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Studies on the Proton Magnetic Resonance Spectra in Aromatic Systems. XVII.[1] On the Electronic Indices of 3- and 4-Substituted Pyridine, 6-Substituted Quinoline and 6-Substituted Quinoxaline Derivatives

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The electronic indices: π-electron charge density ρ, F_r, $S_r^{(E)}$, $S_r^{(R)}$ and $S_r^{(N)}$: were obtained for 3- and 4-substituted pyridine, 6-substituted quinoline and 6-substituted quinoxaline derivatives, and the following results were obtained.

1. The ρ values are linearly related to the substituent constant σ_π.
2. F_r, $S_r^{(E)}$, $S_r^{(R)}$ and $S_r^{(N)}$ are linearly related with σ_π for electron releasing substituent group sites, but this linear relation does not hold for electron attracting substituent group sites.
3. The reliability of the simple sum rule of molecular electronic indices was confirmed.

Introduction

In the previous paper[3] of this series, the corrected ring H-1 chemical shifts of 3- and 4-substituted pyridine, 6-substituted quinoline and 6-substituted quinoxaline derivatives were correlated with the π-electron charge density —ρ value— calculated by a modification of Hueckel's molecular orbital method.

In this paper, in addition to the ρ values for the nitrogen and carbon atom without the H-1 atom, the free valence F_r, electrophilic $S_r^{(E)}$, free radical $S_r^{(R)}$ and nucleophilic $S_r^{(N)}$ superdelocalizabilities are reported.

Result and Discussion

1. π-Electron Charge Density

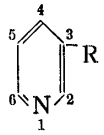
The ρ values for carbon atoms with a substituent group summarized in Table Ia—d are linearly proportional to those of carbon atoms of monosubstituted benzene derivatives,[1] as shown in Fig. 1a, whereas those for carbon atoms without a substituent and nitrogen are linearly related with the substituent constant σ_π (*cf.* Fig. 1a—d).

2. Free Valence Fr, Electrophilic $S_r^{(E)}$, Free Radical $S_r^{(R)}$ and Nucleophilic $S_r^{(N)}$ Superdelocalizabilities

These parameters are summarized in Tables IIa—d, IIIa—d, IVa—d and Va—d. As shown in Fig. 2a, 3a, 4a and 5a, the above indices for carbon atoms with a substituent group were linearly related with those of monosubstituted benzene derivatives, whereas those of nitrogen and carbon atoms without a hydrogen atom were linearly related with the substituent constant σ_π in the electron releasing substituent group site. However, in the electron attracting substituent group sites, these linear relations are confused in $S_r^{(R)}$ and $S_r^{(N)}$, respectively.

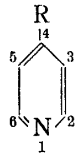
1) Part XVI: Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **11**, 1759 (1969).
2) Location: *Toneyama 6–5, Toyonaka, Osaka.*
3) Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **17**, 1090 (1969); Y. Sasaki and M. Suzuki **17**, 1799 (1969).

Table Ia. π-Electron Charge Densities for 3-Substituted Pyridine Derivatives (1 and 3 Positions)



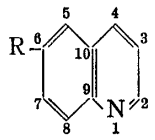
Substituent R	1-N	3-C	Substituent R	1-N	3-C
NH_2	1.076	0.969	CO_2Me	1.048	1.001
OMe	1.063	0.971	COMe	1.045	0.997
Me	1.057	0.978	NO_2	1.046	0.964
Br	1.057	0.994			

Table Ib. π-Electron Charge Densities for 4-Substituted Pyridine Derivatives (1 and 4 Positions)



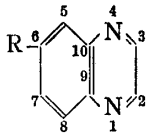
Substituent R	1-N	4-C	Substituent R	1-N	4-C
NH_2	1.103	0.961	CO_2Me	1.033	0.994
OMe	1.087	0.963	COMe	1.025	0.990
Me	1.064	0.969	NO_2	1.021	0.957
H	1.055	0.988			

Table Ic. π-Electron Charge Densities for 6-Substituted Quinoline Derivatives (1,6,9 and 10 Positions)



Substituent R	1-N	6-C	9-C	10-C
NH_2	1.0626	0.96928	1.01145	1.0051
OMe	1.06175	0.97159	1.00484	1.00249
Me	1.05973	0.97931	0.99427	0.99913
Br	1.05958	0.99549	0.99302	0.99891
H	1.05893	0.99891	0.98977	0.99788
CO_2Me	1.05617	1.00413	0.97791	0.99388
NO_2	1.05389	0.96552	0.97204	0.99074

Table Id. π-Electron Charge Densities for 6-Substituted Quinoxaline Derivatives



Substituent R	1-N	4-N	6-C	9-C	10-C
NH_2	1.04876	1.05960	0.96568	1.00891	0.99506
OMe	1.04706	1.05448	0.96836	1.00252	0.99243
Me	1.04471	1.04695	0.97573	0.99220	0.98878
Cl	1.04481	1.04669	0.99255	0.99116	0.98883
H	1.04400	1.04400	0.99555	0.98763	0.98763
CO_2Me	1.04160	1.03709	1.00117	0.97578	0.98392
NO_2	1.03968	1.03151	0.96295	0.96985	0.98149

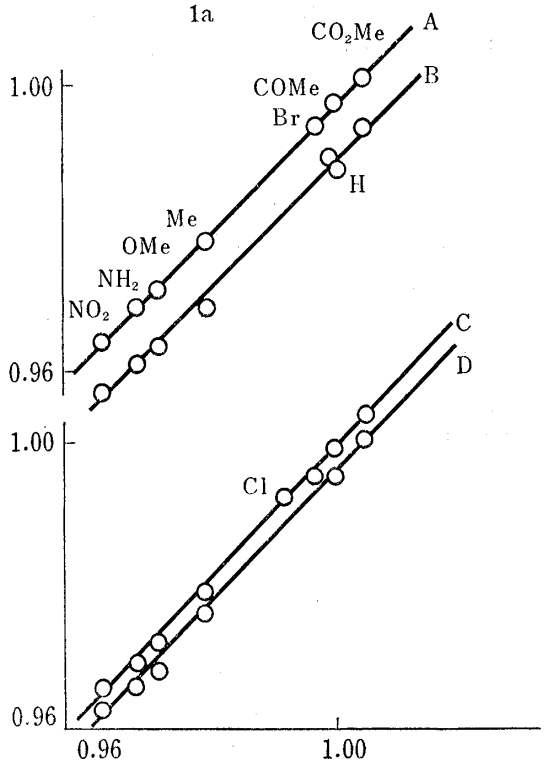
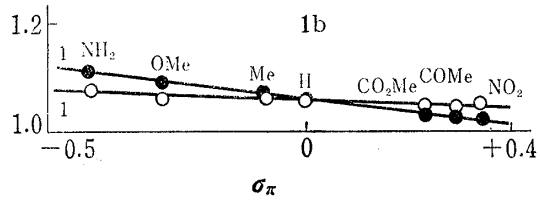


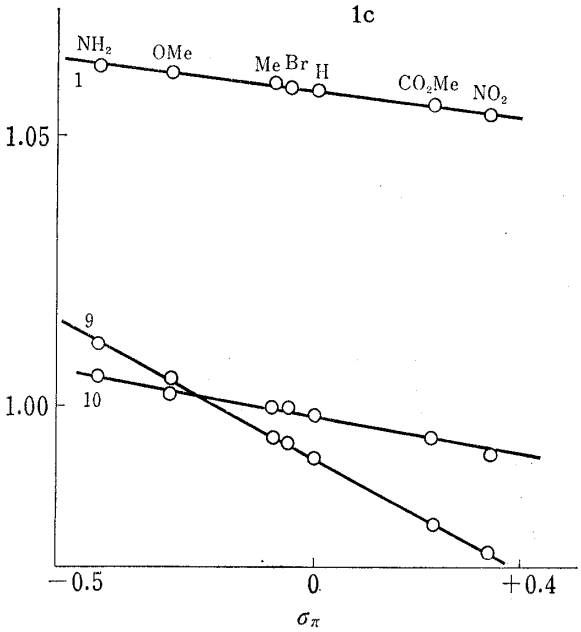
Fig. 1a. π-Electron Charge Densities Carbon Atoms with a Substituent Group

horizontal axis: π-electron charge densities for carbon atoms with a substituent group in mono-substituted benzene derivatives
vertical axis: π-electron charge densities for carbon atoms with a substituent group in
A: 3-pyridine B: 4-pyridine
C: 6-quinoline D: 6-quinoxaline derivatives

Fig. 1b. π-Electron Charge Densities for the Nitrogen Atom in 3- and 4-Pyridine Derivatives *vs.* the Substituent Constant σ_π

The vertical axis shows the π-elclectron charge density.
○: 3-pyridine ●: 4-pyridine





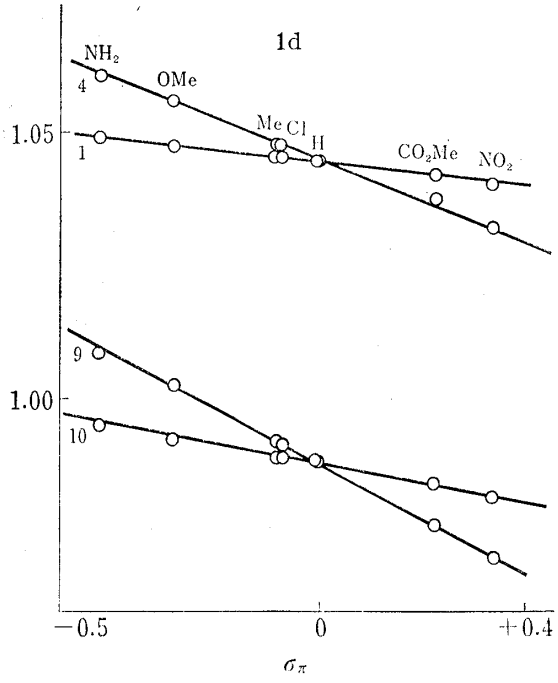


Fig. 1c. π-Electron Charge Densities for 6-Quinoline Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the π-elecrtron charge density.
The numbers on the diagonal lines show the positions of carbon and nitrogen atoms.

Fig. 1d. π-Electron Charge Densities for 6-Quinoxaline Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the π-electron charge density.
The numbers on the diagonal lines show the positions of the carbon and nitrogen atoms.

Table IIa. Free Valence F_r for 3-Substituted Pyridine Derivatives

Substituent R	1-N	2-C	3-C	4-C	5-C	6-C
NH_2	0.39861	0.44935	0.09991	0.44621	0.39438	0.41962
OMe	0.40007	0.43191	0.14038	0.42915	0.39577	0.41117
Me	0.40237	0.40736	0.26560	0.40556	0.39796	0.40166
Br	0.40242	0.40656	0.26039	0.40516	0.39803	0.40278
CO_2Me	0.39909	0.44577	0.10948	0.44561	0.39459	0.41849
COMe	0.39829	0.45739	0.08991	0.45718	0.39377	0.42563

Table IIb. Free Valence F_r for 4-Substituted Pyridine Derivatives

Substituent R	1-N	2-C	3-C	4-C
NH_2	0.43398	0.39556	0.44486	0.09696
OMe	0.42165	0.39706	0.42818	0.13687
Me	0.40652	0.39957	0.40481	0.26416
H	0.40299	0.40041	0.39856	0.39930
CO_2Me	0.41386	0.39691	0.44520	0.11143
COMe	0.41847	0.39613	0.45706	0.09179
NO_2	0.42560	0.39565	0.46733	0.13740

Table IIc. Free Valence F_r for 6-Substituted Quinoline Derivatives

Substituent R	1-N	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9-C	10-C
OMe	0.45652	0.40853	0.40404	0.45583	0.48769	0.14411	0.43093	0.44831	0.11206	0.10219
Me	0.45772	0.40661	0.40406	0.45376	0.45986	0.27090	0.41058	0.45170	0.10666	0.10389
Br	0.45765	0.40695	0.40406	0.45406	0.45978	0.26434	0.40954	0.45160	0.10704	0.10393
H	0.45796	0.40648	0.40406	0.45355	0.45285	0.40425	0.40448	0.45243	0.10568	0.10434
CO_2Me	0.45639	0.41065	0.40402	0.45789	0.50589	0.11367	0.44321	0.44599	0.11461	0.10112
NO_2	0.45526	0.41609	0.40400	0.46322	0.53676	0.14335	0.45662	0.44397	0.12262	0.10046

Table IId. Free Valence F_r for 6-Substituted Quinoxaline Derivatives

Substituent R	1-N	2-C	3-C	4-N	5-C	6-C	7-C	8-C	9-C	10-C
OMe	0.45299	0.40877	0.40689	0.45967	0.48662	0.14319	0.43126	0.44839	0.11223	0.10343
Cl	0.45431	0.40748	0.40694	0.45599	0.46021	0.25570	0.41013	0.45172	0.10736	0.10531
H	0.45470	0.40695	0.40695	0.45470	0.45267	0.40457	0.40457	0.45267	0.10580	0.10580
CO_2Me	0.45348	0.41137	0.40698	0.45667	0.50641	0.11424	0.44312	0.44633	0.11456	0.10270
NO_2	0.45242	0.41691	0.40701	0.45962	0.53734	0.14295	0.45676	0.44422	0.12277	0.10190

Table IIIa. Electrophilic Supperdelocalizability $S_r^{(E)}$ for 3-Substituted Pyridine Derivatives

Substituent R	1-N	2-C	3-C	4-C	5-C	6-C
NH_2	0.85023	1.14824	0.79332	1.13837	0.85240	1.11925
OMe	0.84220	0.99687	0.80386	0.99052	0.84391	0.97862
Me	0.82933	0.83459	0.82157	0.83267	0.83033	0.83103
Br	0.82682	0.84345	0.81834	0.84190	0.82774	0.83927
CO_2Me	0.80650	0.77810	0.73914	0.78180	0.80677	0.76170
COMe	0.80395	0.75971	0.72034	0.76504	0.80433	0.73877

Table IIIb. Electrophilic Superdelocalizability $S_r^{(E)}$ for 4-Substituted Pyridine Derivatives

Substituent R	1-N	2-C	3-C	4-C
NH_2	1.13115	0.82137	1.15898	0.75432
OMe	0.99892	0.81376	1.01708	0.76849
Me	0.85738	0.80140	0.86157	0.79099
H	0.82295	0.79526	0.82365	0.79493
CO_2Me	0.79303	0.78090	0.81004	0.71598
COMe	0.77165	0.77920	0.78307	0.69903
NO_2	0.76215	0.77323	0.78500	0.69516

Table IIIc. Electrophilic Superdelocalizability $S_r^{(E)}$ for 6-Substituted Quinoline Derivaties

Substituent R	1-N	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9-C	10-C
OMe	0.99131	0.88608	0.87704	1.00718	1.31246	0.85007	0.95821	1.01647	0.77386	0.70652
Me	0.98290	0.82476	0.86818	0.94479	1.04194	0.86695	0.87587	0.99827	0.70389	0.70148
Br	0.98149	0.82769	0.86719	0.94749	1.05605	0.86317	0.88047	0.99408	0.70741	0.70034
H	0.97905	0.80948	0.86454	0.92906	0.97672	0.86833	0.85598	0.98895	0.68672	0.69868
CO_2Me	0.96773	0.78605	0.85832	0.90330	0.92413	0.77699	0.86034	0.96290	0.67000	0.68972
NO_2	0.95658	0.76760	0.85202	0.88396	0.86632	0.74703	0.85618	0.94703	0.65560	0.68365

Table IIId. Electrophilic Superdelocalizability $S_r^{(E)}$ for 6-Substituted Quinoxaline Derivatives

Substituent R	1-N	2-C	3-C	4-N	5-C	6-C	7-C	8-C	9-C	10-C
OMe	0.92860	0.87853	0.81494	0.99362	1.30031	0.83000	0.95456	0.99778	0.76872	0.69024
Cl	0.92166	0.82519	0.80641	0.94088	1.06577	0.84548	0.88136	0.97770	0.70719	0.68445
H	0.91981	0.80372	0.80372	0.91981	0.97278	0.85230	0.85230	0.97278	0.68277	0.68277
CO_2Me	0.91169	0.78164	0.79885	0.89765	0.92413	0.76414	0.85559	0.94877	0.66589	0.67460
NO_2	0.90290	0.76401	0.79348	0.88040	0.86856	0.73621	0.85056	0.93431	0.65127	0.66912

Table IVa. Free Radical Superdelocalizability $S_r^{(R)}$ for 3-Substituted Pyridine Derivatives

Substituent R	1-N	2-C	3-C	4-C	5-C	6-C
NH_2	0.82716	0.96630	0.76978	0.95738	0.82930	0.93822
OMe	0.82888	0.90250	0.79044	0.89648	0.83058	0.88457
Me	0.83177	0.84277	0.82400	0.84086	0.83276	0.83922
Br	0.83167	0.85230	0.82319	0.85074	0.83259	0.84810
CO_2Me	0.82988	0.95748	0.76271	0.96166	0.83010	0.94161
COMe	0.82860	1.04552	0.74542	1.05174	0.82897	1.02562

Table IVb. Free Radical Superdelocalizability $S_r^{(R)}$ for 4-Substituted Pyridine Derivatives

Substituent R	1-N	2-C	3-C	4-C
NH_2	0.92506	0.82758	0.95296	0.76122
OMe	0.87618	0.83010	0.89444	0.78519
Me	0.83505	0.83421	0.83927	0.82383
H	0.83268	0.83561	0.83336	0.83527
CO_2Me	0.94498	0.83516	0.96142	0.77083
COMe	1.03677	0.83554	1.05696	0.75649
NO_2	1.40219	0.83895	1.42231	0.76488

Table IVc. Free Radical Superdelocalizability $S_r^{(R)}$ for 6-Substituted Quinoline Derivaties

Substituent R	1-N	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9-C	10-C
OMe	0.99049	0.89300	0.87272	1.01358	1.09497	0.82931	0.91385	0.99017	0.73137	0.70082
Me	0.99302	0.87821	0.87273	0.99880	1.00431	0.86384	0.87870	0.99353	0.70726	0.70286
Br	0.99269	0.88160	0.87275	1.00212	1.01930	0.86250	0.88386	0.99279	0.71111	0.70268
H	0.99364	0.87777	0.89283	0.99842	0.99523	0.87308	0.87387	0.99433	0.70446	0.70320
CO_2Me	0.99021	0.91929	0.87306	1.03962	1.18701	0.79661	0.94342	0.98603	0.74999	0.69982
NO_2	0.98856	1.08931	0.87348	1.20898	1.87449	0.77876	1.12377	0.98246	0.92034	0.69811

Table IVd. Free Radical Superdelocalizability $S_r^{(R)}$ for 6-Substituted Quinoxaline Derivatives

Substituent R	1-N	2-C	3-C	4-N	5-C	6-C	7-C	8-C	9-C	10-C
OMe	0.99698	0.89380	0.87884	1.01468	1.08956	0.82721	0.91637	0.99005	0.73219	0.70213
Cl	1.00254	0.88554	0.88048	1.00844	1.02555	0.86229	0.88767	0.99445	0.71362	0.70447
H	1.00486	0.88109	0.88109	1.00486	0.99694	0.87519	0.87519	0.99694	0.70527	0.70527
CO_2Me	1.00548	0.92599	0.88323	1.05222	1.19719	0.80212	0.94357	0.99087	0.75056	0.70265
NO_2	1.01054	1.11289	0.88741	1.24108	1.93872	0.78880	1.13161	0.99086	0.92951	0.70191

Table Va. Nucleophilic Superdelocalizability $S_r^{(N)}$ for 3-Substituted Pyridine Derivatives

Substituent R	1-N	2-C	3-C	4-C	5-C	6-C
NH_2	0.80409	0.78435	0.74623	0.77639	0.80620	0.75718
OH	0.81556	0.80812	0.77702	0.80245	0.81726	0.79053
Me	0.83420	0.85097	0.82643	0.84906	0.83519	0.84742
Br	0.83652	0.86115	0.82804	0.85957	0.83744	0.85694
CO_2Me	0.85325	1.13687	0.78627	1.14151	0.85343	1.12151
COMe	0.85324	1.33133	0.77050	1.33844	0.85355	1.31247

Table Vb. Nucleophilic Superdelocalizability $S_r^{(N)}$ for 4-Substituted Pyridine Derivatives

Substituent R	1-N	2-C	3-C	4-C
NH_2	0.71897	0.83380	0.74694	0.76808
OMe	0.75343	0.84643	0.77180	0.80189
Me	0.81271	0.86703	0.81698	0.85668
H	0.84240	0.87595	0.84308	0.87562
CO_2Me	1.09692	0.88942	1.11280	0.82567
COMe	1.30190	0.89187	1.32085	0.81395
NO_2	2.04222	0.90467	2.05963	0.83460

Table Vc. Nucleophilic Superdelocalizability $S_r^{(N)}$ for 6-Substituted Quinoline Derivatives

Substituent R	1-N	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9-C	10-C
OMe	0.98963	0.89993	0.86840	1.01998	0.87748	0.80856	0.86948	0.96387	0.68887	0.69512
Me	1.00314	0.93167	0.87729	1.05282	0.96667	0.86073	0.88154	0.98879	0.71063	0.70423
Br	1.00388	0.93551	0.87831	1.05675	0.98255	0.86183	0.88725	0.99151	0.71481	0.70502
H	1.00823	0.94607	0.88113	1.06777	1.01375	0.87783	0.89176	0.99972	0.72220	0.70772
CO_2Me	1.01269	1.05252	0.88780	1.17593	1.44989	0.81623	1.02649	1.00916	0.82999	0.70991
NO_2	1.02054	1.41102	0.89493	1.53401	2.88266	0.81049	1.39135	1.01789	1.18508	0.71257

Table Vd. Nucleophilic Superdelocalizability $S_r^{(N)}$ for 6-Substituted Quinoxaline Derivatives

Substituent R	1-N	2-C	3-C	4-N	5-C	6-C	7-C	8-C	9-C	10-C
OMe	1.06535	0.90907	0.94273	1.03574	0.87880	0.82442	0.87818	0.98222	0.69566	0.71401
Cl	1.08342	0.94590	0.95454	1.07599	0.98533	0.87909	0.89398	1.01120	0.72006	0.72449
H	1.08990	0.95845	0.95845	1.08990	1.02111	0.89807	0.89807	1.02111	0.72778	0.72778
CO_2Me	1.09927	1.07035	0.96760	1.20678	1.47025	0.84010	1.03154	1.03297	0.83524	0.73071
NO_2	1.11818	1.46177	0.98135	1.60176	3.00888	0.84139	1.41266	1.04740	1.20775	0.73471

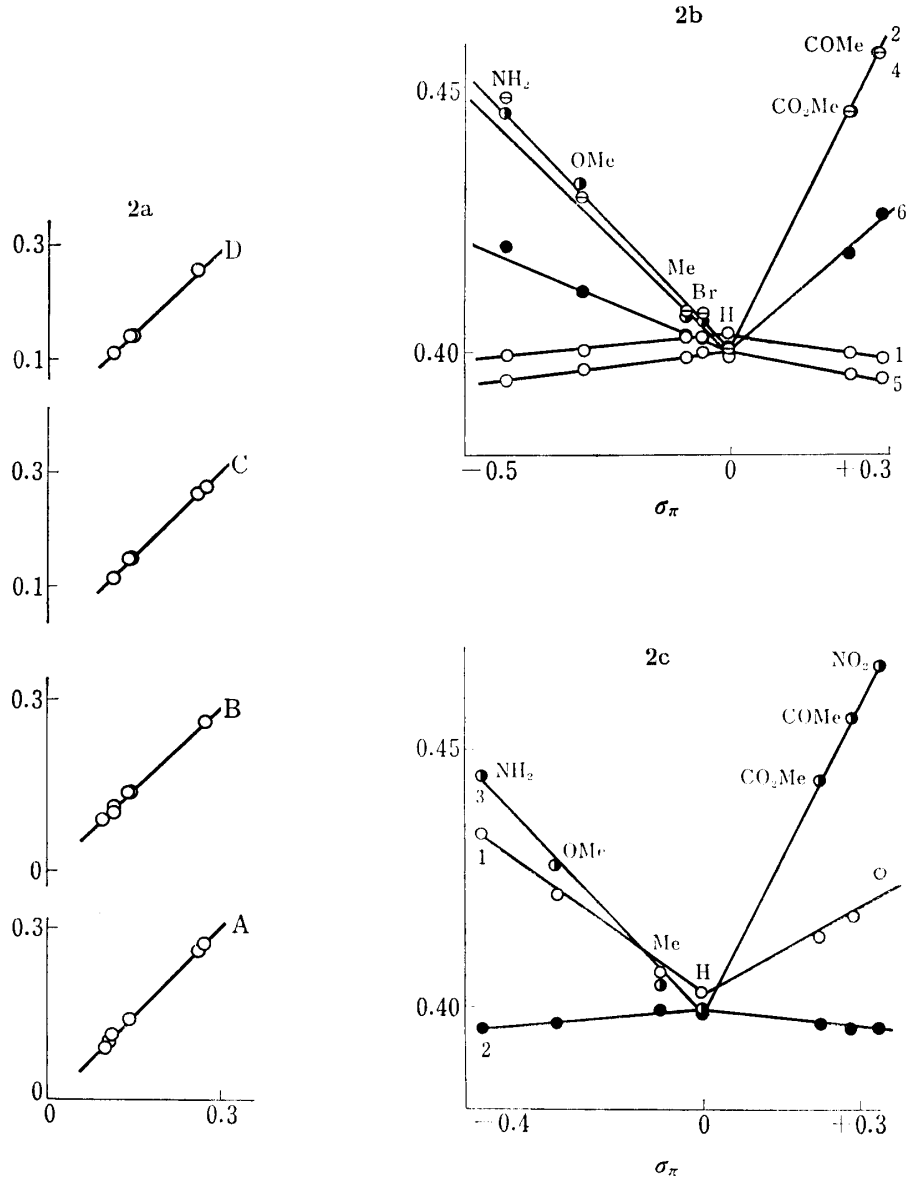


Fig. 2a. Free Valence F_r for Carbon Atoms with a Substituent Group

horizontal axis: F_r of carbon atoms with a substituent group in monosubstituted benzene derivatives
vertical axis: E_r for carbon atoms with a substituent group in
A: 3-pyridine B: 4-pyridine
C: 6-quinoline D: 6-quinoxaline derivatives

Fig. 2b. Free Valence F_r for 3-Pyridine Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the F_r. The numbers on the diagonal lines show the positions of the carbon or nitrogen.

Fig. 2c. Free Valence F_r for 4-Pyridine Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the F_r.The numbers on the diagonal lines show the position of the carbon or nitrogen.

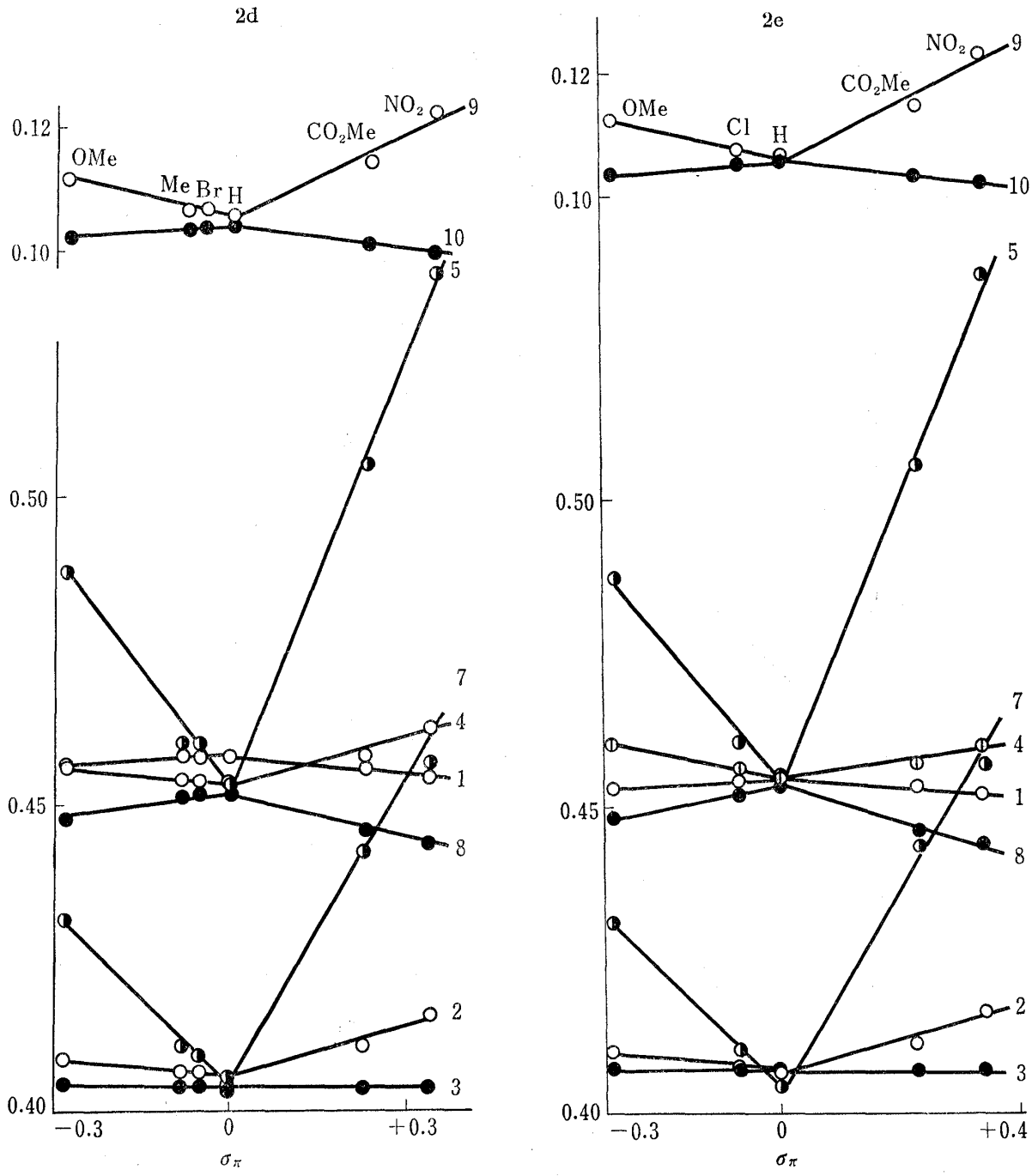


Fig. 2d. Free Valence F_r for 6-Quinoline Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the F_r. The numbers on the diagonal lines show the positions of the carbon or nitrogen.

Fig. 2e. Free Valence F_r for 6-Quinoxaline Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the F_r. The numbers on the diagonal lines show the positions of the carbon or nitrogen.

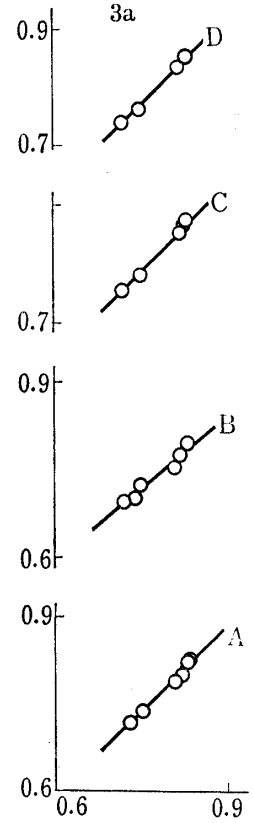


Fig. 3a. Electrophilic Superdelocalizability $S_r^{(E)}$ for Carbon Atoms with a Substituent Group

horizontal axis: $S_r^{(E)}$ for carbon atoms with a substituent group in monosubstituted benzene derivatives
vertical axis: $S_r^{(E)}$ for carbon atoms with a substiutuent group in
A: 3-pyridine
B: 4-pyridine
C: 6-quinoline
D: 6-quinoxaline derivatives

Fig. 3b. Electrophilic Superdelocalizability $S_r^{(E)}$ for 3-Pyridine Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the $S_r^{(E)}$. The numbers on the diagonal lines show the positions of the carbon or nitrogen.

Fig. 3c. Electrophilic Superdelocalizability $S_r^{(E)}$ for 4-Pyridine Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the $S_r^{(E)}$. The numbers on the diagonal lines show the positions of the carbon or nitrogen.

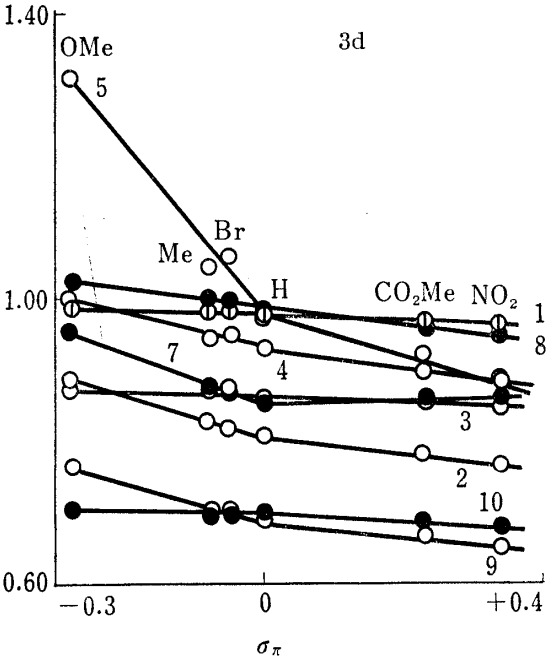
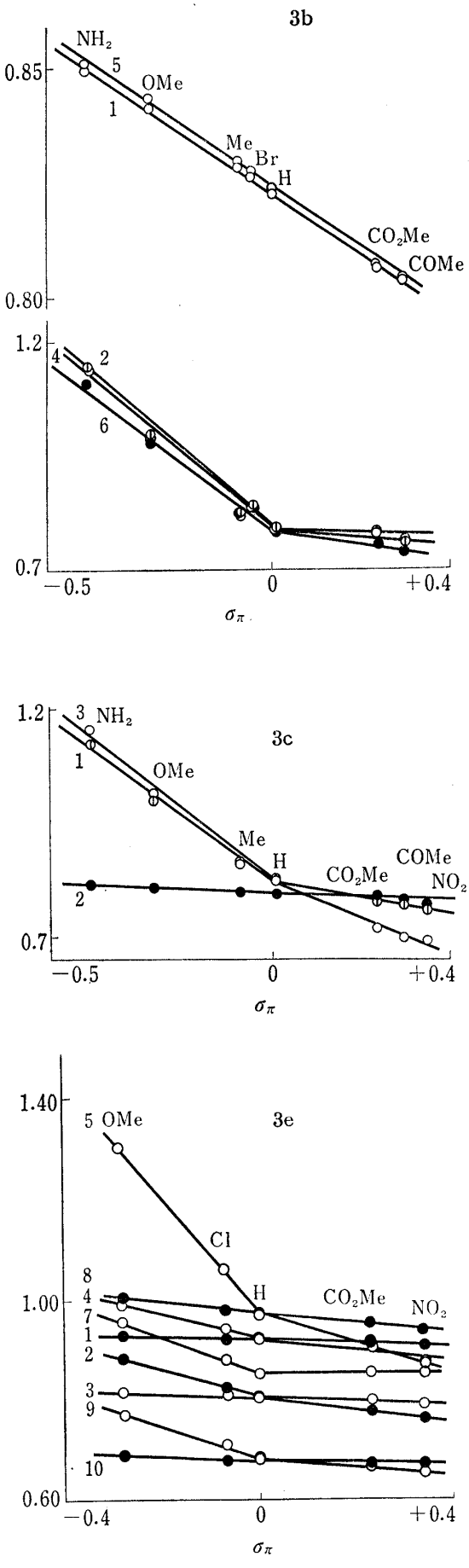


Fig. 3d. Electrophilic Superdelocalizability $S_r^{(E)}$ for 6-Quinoline Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the $S_r^{(E)}$. The numbers on the diagonal lines show the positions of the carbon or nitrogen.

Fig. 3e. Electrophilic Superdelocalizability $S_r^{(E)}$ for 6-Quinoxaline Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the $S_r^{(E)}$. The numbers on the diagonal lines show the positions of the carbon or nitrogen.



4a

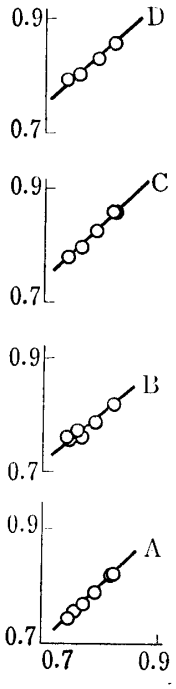
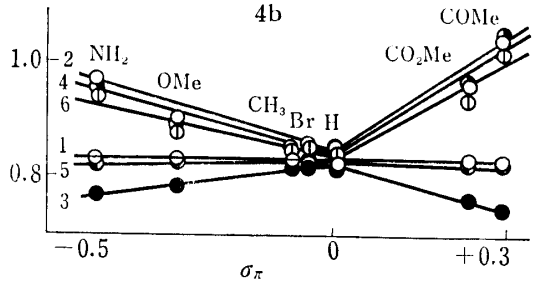


Fig. 4a. Free Radical Superdelocalizability $S_r^{(h)}$ for Carbon Atoms with a Substituent Group

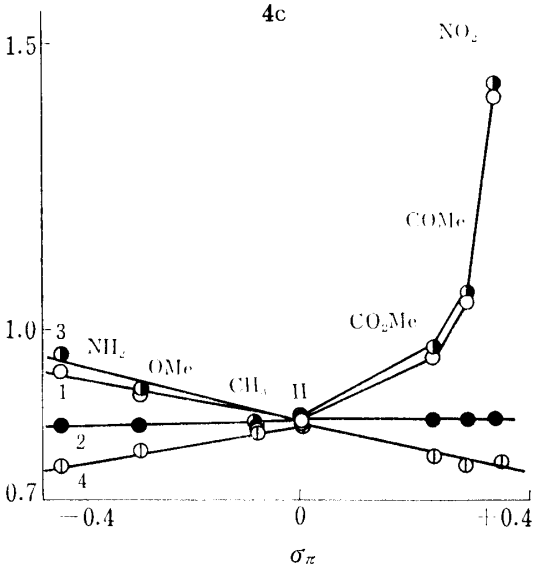
horizontal axis: $S_r^{(R)}$ for carbon atoms with a substituent group in monosubstituted benzene derivatives
vertical axis: $S_r^{(R)}$ for carbon atoms with a substituent group in

A: 3-pyridine
B: 4-pyridine
C: 6-quinoline
D: 6-quinoxaline derivatives

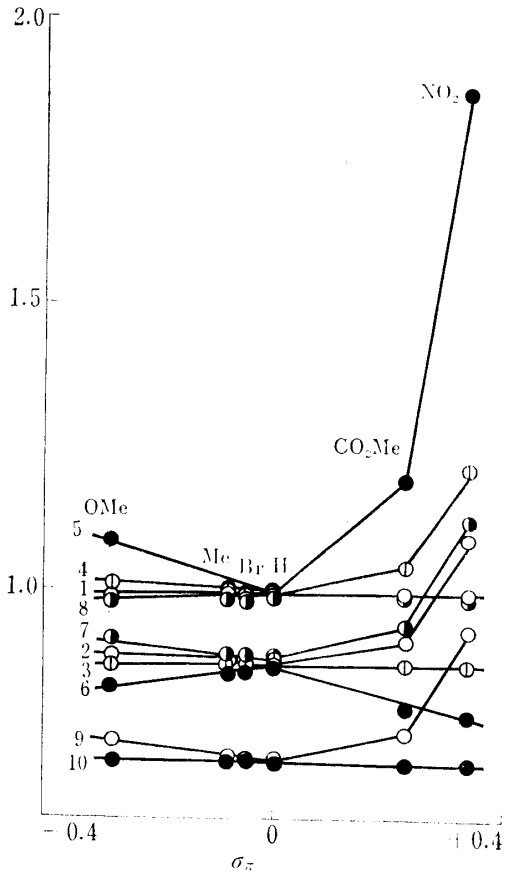
4b



4c



4d



4e

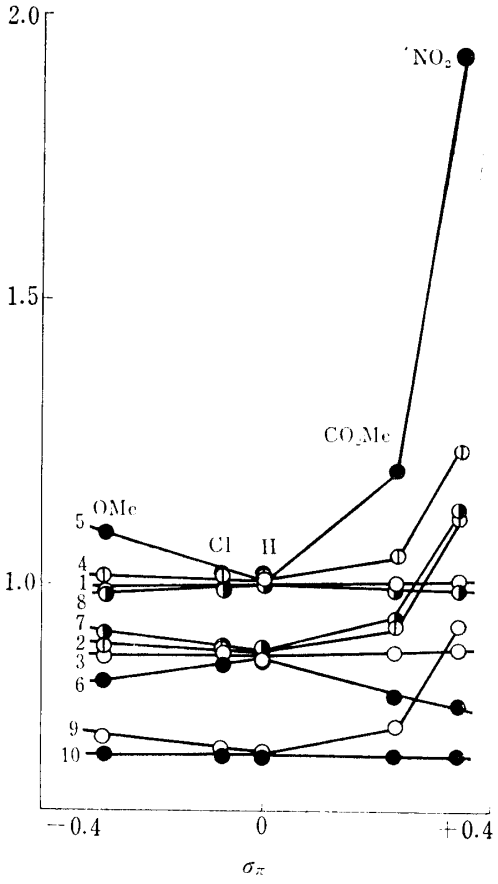


Fig. 4b. Free Radical Superdelocalizability $S_r^{(R)}$ for 3-Pyridine Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the $S_r^{(R)}$. The numbers on the diagonal lines show the positions of the carbon or nitrogen.

Fig. 4c. Free Radical Superdelocalizability $S_r^{(R)}$ for 4-Pyridine Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the $S_r^{(R)}$. The numbers on the diagonal lines show the positions of the carbon or nitrogen.

Fig. 4d. Free Radical Superdelocalizability $S_r^{(R)}$ for 6-Quinoline Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the $S_r^{(R)}$. The numbers on the diagonal lines show the positions of the carbon or nitrogen.

Fig. 4e. Free Radical Superdelocalizability $S_r^{(R)}$ for 6-Quinoxaline Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the $S_r^{(R)}$. The numbers on the diagonal lines show the positions of the carbon or nitrogen.

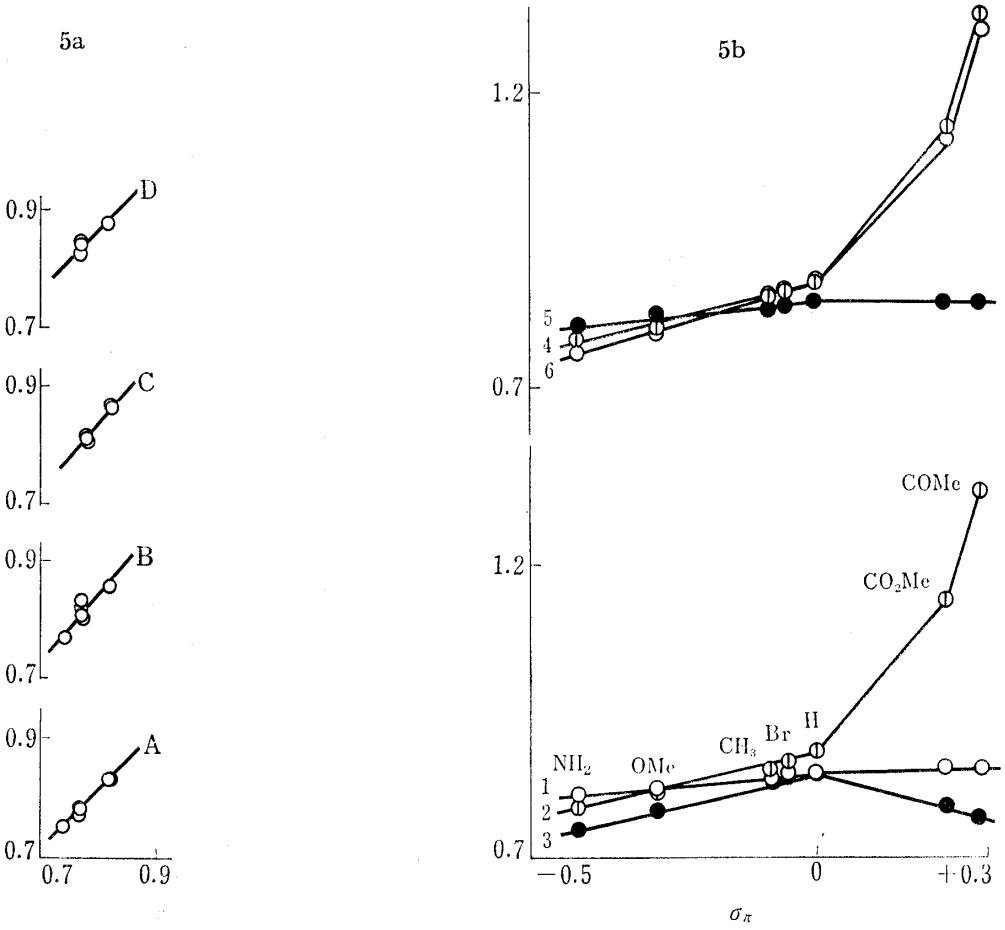


Fig. 5a. Nucleophilic Superdelocalizability $S_r^{(N)}$ for the Carbon Atoms with a Substituent Group

horizontal axis: $S_r^{(N)}$ for carbon atoms with a substituent group in monosubstituted benzene derivatives
vertical axis: $S_r^{(N)}$ for carbon atoms with a substituent group in
A: 3-pyridine B: 4-pyridine
C: 6-quinoline D: 6-quinoxaline derivatives

Fig. 5b. Nuclophilic Superdelocalizability $S_r^{(N)}$ for 3-Pyridine Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the $S_r^{(N)}$. The numbers on the diagonal lines show the positions of the carbon or nitrogen.

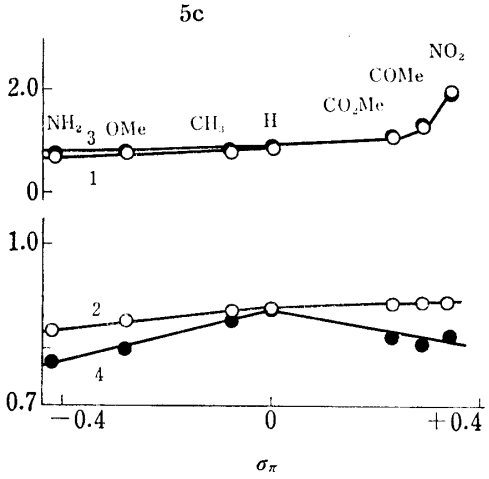
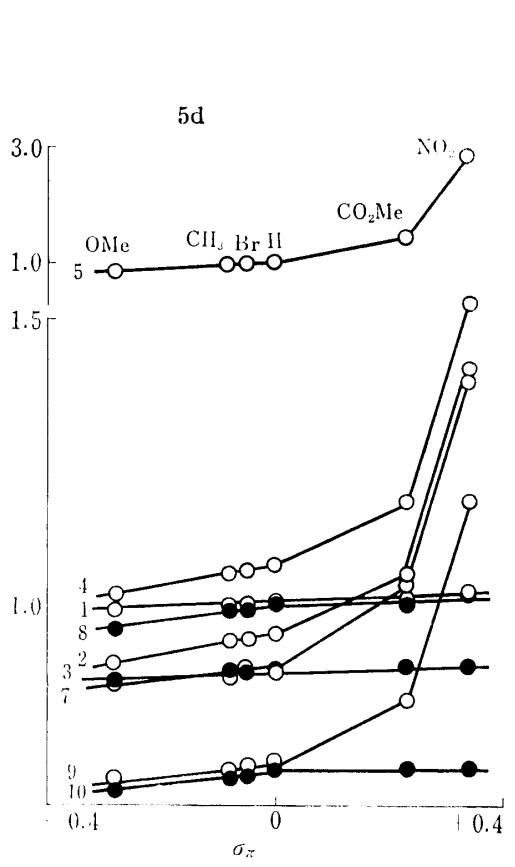


Fig. 5c. Nucleophilic Superdelocalizability $S_r^{(N)}$ for 4-Pyridine Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the $S_r^{(N)}$. The numbers on the diagonal lines show the positions of the carbon or nitrogen.



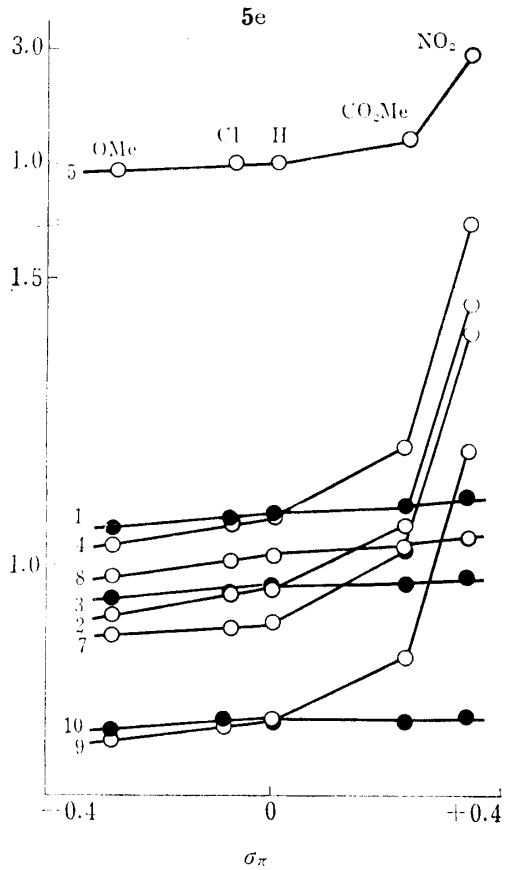


Fig. 5d. Nucleophilic Superdelocalizability $S_r^{(N)}$ for 6-Quinoline Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the $S_r^{(N)}$. The numvbers on the diagonal lines show the positions of the carbon or nitrogen.

Fig. 5e. Nucleophilic Superdelocalizability $S_r^{(N)}$ for 6-Quinoxaline Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the $S_r^{(N)}$. The numbers on the diagonal lines show the positions of the carbon or nitrogen.

3. Simple Sum Rule of Electronic Indices

From the data shown in the preceding section, we could estimate the excess value Δ of the above index with reference to benzene, and calculate those values for the substituted compounds from the following scheme.

$$\rho_{cal}=\rho_{ref.}+\sum\Delta\rho$$
$$F_r{}_{cal}=F_r{}_{ref.}+\sum\Delta F_r$$
$$S_r{}_{cal}=S_r{}_{cal}+\sum\Delta S_r$$

where $\Delta\rho=\rho-1.0000$

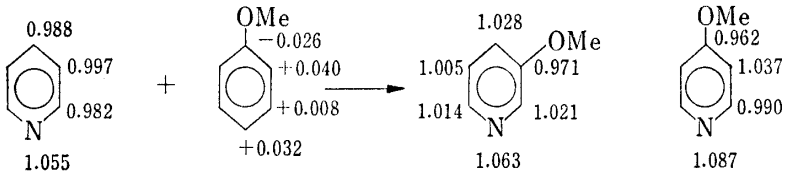
$\Delta F_r=F_r-0.43000$

$\Delta S_r=S_r-0.83000$

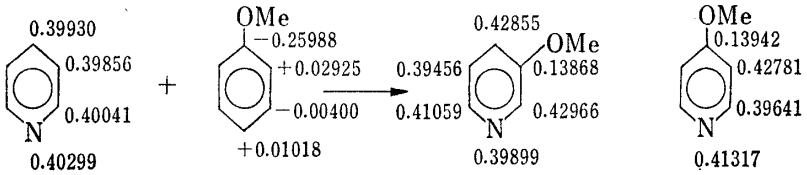
in monosubstituted benzene derivatives[1].

For example, the molecular electronic indices for 3- and 4-methoxy pyridine are presented below, and results agree with those obtained by molecular orbital treatment.[1,3]

a. π-Electron Charge Density

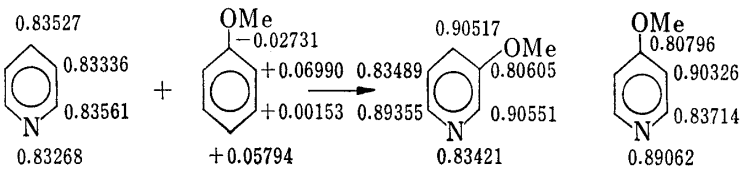


b. F_r

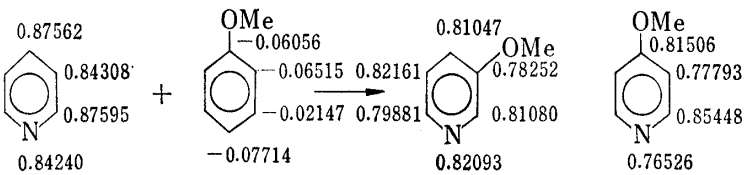


c. $S_r^{(E)}$

d. $S_r^{(R)}$



e. $S_r^{(N)}$



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