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Studies on the Proton Magnetic Resonance Spectra in Aromatic Systems. IX.[1) Calculation of π-Electron Charge Density Distribution of the Substituted Benzene and Naphthalene Derivatives and ω-Technique[2)

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ρ_{NMR}—π-electron charge density estimated from the revised shielding parameter—showed appreciable disagreement with that from HMO calculation using Streitwieser's parameter especially at *meta* position.

The ω-technique has been applied to settle this problem and parameters for above treatment have been arranged so as to reconcile with ρ_{NAR}.

Above treatments have also been applied to 1-substituted-3,4-dimethoxybenzene, 2-substituted- and 2-substituted-6-methoxynaphthalene series, and favorable results have been acknowledged.

In the previous papers,[4-6) the correlation among substituent shielding parameter in monosubstituted benzene series and π-electron charge density —ρ value—has been examined and revised shielding parameter $d_{rev.}$ ascribed to ρ value has been proposed (*cf.* Table I).

The above parameter has also been proved reliable for ρ value estimation in polysubstituted benzene series.

Nevertheless, ρ_{NMR}[7) has showed appreciable disagreement with $\rho_{calcd.}$[8) from HMO method using Streitwieser's parameter[6b) at *meta* position, and the latter is somewhat underestimated in electron releasing and overestimated in electron attracting substituent group.

Formerly, Schug[9,10) has suggested the following equation to express the correlation among chemical shift and local excess ρ value of the attached carbon, instead of $\delta=10.7\ \rho$:

$$\delta=aq+a'q'$$

where

δ=ring ^{1}H chemical shift (ppm)
q=excess ρ value on the attached carbon atom
q'=sum of excess ρ value on both next-nearest carbon atoms
a=proportional constant 6.15
a'=proportional constant 1.56

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1) Part VIII: Y. Sasaki, M. Hatanaka, I. Shiraishi, M. Suzuki, and K. Nishimoto, *Yakugaku Zasshi*, **89**, 21 (1969).
2) This work was presented at 88th Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, April 1968 and 21th Annual Meeting of the Chemical Society of Japan, Osaka, April 1968.
3) Location: *Toneyama* 6-5, *Toyonaka, Osaka.*
4) Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **15**, 1429 (1967); *ibid.*, **16**, 1187 (1968).
5) Y. Sasaki and M. Suzuki, Abstract Papers of the Symposium on the Hammett Relationship, Kyoto, October 1967, p. 46.
6) *a*) Y. Sasaki and M. Suzuki, Abstract Papers of the 6th NMR Symposium, Kyoto, October 1967, p. 17; *b*) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York, 1961, p. 135; *c*) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, 1961, p. 335, 342.
7) $\rho_{NMR}=\rho$ value from ^{1}H chemical shift.
8) $\rho_{calcd.}=\rho$ value from quantum chemical calculation.
9) J.C. Schug and J.C. Deck, *J. Chem. Phys.*, **37**, 2618 (1962).
10) J.C. Schug, *J. Chem. Phys.*, **46**, 2447 (1967).

Table I. Revised Shielding Parameter, ρ_{NMR}, ρ_{calcd} and L_Y^ω in Mono Substituted Benzene Series

Substituent		$\delta_{rev.ppm}$	ρ_{NMR}	$\rho_{calcd.}$		L_Y^ω
				HMO	ω–Technique	
NH_2	*o*	+0.61	1.057	1.037	1.056	
	m	+0.12	1.011	0.998	1.012	
	p	+0.50	1.047	1.029	1.046	1.36
OCH_3	*o*	+0.43	1.040	1.025	1.040	
	m	+0.08	1.007	0.999	1.008	
	p	+0.34	1.032	1.020	1.032	1.51
CH_3	*o*	+0.12	1.011	1.005	1.013	
	m	+0.03	1.003	1.000	1.003	
	p	+0.10	1.009	1.003	1.009	1.84
Cl	*o*	+0.11	1.010	0.979	1.011	
	m	+0.02	1.002	1.001	1.002	
	p	+0.09	1.008	0.987	1.008	1.67
Br	*o*	+0.08	1.007	0.984	1.008	
	m	+0.02	1.002	1.001	1.002	
	p	+0.07	1.007	0.990	1.007	1.71
$COOCH_3$	*o*	−0.33	0.969	0.940	0.972	
	m	−0.06	0.994	1.002	0.994	
	p	−0.27	0.975	0.948	0.975	1.80
NO_2	*o*	−0.49	0.954	0.941	0.965	
	m	−0.09	0.992	0.998	0.990	
	p	−0.40	0.963	0.932	0.963	1.92
CHO	*o*	−0.42	0.961	0.935	0.964	
	m	−0.08	0.993	1.001	0.991	
	p	−0.34	0.968	0.941	0.967	1.87

Consequently, modification has been noted for *meta* position, to predict the correct sign for δ.

In trying to improve the agreement among calculated and empirical ρ value, Schug[10] has estimated Δh_X and Δk_X using atom–atom and bond–atom polarizabilities for Streitwieser's parameter, but above treatment was unfavorable because all chemical shifts have been ascribed to ρ values. Generally speaking, it is obvious that ^1H chemical shift at *ortho* position of an electron attracting group is afforded from several contributions—for example, resonance, inductive and magnetic anisotropy effect, *etc.* Matsen[11] has suggested that h_X is derived from an ionization potential of the corresponding hydride, since kc-x is not involved in this case. Streitwieser[12] has adopted this suggestion and obtained h_X and k_X for ω-technique. But $\rho_{calcd.}$ from ω-technique using above parameter does not coincide with ρ_{NMR}.

In the present work, ω–technique was used to promote the agreement among $\rho_{calcd.}$ and ρ_{NMR} at *meta* position by rearranging the deviation of π–electron distribution from HMO calculation and the parameters h_X and k_X wihch represent ρ_{NMR} were discussed.

Results and Discussion

The Coulomb integral of ω–technique is defined as below:

$$\alpha'_X = \alpha_X + (n_X - \rho_X)\omega\beta_0$$

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[11] F.A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950).

[12] A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).

where

n_x = number of π-electron given by atom x
ρ_x = value on atom x
ω = proportional constant

In the first step, to determine ω empirically, ω is varied between 0.65[13] and 1.4,[14] fixing h_X and k_X at 1.7 and 0.9.[12] The converged ρ_o/ρ_p[15] and ρ_m/ρ_o[15] ratios are calculated at ω variable, and when ω=1.4, ρ_X diverges.

Table II. Effect on ω on Charge Density Ratios of 1-Substituted Benzene Series

ω	o/p	m/p	ω	o/p	m/p
0.65	1.33	0.20	0.95	1.31	0.29
0.75	1.32	0.23	1.00	1.31	0.31
0.85	1.32	0.26	1.10	1.31	0.34
0.90	1.32	0.28	1.20	1.30	0.35

As is showh in Table II, ρ_o/ρ_p is independent, but ρ_m/ρ_p is sensitive to ω, and ω=0.85 is the most favorable to represent ρ_m/ρ_p=0.25 and ρ_o/ρ_p=1.25 from the revised shielding parameter. Here the ρ value ratios among ρ_o, ρ_m and ρ_p are settled and h_X and k_X are obtained from trial and error (*cf.* Table III).

Table III. Parameters for ω–Technique

Substituent	h_x	k_x	Substituent	h_x	k_x
NH_2	0.8	0.9	CHO	0.9	0.9
OH	1.1	0.8	$COOCH_3$	$h_{\ddot{O}} = 1.1$	$k_{C-O} = 0.8$
CH_3	3.5	0.7		$h_{\dot{O}} = 0.9$	$k_{C=O} = 0.9$
Cl	0.6	0.3	NO_2	$h_{\ddot{N}} = 2.2$	$k_{N-O} = 1.35$
Br	0.7	0.3		$h_{\dot{O}} = 1.4$	$k_{N-C} = 1.2$

Correlation among omega localization energy[6c]—L_γ^ω, ω/r—calculated from new h_X, k_X and σ_π is satisfactory, except CH_3 from hetero atom model treatment (*cf.* Fig. 1 and Table I).

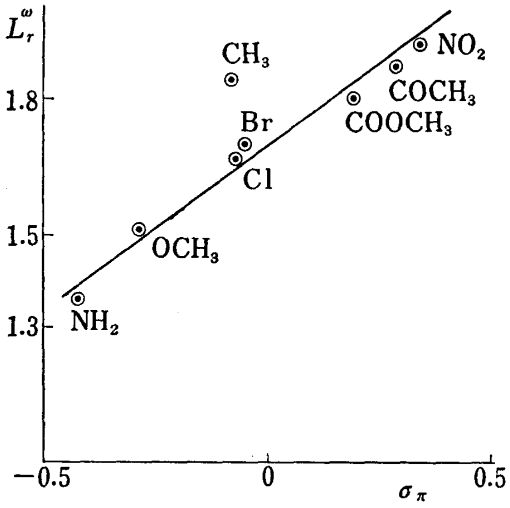

Fig.1. Correlation among Omega Localization Energy and σ_π

The $\rho_{calcd.}$ in monosubstituted benzene series obtained from ω-technique using new h_X and k_X is shown in Table I, and agreement among $\rho_{calcd.}$ and ρ_{NMR} is observed in general. In the next place, the revised chemical shift and h_X and k_X for ω–technique were applied to 1-substituted-3,4-dimethoxybenzene, 2-substituted- and 2-substituted-6-methoxynaphthalene series.

In 1-substituted-3,4-dimethoxybenzene series[16] (*cf.* Table IV), the first column shows

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13) J. Morris, "HMϕ-II Operator's Handbook."
14) A. Streitwieser, Jr. and P.M. Nair, *Tetrahedron*, **5**, 149 (1959).
15) ρ_o, ρ_m, ρ_p=ρ value of *ortho, meta* and *para* position.
16) Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **16**, 1193 (1968).

simple sum of revised shielding parameter, and an agreement among ρ_{NMR} and $\rho_{calcd.}$ from ω–technique is observed, but unsatisfactory with that from HMO method.

Table IV. Simple Sum of Revised Shielding Parameters, ρ_{NMR} and $\rho_{calcd.}$ in 1-Substituted-3,4-dimethoxy Benzene Series

Substituent		$\delta_{rev.}$ppm	ρ_{NMR}	$\rho_{calcd.}$	
				HMO	ω-Technique
NH_2	2	+1.12	1.105	1.062	1.103
	5	+0.63	1.059	1.022	1.058
	6	+1.03	1.096	1.054	1.091
OCH_3	2	+0.94	1.088	1.050	1.088
	5	+0.59	1.055	1.023	1.056
	6	+0.85	1.079	1.042	1.076
CH_3	2	+0.63	1.059	1.030	1.060
	5	+0.54	1.050	1.024	1.053
	6	+0.54	1.050	1.022	1.049
H	2	+0.51	1.048	1.025	1.046
	5	+0.51	1.048	1.025	1.046
	6	+0.42	1.039	1.018	1.037
Br	2	+0.59	1.055	1.009	1.057
	5	+0.53	1.050	1.026	1.051
	6	+0.50	1.047	1.002	1.046
CHO	2	+0.09	1.008	0.963	1.019
	5	+0.43	1.040	1.024	1.036
	6	+0.00	1.000	0.951	0.997
$COOCH_3$	2	+0.18	1.017	0.968	1.025
	5	+0.45	1.042	1.025	1.040
	6	+0.09	1.008	0.957	1.006
NO_2	2	+0.02	1.002	0.973	1.022
	5	+0.42	1.039	1.017	1.032
	6	−0.07	0.993	0.951	0.995

In 2-substituted naphthalene series[17] as is shown in Table V, the first column is the observed shift δ, and the second is the corrected one $\delta_{corr.}$ from induced ring current effect by the neighbouring ring[18]—namely, +0.5 and +0.16 ppm for α- and β-^{1}H, respectively. In the third, $\delta_{rev.}$ is estimated as in the previous paper.[17]

When $\rho_{calcd.}$ from ω–technique is compared with that from HMO method, it is found that both the sign of excess charge in 4 position and underestimating in electron releasing group are improved in the former treatment. But quantitative agreement among ρ_{NMR} and $\rho_{calcd.}$ from ω–technique is unsatisfactory.

It is probable that owing to the lack of d_p[19] in 2-substituted naphthalene series, revised chemical shifts estimated against σ_π are overestimated.

In 2-substituted-6-methoxynaphthalene series[17] (*cf.* Table VI), revised chemical shifts are estimated by simple sum of 2-substituted naphthalene series, and agreement among $\rho_{calcd.}$ from ω–technique and simple sum rule is ascertained (*cf.* Table VII).

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[17] Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **16**, 1367 (1968).

[18] J.A. Pople, W.G. Schneider, and H.J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, p. 252.

[19] Shielding parameter of *para* position.

Table V. Chemical Shifts, Corrected Chemical Shifts, Revised Chemical Shifts, ρ_{NMR} and $\rho_{calcd.}$ in 2-Substituted Naphthalene Series

Substituent		δ_{ppm}	$\delta_{corr.ppm}$	$\delta_{rev.ppm}$	ρ_{NMR}	$\rho_{calcd.}$ HMO	$\rho_{calcd.}$ ω-Technique
NH_2	1	+0.46	+0.96	+1.18	1.110	1.054	1.078
	3	+0.53	+0.69	+0.48	1.045	1.023	1.032
	4	−0.26	+0.24	+0.20	1.019	0.996	1.008
OCH_3	1	+0.25	+0.75	+0.80	1.075	1.037	1.055
	3	+0.16	+0.32	+0.32	1.030	1.016	1.024
	4	−0.37	+0.13	+0.13	1.012	0.997	1.006
CH_3	1	−0.13	+0.37	+0.23	1.022	1.006	1.017
	3	−0.09	+0.07	+0.09	1.008	1.003	1.008
	4			+0.04	1.004	0.999	1.002
Cl	1	−0.53	−0.03	+0.21	1.020	0.973	1.015
	3	−0.18	−0.02	+0.08	1.007	0.985	1.007
	4			+0.03	1.003	1.002	1.001
Br	1	−0.66	−0.16	+0.15	1.014	0.968	1.012
	3	−0.26	−0.10	+0.05	1.005	0.983	1.005
	4			+0.03	1.003	1.003	1.001
$COCH_3$	1	−1.12	−0.62	−0.80	0.925	0.898	0.947
	3	−0.78	−0.62	−0.33	0.969	0.965	0.982
	4	−0.49	0.01	−0.13	0.988	1.004	0.993
$COOCH_3$	1	−1.23	−0.73	−0.64	0.940	0.908	0.961
	3	−0.70	−0.54	−0.26	0.976	0.968	0.985
	4	−0.44	+0.06	−0.10	0.991	1.004	0.995

Table VI. Chemical Shifts, Corrected Chemical Shifts, Revised Chemical Shifts, ρ_{NMR} and $\rho_{calcd.}$ in 2-Substituted-6-methoxynaphthalene Series

Substituent		δ_{ppm}	$\delta_{corr.ppm}$	$\delta_{rev.ppm}$	ρ_{NMR}	$\rho_{calcd.}$ HMO	$\rho_{calcd.}$ ω-Technique
NH_2	1	+0.44	+0.94	+1.24	1.116	1.052	1.080
	3	+0.45	+0.61	+0.61	1.057	1.023	1.037
	4	−0.12	+0.38	+0.37	1.035	1.003	1.017
OCH_3	1	+0.32	+0.82	+0.86	1.080	1.035	1.057
	3	+0.36	+0.52	+0.45	1.042	1.016	1.028
	4	−0.30	+0.20	+0.30	1.028	1.004	1.015
CH_3CH_2	1	−0.17	+0.33	+0.29	1.027	1.005	1.020
	3	+0.08	+0.24	+0.22	1.021	1.003	1.013
	4	−0.29	+0.21	+0.21	1.020	1.006	1.011
H	1	−0.44	+0.06	+0.06	1.006	0.999	1.003
	3	−0.03	+0.13	+0.13	1.012	1.000	1.004
	4	−0.33	+0.17	+0.17	1.016	1.006	1.010
Br	1	−0.56	−0.06	+0.21	1.020	0.978	1.014
	3	−0.11	+0.05	+0.18	1.017	0.988	1.009
	4	−0.29	+0.21	+0.20	1.019	1.008	1.011
$COCH_3$	1	−0.98	−0.48	−0.74	0.931	0.897	0.934
	3	−0.64	−0.48	−0.20	0.981	0.966	0.986
	4	−0.36	+0.14	+0.04	1.004	1.010	1.003
$COOCH_3$	1	−1.17	−0.67	−0.58	0.946	0.907	0.962
	3	−0.68	−0.52	−0.13	0.988	0.968	0.989
	4	−0.36	+0.14	+0.07	1.007	1.010	1.005

Table VII. $\rho_{\text{calcd.}}$ of 2-Substituted-6-methoxynaphthalene Series calculated by Simple Sum Method of ρ Value

Substituent	C_1	C_3	C_4
NH_2	1.081	1.036	1.018
OCH_3	1.058	1.028	1.016
CH_3	1.020	1.012	1.012
Br	1.015	1.009	1.011
$COCH_3$	0.950	0.986	1.003
$COOCH_3$	0.964	0.989	1.005

Conclusion

The combination of revised shielding parameter, parameter for ω-technique and simple sum rule suggest a reasonable and practical procedure for the estimation of π-electron charge density distribution in substituted aromatics.

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