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Studies on the Proton Magnetic Resonance Spectra in Aromatic Systems. XX.[1] Major Factors of the Paramagnetic Shift Parameter of Alkyl Pyridine Derivatives by Tris (dipivalomethanato)-europium

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The induced paramagnetic shift parameters, S values, due to tris (dipivalomethanato)-europium were examined in alkyl pyridine derivatives from the view points of steric, electronic and solvent effects.

1. The log S values are linearly related with $\Delta\Delta E_R$, σ^* and $1-1/\varepsilon$, and expressed by the following type of equation. $S=A.\, e^{-B\times k}$, $k=\Delta\Delta E_R$, σ^* or $1-1/\varepsilon$
2. The three kinds of intercepts are linearly related with each other and decrease regularly from α to γ, whereas a plot of three kinds of slopes, referring to the perturbed state is *zig-zag*.
3. The S values are expressed by the sum of the contributions of ΔE_{steric}, $\Delta E_{elect.}$ and $\Delta E_{solv.}$

Introduction

In the previous reports,[3a,b] the induced paramagnetic shift parameters, S values, of aliphatic amines and alcohols, and of *meta*- and *para*-substituted aniline derivatives by Eu-(DPM)$_3$ were examined from empirical view points, and the important role of the steric requirement in the equilibrium between the shift reagent and the ligand molecule was indicated.

To confirm the previous deductions, in this work the S values of alkyl pyridine derivatives were examined from the view points of steric, electronic and solvent effects.

Experimental

All materials, purchased from commercial sources, were of J.I.S. grade and were used without further purification. Spectra were measured in an Hitachi R-20A-type spectrometer at 34° in $CDCl_3$ with tetramethylsilane as an internal reference. Samples contained 0.3 mole of substrate and a molar ratio of Eu(DPM)$_3$/substrate of less than 0.10. The shift parameters, S values, were determined from the mean values of the slopes of 4 or 5 measurements of the linear relations between the induced shifts and the molar ratios of reagent/substrate. Solvent effects were examined in C_6H_{12} ($\varepsilon=1.99$), CCl_4 ($\varepsilon=2.20$), $CDCl_3$ ($\varepsilon=4.55$) and CH_2Cl_2 ($\varepsilon=9.08$), respectively.

Results and Discussion

S Values of Alkyl Pyridines and $\Delta\Delta$ E$_R$

The S values of alkyl pyridines (Table I) were compared with the steric strain energies, $\Delta\Delta E_R$ (Table II) obtained from the thermal data of BF_3-pyridine complexes.[4]

The correlations between the two are exponential, and the linear relation between log S and $\Delta\Delta E_R$ (Fig. 1a, b) can be expressed by the following equations:

$$S_\alpha = 12.90e^{-0.55\Delta\Delta E_R} \qquad S_\beta = 5.13e^{-0.46\Delta\Delta E_R} \qquad S_\gamma = 4.08e^{-0.55\Delta\Delta E_R}$$

1) Part XIX: Y. Sasaki and M. Sugiura, *Chem. Pharm. Bull.* (Tokyo), **22**, 224 (1974).
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3) *a*) Y. Sasaki, H. Kawaki and Y. Okazaki, *Chem. Pharm. Bull.* (Tokyo), **21**, 917 (1973); *b*) Y. Sasaki, H. Kawaki and Y. Okazaki, *ibid.*, **22**, 50 (1974).
4) H.C. Brown, D. Gintis and H. Podall, *J. Am. Chem. Soc.*, **78**, 5375 (1956).

Table I. S Values and log S Values of Alkyl-pyridine Derivatives

	α-H	β-H	γ-H
4-Me	12.3(1.09)	5.2(0.72)	
3-Me	13.1(1.12)	5.2(0.72)	4.2(0.63)
H	12.3(1.09)	4.8(0.69)	4.4(0.65)
2-Me	4.4(0.65)	1.7(0.24)	1.2(0.09)
2-Et	2.3(0.36)	1.5(0.16)	0.9(0.06)
2,6-Di Me	0	0	0
2,4,6-Tri Me	0	0	0

Table II. Steric Strain Energies $\Delta\Delta E_R$ (kcal./mole) in the Reactions of Pyridine Bases with BF_3

Substituent	$\Delta\Delta E_R$
H	0
4-Me	0
3-Me	0
2-Me	2.2
2-Et	2.8
2,6-di Me	8.5
2,4,6-tri Me	8.0

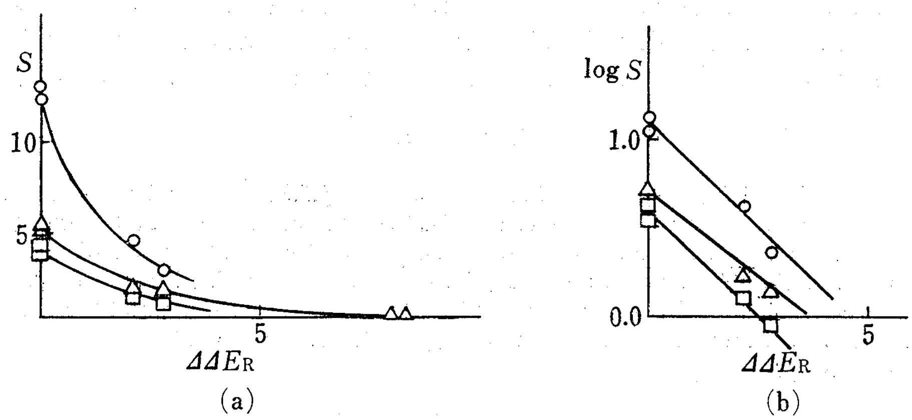

Fig. 1a—b. Correlations of S and log S with $\Delta\Delta E_R$ (kcal./mole) of Alkyl Pyridines

From the above equations, the relative weights of the intercepts A_S and slopes B_S are 1.00: 0.40: 0.32 and 1.00: 0.84: 1.00, respectively.

The intercepts referred to the unperturbed state, where $\Delta\Delta E_R=0$, afford a linear relation with the σ charge densities[5] and decrease regulary from α to γ (Fig. 2a, b).

On the other hand, the slopes, corresponding to the perturbed state, fall in the *zig-zag* manner, as shown in Fig. 3.

5) *a*) J.E. Bloor and D.L. Breen, *J. Am. Chem. Soc.*, **89**, 6835 (1967); *b*) E. Clementi, *J. Chem. Phys.*, **46**, 5731 (1967).

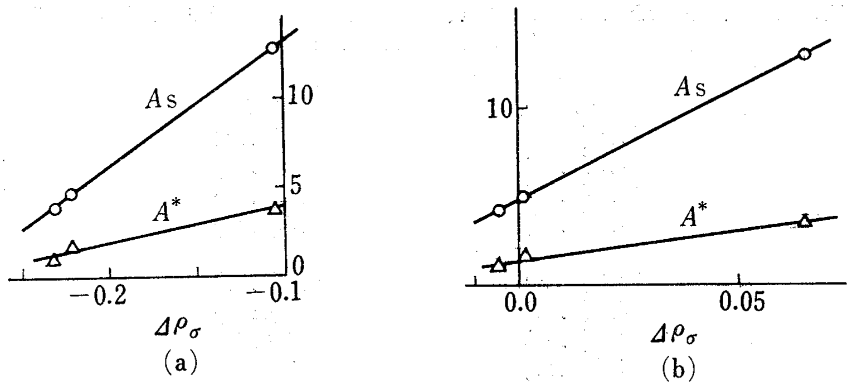

Fig. 2. Correlations of A_s and A^* with Δ of Alkyl Pyridines

(a): Clementi, *et al.* (b): Bloor, *et al.*

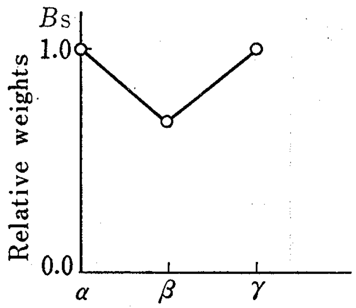

Fig. 3. Relative Weights, B_s, of the α-,β-, and γ-Positions of Alkyl Pyridines

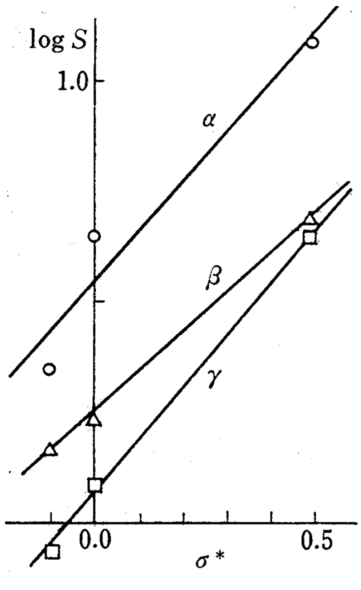

Fig. 4. Correlations between log S Values of α-, β-, and γ-H of Alkyl Pyridines and the Polar Substituent Constants σ^*

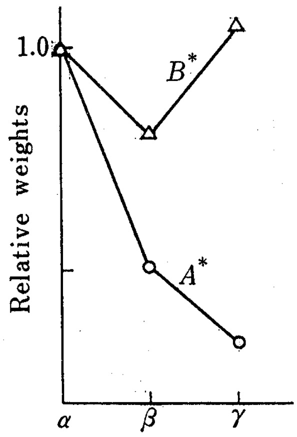

Fig. 5. Relative Weights A^* and B^* of the α-, β-, and γ-Positions of Alkyl Pyridines

S Values of Alkyl Pyridines and σ^*

As shown in Fig. 4, the log S values of alkyl pyridines are also correlated with the polar substituent constants σ^*,[6] and the relation being expressed by the next equations.

$$S_\alpha = 3.54e^{2.60\sigma^*} \qquad S_\beta = 1.78e^{2.07\sigma^*} \qquad S_\gamma = 1.18e^{2.72\sigma^*}$$

The relative weights of the intercepts A^* and slopes B^* are 1.00: 0.50: 0.33 and 1.00: 0.80: 1.05, respectively. The intercepts decrease regularly, whereas the slopes are *zig-zag*. The coefficients show similar relations to those given in the previous section (*cf.* Fig. 2 and 5).

Solvent Effect

The S values are thought to depend on the solvent, *i.e.* the induced shifts in C_6D_6, $CDCl_3$ and MeCN are equivalent to 90, 80—75 and 70—60% of those in CCl_4.[7] This indicates the

6) R.W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 2729, 3120 (1952); **75**, 4231 (1953). The polar substituent constants σ^* are correlated with σ' (J.D. Roberts and W. Moreland, Jr., *J. Am. Chem. Soc.*, **75**, 2167 (1953)) as shown in the following equations. $\sigma' = 0.45\,\sigma^*$ $\sigma' = 1/1.464 \log K/K_0$, where K, K_0 are the dissociation constants of the 4-substituted bicyclo-[2,2,2]-octane-1-carboxylic acid series.

7) L.K.M. Sanders and D.H. Williams, *J. Am. Chem. Soc.*, **93**, 641 (1971).

TABLE III. S Values and log S Values of Pyridine and 3- and 4-Picoline in Various Solvents

Pyridine	α-H	β-H	γ-H
C_6H_{12}	19.4(1.29)	5.8(0.77)	5.8(0.77)
CCl_4	14.7(1.17)	6.2(0.80)	4.5(0.66)
$CDCl_3$	12.3(1.09)	4.8(0.68)	4.8(0.68)
CH_2Cl_2	14.1(1.15)	4.5(0.66)	3.7(0.58)
3-Picoline			
C_6H_{12}	19.0(1.28)	6.5(0.82)	5.5(0.75)
CCl_4	17.3(1.24)	6.3(0.80)	5.7(0.76)
$CDCl_3$	13.4(1.13)	5.3(0.73)	4.5(0.66)
CH_2Cl_2	14.7(1.17)	4.7(0.68)	4.8(0.69)
4-Picoline			
C_6H_{12}	13.4(1.13)	6.4(0.81)	
CCl_4	15.4(1.19)	5.3(0.73)	
$CDCl_3$	12.3(1.09)	5.2(0.72)	
CH_2Cl_2	14.4(1.16)	4.3(0.61)	

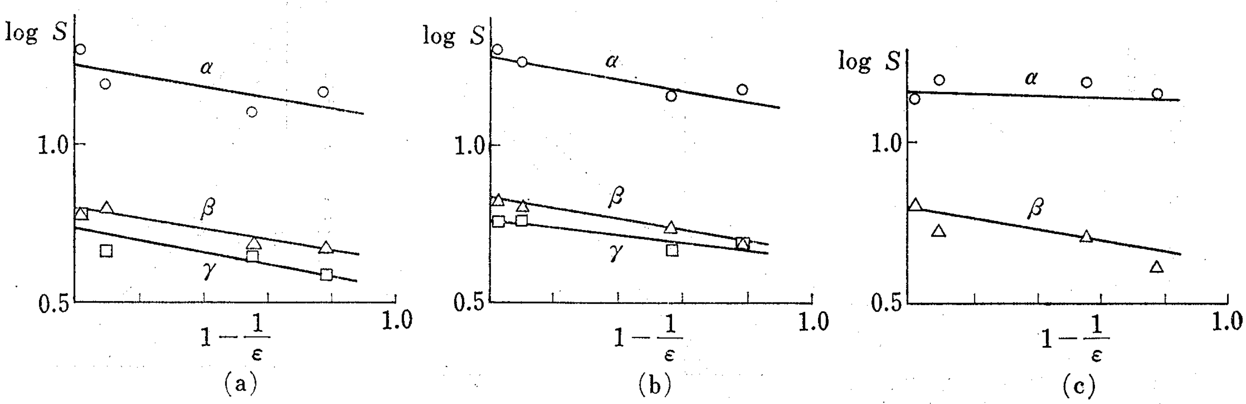

Fig. 6a—c. Correlations between log S Values of α-, β-, and γ-H of Alkyl Pyridines and $1-1/\varepsilon$

(a): pyridine, (b): 3-picoline, (c) 4-picoline

TABLE IV. Intercepts $A_{solv.}$ and Slopes $B_{solv.}$ and Relative Weights

		α-H	β-H	γ-H
$A_{solv.}$	Pyridine	25.1(1.00)	9.33(0.37)	8.12(0.32)
	3-Picoline	26.2(1.00)	10.0 (0.38)	7.41(0.28)
	4-Picoline	15.1(1.00)	9.11(0.60)	
$B_{solv.}$	Pyridine	0.76(1.00)	0.81(1.07)	0.85(1.12)
	3-Picoline	0.74(1.00)	0.81(1.09)	0.53(0.72)
	4-Picoline	0.13(1.00)	0.76(5.85)	

dependency of the S values on the dielectric character of the solvent. In this work, the isotropic dipole-dipole interaction term—electrostatic interaction energy—is taken as the major factor, and the contributions of polarization and dispersion effects are neglected.[8] Previously, Born,[9] and Hoijtink, *et al.*[10] proposed the next equation for estimation of the solvation energy.

$$E_{\mathrm{solv.}} = -k(1-1/\varepsilon) \quad \text{where } k=\text{constant}$$

Then, when the S values are controlled by the solvent effect of the above mechanism, the following relation must be expected.

$$S_{\mathrm{solv.}} = A_{\mathrm{solv.}} \cdot e^{-B_{\mathrm{solv.}} \times (1-1/\varepsilon)}$$

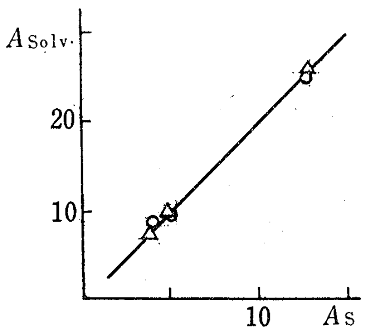

Fig. 7. A_{Solv} and A_{S} of Alkyl Pyridines

The S values and log S values obtained in this work are summarized in Table III.

The correlations between the log S values and $1-1/\varepsilon$ are illustrated in Fig. 6a—c.

The linear relations observed in Fig. 6a—c indicate that the S values can be expressed by the above equation, and the intercepts $A_{\mathrm{solv.}}$ and slopes $B_{\mathrm{solv.}}$ were obtained as shown in Table V.

The intercepts $A_{\mathrm{solv.}}$, linearly related with the intercepts A_{S} in the preceding section (*cf.* Fig. 7), correspond to the state without medium, and as shown in Table IV, the intercepts $A_{\mathrm{solv.}}$ decrease regularly, whereas the slopes $B_{\mathrm{solv.}}$, corresponding to the perturbed state, are irregular, and deviations are prominent at positions α and γ.

8) R. Daudel, "Theorie Quantique de la Reactivite Chimique," Gauthier-Villars, 1967, Chapter 2.
9) M. Born, *Z. Physik.*, **1**, 45 (1920).
10) G.J. Hoijtink, E. DeBoer, P.M. Van Der Meij and W.P. Weijland, *Rec. Trav. Chim.*, **75**, 487 (1956).