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Studies on the Proton Magnetic Resonance Spectra in Aromatic Systems. XV.[1] Discussions on the π-Electron Charge Density Distributions of 3- and 4-Pyridine, 6-Quinoline and 6-Quinoxaline Series

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π-Electron charge density distributions from both corrected ring ^{1}H chemical shift and modified Hueckel Molecular Orbital Method—ω Technique—have been compared in 3- and 4-pyridines, 6-quinolines and 6-quinoxalines.

The plots of above two kinds of charge density distributions against substituent constant σ_π showed similar gradients with each other, but relative intersections are unsatisfactory.

Introduction

In the previous studies of this series, the correlations among substituent's shielding parameters and π-electron charge density distributions -ρ- have been examined with respect to substituent constant σ_π, and several revised *ortho*, *meta* and *para* shielding parameters appropriate to estimate π-electron charge density distributions have been proposed, and those obtained from the simple sum of above parameters showed passable agreements with calculated ones.[3a–d]

In this work, π-electron charge density distributions of 3-[4] and 4-pyridines,[5] 6-quinolines[6] and 6-quinoxalines[7] have been examined according to molecular orbital view point.

Experimental

All materials are prepared by authentic procedures. Spectra are obtained in 0.3 mole$\gtrsim$$C_6H_{12}$ solution except 6-NH_2-, 6-NO_2-quinoline, 6-NO_2-quinoxaline (0.3 mole$\gtrsim$$CCl_4$) and 6-$NH_2$-quinoxaline (0.3 mole$>$ $CDCl_3$). Others are the same as shown in the previous paper.[8]

Analyses of Spectra——3-Pyridines: When substituents are electron attracting groups or halogens, spectra were analysed as ABX type except δ_{2-H} which appeared at the lowest field, on the other hand, when they are electron releasing, the first order analyses are impossible and spin decoupling techniques are utilised.

4-Pyridines: All spectra were analysed as AA'XX' type.[9]

6-Quinolines and 6-Quinoxalines: All spectra were analysed by the first order rule, and results were inspected by dispersion method.[8]

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[1] Part XIV: Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **17**, 1778 (1969).

[2] Location: *Toneyama 6-5, Toyonaka, Osaka.*

[3] *a*) Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **15**, 1492 (1967); *b*) *idem, ibid.*, **16**, 1187 (1968); *c*) *idem, ibid.*, **16**, 1193 (1968); *d*) *idem, ibid.*, **16**, 1367 (1968).

[4] Y. Sasaki, M. Suzuki, I. Shiraishi and K. Nishimoto, *Yakugaku Zasshi*, **89**, 21 (1969).

[5] Y. Sasaki, M. Hattori and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **17**, 1515 (1969).

[6] Y. Sasaki, K. Iwasaki, M. Suzuki and K. Nishimoto, *Yakugaku Zasshi*, **89**, 25 (1969).

[7] Y. Sasaki, M. Hatanaka and M. Suzuki, *Yakugaku Zasshi*, **89**, 64 (1969).

[8] Y. Sasaki, M. Suzuki, T. Hibino and K. Karai, *Chem. Pharm. Bull.* (Tokyo), **15**, 599 (1967).

[9] W. Brügel, *Z. Elektrochem.*, **16**, 159 (1962).

Results and Discussion

Chemical Shift

Recently, Wu and Daily[10] have suggested that if substituent effect of both benzene and pyridine series are closely similar, the chemical shift differences of substituted pyridines from pyridine reference should be approximately similar with those of benzene series, and this assumption has been proved reliable in 4-pyridine series. In this section, the correlations among ring ^1H chemical shift of above series, where an unsubstituted ones are taken as reference, and shielding parameters of monosubstituted benzenes are examined.

In 4-pyridine series, the following results are obtained as is illustrated in Fig. 1.

$\delta_{2\text{-H}} = 1.43 d_m + 0.02$ ppm

$\delta_{3\text{-H}} = 0.88 d_o + 0.05$ ppm

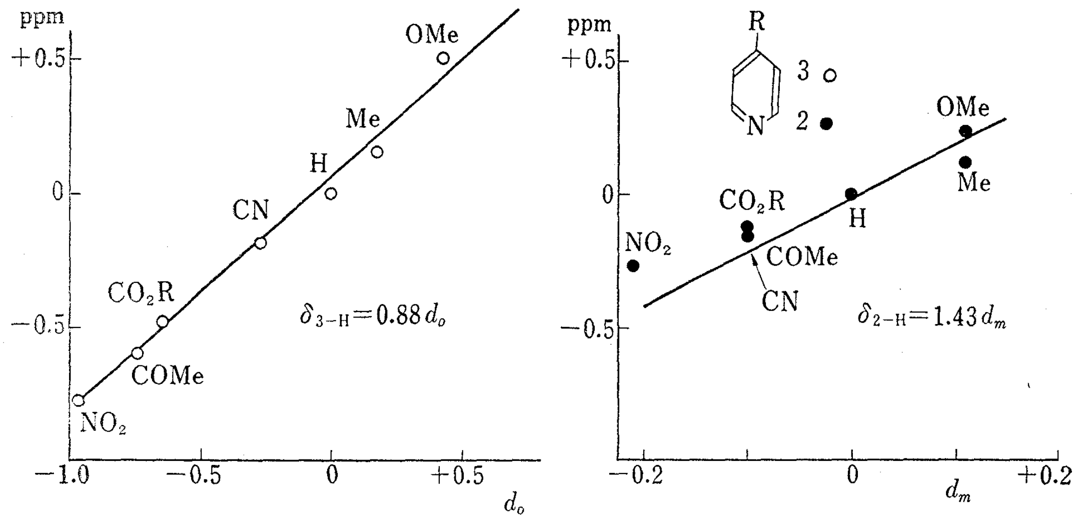

Fig. 1

d_o, d_m, d_p=substituent shielding parameter of *ortho*, *meta*, and *para* positions in monosubstituted benzenes correlations among $\delta_{2\text{-H}}$ (●), $\delta_{2\text{-H}}$ (○) in 4-pyridines and d_o, d_m

In 3-pyridine series

$\delta_{2\text{-H}} = 0.79 d_o - 0.03$ ppm

$\delta_{4\text{-H}} = 1.00 d_o - 0.03$ ppm

$\delta_{5\text{-H}} = 0.61 d_m - 0.03$ ppm

$\delta_{6\text{-H}} = 1.05 d_p + 0.03$ ppm

Formerly, it is concluded that simple sum rule holds with an accuracy of about±0.13 ppm in 1-substituted-3,4-dimethoxybenzene series, and in pyridine series, correlation of chemical shifts against d_0 and d_p are passable (gradient=0.88,1.05,1.00) except $\delta_{2\text{-H}}$ (gradient=0.79) in 3-pyridines, which is adjacent with both substituent group and ring nitrogen. On the other hand, $\delta_{5\text{-H}}$ of 3-pyridines, which is situated on *meta* position from both substituent and ring nitrogen atom, shows same gradient as in 1-substituted-3,4-dimethoxybenzene series,[3c] but $\delta_{2\text{-H}}$ in 4-pyridines, situated *meta* position from substituent and *ortho* from ring nitrogen, afforded larger slope than 1, it is probably due to an additional effect from nitrogen atom.

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[10] T.K. Wu and B.P. Daily, *J. Chem. Phys.*, 41, 3307 (1964).

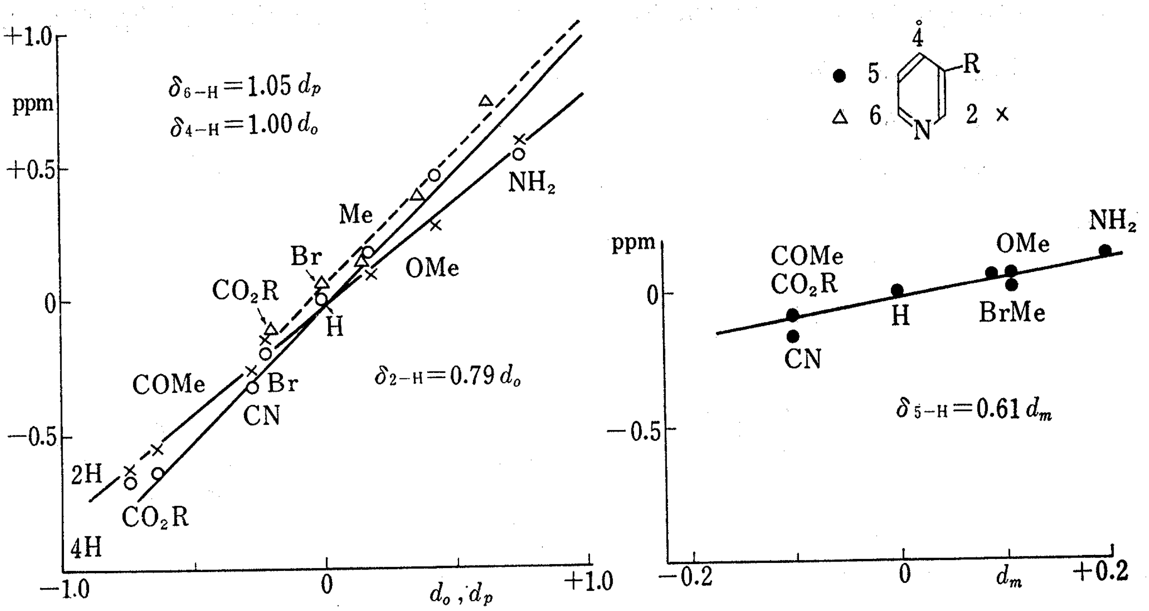

Fig. 2

d_o, d_m, d_p=substituent shielding parameter of *ortho, meta,* and *para* positions in monosubstituted benzenes correlations among $\delta_{2\text{-H}}$ (×), $\delta_{4\text{-H}}$ (○), $\delta_{5\text{-H}}$ (●), $\delta_{6\text{-H}}$ (△) and d_o, d_m, d_p

From above facts, it is assumed that ring ^{1}H chemical shift of monosubstituted pyridines may be estimated by the sum of corresponding substituent's shielding parameter and ring nitrogen contribution.

In 6-substituted quinolines, the following correlations have been acknowledged (*cf.* Fig. 3).

$$\delta_{5\text{-H}}=1.21d_o+0.13\ \text{ppm}$$

$$\delta_{7\text{-H}}=0.73d_o-0.07\ \text{ppm}$$

$$\delta_{8\text{-H}}=1.25d_m-0.06\ \text{ppm}$$

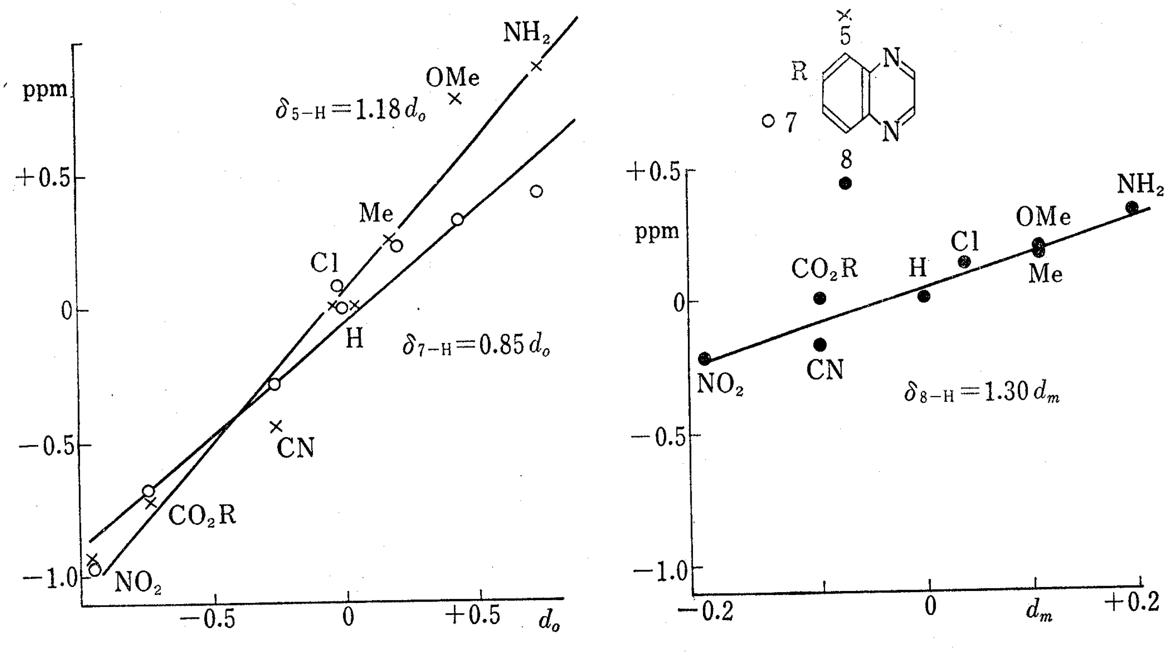

Fig. 3

d_o, d_m, d_p=substituent shielding parameter of *ortho, meta,* and *para* positions in monosubtituted benzenes correlations among $\delta_{5\text{-H}}$ (×), $\delta_{7\text{-H}}$ (○), $\delta_{8\text{-H}}$ (●) in 6-quinolines and d_o, d_m

In 6-substituted quinoxalines, the following results have been observed (*cf.* Fig. 4).

$\delta_{5\text{-H}} = 1.18 d_o + 0.07$ ppm

$\delta_{7\text{-H}} = 0.85 d_o - 0.12$ ppm

$\delta_{8\text{-H}} = 1.30 d_m + 0.05$ ppm

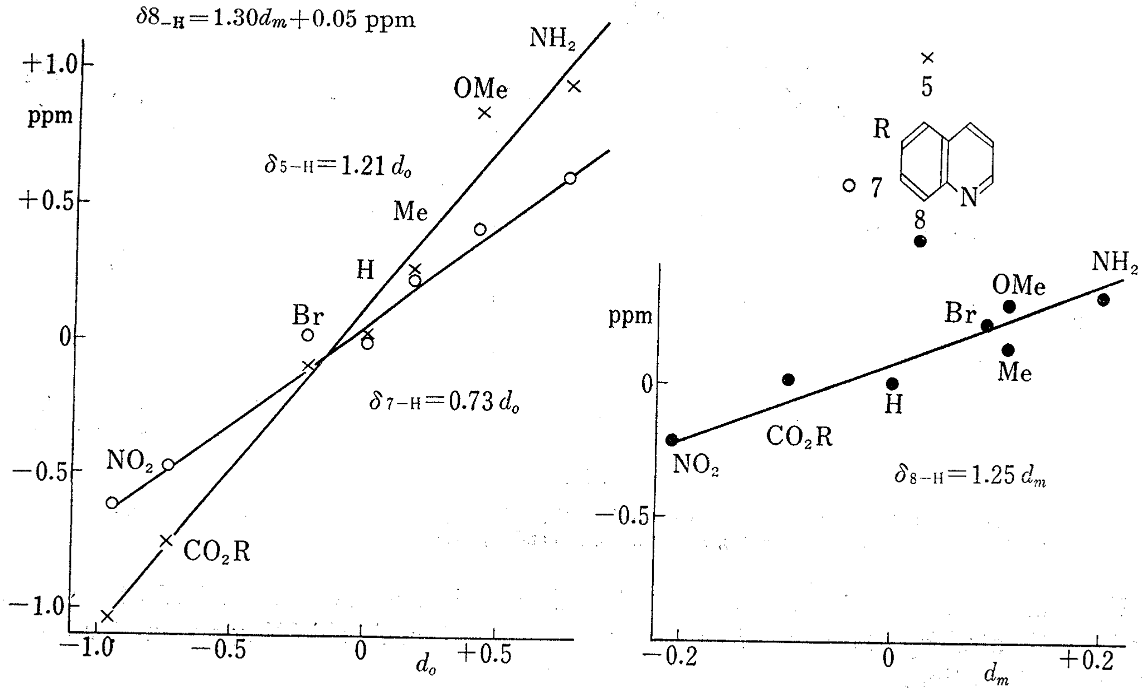

Fig. 4

d_o, d_m, d_p=Substituent shielding parameter of *ortho*, *meta*, and *para* positions in monosubstituted benzenes correlations among $\delta_{5\text{-H}}$ (×), $\delta_{7\text{-H}}$ (○), $\delta_{8\text{-H}}$ (●) in 6-quinoxalines and d_o, d_m

$\delta_{5\text{-H}}$ and $\delta_{7\text{-H}}$ in 6-quinolines and 6-quinoxalines are both *ca.* 20% increase and decrease of d_o, and same results are also acknowledged in 2-substituted and 2-substituted-6-methoxy-naphthalene derivatives.[3d)]

$\delta_{8\text{-H}}$-*peri* position from ring nitrogen–shows larger gradient than 1, whereas in naphthalene series cited before, $\delta_{8\text{-H}}$ affords the gradient of 0.65,0.68, it is probably due to the same reasons as stated in pyridine derivatives.

Correlation between Ring ^{1}H Chemical Shift and *pi*-Electron Charge Density Distribution

In order to estimate π-electron charge density distribution from ring ^{1}H chemical shift of nitrogen heteroaromatics, the following corrections are necessary: namely, ring current

Table I. Correction Terms of Ring ^{1}H Chemical Shift in Nitrogen Heteroaromatics (ppm)[11)]

	^{1}H position	δ_{RC}	δ_{MA}	δ_E	Σ
Pyridine	2	0.06	−0.35	−0.41	−0.70
	3	0.06	0.00	−0.18	−0.12
	4	0.06	0.00	−0.14	−0.08
Quinoline	2	−0.17	−0.35	−0.41	−0.93
	3	−0.17	0.00	−0.18	−0.35
	4	−0.38	0.00	−0.14	−0.52
	5	−0.38	0.00	−0.06	−0.44
	6	−0.17	0.00	−0.03	−0.20
	7	−0.17	0.00	−0.03	−0.20
	8	−0.38	−0.15	−0.16	−0.69
Quinoxaline	2	−0.17	−0.35	−0.61	−1.13
	5	−0.38	−0.15	−0.23	−0.76
	6	−0.17	0.00	−0.07	−0.24

effect due to ring nitrogen, substituent group and neighbouring ring, anisotropic and electric field effect of nitrogen atom[11] (*cf.* Table 1).

Recently, Figeys and Flammang,[12] Yukawa and his coworkers[13] have suggested the contribution from ring current effect on d_o, d_m and d_p of monosubstituted benzenes.

In Table II—V, $\delta_{\text{obs.}}$ indicates corrected ring ^{1}H chemical shift from C_6H_6 reference, and

$$\delta_{\text{corr. I}} = \delta_{\text{obs.}} - (\delta_{\text{RC}} + \delta_{\text{MA}} + \delta_{\text{E}})_{\text{ref.}}$$

$$\delta_{\text{corr. II}} = \delta_{\text{corr. I}} - \delta_{\text{RC}} \text{ substituent}^{12)}$$

where δ_{RC} = Ring current effect contribution

δ_{MA} = Magnetic anisotropy contribution

δ_{E} = Electric field effect contribution

TABLE II. Observed, Corrected, Revised Chemical Shifts (ppm), ρ_{NMR} and $\rho_{\text{calcd.}}$ in 4-Pyridines

Substituent	^{1}H position	$\delta_{\text{obs.}}$	$\delta_{\text{corr. I}}$	$\delta_{\text{corr. II}}$	$\delta_{\text{rev.}}$	ρ_{NMR}	ρ_{omega}
NO_2	3	−0.57	−0.45		−0.24	0.977	0.963
	2	−1.50	−0.80		−0.70	0.935	0.973
CN	3	+0.02	+0.14		−0.09	0.991	
	2	−1.35	−0.65		−0.65	0.940	
$COOCH_3$	3	−0.39	−0.27		−0.04	0.996	0.970
	2	−1.35	−0.65		−0.64	0.940	0.976
$COCH_3$	3	−0.27	−0.15		−0.15	0.986	0.962
	2	−1.39	−0.69		−0.67	0.937	0.974
CH_3	3	+0.37	+0.49		+0.45	1.042	1.010
	2	−1.11	−0.41		−0.48	0.955	0.984
OCH_3	3	+0.71	+0.83	+0.75	+0.75	1.070	1.037
	2	−0.99	−0.29	−0.37	−0.37	0.965	0.991
H	3	+0.21	+0.33	+0.33	+0.33	1.031	0.997
	2	−0.23	−0.53	−0.53	−0.53	0.951	0.982
NH_2	3				+0.99	1.093	1.053
	2				−0.31	0.971	0.995
$N(CH_3)_2$	3				+1.16	1.108	
	2				−0.24	0.978	

Previously, in monosubstituted benzene series, the linear relation $\rho_o/\rho_p = d_o/d_p$ has been observed in electron releasing substituent groups, and deviation from above extention line has been attributed to the sum of factors other than π-electron charge density contribution. In this work, the following treatment has been taken into account, namely

1. Corrections of chemical shift of parent compounds are carried out by Table I.
2. Magnetic anisotropy effect due to Me and OMe are neglected from Pople's[14] conclusion.
3. Corrections due to ring current effect (for example, OMe −0.08 ppm) are utilized from Figeys and Flammang's[12] result.
4. Corrected shift of H, OMe, NH_2 groups were plotted against σ_π, and resulted linear relation was extended to electron attracting substituent groups, and corrected shifts were estimated by extrapolation.

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11) P.J. Black, R.D. Brown and M.L. Heffernan, *Aus. J. Chem.*, **20**, 1305 (1967).

12) H.P. Figeys and R. Flammang, *Mol. Phys.*, **12**, 581 (1967).

13) *a*) Y. Yukawa, Y. Tsuno, H. Yamada and T. Kinugasa, Abstract Papers of the 7th NMR Symposium in Japan, Nagoya, November 1968, p. 61; *b*) H. Yamada, Ph. D. Thesis, Osaka University, 1968.

14) J.A. Pople, *J. Chem. Phys.*, **37**, 60 (1962).

TABLE III. Observed, Corrected, Revised Chemical Shifts (ppm), ρ_{NMR} and $\rho_{calcd.}$ in 3-Pyridines

Substituent	^{1}H position	$\delta_{obs.}$	$\delta_{corr.\,I}$	$\delta_{corr.\,II}$	$\delta_{rev.}$	ρ_{NMR}	ρ_{omega}	ρ_{SCF}
NO_2	2				−1.00	0.903	0.945	0.956
	4				−0.67	0.937	0.953	0.999
	5				+0.24	1.022	0.988	0.970
	6				−0.84	0.921	0.945	0.947
$COOCH_3$	2	−1.86	−1.16		−0.86	0.920	0.954	
	4	−0.86	−0.78		−0.50	0.953	0.961	
	5	+0.12	+0.24		+0.25	1.023	0.990	
	6	−1.35	−0.65		−0.75	0.930	0.959	
$COCH_3$	2	−1.78	−1.08		−0.94	0.912	0.946	
	4	−0.83	−0.75		−0.59	0.945	0.954	
	5	+0.20	+0.24		+0.25	1.023	0.987	
	6	−1.38	−0.68		−0.80	0.925	0.950	
CN	2	−1.50	−0.80		−0.89	0.917		0.888
	4	−0.52	−0.44		−0.53	0.950		0.948
	5	+0.04	+0.16		+0.25	1.023		1.012
	6	−1.42	−0.72		−0.77	0.929		0.890
Br	2	−1.18	−0.48		−0.51	0.952	0.990	
	4	−0.39	−0.31		−0.08	0.992	0.997	
	5	+0.27	+0.39		+0.29	1.027	0.999	
	6	−1.38	−0.68		−0.54	0.950	0.989	
H	2	−1.28	−0.58	−0.58	−0.58	0.946	0.982	0.906
	4	−0.24	−0.16	−0.16	−0.16	0.986	0.988	0.969
	5	+0.16	+0.28	+0.28	+0.28	1.026	0.997	0.988
	6	−1.28	−0.58	−0.58	−0.58	0.946	0.982	0.906
CH_3	2	−1.09	−0.39		−0.46	0.958	0.995	
	4	−0.02	+0.06		−0.05	0.995	1.001	
	5	+0.22	+0.34		+0.29	1.027	0.999	
	6	−1.14	−0.44		−0.51	0.952	0.991	
OCH_3	2	−0.84	−0.14	−0.22	−0.22	0.979	1.021	
	4	+0.27	+0.35	+0.27	+0.27	1.025	1.028	
	5	+0.27	+0.39	+0.31	+0.31	1.029	1.005	
	6	−0.96	−0.26	−0.34	−0.34	0.968	1.014	
NH_2	2				−0.03	0.997	1.037	0.999
	4				+0.47	1.044	1.045	1.029
	5				+0.33	1.031	1.009	0.997
	6				−0.22	0.979	1.029	0.981
$N(CH_3)_2$	2				+0.11	1.010		1.007
	4				+0.64	1.060		1.036
	5				+0.35	1.033		0.998
	6				−0.13	0.988		0.986

From above treatment, following results have been acknowledged (*cf.* Fig. 5—8).

1. Chemical shift of *meta* position from substituent, the magnitude of which is small but linear with σ_π, is dependent on the resonance effect in same direction as in *ortho* and *para* positions.
2. $\delta_{2\text{-H}}$, $\delta_{3\text{-H}}$, $\delta_{4\text{-H}}$ in 6-quinolines and $\delta_{2\text{-H}}$, $\delta_{3\text{-H}}$ in 6-quinoxalines, which are all situated far from substituent groups, are linear with σ_π in electron releasing substituent groups, but in some of electron attracting substituent groups the linearity was unsatisfactory.

TABLE IV. Observed, Corrected, Revised Chemical Shifts (ppm), ρ_{NMR} and $\rho_{calcd.}$ in 6-Quinolines

Substituent	^{1}H posion	$\delta_{obs.}$	$\delta_{corr.\,I}$	$\delta_{corr.\,II}$	$\delta_{rev.}$	ρ_{NMR}	ρ_{omega}	ρ_{SCF}
NO_2	2	−1.77	−1.00		−0.82	0.923	0.962	0.939
	3	−0.24	+0.11		+0.35	1.033	0.993	0.981
	4	−1.20	−0.68		−0.16	0.986	0.971	0.983
	5	−1.48	−1.04		−0.83	0.922	0.942	1.009
	7	−0.96	−0.76		−0.56	0.948	0.982	1.007
	8	−1.04	−0.35		−0.40	0.963	0.993	0.968
$COOCH_3$	2	−1.58	−0.75		−0.77	0.928	0.968	
	3	+0.05	+0.40		+0.39	1.036	0.994	
	4	−0.98	−0.48		−0.12	0.989	0.978	
	5	−1.20	−0.76		−0.56	0.948	0.958	
	7	−0.81	−0.61		−0.42	0.979	0.981	
	8	−0.81	−0.12		−0.32	0.965	0.996	
H	2	−1.51	−0.68	−0.68	−0.66	0.937	0.977	0.875
	3	+0.10	+0.45	+0.45	+0.47	1.042	0.998	1.011
	4	−0.61	−0.09	−0.09	−0.08	0.993	0.985	0.959
	5	−0.41	+0.03	+0.03	+0.03	1.003	0.998	1.010
	7	−0.34	−0.14	−0.14	−0.14	0.988	0.997	1.001
	8	−0.83	−0.14	−0.14	−0.14	0.988	1.001	0.986
Br	2	−1.49	−0.66		−0.63	0.941	0.979	
	3	+0.12	+0.47		+0.48	1.045	0.999	
	4	−0.49	+0.03		−0.05	0.996	0.987	
	5	−0.53	+0.09		+0.15	1.014	1.010	
	7	+0.15	+0.35		−0.07	0.993	1.001	
	8	−0.60	+0.09		−0.10	0.990	1.002	
CH_3	2	−1.42	−0.59		−0.62	0.941	0.980	
	3	+0.16	+0.51		+0.49	1.046	0.999	
	4	−0.53	−0.01		−0.03	0.998	0.988	
	5	−0.17	+0.27		+0.25	1.023	1.015	
	7	−0.12	+0.08		−0.04	0.996	1.005	
	8	−0.69	0.00		−0.07	0.993	1.003	
OH	2				−0.49	0.954		0.943
	3				+0.57	1.053		1.007
	4				+0.04	1.003		0.975
	5				+0.89	1.083		1.035
	7				+0.29	1.027		1.013
	8				+0.14	1.013		1.006
OCH_3	2	−1.35	−0.52		−0.53	0.950	0.988	
	3	+0.19	+0.54		+0.56	1.052	1.002	
	4	−0.53	−0.01		+0.02	1.001	0.995	
	5	+0.41	+0.85	+0.77	+0.77	1.072	1.053	
	7	+0.08	+0.28	+0.20	+0.20	1.019	10.20	
	8	−0.53	+0.16	+0.08	+0.08	1.008	1.006	
NH_2	2	−1.21	−0.37		−0.45	0.958	0.994	0.945
	3	+0.13	+0.48		+0.60	1.056	1.004	1.008
	4	−0.58	−0.06		+0.05	1.004	1.000	0.977
	5	+0.52	+0.96		+1.09	1.102	1.075	1.042
	7	+0.26	+0.46		+0.38	1.036	1.028	1.017
	8	−0.50	+0.19		+0.18	1.017	1.009	1.006
$N(CH_3)_2$	2				−0.40	0.963		0.948
	3				+0.63	1.058		1.009
	4				+0.08	1.007		0.979
	5				+1.44	1.135		1.052
	7				+0.55	1.051		1.022
	8				+0.30	1.028		1.006

TABLE V. Observed, Corrected, Revised Chemical Shifts (ppm), ρ_{NMR} and $\rho_{calcd.}$ in 6-Quinoxalines

Substitueut	^{1}H position	$\delta_{obs.}$	$\delta_{corr.\,I}$	$\delta_{corr.\,II}$	$\delta_{rev.}$	ρ_{NMR}	ρ_{omega}
NO_2	2	−1.68	−0.55		−0.42	0.961	0.960
	3	−1.68	−0.55		−0.35	0.967	0.969
	5	−1.73	−0.97		−0.84	0.931	0.944
	7	−1.24	−1.00		−0.37	0.966	0.980
	8	−0.97	−0.21		−0.13	0.988	0.991
$COOCH_3$	2	−1.42	−0.29		−0.38	0.964	0.966
	3	−1.42	−0.29		−0.33	0.968	0.971
	5	−1.48	−0.72		−0.55	0.949	0.960
	7	−0.98	−0.74		−0.27	0.975	0.980
	8	−0.76	0.00		−0.09	0.991	0.994
CN	2	−1.64	−0.51		−0.39	0.964	
	3	−1.64	−0.51		−0.34	0.967	
	5	−1.23	−0.47		−0.60	0.944	
	7	−0.65	−0.41		−0.28	0.974	
	8	−0.93	−0.17		−0.10	0.991	
H	2	−1.38	−0.25		−0.25	0.977	0.974
	3	−1.38	−0.25		−0.25	0.977	0.974
	5	−0.76	0.00	0.00	0.00	1.000	0.999
	7	−0.33	−0.09	−0.09	−0.09	0.993	0.996
	8	−0.76	0.00	0.00	0.00	1.000	0.999
Cl	2	−1.33	−0.20		−0.22	0.979	0.977
	3	−1.33	−0.20		−0.24	0.978	0.975
	5	−0.74	+0.02		+0.18	1.017	1.012
	7	−0.25	+0.01		−0.03	0.997	1.005
	8	−0.63	+0.13		+0.03	1.003	1.000
CH_3	2	−1.29	−0.16		−0.22	0.979	0.977
	3	−1.29	−0.16		−0.23	0.979	0.975
	5	−0.52	+0.24		+0.23	1.022	1.016
	7	−0.11	+0.13		−0.02	0.998	1.004
	8	−0.59	+0.17		+0.04	1.004	1.000
OCH_3	2	−1.23	−0.11		−0.11	0.989	0.986
	3	−1.29	−0.17		−0.17	0.984	0.979
	5	+0.01	+0.77	+0.69	+0.69	1.064	1.054
	7	−0.01	+0.23	+0.15	+0.15	1.014	1.019
	8	−0.57	+0.19	+0.11	+0.11	1.010	1.004
NH_2	2	−1.27	−0.14		−0.03	0.997	0.991
	3	−1.19	−0.06		−0.13	0.988	0.981
	5	+0.21	+0.97		+1.04	1.097	1.077
	7	+0.18	+0.42		+0.27	1.025	1.027
	8	−0.43	+0.33		+0.17	1.026	1.007

ρ_{NMR}, π-Electron Charge Density Distribution from Corrected Ring ^{1}H Chemical Shift

ρ_{NMR} is estimated from next equation

$$\rho_{NMR}=1+\delta_{corr.}\ \mathrm{ppm}/10.7\ \mathrm{ppm}^{15)}$$

ρ_ω, π-Electron Charge Density Distribution from Modified Hueckel Molecular Orbital Method-ω-Technique

$h_N=0.2$ and $k_{CN}=1.0$, which afford the best ρ_{NMR} at *para* position from ring nitrogen, are proposed to nitrogen atom. ω-Values and substituent's parameters are the same as those

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15) T. Schaefer and W.G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

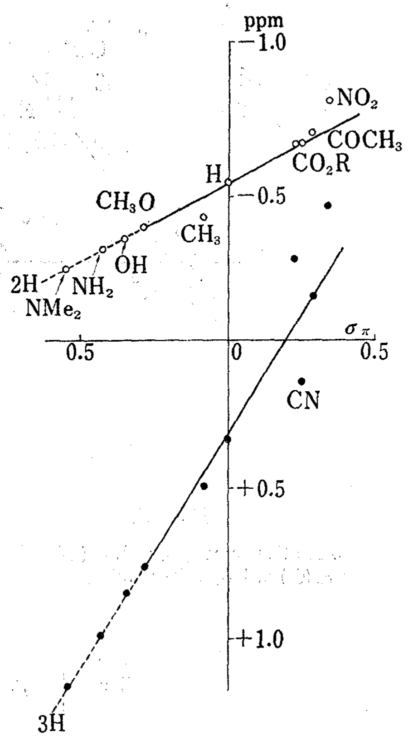


Fig. 5

correlations among $\delta_{corr.}$ 2-H (○), $\delta_{corr.}$ 3-H (●) of 4-pyridines and σ_π

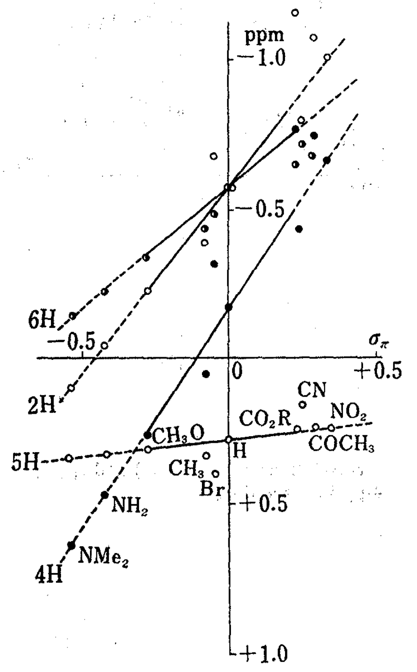
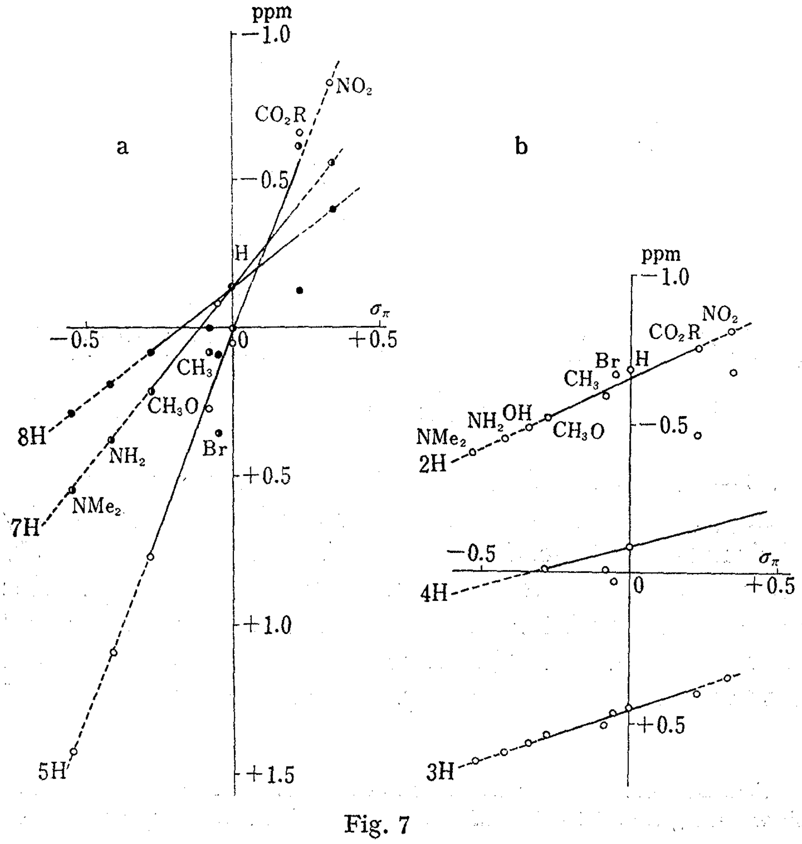


Fig. 6

correlations among $\delta_{corr.}$ 2-H (○), $\delta_{corr.}$ 4-H (●), $\delta_{corr.}$ 5-H (○), $\delta_{corr.}$ 6-H (◑) of 3-pyridines and σ_π



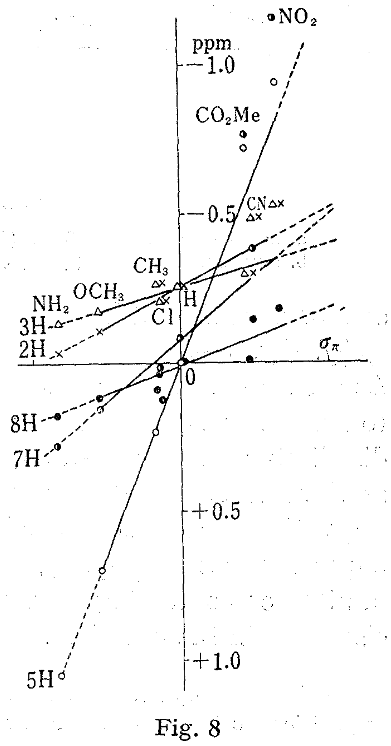


Fig. 7

Fig. 8

a. correlations among $\delta_{corr.}$ 5-H (○), $\delta_{corr.}$ 7-H (◑), $\delta_{corr.}$ 8-H (●) of 6-quinolines and σ_π

b. correlations among $\delta_{corr.}$ 2-H (○), $\delta_{corr.}$ 3-H (○), $\delta_{corr.}$ 4-H (○) of 6-quinolines and σ_π

correlations among $\delta_{corr.}$ 2-H (×), $\delta_{corr.}$ 3-H (△), $\delta_{corr.}$ 5-H (○), $\delta_{corr.}$ 7-H (◑), $\delta_{corr.}$ 8-H (●) of 6-quinoxalines and σ_π

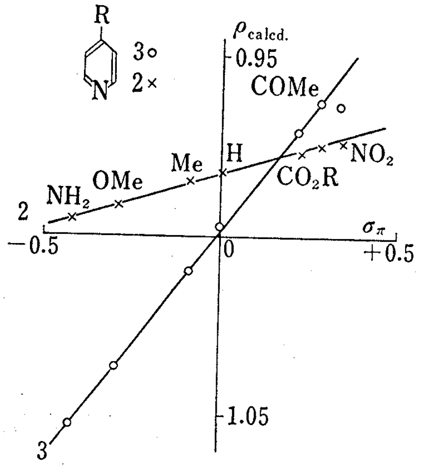


Fig. 9

correlations among ρ_2 (×) and ρ_3 (○) of 4-pyridines and σ_π

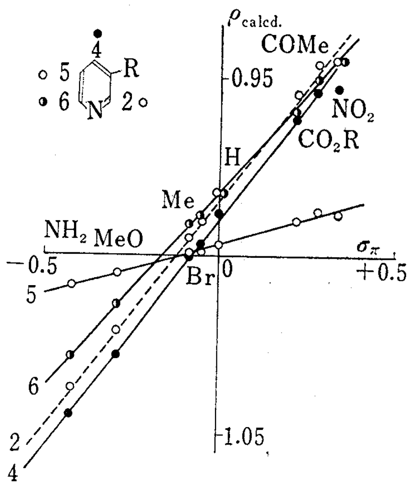


Fig. 10

correlations among ρ_2 (○), ρ_4 (●) ρ_5 (○) and ρ_6 (◑) of 3-pyridines and σ_π

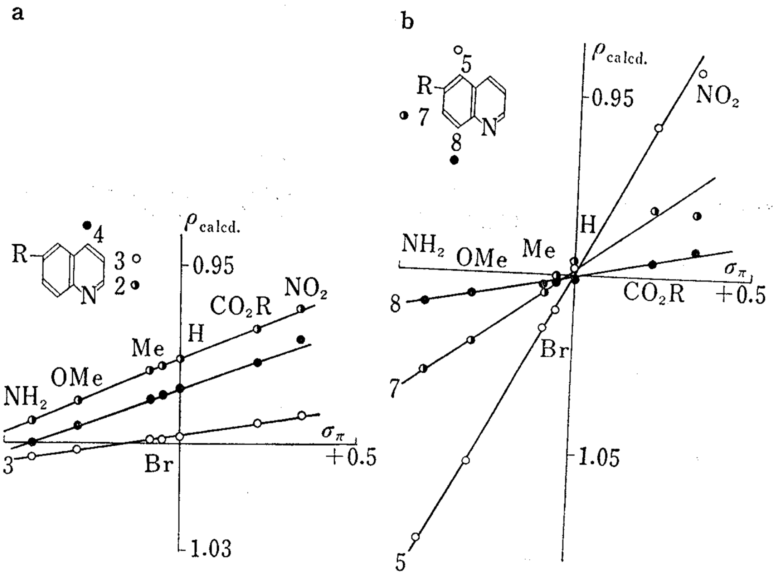


Fig. 11

a. correlations among ρ_2 (◑), ρ_3 (○), ρ_4 (●) of 6-quinolines and σ_π
b. correlations among ρ_5 (○), ρ_7 (◑), ρ_8 (●) of 6-quinolines and σ_π

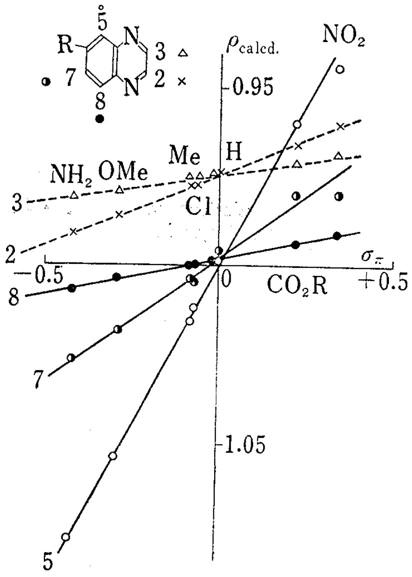


Fig. 12

correlations among ρ_2 (×), ρ_3 (△), ρ_5 (○), ρ_7 (◑), ρ_8 (●) of 6-quinoxalines and σ_π

of monosubstituted benzenes reported in the preceding papers,[16] and all ρ_ω are linear with σ_π (*cf.* Fig. 9—12).

As are shown in Fig. 5—8 and Fig. 9—12, ρ_{NMR} and ρ_ω showed similar gradients with respect to substituent constant σ_π, and both ρ_{NMR} and ρ_{SCF}[17] afford similar trends of charge density distribution in *meta* position, but their relative intersections are unsatisfactory. It is probably ascribed to both additional ring nitrogen correction term and mathematical treatment. This suggestion is also supported from the fact that intersections observed in 6-quinolines and 6-quinoxalines (*cf.* Fig. 7_b, Fig. 11_a and Fig. 8, Fig. 12) showed unfavorable correspondence in nitrogen containing ring, whereas favorable in the other ring. This problem will be solved elsewhere in the due time.

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