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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 paper³⁾ 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 $-\rho$ 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 F_r , 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 ₂ Me	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 ₂ Me	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 ₂ Me	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 ₂ Me	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 -electron 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 -electron 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 ₂ Me	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 ₂ Me	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 ₂ Me	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 IIId. 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 ₂ Me	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 Superdelocalizability $S_r^{(E)}$ 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 ₂ Me	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 ₂ Me	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 Derivatives

Substituent R	1-N	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9-C	10-C
OMe	0.99131	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 ₂ Me	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 IIIId. 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 ₂ Me	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 ₂ Me	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 $S_r^{(h)}$ 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 ₂ Me	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 $S_r^{(h)}$ 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	0.99049	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 ₂ Me	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 ₂ Me	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 ₂ Me	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 ₂ Me	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 ₂ Me	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 ₂ Me	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: F_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 substituent 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.

Fig. 3f. 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.

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. Nucleophilic 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 numbers 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.

$$\begin{aligned}\rho_{\text{cal}} &= \rho_{\text{ref.}} + \sum \Delta\rho \\ Fr_{\text{cal}} &= Fr_{\text{ref.}} + \sum \Delta Fr \\ S_{r\text{ cal}} &= S_{r\text{ cal}} + \sum \Delta S_r \\ \text{where } \Delta\rho &= \rho - 1.0000 \\ \Delta Fr &= Fr - 0.43000 \\ \Delta S_r &= S_r - 0.83000\end{aligned}$$

in monosubstituted benzene derivatives¹⁾.

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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