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Solute-Stationary Phase Interaction in Gas Liquid Chromatography. Relative Retention Values for Monosubstituted Benzene Derivatives and the Role of a New Descriptor for Regression Analysis

Hideko Kawaki

Faculty of Pharmaceutical Sciences, Kinki University, 3–4–1 Kowakae, Higashi-Osaka 577–8502, Japan.

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The descriptor μ^2/α was introduced by the classical equations for the orientation and induction energies. As the descriptor has the dimension of energy, it is not convenient to discuss in detail. The dipole moment in the benzene series μ_{aro} is evaluated from both the bond moment μ_b and the mesomeric moment μ_m. We redefine the new descriptors σ_{bd} and σ_{ms} modified to dimensionless values from μ_b and μ_m for the standard benzene as well as the descriptor σ_{s^o}. The relative retention values $\log\gamma$ on monosubstituted benzene derivatives are analyzed satisfactorily, using σ_{s^o}, σ_{bd}, and σ^+_{ms} for electron-donating group, and a new descriptor $(\sigma_{s^o}\cdot\sigma_{bd})^{1/2}$(N), which has a relation to the dipole moment of the excited state in $C_{ipso}-N$ bond of the aniline series.

$$\log\gamma=4.414(0.561)\sigma_{s^o}+0.209(0.042)\sigma_{bd}+0.336(0.153)\sigma^+_{ms}+1.592(0.441)(\sigma_{s^o}\cdot\sigma_{bd})^{1/2}(\mathrm{N})+0.004(0.096)$$
$$n=22,\quad r=0.981,\quad F=110.21,\quad \mathrm{S.D.}=0.064$$

It is suggested that E_{HB} of aniline or *N,N*-dimethylaniline can be expressed by E_{ES} in gaseous interaction.

Key words gas liquid chromatography; relative retention value $\log\gamma$; dispersion energy; hydrogen bonding interaction; monosubstituted benzene derivative; new descriptor $(\sigma_{s^o}\cdot\sigma_{bd})^{1/2}$

Introducing linear free energy relationships (LFER), Yukawa and Tsuno showed that the enthalpy change ΔH was expressed as a linear combination of the descriptors σ_i and σ_π which were representatives of the inductive/field and the resonance effects respectively.[1] Hansch and Fujita,[2] by adding the hydrophobic parameter $\log P$ to the Yukawa–Tsuno equation, succeeded in the development of some chemicals. Comparative molecular field analysis (CoMFA),[3] which is one of the 3D-QSAR, has been proposed recently; however, it is not easy to decide the three-dimentional molecular structure necessary for the activity. Using molecular dynamics and/or molecular kinetics, is a direct method to find the intermolecular interaction energy under discussion but it is difficult, because the 3D structure of the active site is not well known. Accordingly, going back to the Hansch–Fujita equation, a discussion on the parameters and the collection of the information are necessary. It has been pointed out that the hydrophobic parameter $\log P$ includes both steric and electric terms.[4] We have improved and evaluated each descriptor having a single chemical meaning, by gas liquid chromatography (GLC) of monosubstituted benzene derivatives. The relative retention values, $\log\gamma$, obtained from the experimental results, were expressed by the regression analysis of σ_{s^o}[5] and μ^2/α[5] plus σ_R.[6] The dispersion E_{dis} and repulsion E_{rep}, orientation E_{ori} and induction E_{ind} and charge transfer interaction E_{CT} energies are evaluated by these descriptors respectively. The value μ^2/α is not suitable for the regression analysis descriptor because of the energy dimension, thus we divided it into the two components of the dipole moment μ_b[7] and μ_m,[8] and made them dimensionless. Introducing the parameter $\mathrm{p}K_a$ to the aniline series as the CH/N contribution, we obtained good results in the previous report.[9]

We have, however, doubts on the overlapping energies, since the coefficient of the descriptor (μ^2_{aro}/α) was minus and that of $\mathrm{p}K_a$ became plus (Eq. 12). The relation of $(E_{\mathrm{ori}}+E_{\mathrm{ind}})$ and E_{CT} is so complicated that regression analyses using both descriptors would be fairly difficult. The weak molecular interaction energy is expressed in general by the sum of the van der Waals interaction energy E_{VDW}, the electrostatic energy E_{ES} and the charge transfer interaction energy E_{CT}. These energies are also evaluated by the descriptors σ_{s^o}, σ_{bd} and σ_{ms}, and $(\sigma_{s^o}\cdot\sigma_{bd})^{1/2}$, respectively. The new descriptor $(\sigma_{s^o}\cdot\sigma_{bd})^{1/2}$ was introduced to represent the difference, $E_{\mathrm{total}}-[(E_{\mathrm{dis}}+E_{\mathrm{rep}})+(E_{\mathrm{ori}}+E_{\mathrm{ind}})]$, that is E_{CT}. The values $\log\gamma$ are analyzed using $(\sigma_{s^o}\cdot\sigma_{bd})^{1/2}$ instead of $\mathrm{p}K_a$ this time and we discuss the chemical meaning of the descriptor by an analysis of a proton transfer reaction in solution.

Experimental

Regression Analysis Regression analyses were carried out using the program MVA,[10] and $\log\gamma$ values were done according to Eq. 1;

$$\log\gamma=a\sigma_{s^o}+b\sigma_{bd}+c\sigma_{ms}+d(\sigma_{s^o}\cdot\sigma_{bd})^{1/2}+e \tag{1}$$

where the four descriptors σ_{s^o}, σ_{bd} and σ_{ms}, and $(\sigma_{s^o}\cdot\sigma_{bd})^{1/2}$ represent [E_{dis} and E_{rep}], [E_{ind} and E_{ori}] and E_{CT}, respectively.

Descriptors for Regression Analyses Substituent Entropy Constant σ_{s^o}: This descriptor is derived from the absolute entropy $S^o_{298}(g)$[11] by Eq. 2;

$$\sigma_{s^o}=\log[S^o_{298}(g)(B)/S^o_{298}(g)(A)] \tag{2}$$

where A and B represent benzene for the reference and its derivatives, respectively.

All of the descriptors for monosubstituted benzene derivatives were taken from our previous report.[9,12]

Descriptors σ_{bd} and σ_{ms}: Dipole Moment μ: All experimental data [$\mu_{aro}(g)$ and $\mu_{ali}(g)$] are cited from the literature values.[13] The calculated values μ_{aro}(cal.) and μ_{ali}(cal.) were estimated with the program system MOPAC with the PM3 parameterization.[14] Geometries were fully optimized using the PRECISE option in MOPAC. The calculations were performed on a SX-3R/NEC in the Computer Center of Osaka University.[15]

Polarizability α: Polarizability values are given by the Clausius–Mosotti equation, using the observed refractive indices given by the sodium D line at 293 K.[16] By another method, α is calculated using POLAR option in MOPAC. The descriptors σ_{bd} and σ_{ms} are defined by the following equations;

$$\sigma_{bd}=\log[(\mu^2_b/\alpha)(B)/(\mu^2_b/\alpha)(A)] \tag{3}$$

Table 1. The Values of Dipole Moments

R	μ_b[a]	μ_m[b]	$\mu_{ali}(g)$[c]	μ_{ali}(cal.)[d]	$\mu_{aro}(g)$[e]	μ_{aro}(cal.)[f]
1 NMe_2	—	−1.66	0.83	1.02	1.61	1.17
2 NH_2	—	−1.02	1.34	1.31	1.49	1.30
3 OH	1.68	−0.60	1.70	1.51	1.60	1.16
4 OMe	1.68	−0.80	1.30	1.34	1.28	1.19
5 OEt	—	—	1.22	1.22	1.41	1.13
6 Me	0.30	−0.35	0.00	0.01	0.37	0.25
7 H	0.31[g]	0.32[h]	0.00	0.00	0.00	0.00
8 F	1.81	−0.41	1.81	1.83	1.59	1.60
9 Cl	1.87	−0.41	1.57	1.72	1.73	0.93
10 Br	1.80	−0.43	1.78	2.02	1.71	1.05
11 I	1.64	−0.50	1.62	2.04	1.71	0.60
12 COMe	2.28	0.46	2.75	2.68	2.88	2.79
13 COEt	—	—	2.77	2.62	—	2.68
14 CO_2Me	1.98	0.56	1.67	1.88	2.08	2.08
15 CO_2Et	—	—	1.78	1.77	1.95	2.11
16 CN	3.00	0.45	3.60	3.47	4.05	3.61
17 NO_2	2.76	0.76	3.25	4.50	4.01	5.33

a) Bond moment. *b*) Mesomeric moment. *c*) Experimental values of gases monosubstituted methanes. *d*) Calculated values of monosubstituted bicyclo[2.2.2] octanes. *e*) Experimental values of gases monosubstituted benzene derivatives. *f*) Calculated values. *g*) Dipole moment of C_{sp^3}–H.[17] *h*) Difference of the dipole moment $[C_{sp^3}–H−C_{sp^3}–H]$.[17b,18]

$$\sigma_{ms}=\log[(\mu_m^2/\alpha)(B)/(\mu_m^2/\alpha)(A)] \qquad (4)$$

where *A* and *B* represent benzene for the reference and its derivatives, respectively. The values μ_b and μ_m of benzene for the reference were set at 0.31 D[17] and 0.32 D[17b,18] for $\mu_{C_{sp^3}-H}$ and $[\mu_{C_{sp^2}-H}-\mu_{C_{sp^3}-H}]$.

Results and Discussion

Dipole Moments of Aliphatic Compound μ_{ali} and Bond Moment μ_b Dipole moment data, $\mu_{ali}(g)$, of monosubstituted methane derivatives in gas phase, and calculated values of monosubstituted bicyclo[2.2.2] octane derivatives, μ_{ali}(cal.), and μ_b are listed in Table 1. The correlations between $\mu_{ali}(g)$ and bond moment μ_b[7] as well as μ_{ali}(cal.) showed positive lines as shown in Figs. 1 and 2. The regression analyses Eqs. 5 and 6 are given by

$$\mu_{ali}(g)=1.38(0.20)\mu_b-0.65(0.40) \qquad (5)$$

$n=11$, $r=0.982$, $F=246.6$, S.D.$=0.19$

$$\mu_{ali}(\text{cal.})=1.08(0.18)\mu_{ali}(g)-0.05(0.36) \qquad (6)$$

$n=17$, $r=0.956$, $F=159.3$, S.D.$=0.34$

In these equations, *n*, *r*, *F* and S.D. denote the number of observations, correlation coefficient, variance ratio and standard deviation, respectively. S.D. is given by S.D.$=[S_{se}/(n-k-1)]^{1/2}$, where *n* and *k* denote the number of observations and variables, and S_{se} denotes the sum of the square of the residuals. The values in the parentheses in the regression equations denote the 95% confidence intervals. As the calculated value of the NO_2 group becomes significantly larger than the experimental one,[19] Eq. 7 is obtained by excluding the data for the NO_2 group.

$$\mu_{ali}(\text{cal.})=0.95(0.09)\mu_{ali}(g)+0.10(0.17) \qquad (7)$$

$n=16$, $r=0.987$, $F=521.1$, S.D.$=0.15$

μ_{aro} and Mesomeric Moment μ_m Data on the calculated μ_{aro}(cal.) and experimental $\mu_{aro}(g)$ dipole moments and μ_m[8] are summarized in Table 1. The plots of μ_{aro}(cal.) and $\mu_{aro}(g)$ are shown in Fig. 3 and the regression equation is given by Eq. 8.

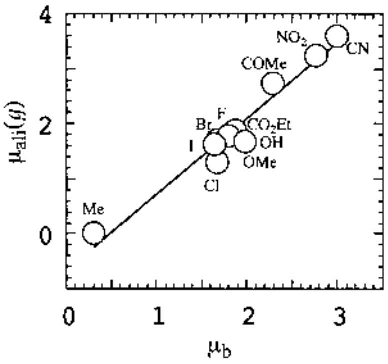

Fig. 1. Correlation between Experimental Dipole Moment of the Gases Monosubstituted Methane Derivatives $\mu_{ali}(g)$ and Bond Moment μ_b

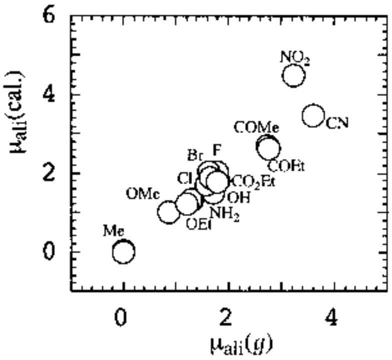

Fig. 2. Correlation between Calculated Dipole Moment for Monosubstituted Bicyclo[2.2.2] Octane Derivatives μ_{ali}(cal.) and $\mu_{ali}(g)$

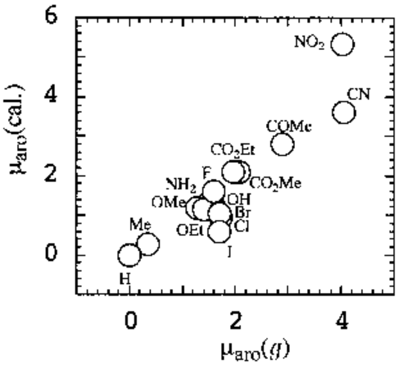

Fig. 3. Correlation between Calculated Dipole Moment μ_{aro}(cal.) and Experimentals under Gases Condition $\mu_{aro}(g)$ in Monosubstituted Benzene Derivatives

$$\mu_{aro}(\text{cal.})=1.16(0.27)\mu_{aro}(g)-0.49(0.57) \qquad (8)$$

$n=16$, $r=0.928$, $F=86.3$, S.D.$=0.52$

Equation 9 is obtained by excluding the calculated values of NO_2 and halogen groups except *F*.

$$\mu_{aro}(\text{cal.})=0.94(0.13)\mu_{aro}(g)-0.06(0.25) \qquad (9)$$

$n=12$, $r=0.982$, $F=267.5$, S.D.$=0.20$

The values of μ_{aro}(cal.) were expressed by the sum of μ_{ali}(cal.) and μ_m (Eq. 10).

$$\mu_{aro}(\text{cal.})=0.93(0.10)\mu_{ali}(\text{cal.})+0.29(0.26)\mu_m^{+} +1.26(0.62)\mu_m^{-}-0.27(0.30) \qquad (10)$$

$n=9$, $r=0.997$, $F=264.4$, S.D.$=0.10$

Table 2. Retention Values $\log \gamma$ for Monosubstituted Benzene Derivatives and Their Descriptors

	R	$\log \gamma$	σ_{s^o}	σ_{bd}	$\sigma^{*\,a)}_{bd}$	σ_{ms}	$(\sigma_{s^o} \cdot \sigma_{bd})^{1/2}$
1	H	0.000	0.000	0.000	0.000	0.000	0.000
2	Me	0.301	0.076	0.000	0.000	0.000	0.000
3	Et	0.538	0.127	0.000	0.000	0.000	0.000
4	*n*-Pr	0.760	0.173	0.000	0.000	0.000	0.000
5	iso-Pr	0.684	0.159	0.000	0.000	0.000	0.000
6	*n*-Bu	1.007	0.213	0.000	0.000	0.000	0.000
7	iso-Bu	0.895	0.200	0.000	0.000	0.000	0.000
8	*sec*-Bu	0.896	0.202	0.000	0.000	0.000	0.000
9	*tert*-Bu	0.853	0.173	0.000	0.000	0.000	0.000
10	OMe	0.595	0.127	1.144	0.000	−0.694	0.000
11	OEt	0.781	0.175	1.034	0.000	−0.640	0.000
12	NH_2	0.670	0.074	1.327	0.691	−0.941	0.313
13	NHMe	0.939	0.103	1.342	—	−1.113	0.371
14	NMe_2	1.051	0.134	1.211	0.786	−1.238	0.402
15	NHEt	1.104	0.116	1.290	—	−1.055	0.387
16	NEt_2	1.340	0.157	1.236	0.875	−1.149	0.440
17	COMe	0.940	0.142	1.750	0.000	0.170	0.000
19	CO_2Me	1.003	0.185	1.298	0.000	0.322	0.000
20	CO_2Et	1.179	0.219	1.308	0.000	0.276	0.000
22	NO_2	0.977	0.115	1.945	0.000	0.656	0.000

a) The values are estimated by the excited dipole moment $\mu^*_{NH_2}=3.42$ D, $\mu^*_{NMe_2}=3.86$ D and $\mu^*_{NEt_2}=4.87$ D.

Here, the descriptor μ^+_m can be omitted from the 95% confidence level of the regression coefficient, thus Eq. 11 is obtained.

$$\mu_{aro}(\text{cal.})=0.92(0.14)\mu_{ali}(\text{cal.})+0.74(0.58)\mu^-_m-0.00(0.25) \qquad (11)$$
$$n=9, \quad r=0.992, \quad F=178.1, \quad \text{S.D.}=0.15$$

These results suggest that μ_{aro}(cal.) contains both inductive and mesomeric moments.

Regression Analyses of $\log \gamma$ In our previous report,[9] $\log \gamma$ values were expressed using σ_{s^o}, μ^2_{aro}/α and σ_π, which is the pK_a for the aniline series as in Eq. 12.

$$\log \gamma=4.736(0.490)\sigma_{s^o}-0.238(0.140)\mu^2_{aro}/\alpha-0.549(0.412)\sigma^-_\pi$$
$$+0.090(0.011)\text{p}K_a-0.045(0.081) \qquad (12)$$
$$n=22, \quad r=0.989, \quad F=190.3, \quad \text{S.D.}=0.050$$

In this paper, these regression analyses are carried out using σ_{s^o}, σ_{bd}, $\sigma^\pm_{ms}$ and the new descriptor $(\sigma_{s^o} \cdot \sigma_{bd})^{1/2}$(N) instead of p$K_a$, and all data and their descriptors are listed in Table 2.

$$\log \gamma=4.412(0.580)\sigma_{s^o}+0.205(0.071)\sigma_{bd}+0.329(0.183)\sigma^+_{ms}$$
$$+0.026(0.328)\sigma^-_{ms}+1.585(0.462)(\sigma_{s^o} \cdot \sigma_{bd})^{1/2}(\text{N})+0.004(0.100) \qquad (13)$$
$$n=22, \quad r=0.981, \quad F=83.1, \quad \text{S.D.}=0.066$$

Here, the descriptor σ^-_{ms} for the electron-attracting group (EA) can be omitted from the 95% confidence level of the regression coefficient, and rewritten as Eq. 14.

$$\log \gamma=4.414(0.561)\sigma_{s^o}+0.209(0.042)\sigma_{bd}+0.336(0.153)\sigma^+_{ms}$$
$$+1.592(0.441)(\sigma_{s^o} \cdot \sigma_{bd})^{1/2}(\text{N})+0.004(0.096) \qquad (14)$$
$$n=22, \quad r=0.981, \quad F=110.2, \quad \text{S.D.}=0.064$$

The coefficients of all the descriptors became plus and the regression results were better than in Eq. 12. The evaluation of σ^+_{ms} can correspond to increased π electron introduced for the electron-donating group (ED).

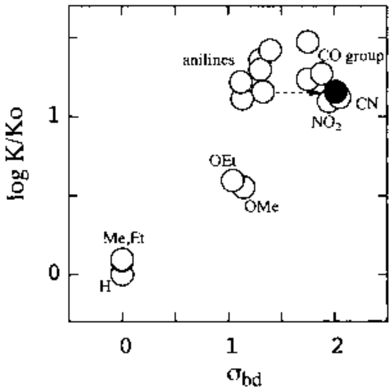

Fig. 4. Plots of $\log K/K_o$ for Phenol *vs*. σ_{bd} with Substituted Benzene Derivatives in CCl_4

● = σ^*_{bd} estimated by $\mu^*_{NH_2}=3.42$ D.

Table 3. $\log K/K_o$ for Phenol with Substituted Benzene Derivatives, and Their Descriptors

	R	$\log K/K_o$	σ_{bd}	$\sigma^{*\,a)}_{bd}$	σ_{ms}	$(\sigma_{s^o} \cdot \sigma_{bd})^{1/2}$
1	H	0.000	0.000	0.000	0.000	0.000
2	Me	0.084	0.000	0.000	0.000	0.000
3	Et	0.097	0.000	0.000	0.000	0.000
4	$CH=CH_2$	—	0.000	0.000	0.000	0.000
5	OMe	0.553	1.144	0.000	−0.694	0.000
6	OEt	0.594	1.034	0.000	−0.640	0.000
7	NH_2	1.155	1.327	0.691	−0.941	0.313
8	NHMe	—	1.342	—	−1.113	0.371
9	NMe_2	—	1.211	0.786	−1.238	0.402
10	1,2-Me, NH_2	1.109	1.129	—	−0.744	0.375
11	1,3-Me, NH_2	1.216	1.125	—	−0.740	0.379
12	1,4-Me, NH_2	1.301	1.161	—	−0.776	0.365
13	1,4-OMe, NH_2	1.422	1.397	—	−0.986	0.473
14	NO_2	1.097	1.945	0.000	0.656	0.000
15	CN	1.121	2.051	0.000	0.217	0.000
16	COMe	1.472	1.750	—	0.170	0.493
17	CHO	1.234	1.754	—	0.229	0.470
18	CO_2Et	1.359	1.308	—	0.276	0.535
19	1,4-NO_2, CO_2Et	1.269	1.880	—	0.477	0.522

a) The values are estimated by the excited dipole moment $\mu^*_{NH_2}=3.42$ D and $\mu^*_{NMe_2}=3.86$ D.

Regression Analyses of $\log K/K_o$ for Phenol and Aniline in Substituted Benzene Derivatives The logarithm of H^+ transfer equilibrium[20] based on benzene $\log K/K_o$ had a linear relation to σ_{bd} with the exception of the NR_2, COR and CO_2R groups, the so-called hydrogen bonding groups (Fig. 4) (Table 3). We obtained a regression equation using $(\sigma_{s^o} \cdot \sigma_{bd})^{1/2}$(N) and $(\sigma_{s^o} \cdot \sigma_{bd})^{1/2}$(CO).

$$\log K/K_o=0.496(0.094)\sigma_{bd}+1.442(0.338)(\sigma_{s^o} \cdot \sigma_{bd})^{1/2}(\text{N})$$
$$+0.866(0.302)\sigma_{s^o} \cdot \sigma_{bd})^{1/2}(\text{CO})+0.068(0.116) \qquad (15)$$
$$n=16, \quad r=0.985, \quad F=126.5, \quad \text{S.D.}=0.099$$

Now, we will consider the detail of this interaction in the aniline series. Two important conformational changes of para-substituted *N*,*N*-dimethylaniline derivatives have been proposed to explain the delocalized excited state.[21] The first is the twisting, the so-called "twisted internal charge transfer (TICT)" state of the dimethyl group with respect to the benzene ring. The second is the pyramidalization of the dimethylamino nitrogen. This change from planer (sp^2) to pyramidal (sp^3) hybrization of the dimethylamino nitrogen has been recently proposed by Schuddeboom *et al.*,[22] and this mechanism is called the "wagged internal charge transfer (WICT)" by A.-D. Gorse *et al.*[23] A.-D. Gorse *et al.* came to the conclusion that the solvent effects could be related to the TICT state more than the WICT state under strong polar solvent. Consequently, they suggested that a strong dipole moment would be produced by the effect of TICT in solution. It was reported recently that the values for aniline, dimethylaniline and diethylaniline were 2.1, 3.0 and 3.1 D from the AM1 method, respectively,[24] as the dipole moment increased upon the excitation. The $\log K/K_o$ values could be analyzed again using σ^*_{bd} estimated from the excited dipole moment (Fig. 4) except COMe, CO_2Me, *etc.*, then the linear relation would hold.

$$\log K/K_o = 0.528(0.055)(\sigma_{bd} + \sigma^*_{bd}) + 0.047(0.073) \qquad (16)$$
$$n = 8, \quad r = 0.995, \quad F = 559.6, \quad \text{S.D.} = 0.055$$

These results suggested that new descriptor $(\sigma_{s^o} \cdot \sigma_{bd})^{1/2}$ can be expressed by the change of the excited dipole moment in hydrogen bonding in the aniline series. The COR and CO_2R in Eq. 17 can be explained by the increased dipole moment the same as the aniline series. Substituting σ^*_{bd} to Eq. 14 instead of $(\sigma_{s^o} \cdot \sigma_{bd})^{1/2}$(N), a good result is given by

$$\log \gamma = 4.426(0.661)\sigma_{s^o} + 0.223(0.041)(\sigma_{bd} + \sigma^*_{bd}) + 0.332(0.179)\sigma^+_{ms}$$
$$-0.001(0.114)$$
$$n = 20, \quad r = 0.975, \quad F = 100.7, \quad \text{S.D.} = 0.076$$

Conclusion

The new descriptor $(\sigma_{s^o} \cdot \sigma_{bd})^{1/2}$ can be used satisfactory in the evalution of the interaction as hydrogen bonding and it is clear that the change of the dipole moment of the excited state for C_{ipso}–N in intermolecular interaction is expressed by σ^*_{bd}. The hydrogen bonding energy E_{HB} of the aniline series (especially aniline, *cf.* Eq. 16) could be expressed by E_{ES} in gaseous and non-aqeous interaction, but COR and CO_2R could not be determined at this time which is EES or ECT.

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