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Shift Parameter Induced by Tris (dipivalomethanato) Europium and Steric Strain Energies of Aliphatic Amines

Treatment of organic molecules having a lone pair of electrons on a nitrogen atom with tris (dipivalomethanato) europium, $Eu(DPM)_3$,[1] is known to induce a paramagnetic shift of the proton magnetic resonance spectrum. The magnitude of the induced shift is thought to depend on the angle and spatial distance of the pseudocontact interaction. However, an anomalous shift observed for a proton situated two or three bonds from the coordination site is affected by a contribution due to an additional contact term.[2a,b] This communication reports the induced shift parameters, S values,[3] of simple aliphatic amines in dilute $CDCl_3$ solution at 34°. (*cf.* Table I). Values are compared with the steric strain energies, $\Delta\Delta E_R$, of amine-BMe_3 addition compounds[4a-c] (*cf.* Table II), because these two parameters can be expected to reflect an analogous mode of reaction. The correlations between the S values and steric strain energies of these addition compounds are shown in Fig. 1. This curve suggests

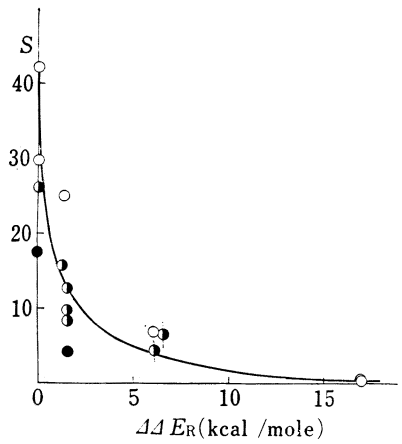

Fig. 1. Correlations between S Values and Steric Strain Energies, $\Delta\Delta E_R$, of Simple Aliphatic Amines

○: S_α; ◑: S_β; ●: S_γ

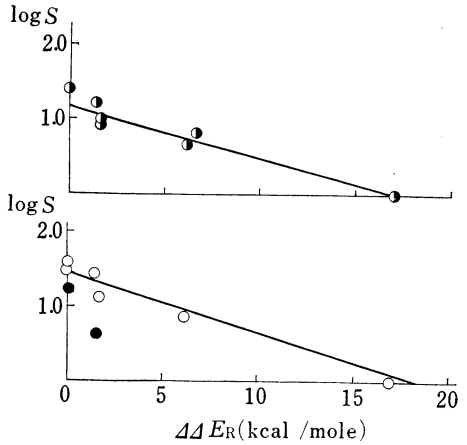

Fig. 2. Correlations between log$S$ and Steric Strain Energies, $\Delta\Delta E_R$, of Simple Aliphatic Amines

○: S_α; ◑: S_β; ●: S_γ

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

Amine	S_α	S_β	S_γ
n-$C_3H_7NH_2$	42.0	26.0	17.5
n-$C_4H_9NH_2$	29.5		
iso-$C_3H_7NH_2$	25.0	15.5	
s-$C_4H_9NH_2$	12.5	Me 9.5	4.0
		CH_2 8.0	
t-$C_4H_9NH_2$		6.5	
Et_2NH	7.0	4.5	
Et_3N	0	0	

1) C.C. Hinckley, M.R. Klotz, and F. Patil, *J. Am. Chem. Soc.*, **93**, 2417 (1970).
2) *a*) G.H. Wahl, Jr., and M.R. Peterson, Jr., *Chem. Comm.*, **1970**, 1167; *b*) C.C. Hinckley, *J. Am. Chem. Soc.*, **93**, 2417 (1971).
3) A.F. Cockerill and D.M. Rackham, *Tetrahedron Letters*, **1970**, 5149, 5153.
4) *a*) H.C. Brown, M.D. Taylor, and S. Sujishi, *J. Am. Chem. Soc.*, **73**, 2464 (1951); *b*) H.C. Brown and K. Barbaras, *J. Am. Chem. Soc.*, **75**, 6 (1953); *c*) R.W. Taft, Jr., *J. Am. Chem. Soc.*, **75**, 4534 (1953).

TABLE II. Steric Strain Energies, $\Delta\Delta E_R$, (kcal/mole) of Amine-BMe_3 Addition Compounds

Amine	$\Delta\Delta E_R$ kcal/mole
n-$C_3H_7NH_2$	0.0
n-$C_4H_9NH_2$	0.0
iso-$C_3H_7NH_2$	1.4
s-$C_4H_9NH_2$	1.6
t-$C_4H_9NH_2$	6.6
Et_2NH	6.1
Et_3N	17

that the S value is an exponential function of $\Delta\Delta E_R$, and log S is linearly related to $\Delta\Delta E_R$, as shown in Fig. 2. These relations can be expressed by the following empirical equations:

$$S_\alpha = 28.9\, e^{-0.21\Delta\Delta E_R} \qquad S_\beta = 11.6\, e^{-0.16\Delta\Delta E_R}$$

where S_α and S_β= Shift parameters of α- and β-H, respectively, induced by Eu(DPM)$_3$
$\Delta\Delta E_R$= Steric strain energy (kcal/mole) of the amine-BMe_3 addition reaction

Thus there seems to be an analogy between the coordination scheme of the shift reagent and BMe_3 on the lone pair of electrons on the nitrogen, and the contribution of the steric strain is probably a major factor in determining the magnitude of the S value. Details of this works will be published elsewhere.

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Enzymic Synthesis of 2-Alanyl-3-isoxazolin-5-one from O-Acetylserine and Isoxazolin-5-one by Pisum Seedling Extracts

In recent years two UV-sensitive heterocyclic amino acids, that may be regarded as β-substituted alanines, have been isolated by Lambein, *et al.* from pea (*Pisum sativum*) seedlings.[1,2] These amino acids are not present in the dry seeds, but they can be detected after germination for two or three days. The structures assigned on the basis of chemical and spectroscopic methods were 2-alanyl-3-isoxazolin-5-one (I) and 2-(β-D-glucopyranosyl)-4-alanyl-3-isoxazolin-5-one.

1) F. Lambein, N. Schamp, L. Vandendriessche, and R. Van Parijs, *Biochem. Biophys. Res. Comm.*, **37**, 375 (1969).
2) F. Lambein and R. Van Parijs, *Biochem. Biophys. Res. Comm.*, **40**, 557 (1970).