CHEMICAL & PHARMACEUTICAL BULLETIN

Vol. 23, No. 9 September 1975

Regular Articles

[Chem. Pharm. Bull. 23(9)1899—1904(1975)]

UDC 547.26.03 : 547.233.03 : 543.422.25 : 546.661.09

Studies on the Proton Magnetic Resonance Spectra in Aliphatic Systems. VI.[1] Tris (dipivalomethanato)europium Induced Paramagnetic Shifts of Aliphatic Amines and Alcohols: Steric, Electronic and Solvent Effects

Yoshio Sasaki,[2a] Hideko Kawaki and Yuko Okazaki[2b]

Faculty of Pharmaceutical Sciences, Osaka University[2a] and Faculty of Pharmacy, Kinki University[2b]

(Received February 21, 1974)

Tris (dipivalomethanato) europium induced paramagnetic shifts of aliphatic amines and alcohols were examined with respect to steric, electronic and solvent effects. The paramagnetic shifts are an exponential function of the three effects, and can be expressed by the following type of equation:

$$S = A \cdot e^{-B \times k}$$

where k=parameters of the steric, electronic and solvent effects

The intercepts A, referred to the unperturbed state, decrease regulary from α to γ, whereas the slopes B, referred to the perturbed state, decrease in a *zig-zag* manner.

Introduction

In the previous paper of this series,[1] the tris (dipivalomethanato) europium induced paramagnetic shift parameters of aliphatic amines and alcohols were correlated with Brown's steric strain energies[3] of the thermal dissociation energies of amine-BMe_3 addition compounds, and the important role of the steric factor in such equilibrium reactions was indicated. In this work, Taft's steric substituent constants E_s[4] and the polar substituent constant σ^*,[5] obtained in kinetical studies, are tentatively utilized as reference parameters, and more elaborate factors are explored.

Experimental

All materials purchased from commercial sources were of J.I.S. grade, and were used without further purification. Spectra were measured in a Hitachi Perkin-Elmer, R-20A type, spectrometer in 0.3 mole $CDCl_3$ solution with tetramethylsilane as internal reference, and chemical shifts were measured using a frequency counter. The induced paramagnetic shift parameters, S values, were determined from the mean values of 4 or 5 measurements of the slopes of plots of the induced shifts against the $Eu(DPM)_3$/substrate mole ratios. The observed S values and log S values of aliphatic amines and alcohols are summarized in Tables I and II.

1) Part V: Y. Sasaki, H. Kawaki, and Y. Okazaki, *Chem. Pharm. Bull.* (Tokyo), **21**, 2488 (1973).
2) *a) Yamadakami 133–1, Suita, Osaka; b) Kowakae 321, Higashi-Osaka, Osaka.*
3) H.C. Brown, M.D. Taylor and S. Sujishi, *J. Am. Chem. Soc.*, **73**, 2464 (1951); H.C. Brown and G.K. Barbaras, *ibid.*, **75**, 6 (1953).
4) R.W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 3120 (1952).
5) R.W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 2929 (1952); *ibid.*, **75**, 4231 (1953).

Table I. $Eu(DPM)_3$ Induced Shift Parameters, S Values, and log S Values of Simple Aliphatic Amines

Amine	α-H	β-H	γ-H	δ-H
n-$C_3H_7NH_2$	23.5(1.37)	13.5(1.13)	8.5(0.93)	
n-$C_4H_9NH_2$	28.2(1.45)	12.9(1.11)	9.78(0.99)	5.0(0.70)
iso-$C_3H_7NH_2$	21.5(1.33)	12.5(1.10)		
iso-$C_4H_9NH_2$	28.0(1.45)	17.5(1.24)	9.00(0.95)	
s-$C_4H_9NH_2$	17.4(1.24)	Me 12.4(1.09)	5.50(0.74)	
		CH_2 10.3(1.01)		
t-$C_4H_9NH_2$		6.5(0.81)		
Et_2NH	7.0(0.85)	4.5(0.65)		
Et_3N	0	0		

Table II. $Eu(DPM)_3$ Induced Shift Parameters, S Values, and log S Values of Simple Aliphatic Alcohols

Alcohol	α-H	β-H	γ-H
C_2H_5OH	7.5(0.88)	4.0(0.60)	
n-C_3H_7OH	10.3(1.01)	5.2(0.71)	3.8(0.57)
iso-C_3H_7OH	7.0(0.85)	5.5(0.74)	
iso-C_4H_9OH	7.6(0.98)	5.4(0.74)	3.0(0.49)
s-C_4H_9OH	6.5(0.81)	CH_2 4.1(0.61)	3.1(0.49)
		Me 4.3(0.64)	
t-C_4H_9OH		4.5(0.65)	
neo-$C_5H_{11}OH$	8.4(0.83)		2.0(0.49)

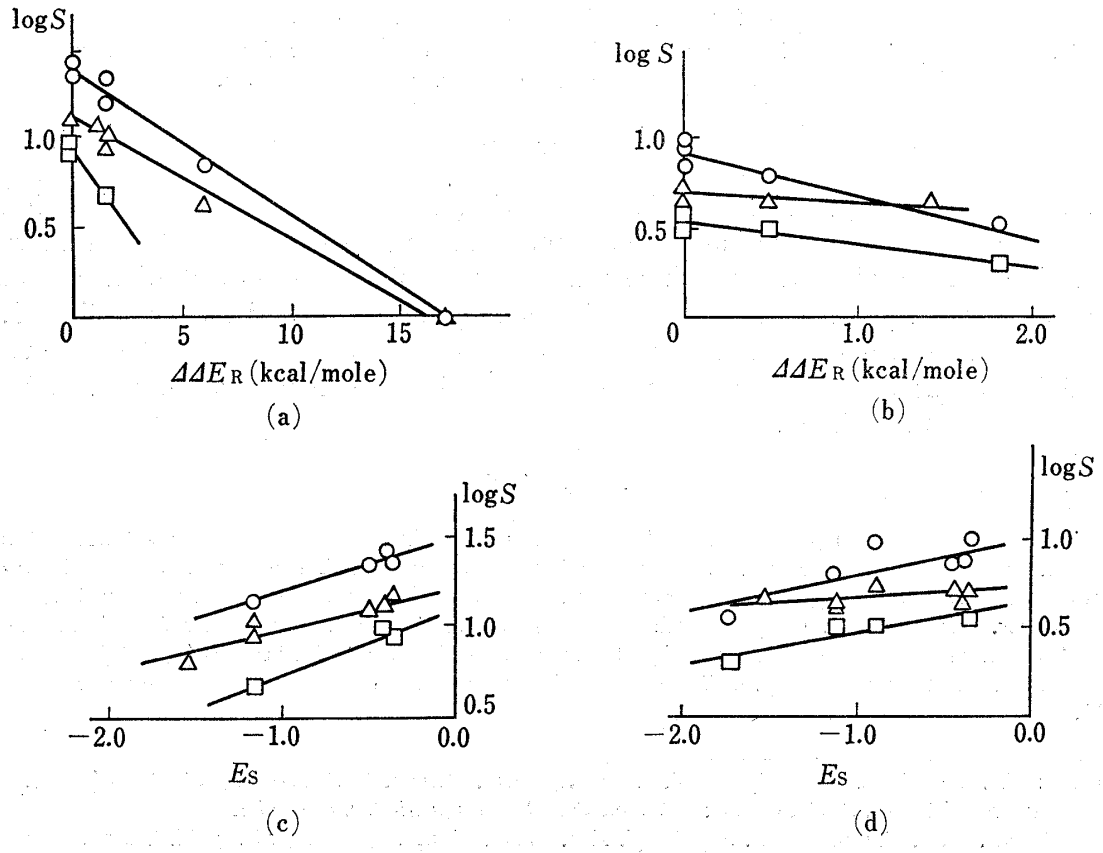

Fig. 1a—d Correlations between log S Values of α-, β-, and γ-H of Simple Aliphatic Amines and Alcohols *vs.* Steric Strain Energies, $\Delta\Delta E_R$ and E_S

(a), (c): amines; (b), (d): alcohols

Results and Discussion

Steric Factor

As shown in Fig. 1a—d, there are exponential, linear relations between the S values and log S *vs.* $\Delta\Delta E_R$[3] and E_s.[4]

The parameters $\Delta\Delta E_R$ are deduced from the thermal equilibrium, whereas E_s values are kinetic values, but the two are linearly related (*cf.* Fig. 2).

The following equations are deduced from the linear relations in Fig. 1b and 2b.

$$S = A_s \cdot e^{-B_s \times k} \qquad k = E_s \text{ or } \Delta\Delta E_R$$

The intercepts A_s and slopes B_s are summarized in Table III.

The intercepts A_s and slopes B_s are ascribed to unperturbed and perturbed states, respectively. The intercepts A_s decreased in the normal order, $\alpha > \beta > \gamma$, whereas B_s showed a *zig-zag* relation as shown in Fig. 3.

The intercepts A_s also corresponded well with the *sigma* charge densities, calculated by the *sigma*-included *omega*-Technique[6] (*cf.* Fig. 4).

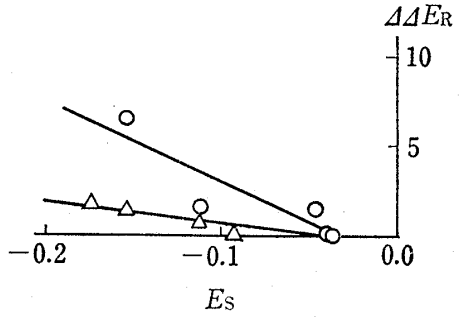

Fig. 2. $\Delta\Delta E_R$ and E_S
○: amines, △: alcohols

Electronic Factor

The S values were examined with respect to the polar substituent constants σ^* of kinetic origin, because these parameters are believed to be the scale of the inductive effect. It was

Table III. Intercepts A_s and Slopes B_s of Amines and Alcohols and Relative Weights

		$\Delta\Delta E_R$		E_S	
		Amine	Alcohol	Amine	Alcohol
A_S	$S\alpha$	28.9(1.00)	7.77(1.00)	33.9(1.00)	9.78(1.00)
	$S\beta$	11.6(0.40)	5.02(0.65)	16.6(0.49)	5.37(0.55)
	$S\gamma$		3.47(0.45)	13.8(0.38)	4.37(0.45)
B_S	$S\alpha$	0.21(1.00)	0.44(1.00)	0.87(1.00)	0.58(1.00)
	$S\beta$	0.16(0.76)	0.14(0.32)	0.60(0.70)	0.21(0.36)
	$S\gamma$		0.30(0.68)	1.08(1.24)	0.36(0.67)

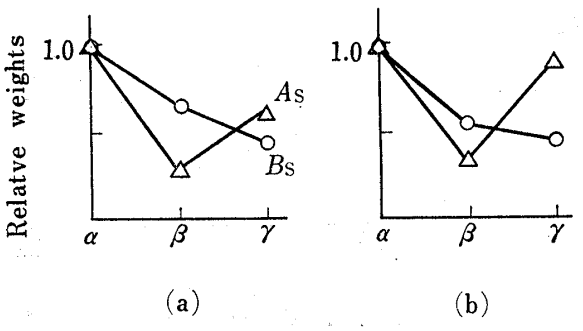

Fig. 3a—b Relative Weights A_s and B_s of α, β, and γ positions of Simple Aliphatic Amines and Alcohols
(a): amines, (b): alcohols

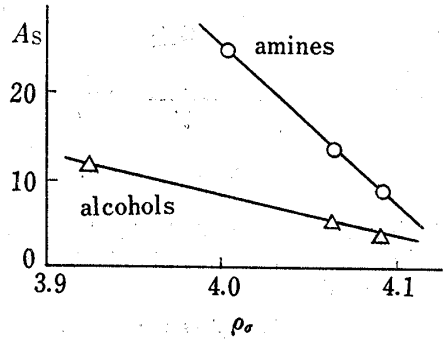

Fig. 4. Correlations between A_S *vs.* *Sigma* Charge Densities ρ_σ of Simple Aliphatic Amines and Alcohols
○: amines, △: alcohols

6) G. Miyajima, H. Akiyama and K. Nishimoto, *Org. mag. Res.*, **4**, 811 (1972).

found that values of σ^* are correlated with σ',[7] obtained from the equilibrium constants, by the following equation.

$$\sigma' = 0.45\sigma^* \qquad \sigma' = 1/1.464 \log K/K_0$$

K, K_0=Dissociation constants of 4-substituted bicyclo-[2,2,2]-octane-1-carboxylic acids

From the above reasons, the parameter σ^* could be used as measures of the chemical equilibrium. The observed log S values of aliphatic amines and alcohols are correlated with σ^* as shown in Fig. 5a—b.

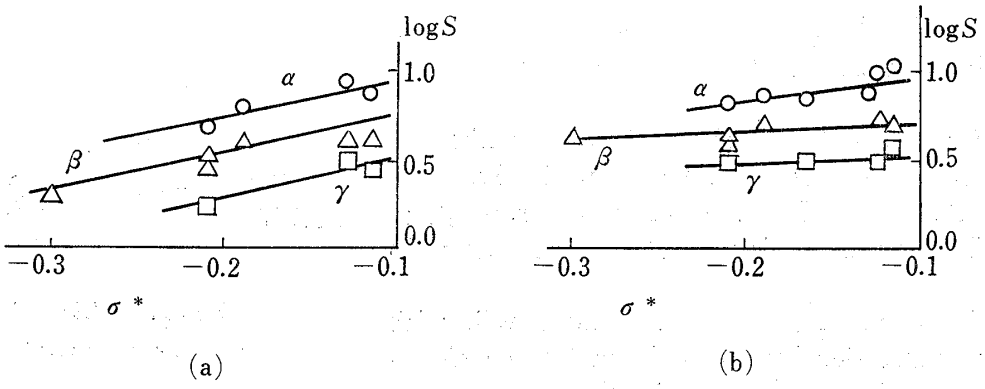

Fig. 5a—b. Correlations between log S of α, β, and γ-H Aliphatic Amines and Alcohols and Polar Substituent Constant σ^*

(a): amines, (b): alcohols

The linear relations in Fig. 5a and 5b show that S values could be expressed as follows;

$$S = A_i \cdot e^{+B_i \times \sigma^*}$$

The intercepts A_i and slopes B_i, summarized in Table IV, show analogous trends to those described in the previous section (*cf.* Fig. 6a—b).

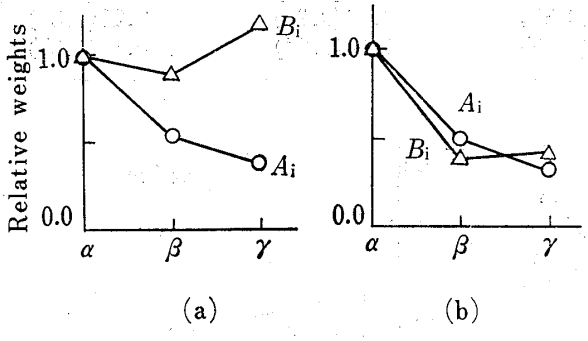

Fig. 6. Relative Weights A_i and B_i of α, β, and γ Positions of Simple Aliphatic Amines and Alcohols

(a): amines, (b): alcohols

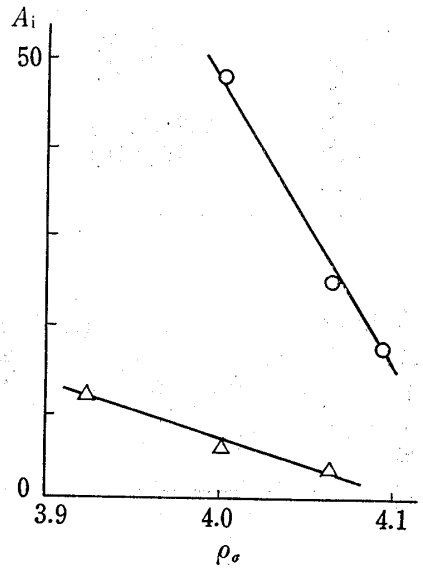

Fig. 7. Correlations between A_i *vs. Sigma* Charge Densities of Simple Aliphatic Amines and Alcohols

○: amines, △: alcohols

7) J.D. Roberts and W. Moreland, Jr., *J. Am. Chem. Soc.*, **75**, 2167 (1953).

TABLE IV. Intercepts A_i and Slopes B_i of Amines and Alcohols and Relative Weights

		Amine	Alcohol
A_i	$S\alpha$	47.9(1.00)	12.30(1.00)
	$S\beta$	25.2(0.53)	6.03(0.49)
	$S\gamma$	17.8(0.37)	3.90(0.32)
B_i	$S\alpha$	4.74(1.00)	3.02(1.00)
	$S\beta$	4.19(0.88)	1.18(0.39)
	$S\gamma$	5.46(1.15)	1.27(0.42)

The intercepts A_i represent the contributions from the unperturbed state or from the state of maximum contribution of the hyperconjugation effect, and correspond well with the σ change densities (*cf.* Fig. 7).

On the other hand, the slopes indicate the contributions from the perturbed state, and show a zig-zag analogous to those in Fig. 3a—b.

These results show that the S values decrease exponentially with increase in $\Delta\Delta E_R$ or σ^*, indicating the additive contributions of these two factors, operating in the same direction.

Solvent Effect on *n*-PrOH

The solvent effects, examined in CCl_4 (ε=2.20), C_6H_{12} (ε=1.99), $CDCl_3$ (ε=4.55) and CH_2Cl_2 (ε=9.08), gave the S values and log S values summarized in Table V. The latter were linearly related with $1-1/\varepsilon$, as shown in Fig. 8.

TABLE V. S Values and log S Values of *n*-Propyl Alcohol in Various Solvents

	α-H	β-H	γ-H
C_6H_{12}	12.3(1.09)		5.0(0.70)
CCl_4	12.0(1.08)	6.6(0.82)	4.4(0.65)
$CDCl_3$	10.4(1.02)	5.1(0.71)	3.8(0.58)
CH_2Cl_2	9.3(0.97)	5.6(0.75)	3.1(0.50)

TABLE VI. Intercepts $A_{solv.}$, Slopes $B_{solv.}$ and Relative Weights of Solvent Effects on *n*-Propyl Alcohol

	α-H	β-H	γ-H
$A_{solv.}$	17.7(1.00)	8.70(0.49)	7.4 (0.42)
$B_{solv.}$	0.69(1.00)	0.58(0.84)	1.13(1.64)

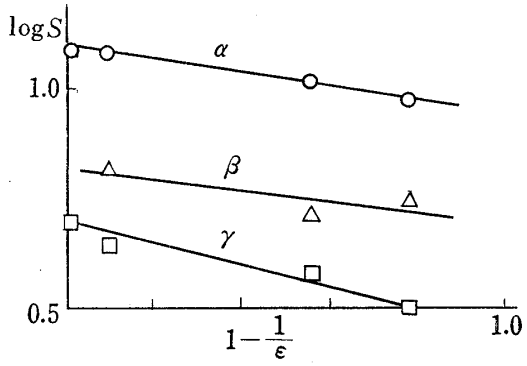

Fig. 8. Correlations between log S Values of α-, β-, and γ-H of *n*-Propyl Alcohol and $1-1/\varepsilon$

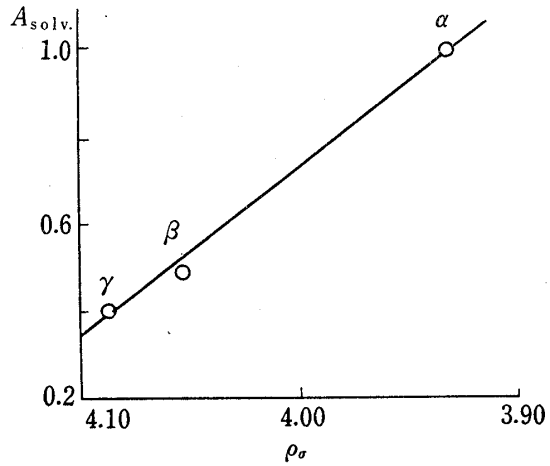

Fig. 9. $A_{solv.}$ and ρ_σ of Propyl Alcohol

The linear relations in Fig. 8, show that the contributions of the solvent effects to S values can be expressed as follows;

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

The intercepts $A_{\text{solv.}}$ and slopes $B_{\text{solv.}}$ are analogous with the results reported in the previous sections. Namely, the intercepts $A_{\text{solv.}}$, comparable with the *sigma* charge densities (*cf.* Fig. 9), refer to the state without medium, whereas $B_{\text{solv.}}$ refer to the perturbed state where medium effects operate.