another Factor A}$$

$$d_B = \pi\text{-Factor B} + \text{Another Factor B}$$

$$\vdots$$

$$d_Z = \pi\text{-Factor Z} + \text{Another Factor Z}$$

$$d_{(A+B+\cdots+Z)} = \pi\text{-Factor}(A+B+\cdots+Z) + \text{Another Factor }(A+B+\cdots+Z)$$

where d_A, d_B, .., d_Z=shielding parameter of substituent, A, B,.., Z. π-Factor A, B,.., Z=re-

24) Y. Sasaki, M. Suzuki, T. Hibino, and K. Karai, *Chem. Pharm. Bull.* (Tokyo), **15**, 599 (1967); Y. Sasaki, M. Suzuki, A. Shimazu (Hoshi), and A. Misaki, *ibid.*, **15**, 1083 (1967).

vised shielding parameter of substituent, A, B,.., Z, Another Factor A, B,.., Z=contribution other than π-electron charge density.

In the following, we have compared both π-electron densities from revised shielding parameter and HMO method in several series of compounds (*cf.* Table II, III, IV, V, VI), and the apparent discrepancies have been observed in *meta* position.

Table II. π-Electron Densities in Methoxybenzene Series

OCH_3 position	H position	ρ_{calcd}[25]	ρ_{nmr}	OCH_3 position	H position	ρ_{calcd}[25]	ρ_{nmr}
1	2, 6	1.040	1.042	1, 2, 4	3	1.079	1.088
	3, 5	0.998	1.008		5	1.066	1.079
	4	1.030	1.032		6	1.037	1.050
1, 2	3, 6	1.040	1.048	2, 4, 6	1, 3, 5	1.109	1.112
	4, 5	1.025	1.039	1, 2, 3, 4	5, 6	1.064	1.087
1, 3	2	1.082	1.080	1, 2, 3, 5	4, 6	1.106	1.120
	4, 6	1.068	1.072				
	5	0.996	1.015	1, 2, 4, 5	3, 6	1.078	1.095
1, 4	2, 3, 5, 6	1.037	1.048	2, 3, 4, 5, 6	1	1.104	1.127
1, 2, 3	4, 6	1.066	1.080				
	5	1.024	1.047				

Table III. π-Electron Densities in Mono-substituted Benzene Series

Substituent		ρ_{calcd}[19]	ρ_{nmr}	Substituent		ρ_{calcd}[19]	ρ_{nmr}
NH_2	*p*	1.03667	1.0467	Br	*p*	1.00542	1.0065
	m	0.99773	1.0112		*m*	0.99964	1.0019
	o	1.04843	1.0635		*o*	1.00728	1.0075
OCH_3	*p*	1.03063	1.0318	I	*p*	1.00331	1.004
	m	0.9902	1.0075		*m*	0.99982	1.000
	o	1.04138	1.0403		*o*	1.00423	1.004
F	*p*	1.01583	1.0140	NO_2	*p*	0.92860	0.9618
	m	0.99875	1.0037		*m*	0.99499	0.9916
	o	1.02270	1.0159		*o*	0.95045	0.9542
CH_3	*p*	1.01331	1.0094	CHO	*p*	0.95269	0.976
	m	0.99888	1.0028		*m*	1.00146	1.000
	o	1.01982	1.0112		*o*	0.94596	0.972
Cl	*p*	1.0075	1.0084				
	m	0.99947	1.0019				
	o	1.01042	1.0103				

Table IV. π-Electron Densities in Symmetrically *para*-Disubstituted Benzene Series

Substituent	ρ_{calcd}[19]	ρ_{nmr}	Substituent	ρ_{calcd}[19]	ρ_{nmr}
NH_2	1.04536	1.0747	Br	1.00689	1.0094
OCH_3	1.03879	1.0477	I	1.00403	1.005
F	1.02134	1.0192	NO_2	0.95315	0.9458
CH_3	1.01855	1.0140	CHO	0.95069	0.967
Cl	1.00984	1.0122			

25) A. Zweig, J.E. Lehnsen, J.E. Lancaster, and M.T. Neglia, *J. Am. Chem. Soc.*, **85**, 3940 (1963).

Table V. π-Electron Densities in Hydroxy Substituted Benzene Series

OH position	H position	ρ_{calcd} J.C. Schug J.C. Deck[26]	ρ_{calcd} R. Fujishiro K. Nishimoto[27]	ρ_{nmr}
1	2, 6	1.0990	1.075[28]	1.0532
	3, 5	0.9968	0.990	1.0084
	4	1.0831	1.038	1.0383
1, 4	2, 6, 3, 5	1.0928	1.036	1.0626
1, 2	3, 6	1.1187	1.038	1.0626
	4, 5	1.0768	1.026	1.0467
1, 3	2	1.2117	1.107	1.1082
	4, 6	1.1711	1.024	1.0925
	5	0.9928	1.030	1.0169
1, 2, 3	4, 6	1.1704		1.1090
	5	1.0694		1.0552
1, 3, 5	2, 4, 6		1.103	1.1485
1, 2, 4, 5	3, 6		1.037	1.1252

Table VI. π-Electron Densities in Cyano Substituted Benzene Series

CN position	H position	ρ_{calcd} H.E. Popkie J.B. Moffat[29]	ρ_{nmr}
1	2, 6	0.9892	0.9764
	3, 5	0.9880	0.9935
	4	0.9904	0.9720
1, 2	3, 6	0.9878	0.9599
	4, 5	0.9891	0.9655
1, 3	2	0.9790	0.9332
	4, 6		0.9383
	5	0.9963	0.9869
1, 4	2, 3, 5, 6	0.9878	0.9599
1, 2, 4, 5	3, 6	0.9771	0.9195

Conclusion

In substituted benzene series, the π-electron charge density estimated from the revised substituent shielding parameter showed good correspondence with those from HMO method, except *meta* position, and in the present step it is concluded that π-electronic effect is a dominant factor in determining the ring ^1H shift, and the contribution from the so-called "electric field effect" in *meta* position is doubtful. In addition, the anomalous *meta* ^1H shifts observed in halogen series are somewhat puzzling.

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26) J.C. Schug and J.C. Deck, *J. Chem. Phys.*, **37**, 2618 (1962). HMO
27) R. Fujishiro and K. Nishimoto, *Bull. Chem. Soc. Japan*, **32**, 699 (1959). HMO
28) K. Nishimoto, *Theoret. Chim. Acta*, **5**, 74 (1966). S.C.F.
29) H.E. Popkie and J.B. Moffat, *Can. J. Chem.*, **43**, 624 (1965). S.C.F.