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Studies on the Proton Magnetic Resonance Spectra in Aromatic Systems. XVI.[1] On the Electronic Indices of Substituted Benzene and Naphthalene 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 monosubstituted-benzene, 1-substituted-3,4-dimethoxybenzene, 2-substituted-naphthalene and 2-substituted-6-methoxy-naphthalene derivatives, and the following results were obtained.

1. The ρ values are linearly related with the substituent constant σ_π.
2. F_r, $S_r^{(E)}$ $S_r^{(R)}$ and $S_r^{(N)}$ are linearly related with the substituent constant σ_π when the substituent groups are electron releasing, but not when they are electron attracting.
3. The electronic indices of polysubstituted benzene derivatives expressed by the simple sum of the excess value Δ with reference to benzene are comparable with calculated values.

Introduction

In the preceding papers of this series,[1,3] the correlations between the ring H-1 chemical shifts for substituted aromatic and heteroaromatic compounds and the π-electron charge densities (ρ values) were examined by a modification of the Hueckel molecular orbital calculation (*omega* technique) and the substituent constants σ_π.

In this work, in addition to the ρ values of carbon atoms with substituent groups and those without H-1 atoms, the following electronic indices (the free valence *Fr*, electrophilic $S_r^{(E)}$, free radical $S_r^{(R)}$ and nucleophilic $S_r^{(N)}$ superdelocalizabilities) were obtained by the methods described previously[1,3] for monosubstituted benzene and 1-substituted-3,4-dimethoxybenzene derivatives as well as 2-substituted- and 2-substituted-6-methoxy-naphthalene derivatives, respectively.

Result and Discussion

π-Electron Charge Density

From the H-1 resonance chemical shift, the ρ value on a carbon atom with an H-1 atom is readily estimated, whereas it is impossible to estimate that of a carbon atom without a hydrogen atom. However, for molecular orbital treatment, the presence of an H-1 atom is not essential (*cf.* Table Ia–d).

From the results in Table Ia–d, it is deduced that the ρ values of carbon atoms with a substituent group are linearly related to each other, while those of carbon atoms without an H-1 atom are linealy related with the substituent constant σ_π.[4]

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

The electronic indices F_r, $S_r^{(E)}$, $S_r^{(R)}$ and $S_r^{(N)}$ are summarized in Tables IIa–d, IIIa–d, IVa–d and Va–d, respectively.

1) Part XV: Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **17**, 1799 (1969).
2) Location: *Toneyama 6–5, Toyonaka, Osaka.*
3) Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **16**, 1090 (1969).
4) Y. Yukawa and Y. Tsuno, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **86**, 873 (1965).

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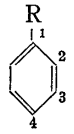
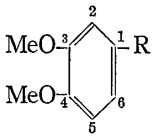
TABLE Ia. π-Electron Charge Density for the Carbon Atom with a Substituent Group in Monosubstituted Benzene Derivatives



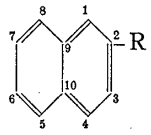
Substituent R	C-1
NH_2	0.971
OMe	0.974
Me	0.981
H	1.000
Br	0.997
Cl	0.993
CHO	0.999
CO_2Me	1.004
NO_2	0.966

TABLE Ib. π-Electron Charge Density of 1-Substituted-3,4-dimethoxybenzene Derivatives



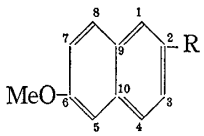
Substituent R	1	2	3	4	5	6	3—O	4—O
NH_2	1.003	1.103	1.019	1.046	1.058	1.091	1.905	1.907
OMe	1.008	1.088	1.020	1.052	1.056	1.076	1.906	1.911
Me	1.019	1.060	1.010	1.016	1.053	1.049	1.905	1.907
H	1.038	1.049	1.008	1.008	1.049	1.038	1.904	1.904
Br	1.034	1.057	1.009	1.013	1.051	1.046	1.905	1.906
Cl	1.032	1.058	1.009	1.014	1.051	1.046	1.905	1.906
CHO	1.031	1.019	0.997	0.966	1.036	0.997	1.902	1.880
CO_2Me	1.038	1.025	1.000	0.977	1.040	1.006	1.903	1.888
NO_2	0.994	1.022	0.994	0.956	1.032	0.995	1.902	1.872

TABLE Ic. π-Electron Charge Density of 2-Substituted Naphthalene Derivatives



Substituent R	1	2	3	4	5	6	7	8	9	10
NH_2	1.078	0.970	1.026	1.008	1.004	1.016	1.006	1.015	1.007	1.022
OMe	1.055	0.973	1.025	1.006	1.003	1.011	1.004	1.010	1.005	1.015
Me	1.017	0.980	1.008	1.002	1.001	1.003	1.001	1.003	1.001	1.004
Cl	1.015	0.992	1.007	1.001	1.001	1.003	1.001	1.003	1.001	1.004
Br	1.012	0.997	1.005	1.001	1.001	1.002	1.001	1.002	1.001	1.003
CO_2Me	0.961	1.005	0.985	0.995	0.997	0.991	0.996	0.992	0.996	0.989
COMe	0.947	1.000	0.980	0.993	0.996	0.987	0.995	0.989	0.994	0.985

TABLE Id. π-Electron Charge Density of 2-Substituted 6-methoxy Naphthalene Derivatives



Substituent R	1	2	3	4	5	6	7	8	9	10
NH_2	1.080	0.978	1.037	1.017	1.058	0.987	1.030	1.019	1.021	1.026
OMe	1.057	0.982	1.028	1.015	1.057	0.982	1.028	1.015	1.019	1.019
Et	1.020	0.991	1.013	1.011	1.055	0.975	1.025	1.008	1.016	1.009
H	1.003	1.011	1.004	1.010	1.055	0.973	1.024	1.006	1.015	1.005
Cl	1.015	1.007	1.009	1.011	1.055	0.975	1.025	1.008	1.016	1.008
Br	1.014	1.007	1.009	1.011	1.055	0.975	1.025	1.009	1.016	1.008
CO_2Me	0.962	1.015	0.989	1.005	1.051	0.962	1.020	0.997	1.011	0.993
COMe	0.950	1.010	0.986	1.003	1.049	0.985	1.018	0.993	1.009	0.989

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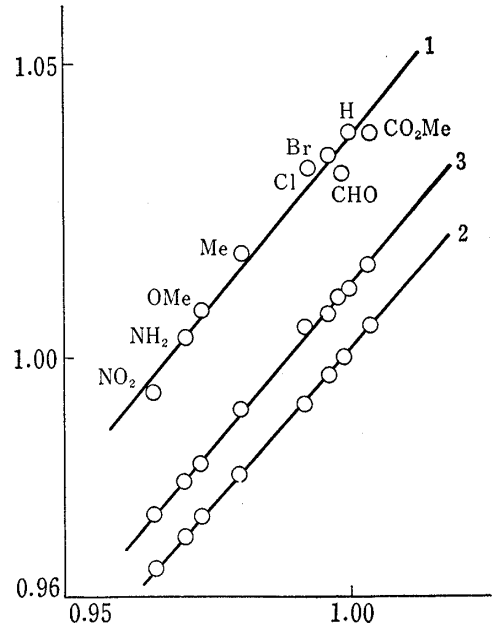


Fig. 1a. π-Electron. Charge Densities for Carbon Atoms with a Substituent Group

horizontal axis: π-electron charge density distribution for carbon atoms with a substitutent group in monosubstituted benzene derivatives
vertical axis: π-electron charge density distribution for carbon atoms with a substituent group in
1: 1-substituted-3,4-dimethoxybenzene derivatives
2: 2-substituted-naphthalene derivatives
3: 2-substituted-6-methoxy-naphthalene derivatives

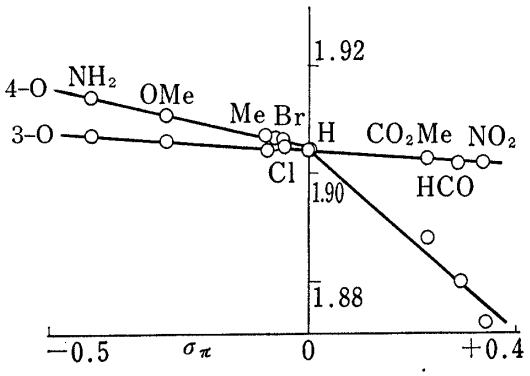


Fig. 1b. π-Electron Charge Densities for 1-Substituted 3,4-dimethoxybenzene Derivatives *vs.* Substituent Constant σ_π

The vertical axis swhows the π-electron charge density distribution.
The numbers on the diagonal lines shows the position of the carbon atom.

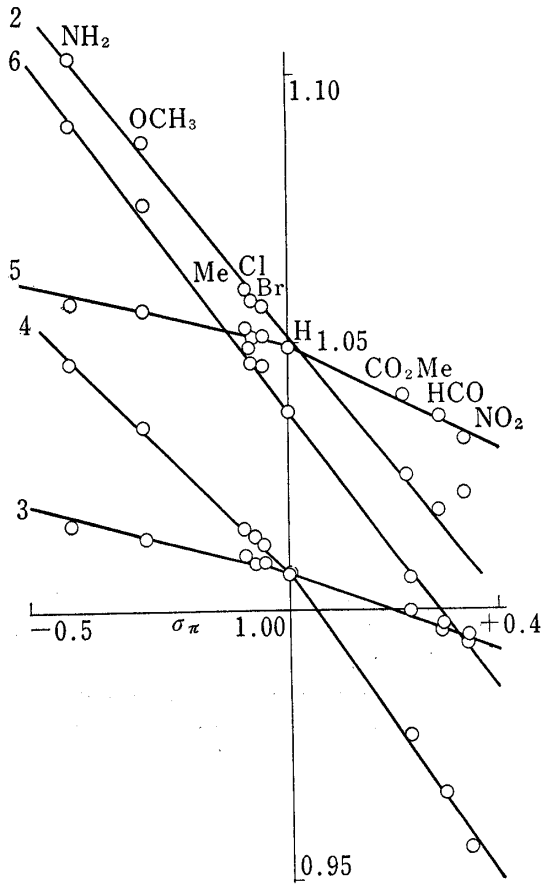
These tables show that the electronic indices of carbon atoms with a substituent group are linealy related with each other, as shown in the Fig. 2a, 3a, 4a and 5a, respectively, whereas those of carbons without substituent groups are linearly related with the substituent constant σ_π in cases where the substituent groups are electron releasing. However, when the substituent groups are electron attracting, these relations are disturbed (*cf.* Fig.2 b-e, Fig. 3b-e, Fig. 4b-e and Fig. 5b-e)

Simple Sum Rule for Fr, $S_r^{(E)}$, $S_r^{(R)}$ and $S_r^{(N)}$

From the correlations shown in Fig. 2b, 3b, 4b and 5b, it is concluded that the electronic indices for benzene are:

$$Fr = 0.40000$$
$$S_r^{(E)} = S_r^{(R)} = S_r^{(N)} = 0.83000$$

Next, the excess indices Δ with reference to benzene due to the substituent groups were estimated. For example, the following Δ values were obtained for anisole (*cf.* Table VI).



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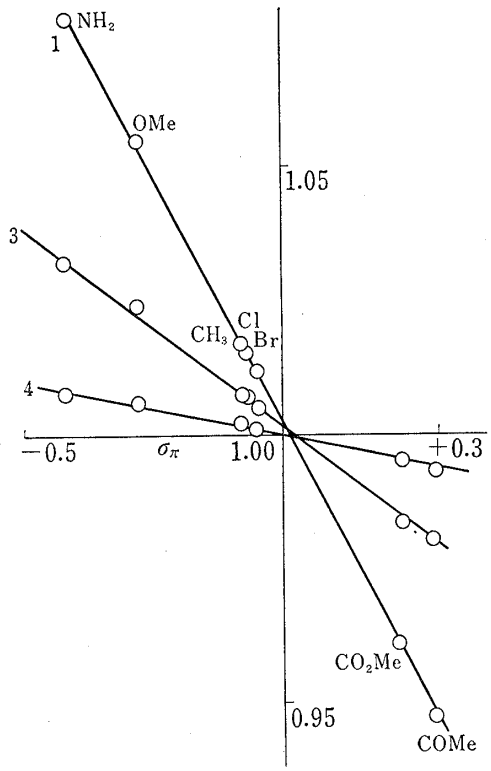


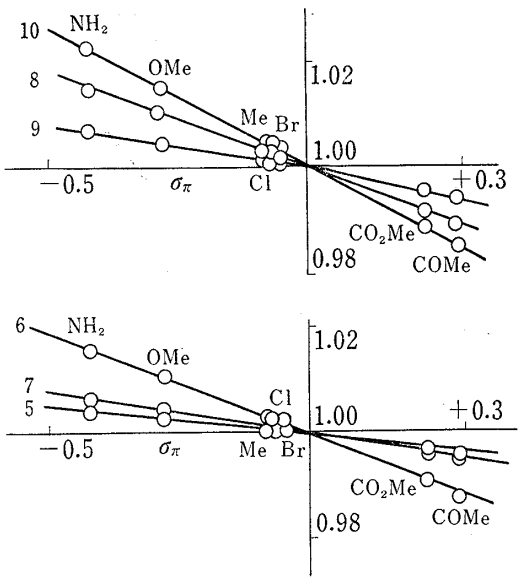
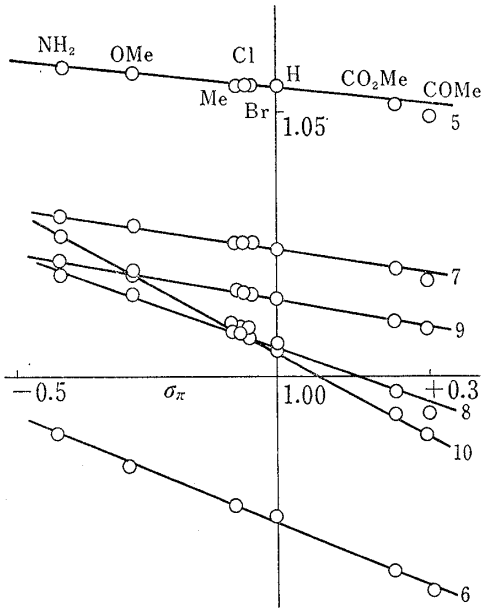


Fig. 1c. π-Electron Charge Densities for 2-Substituted Naphthalene Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the π-electron charge density distribution. The numbers on the diagonal lines show the position of the carbon atom.



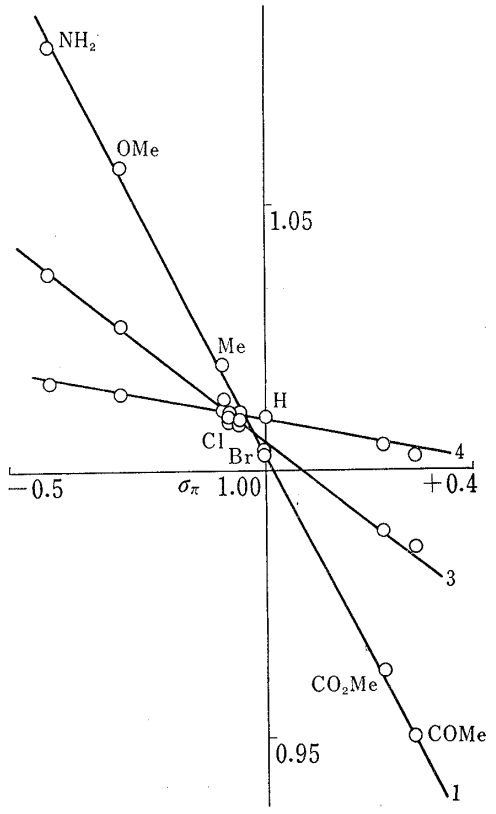


Fig. 1d. π-Electron Charge Densities for 2-Substituted-6-methoxy naphthalene Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the π-electron charge density distribution. The numbers on the diagonal lines show the position of the carbon atom.

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TABLE IIa. Free Valence *Fr* for Menosubstitued Benzene Derivatives

Substituent R	1 C–R	2 *ortho*	3 *meta*	4 *para*
NH_2	0.10835	0.44640	0.39449	0.41590
OMe	0.14012	0.42925	0.39600	0.41018
Me	0.26548	0.40525	0.39815	0.40025
Cl	0.25353	0.40573	0.39808	0.40114
Br	0.26029	0.40471	0.39819	0.40121
CO_2Me	0.10974	0.44463	0.39471	0.41641
CHO	0.09544	0.45311	0.39411	0.42162
NO_2	0.13865	0.46661	0.39382	0.43364

TABLE IIb. Free Valence for 1-Substituted-3,4-dimethoxybenzene Derivatives

Substituent R	1	2	3	4	5	6	3–O	4–O
NH_2	0.11235	0.47421	0.17108	0.20319	0.42410	0.45965	1.41306	1.44234
OMe	0.15466	0.45679	0.17238	0.19248	0.42538	0.44140	1.41336	1.43375
Br	0.27793	0.43279	0.17424	0.17830	0.42671	0.41478	1.41425	1.41829
Cl	0.27179	0.43339	0.17420	0.17871	0.42667	0.41539	1.41424	1.41860
H	0.40843	0.42705	0.17468	0.17468	0.42705	0.40843	1.41445	1.41445
CO_2Me	0.11500	0.47364	0.16966	0.17663	0.42051	0.44920	1.41531	1.37802
CHO	0.09450	0.48438	0.16384	0.17837	0.41930	0.45924	1.41452	1.36278
NO_2	0.15125	0.49103	0.16758	0.18364	0.42045	0.46957	1.40961	1.33805

TABLE IIc. Free Valence for 2-Substituted Naphthalene Derivatives

Substituent R	1	2	3	4	5	6	7	8	9	10
NH_2	0.50882	0.10287	0.44406	0.44608	0.45083	0.40896	0.40428	0.45760	0.10114	0.11475
OMe	0.48786	0.14389	0.43047	0.44851	0.45162	0.40679	0.40430	0.45541	0.10224	0.11043
Me	0.45987	0.27082	0.41032	0.45200	0.45262	0.40460	0.40432	0.45311	0.10396	0.10526
Cl	0.46070	0.25807	0.41042	0.45181	0.45254	0.40481	0.40432	0.45332	0.10390	0.10570
Br	0.45977	0.26416	0.40932	0.45193	0.45254	0.40488	0.40432	0.45337	0.10400	0.10570
COMe	0.52049	0.09368	0.45162	0.44485	0.45044	0.41019	0.40428	0.45884	0.10057	0.11703

TABLE IId. Free Valence for 2-Substituted-6-methoxy-naphthalene Derivatives

Substituent R	1	2	3	4	5	6	7	8	9	10	6–O
OMe	0.48746	0.14840	0.43050	0.45145	0.48746	0.14840	0.43050	0.45145	0.10847	0.10847	1.39940
Me	0.45895	0.27443	0.41029	0.45477	0.48800	0.14488	0.43047	0.44896	0.11007	0.10317	1.39401
Cl	0.45949	0.26323	0.40973	0.45453	0.48773	0.14498	0.43048	0.44925	0.11002	0.10374	1.39342
Br	0.45870	0.27001	0.40930	0.45462	0.48776	0.14485	0.43047	0.44914	0.11005	0.10355	1.39326
H	0.45162	0.40679	0.40430	0.45541	0.48786	0.14389	0.43047	0.44851	0.11043	0.10224	1.39165
CO_2Me	0.50294	0.11495	0.44318	0.44840	0.48482	0.14387	0.43048	0.45189	0.10672	0.11084	1.37943
COMe	0.51702	0.09453	0.45141	0.44666	0.48396	0.14426	0.43051	0.45356	0.10599	0.11406	1.37394

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TABLE IIIa. Electrophilic Superdelocalizability $S_r^{(E)}$ for Mono substituted Benzene Derivatives

Substituent R	1 C–R	2 *ortho*	3 *meta*	4 *para*
NH_2	0.81179	1.13271	0.86604	1.11575
OMe	0.81594	1.03495	0.85453	1.02302
Me	0.83187	0.87248	0.84030	0.87054
Cl	0.82922	0.87835	0.83931	0.87544
Br	0.82834	0.88153	0.83744	0.87864
CO_2Me	0.74685	0.81687	0.81549	0.79612
CHO	0.73063	0.79710	0.81014	0.77199
NO_2	0.72232	0.79058	0.80620	0.76176

TABLE IIIb. Electrophilic Superdelocalizability $S_r^{(E)}$ for 1-Substituted-3,4-dimethoxybenzene Derivatives

Substituent R	1	2	3	4	5	6	3–O	4–O
NH_2	1.16280	1.44182	1.17482	1.63171	1.16071	1.62496	1.98633	2.22658
OMe	1.12177	1.26578	1.13229	1.36870	1.12434	1.36868	1.96380	2.09287
Br	1.08139	1.11162	1.07767	1.12936	1.07949	1.13705	1.93351	1.96131
Cl	1.08250	1.11998	1.07924	1.14125	1.08090	1.14876	1.93435	1.96721
H	1.07341	1.06817	1.06418	1.06418	1.06817	1.07341	1.92598	1.92598
CO_2Me	0.93297	1.06461	1.00813	0.95957	1.01990	1.01295	1.89623	1.82375
CHO	0.89336	1.05814	0.99135	0.91348	1.00443	0.98276	1.88648	1.78077
NO_2	0.87220	1.05206	0.97202	0.87867	0.98933	0.95721	1.87335	1.74107

TABLE IIIc. Electrophilic Superdelocalizability $S_r^{(E)}$ for 2-Substituted–Naphthalene Derivatives

Substituent R	1	2	3	4	5	6	7	8	9	10
NH_2	1.59831	0.84662	1.04821	1.03560	1.01428	1.01725	0.89189	1.14122	0.71402	0.85452
OMe	1.33575	0.85580	0.97399	1.02305	1.00806	0.95470	0.88585	1.07779	0.71113	0.78884
Me	1.06084	0.87186	0.89258	1.00400	0.99861	0.88951	0.87675	1.01144	0.70598	0.71992
Cl	1.07057	0.86836	0.89610	1.00155	0.99784	0.89134	0.87626	1.01311	0.70531	0.72238
Br	1.07477	0.86805	0.89719	0.99974	0.99712	0.89225	0.87572	1.01390	0.70483	0.72350
COMe	0.89919	0.75914	0.87419	0.96314	0.97971	0.83044	0.86626	0.94797	0.69231	0.67746

TABLE IIId. Electrophilic Superdelocalizability $S_r^{(E)}$ for 2-Substituted-6-methoxy-naphthalene Derivatives

Substituent R	1	2	3	4	5	6	7	8	9	10	6–O
OMe	1.37669	0.95408	0.98809	1.11873	1.37669	0.95408	0.98809	1.11973	0.80204	0.80204	1.85538
Me	1.07867	0.95761	0.90507	1.09035	1.34653	0.87598	0.97811	1.04254	0.79307	0.72862	1.81217
Cl	1.10811	0.95271	0.91412	1.08615	1.34523	0.88218	0.97742	1.04866	0.79207	0.73605	1.81429
Br	1.09214	0.95301	0.90970	1.08550	1.34420	0.87809	0.97709	1.04466	0.79177	0.73206	1.81220
H	1.00806	0.95470	0.88585	1.07779	1.33575	0.85580	0.97399	1.02305	0.78884	0.71113	1.79968
CO_2Me	0.94229	0.84725	0.89356	1.04022	1.29917	0.81488	0.96511	0.98522	0.77319	0.69363	1.76273
COMe	0.90187	0.81909	0.89112	1.03067	1.28507	0.79387	0.96353	0.96560	0.76823	0.68346	1.74447

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Table IVa. Free Radical Superdelocalizability $S_r^{(R)}$ for Mono-substituted Benzene Derivatives

Substituent R	1 C–R	2 *ortho*	3 *meta*	4 *para*
NH_2	0.77619	0.93300	0.83129	0.91596
OMe	0.79269	0.89990	0.83153	0.88794
Me	0.82460	0.84036	0.83304	0.83842
Cl	0.82271	0.84653	0.83280	0.84362
Br	0.82366	0.84989	0.83276	0.84701
CO_2Me	0.76082	0.95511	0.82938	0.93438
CHO	0.74937	1.01568	0.82862	0.99062
NO_2	0.74486	1.35083	0.82785	1.32219

Table IVb. Free Radical Superdelocalizability $S_r^{(R)}$ for 1-Substituted-3,4-dimethoxybenzene Derivatives

Substituent R	1	2	3	4	5	6	3-O	4-O
NH_2	0.91841	1.04808	0.93761	1.13715	0.93762	1.14320	1.02889	1.14401
OMe	0.90843	0.97107	0.91945	1.01674	0.92273	1.02500	1.01821	1.07904
Br	0.90436	0.91760	0.89773	0.91911	0.90623	0.93100	1.00415	1.01724
Cl	0.90444	0.92135	0.89839	0.92460	0.90680	0.93646	1.00454	1.02011
H	0.90429	0.90212	0.89244	0.89244	0.90212	0.90429	1.00066	1.00066
CO_2Me	0.79554	1.00981	0.86759	0.93572	0.88246	0.98916	0.98615	0.97644
CHO	0.76589	1.07099	0.86026	0.97753	0.87679	1.04570	0.98134	0.97652
NO_2	0.76374	1.22530	0.85877	1.14991	0.88140	1.22461	0.97682	1.03278

Table IVc. Free Radical Superdelocalizability $S_r^{(R)}$ for 2-Substituted Naphthalene Derivatives

Substituent R	1	2	3	4	5	6	7	8	9	10
NH_2	1.20607	0.80936	0.94589	0.99009	0.99177	0.91582	0.87360	1.03751	0.69936	0.75491
OMe	1.09909	0.83019	0.91171	0.99121	0.99272	0.89322	0.87327	1.01473	0.70092	0.72860
Me	1.00472	0.86399	0.87753	0.99388	0.99418	0.87475	0.87302	0.99616	0.70283	0.70554
Cl	1.01397	0.86176	0.88113	0.99327	0.99390	0.87659	0.87301	0.99795	0.70266	0.70795
Br	1.01954	0.86263	0.88270	0.99307	0.99378	0.87793	0.87300	0.99925	0.70265	0.70946
COMe	1.32431	0.77550	0.98739	0.98192	0.98817	0.94221	0.87306	1.06287	0.69828	0.78604

Table IVd. Free Radical Superdelocalizability $S_r^{(R)}$ for 2-Substituted-6-methoxy-naphthalene Derivatives

Substituent R	1	2	3	4	5	6	7	8	9	10	6-O
OMe	1.11540	0.86348	0.91224	1.02084	1.11540	0.86348	0.91224	1.02084	0.73011	0.73011	0.97098
Me	1.00663	0.88768	0.87756	1.01663	1.10336	0.83521	0.91180	0.99515	0.72927	0.70408	0.95181
Cl	1.02781	0.88481	0.88485	1.01540	1.10278	0.83952	0.91189	0.99953	0.72903	0.70955	0.95319
Br	1.02098	0.88568	0.88275	1.01538	1.10237	0.83780	0.91186	0.99792	0.72899	0.70783	0.95222
H	0.99272	0.89322	0.87327	1.01473	1.09909	0.83019	0.91177	0.99121	0.72860	0.70092	0.94678
CO_2Me	1.16070	0.80314	0.94332	0.99758	1.08021	0.85242	0.91278	1.01819	0.72155	0.74286	0.94163
CHO	1.28164	0.77774	0.98347	0.99053	1.07238	0.87424	0.91369	1.04230	0.71893	0.77352	0.94397

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Table Va. Nucleophilic Superdelocalizability $S_r^{(N)}$ for Mono-substituted Benzene Derivatives

Substituent R	1 C–R	2 *ortho*	3 *meta*	4 *para*
NH_2	0.74064	0.73330	0.79654	0.71617
OMe	0.76944	0.76485	0.80853	0.75286
Me	0.81733	0.80824	0.82577	0.80630
Cl	0.81620	0.81471	0.82630	0.81180
Br	0.81898	0.81826	0.82809	0.81537
CO_2Me	0.77480	1.09335	0.84327	1.07264
CHO	0.76810	1.23426	0.84709	1.20926
NO_2	0.76741	1.91108	0.84950	1.88261

Table Vb. Nucleophilic Superdelocalzability $S_r^{(N)}$ for 1-Substituted-3,4-dimethoxybenzene Derivatives

Substituent R	1	2	3	4	5	6	3-O	4-O
NH_2	0.67402	0.65433	0.70041	0.64258	0.71452	0.66143	0.07145	0.06144
OMe	0.69509	0.67636	0.70661	0.66478	0.72112	0.68132	0.07261	0.06521
Br	0.72733	0.72359	0.71779	0.70886	0.73297	0.72459	0.07478	0.07317
Cl	0.72638	0.72271	0.71754	0.70794	0.73270	0.72417	0.07473	0.07301
H	0.73643	0.73608	0.72070	0.72070	0.73608	0.73643	0.07534	0.07534
CO_2Me	0.65812	0.95501	0.72704	0.91186	0.74502	0.96537	0.07607	0.12912
CHO	0.63843	1.08384	0.72918	1.04157	0.74916	1.10863	0.07619	0.17226
NO_2	0.65527	1.39855	0.74551	1.42116	0.77347	1.49200	0.08029	0.32450

Table Vc. Nucleophilic Superdelocalizability $S_r^{(N)}$ for 2-Substituted Naphthalene Derivatives

Substituent R	1	2	3	4	5	6	7	8	9	10
NH_2	0.81382	0.77210	0.84356	0.94458	0.96926	0.81439	0.85532	0.93381	0.68470	0.65533
OMe	0.86242	0.80457	0.84954	0.95937	0.97738	0.83173	0.86069	0.95167	0.69070	0.66837
Me	0.94859	0.85613	0.86248	0.98375	0.98974	0.85998	0.86929	0.98089	0.69968	0.69117
Cl	0.95737	0.85516	0.86616	0.98498	0.98996	0.86183	0.86976	0.98279	0.70000	0.69352
Br	0.96431	0.85722	0.86821	0.98640	0.99044	0.86362	0.87028	0.98460	0.70047	0.69542
COMe	1.74943	0.79186	1.10060	1.00070	0.99662	1.05398	0.87987	1.17778	0.70425	0.89463

Table Vd. Nucleophilic Superdelocalizability $S_r^{(N)}$ for 2-Substituted-6-methoxynaphthalene Derivatives

Substituent R	1	2	3	4	5	6	7	8	9	10	6-O
OMe	0.85411	0.77288	0.83640	0.92294	0.85411	0.77288	0.83640	0.92294	0.65818	0.65818	0.08675
Me	0.93459	0.81776	0.85006	0.94292	0.86020	0.79444	0.84549	0.94777	0.66548	0.67953	0.09145
Cl	0.94751	0.81692	0.85559	0.94464	0.86033	0.79685	0.84636	0.95040	0.66600	0.68304	0.09209
Br	0.94981	0.81835	0.85579	0.94526	0.86055	0.79751	0.84664	0.95118	0.66621	0.68361	0.09223
H	0.97738	0.83173	0.86069	0.95167	0.86242	0.80457	0.84954	0.95937	0.66837	0.69070	0.09389
CO_2Me	1.37911	0.75903	0.99308	0.95494	0.86126	0.88997	0.86045	1.05117	0.66991	0.79210	0.12054
CHO	1.66142	0.73639	1.07582	0.95040	0.85970	0.95461	0.86385	1.11899	0.66962	0.86359	0.14347

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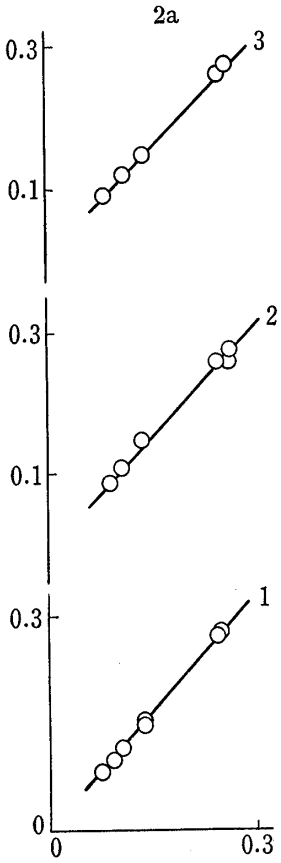
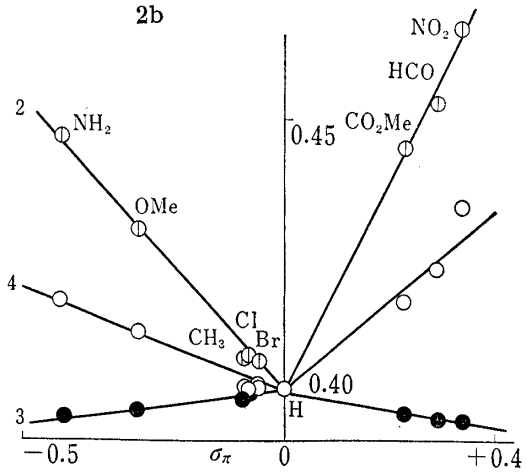


Fig. 2a. Free Valence for Carbon Atoms with a Substituent Group

horizontal axis: *Fr* for carbon atoms with a substituent group in mono-substituted benzene derivatives
vertical axis: *Fr* for carbon atoms with a substituent group in
1: 1-substituted-3,4-dimethoxybenzene derivatives
2: 2-substituted-naphthalene derivatives
3: 2-substituted-6-methoxy-naphthalene derivatives

Fig. 2b. Free Valence for Monosubstituted benzene Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the *Fr*.
The numbers on the diagonal lines show the position of the carbon atom.



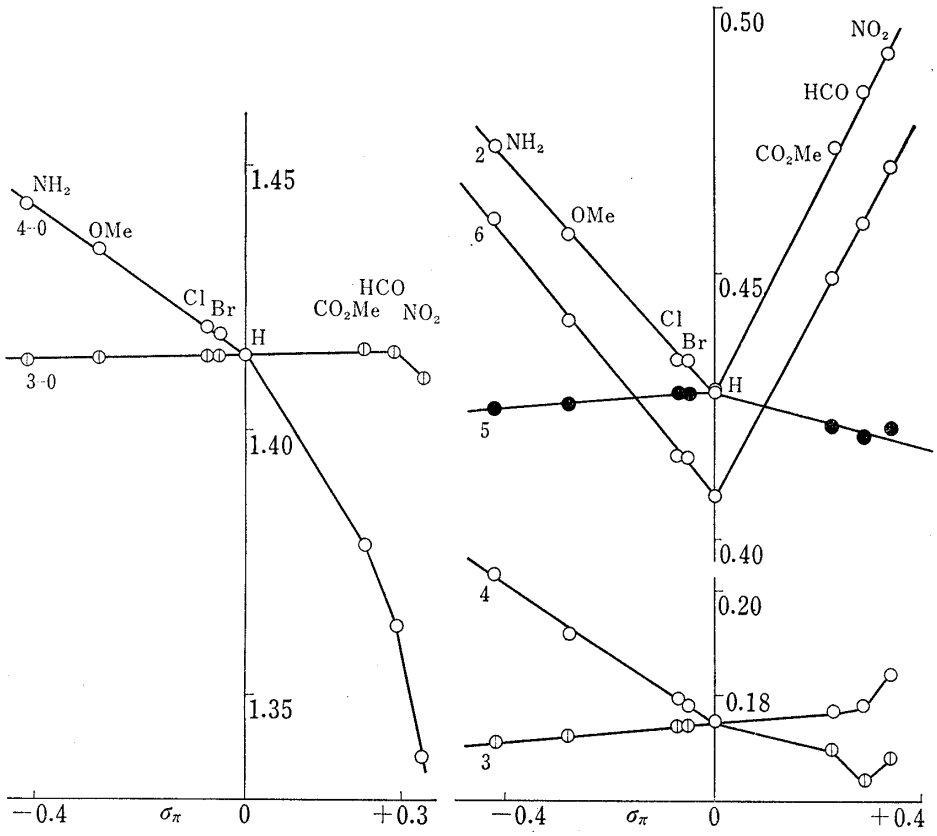


Fig. 2c. Free Valence for 1-Substituted-3,4-dimethoxybenzene Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the *Fr*. The numbers on the diagonal lines show the position of the carbon atom.

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The simple sum rule of Δ values was applicable for polysubstituted benzene derivatives. For example, the electronic indices of 1,3,4-trimethoxy benzene summarized in Table VII are comparable with those calculated by the molecular orbital treatment.

From the above results, we deduced the following equation:

$$F_r = 0.40000 + \sum \Delta F_r$$
$$S_r^{(E)} = S_r^{(R)} = S_r^{(N)} = 0.83000 + \sum \Delta$$
where $\Delta = \Delta S_r^{(E)}, \Delta S_r^{(R)}, \Delta S_r^{(N)}$

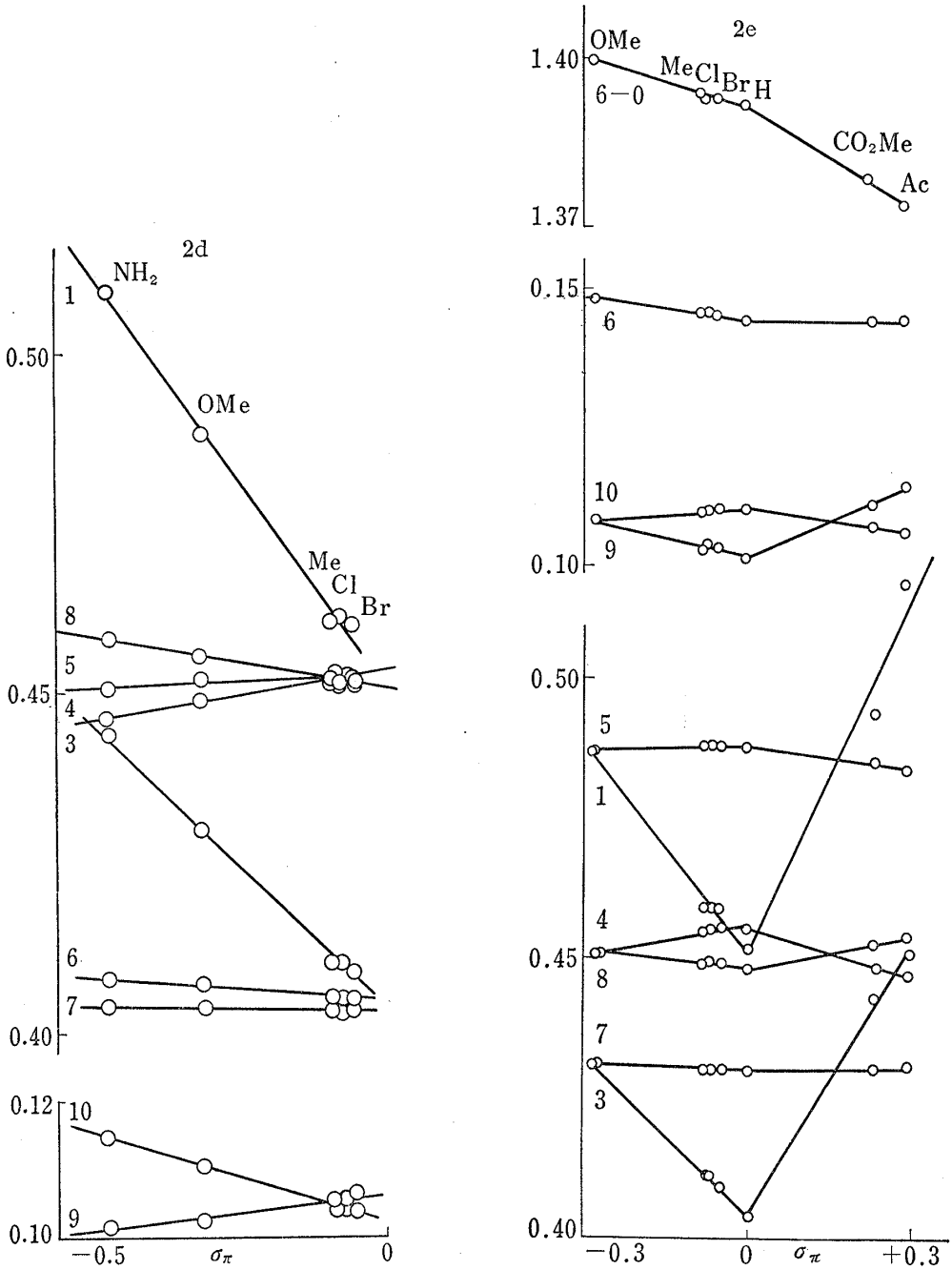

Fig. 2d. Free Valence for 2-Substituted-naphthaleen Derivatives *vs.* Substituent Constant σ_π

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

Fig. 2e. Free Valence for 2-Substituted-6-methoxy-naphthalene Derivatives *vs.* Substituent Constant σ_π

The vertical axis shows the Fr. The numbers on the diagonal lines show the position of the carbon atom.

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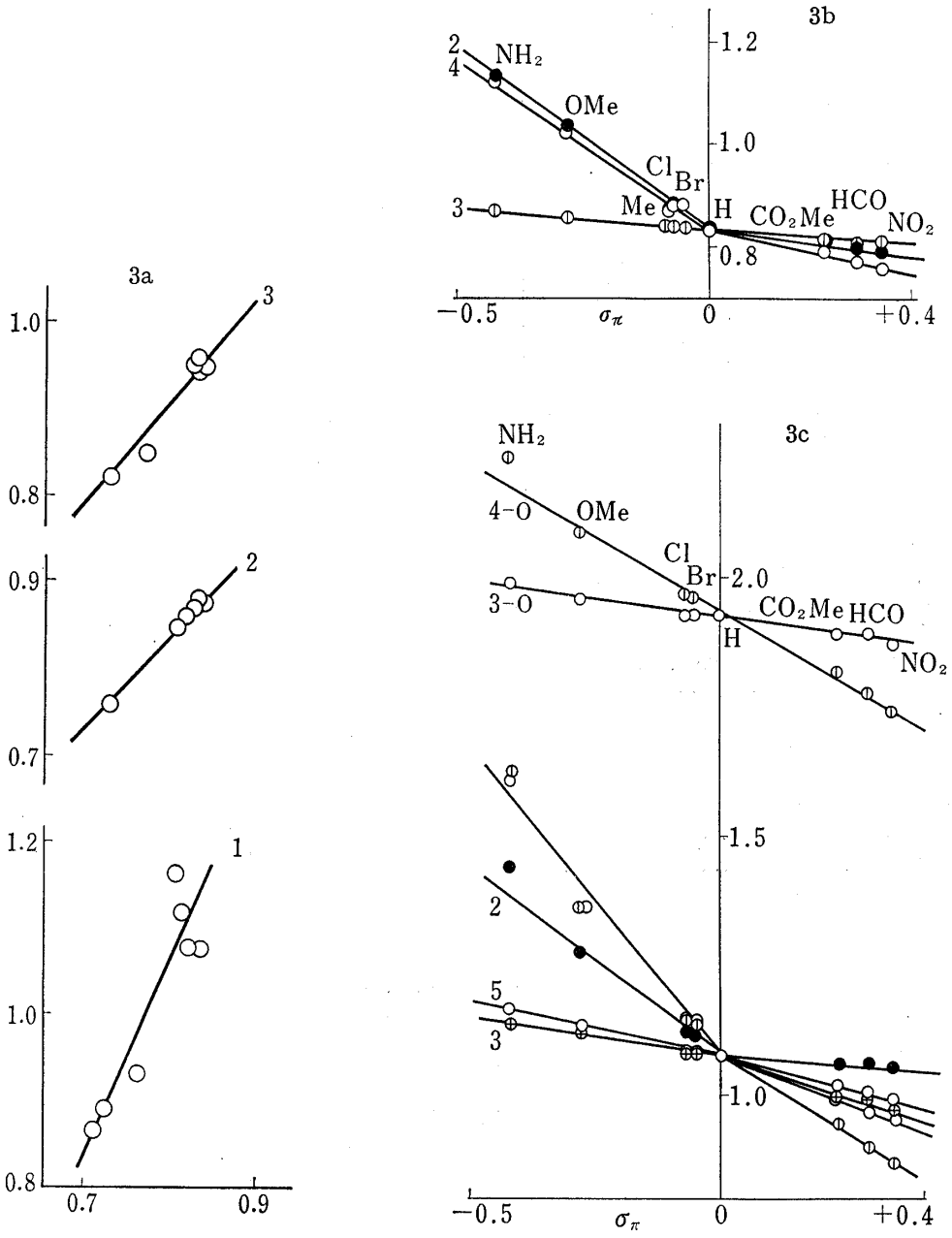

Fig. 3a. Electrophilic Superdelocalizability $S_r^{(E)}$ for Carbon Atoms with a Substituent Group

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 substituent group in
1: 1-substituted-3,4-dimethoxybenzene derivatives
2: 2-substituted-naphthalene derivatives
3: 2-substituted-6-methoxy-naphthalene derivatives

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

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

Fig. 3c. Electrophilic Superdelocalizability $S_r^{(E)}$ for 1-Substituted-3,4-dimethoxybenzene Derivatives *vs.* Substituent Constant σ_π

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

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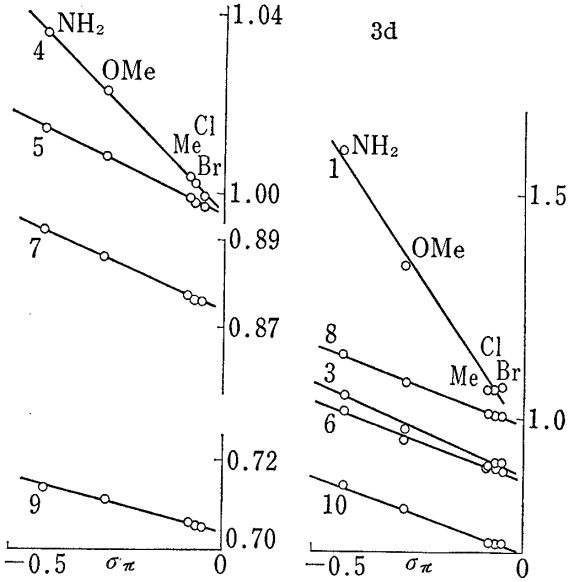


Fig. 3d. Electrophilic Superdelocalizability $S_r^{(E)}$ for 2-Substituted-naphthalene Derivatives *vs.* Substituent Constant σ_π

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

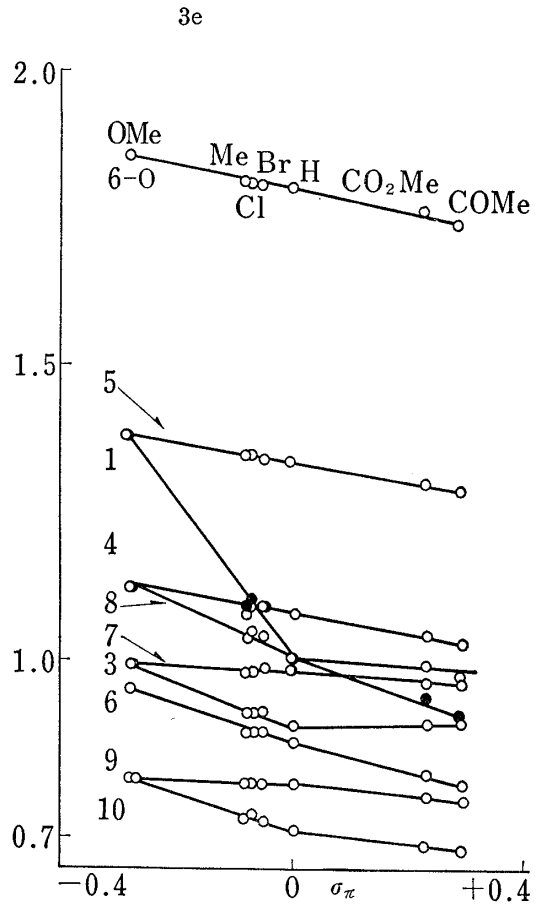


Fig. 3e. Electrophilic Superdelocalizability $S_r^{(E)}$ for 2-Substituted-2-methoxy-naphthalene Derivatives *vs.* Substituent Constant σ_π

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

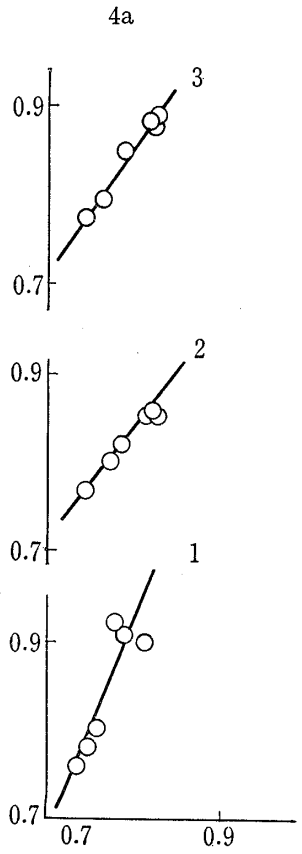


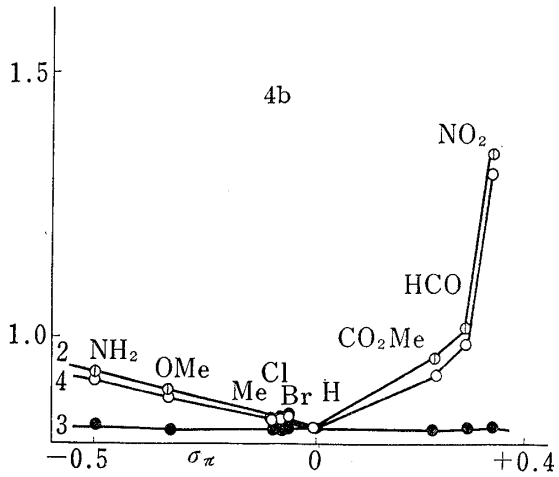
Fig. 4a. Free Radical Superdelocalizability $S_r^{(R)}$ for Carbon Atoms with Substituent Group

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

1: 1-substituted-3,4-dimethoxybenzene derivatives
2: 2-substituted-naphthalene derivatives
3: 2-substituted-6-methoxy-naphthalene derivatives

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

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



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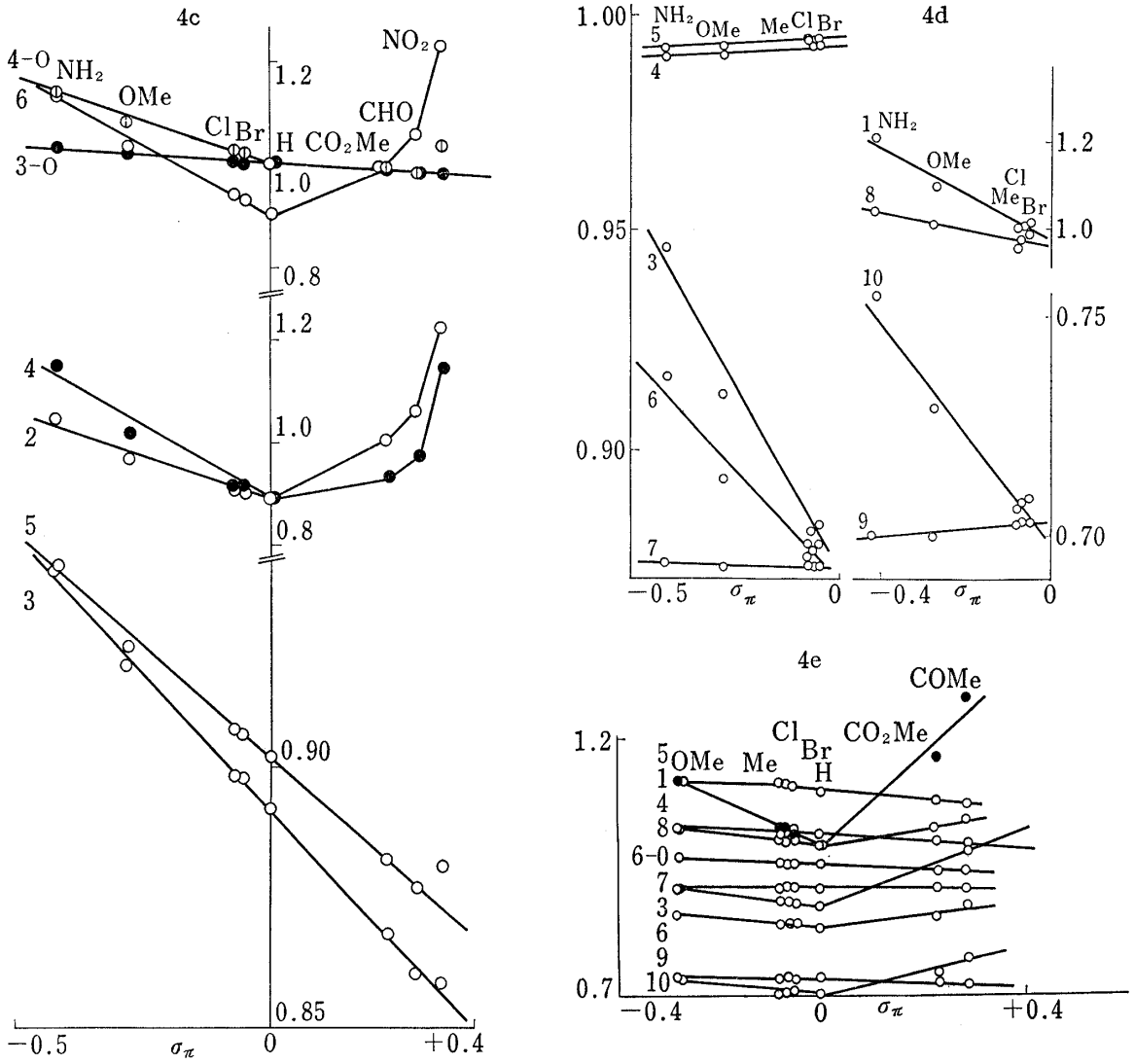

Fig. 4c. Free Radical Superdelocalizability $S_r^{(R)}$ for 1-Substituted-3,4-dimethoxybenzene Derivatives *vs.* Substituent Constant σ_π

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

Fig. 4d. Free Radical Superdelocalizability $S_r^{(R)}$ for 2-Substituted-naphthalene Derivatives *vs.* Substituent Constant σ_π

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

Fig. 4e. Free Radical Superdelocalizability $S_r^{(R)}$ for 2-Substituted-6-methoxy-naphthalene Derivatives *vs.* Substituent Constant σ_π

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

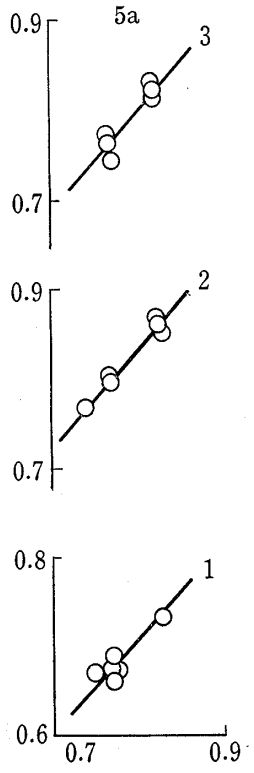

Fig. 5a. Nucleophilic Superdelocalizability $S_r^{(N)}$ for Carbon Atoms witha Substituent Group

horizontal axixs: $S_r^{(N)}$ for carbon atoms with a substituent group in monosubstituted benzene derivatives
vertical axis: $S_r^{(N)}$, for carbon atoms with a substituent group in
1: 1-substituted-3,4-dimet oxybenzene derivatives
2: 2-substituted-naphthalene derivatives
3: 2-substituted-6-methoxy-naphthalene derivatives

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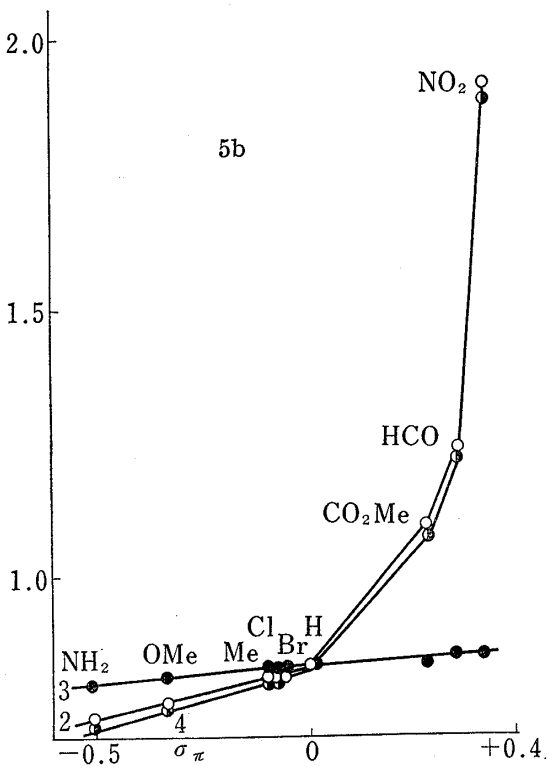


Fig. 5b. Nucleophilic Superdelocalizability $S_r^{(N)}$ for Monosubstituted benzene Derivatives *vs.* Substituent Constant σ_π

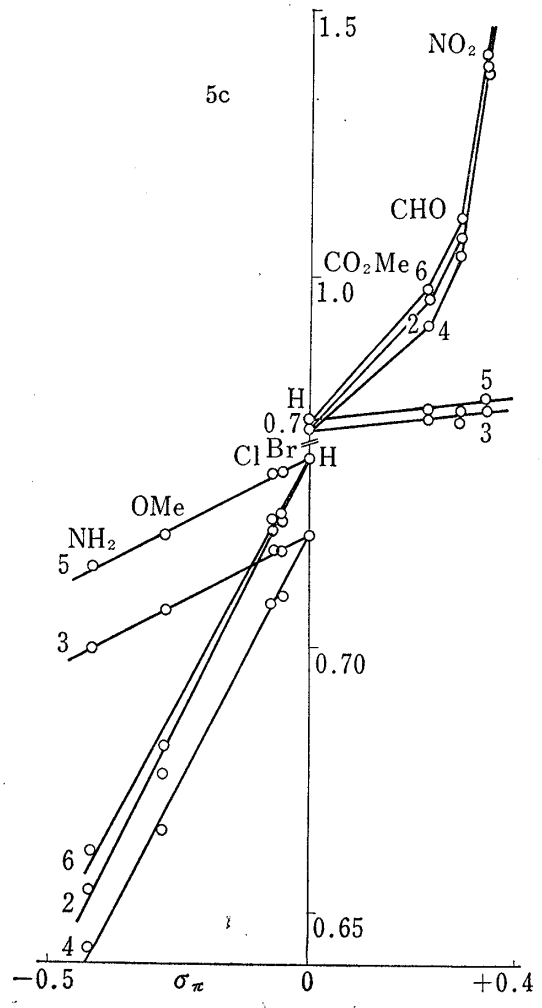
The vertical axis shows the $S_r^{(N)}$. The numbers on the diagonal lines shows the position of the carbon atom.

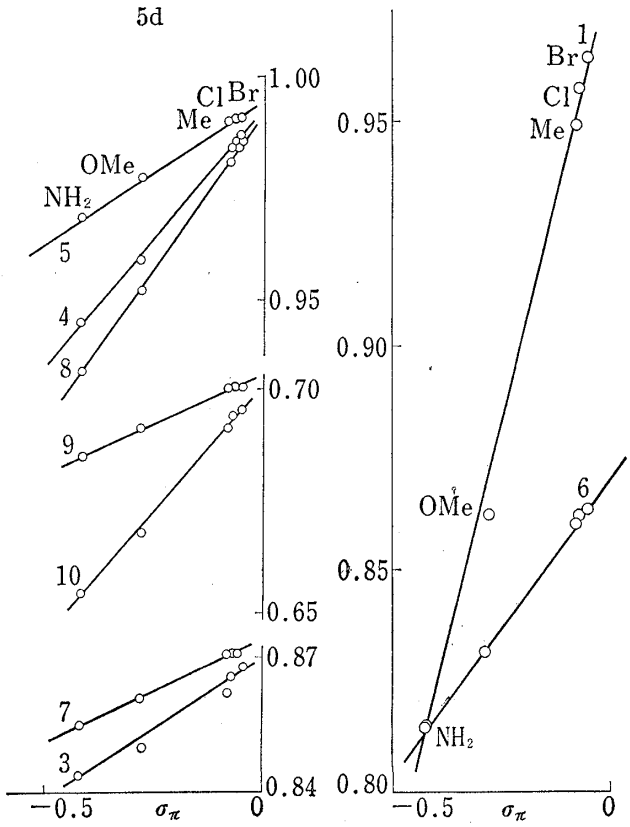
Fig. 5c. Nucleophilic Superdelocalizability $S_r^{(N)}$ for 1-Substituted-3,4-dimethoxybenzene Derivatives *vs.* Substituent Constant σ_π

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

Fig. 5d. Nucleophilic Superdelocalizability $S_r^{(N)}$ for 2-Substituted-naphthalene Derivatives *vs.* Substituent Constant σ_π

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





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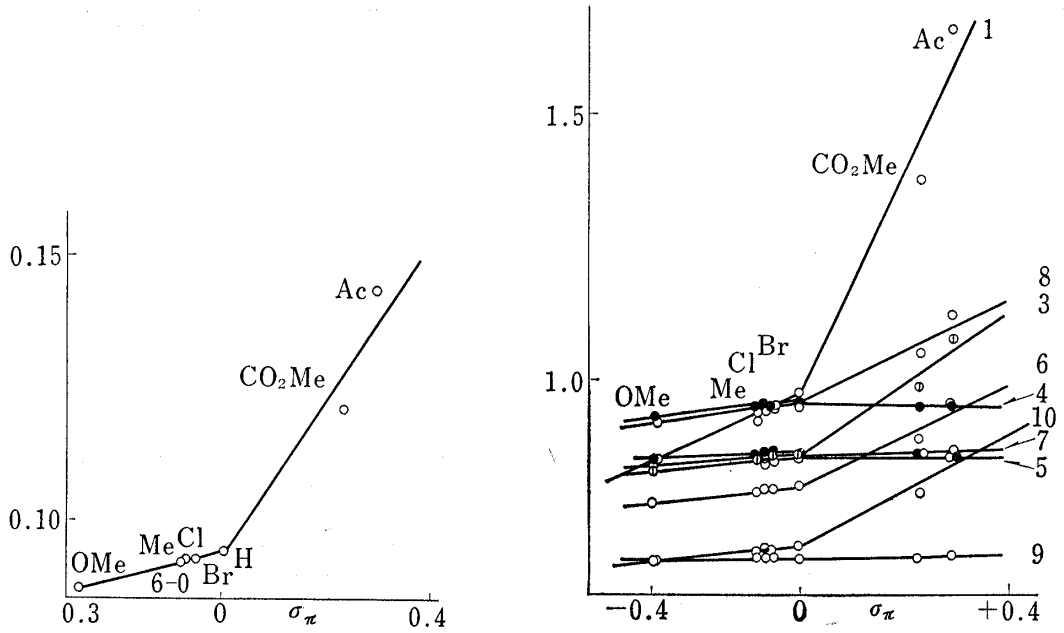

Fig. 5e. Nucleophilic Superdelocalizability $S_r^{(N)}$ for 2-Substituted-6-methoxynaphthalene Derivatives *vs.* Substituent Constant σ_π

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

TABLE VI. ΔF_r, $\Delta S_r^{(E)}$, $\Delta S_r^{(R)}$, and $\Delta S_r^{(N)}$ for Anisole

	C–OMe	*ortho*	*meta*	*para*
ΔFr	−0.25988	+0.02925	−0.00400	+0.01018
$\Delta S_r^{(E)}$	−0.01406	+0.20495	+0.02453	+0.19302
$\Delta S_r^{(R)}$	−0.03731	+0.06990	+0.00153	+0.05794
$\Delta S_r^{(N)}$	−0.06056	−0.06515	−0.02147	−0.07714

TABLE VII. Calculated Values of F_r, $S_r^{(E)}$, $S_r^{(R)}$ and $S_r^{(N)}$ for 1,3,4-Trimethoxybenzene

	1	2	3	4	5	6
Fr	0.14630	0.45450	0.16537	0.17955	0.42575	0.44140
$S_r^{(E)}$	1.03349	1.26443	1.04542	1.21391	1.08401	1.25250
$S_r^{(R)}$	0.85216	0.97133	0.89990	0.92053	0.90296	0.95937
$S_r^{(N)}$	0.67083	0.67823	0.69282	0.62715	0.72191	0.66624

Acknowledgement Mathematical calculations were made in a NEAC Model 2200 Electric Computer, and we are grateful to the staff of Osaka University Computer Center for making these calculations.

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