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Studies on the Proton Magnetic Resonance Spectra in Aliphatic Systems. V.[1] Tris(dipivalomethanato)europium Induced Shift Parameters of Aliphatic Amines and Alcohols

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The induced paramagnetic shift parameters, S values, of simple aliphatic amines and alcohols, and the α-substituted propane and β-substituted ethanol series were measured at a mole ratio of Eu(DPM)$_3$/ligand in CDCl$_3$ of below 0.10. The S value is a measure of the equilibrium between the shift reagent and ligand, for which the steric and electronic effects are responsible, and is expressed by the equation, $S=A.\ e^{-B\Delta E}$ where $\Delta E=\Delta E_{\text{elect}}+\Delta E_{\text{steric}}$

Introduction

In the preceding communication,[3] the tris(dipivalomethanato)europium Eu(DPM)$_3$ induced paramagnetic shift parameters, S values, of aliphatic amines were examined with respect to the steric strain energies, $\Delta\Delta E_R$, of amine–BMe$_3$ addition reactions.[4a,b] The linear relations found between log S and $\Delta\Delta E_R$ suggested that the contribution of the steric strain energies was largely responsible for the estimated S values. This result also suggests that there is an analogous equilibrium reaction between metal–ligand complex formation and the amine–BMe$_3$ addition reaction. In this work, simple aliphatic amines and alcohols were examined from the view point of steric strain energies and polar effects, and reasonable results were obtained.

Experimental

All materials were purchased commercially. They were of J.I.S. grade, and were used without further purification. All spectra were measured in an Hitachi R-20A type spectrometer (solvent, CDCl$_3$; int. ref., SiMe$_4$) at 34°. The induced paramagnetic shift parameters, S values, were obtained from the slopes of the linear relations of the induced shifts *vs.* Eu(DPM)$_3$/ligand mole. ratios below 0.10, where the ligand concentrations were 0.3 mole. Some examples are presented in Fig. 1a, b and Fig. 2a, b.

Result and Discussion

Aliphatic Amines

The S values of the simple aliphatic amines examined are summarized in Table I. The coordination of the shift reagent on the nitrogen lone pair electrons is a typical equilibrium reaction of acid and base, and the chelation of the shift reagent on the nitrogen atom resembles the mode of the amine–BMe$_3$ addition reaction. Formerly, Brown, *et al.*[4] estimated the steric strain energies, $\Delta\Delta E_R$ (*cf.* Table II) of the above reactions. In this work, we compared the S values of aliphatic amines with the corresponding $\Delta\Delta E_R$ values, and exponential rela-

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[1] Part IV: Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **18**, 1478 (1970).

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[3] Y. Sasaki, H. Kawaki, and Y. Okazaki, *Chem. Pharm. Bull.* (Tokyo), **21**, 917 (1973).

[4] *a*) H.C. Brown, M.D. Taylor, and S. Sujishi, *J. Am. Chem. Soc.*, **73**, 2464 (1951); *b*) H.C. Brown and G.K. Barbaras, *ibid.*, **75**, 6 (1953).

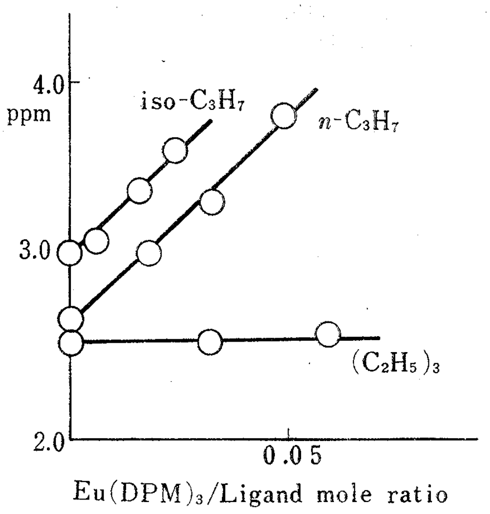

Fig. 1-a Correlations between α-H Chemical Shifts of Aliphatic Amines and Eu(DPM)$_3$/Ligand Mole Ratios

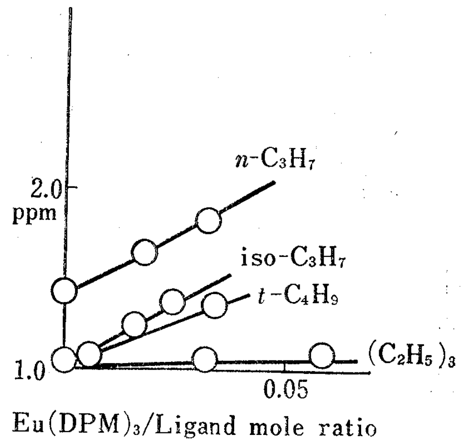

Fig. 1-b Correlations between β-H Chemical Shifts of Aliphatic Amines and Eu(DPM)$_3$/Ligand Mole Ratios

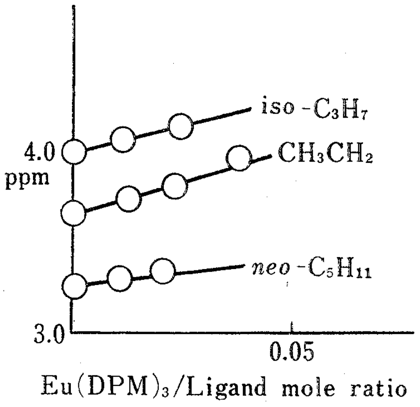

Fig. 2-a Correlations between α-H Chemical Shifts of Aliphatic Alcohols and Eu(DPM)$_3$/Ligand Mole Ratios

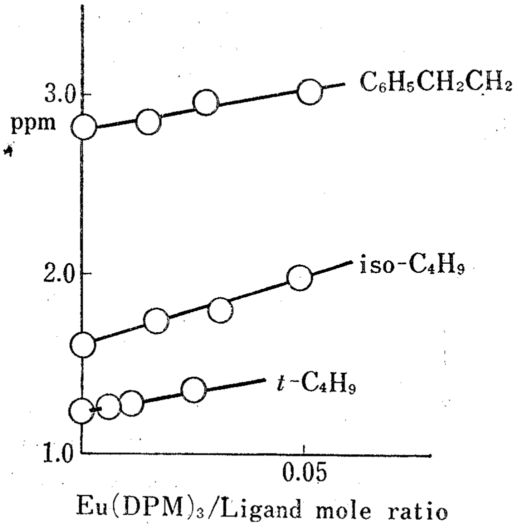

Fig. 2-b Correlations between β-H Chemical Shifts of Aliphatic Alcohols and Eu(DPM)$_3$/Ligand Mole Ratios

TABLE I. Eu(DPM)$_3$ Induced Shift Parameters, S Values, of Simple Aliphatic Amines, RNH_2, R_2NH and R_3N

R	S_α	S_β	S_γ	S_δ
n-C_3H_7	23.5	13.5	8.5	
iso-C_3H_7	21.5	12.5		
n-C_4H_9	28.5	13.0	9.9	5.0
iso-C_4H_9	28.0	17.5	9.0	
sec-C_4H_9	12.5	Me 9.5	4.0	
		CH_2 8.0		
t-C_4H_9		6.5		
Et_2NH	7.0	4.5		
Et_3N	0	0		

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

Amine	$\Delta\Delta E_R$kcal/mole	Amine	$\Delta\Delta E_R$ kcal/mole
n-C_3H_7	0.0	*sec*-C_4H_9	1.6
iso-C_3H_7	1.4	t-C_4H_9	6.6
n-C_4H_9	0.0	Et_2	6.1
iso-C_4H_9	—	Et_3	17

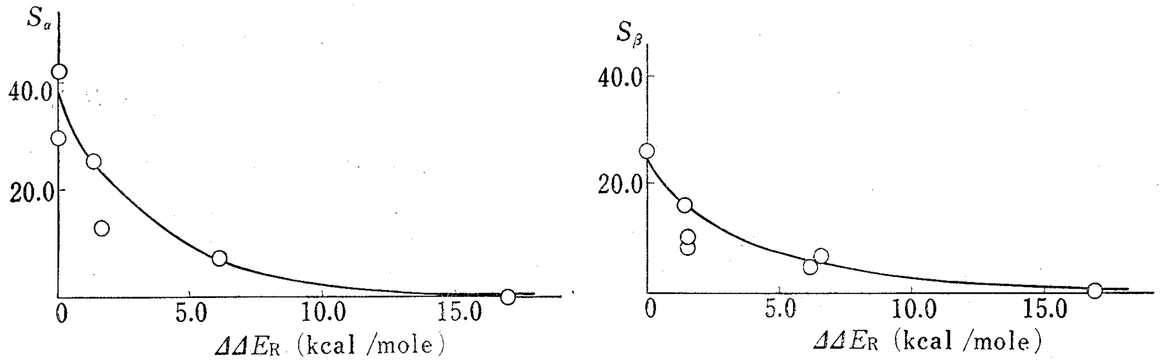

Fig. 3. Correlations between Shift Parameters S_α and S_β of Simple Aliphatic Amines and Steric Strain Energies, $\Delta\Delta E_R$ (kcal/mole)

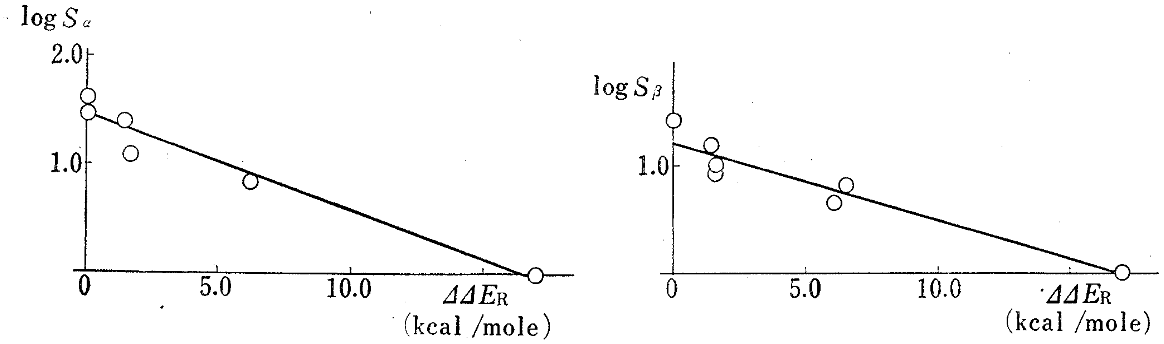

Fig. 4. Correlations between Shift Parameters log S_α and log S_β of Simple Aliphatic Amines and Steric Strain Energies $\Delta\Delta E_R$ (kcal/mole)

tions were observed (*cf.* Fig. 3), which were also plotted as linear relations between log S and $\Delta\Delta E_R$ (*cf.* Fig. 4). The empirical equations for α- and β-H are expressed as follows:

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

where S_α and S_β are the S values of α- and β-H. A few years ago, the abnormal induced shift observed for H-1 situated 2- or 3-bonds away from the coordination site was suggested to be due to an additional contact term[5a,b] together with the pseudocontact term. In the present work, we were unable to identify the induced contact term with the steric strain energy, but results suggested that the steric factor is important in the equilibrium reaction between the shift reagent and the nitrogen lone pair electrons.

Aliphatic Alcohols

The S values of simple aliphatic alcohols are summarized in Table III. The exponential plots of S values with respect to the steric strain energies, $\Delta\Delta E_R$, of aliphatic alcohols[6] (*cf.*

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5) *a*) G.W. Wahl, Jr. and M.R. Peterson, Jr., *Chem. Comm.*, 1970, 1167; *b*) C.C. Hinckley, *J. Am. Chem. Soc.*, 93, 2417 (1971).

6) R.W. Taft, Jr., *J. Am. Chem. Soc.*, 75, 4536 (1953).

TABLE III. Eu(DPM)$_3$ Induced Shift Parameters, S Values, of Simple Aliphatic Alcohols, ROH

R	S_α	S_β	S_γ
n-C_3H_7	9.5	5.0	3.5
iso-C_3H_7	9.5	5.5	
iso-C_4H_9	11.5	7.5	4.0
sec-C_4H_9	5.5	4.0	3.5
		4.0	
t-C_4H_9		4.5	
neo-C_5H_{11}	3.5		2.0
C_2H_5	7.5	4.0	
$PhCH_2CH_2$	7.0	4.5	

TABLE IV. Sterric Strain Energies, $\Delta\Delta E_R$ (kcal/mole), of Aliphatic Groups in Rates of Esterification and Hydrolysis

Alcohol	$\Delta\Delta E_R$ kcal/mole	Alcohol	$\Delta\Delta E_R$ kcal/mole
C_2H_5	0.0	sec-C_4H_9	0.5
n-C_3H_7, n-C_4H_9	0.0	t-C_4H_9	1.4
iso-C_3H_7	0.0	neo-C_5H_{11}	1.8
iso-C_4H_9	0.0	$PhCH_2CH_2$	0

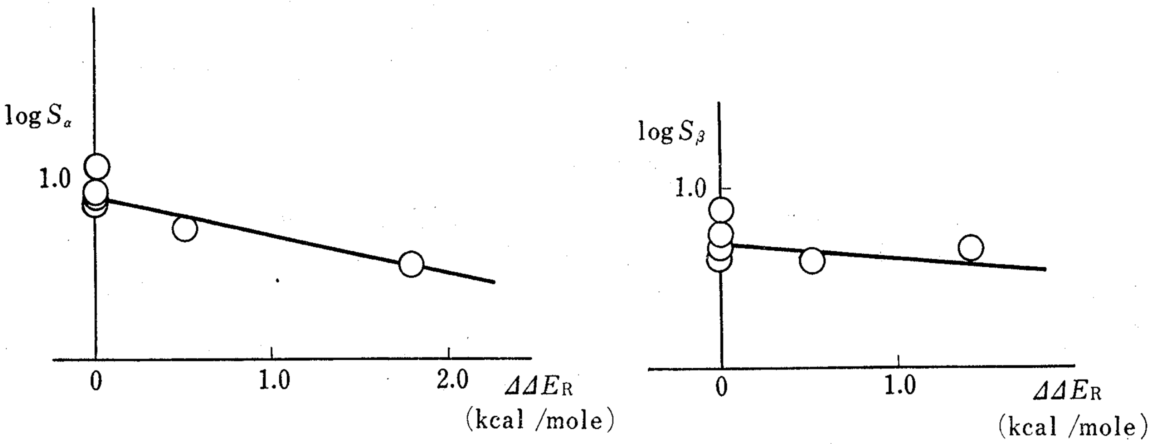

Fig. 5. Correlations between log S_α and log S_β and Steric Strain Energies, $\Delta\Delta E_R$ (kcal/mole), of Aliphatic Groups

Table IV), which are about 1/4 of those of aliphatic amines, were also found to give linear relations between log S and $\Delta\Delta$ E_R (*cf.* Fig. 5), and the following empirical equations were obtained:

$$S_\alpha = 8.22e^{-0.50\Delta\Delta E_R} \qquad S_\beta = 4.98e^{-0.15\Delta\Delta E_R}$$

where S_α and S_β are the S values of α- and β-H.

S Value Ratio of Amines and Alcohols

The steric strain energies of alkyl groups in the rates of esterification and ester hydrolysis were presented by Taft.[6] These parameters were equivalent to 1/4 of those proposed for the amine–BMe$_3$ addition reaction. The S values of amines and alcohols with the same steric requirements were compared, and linear relations were obtained, as shown in Fig. 6. The slopes of these linear relations are ~4.0. This result affords positive support for the kinetical evidence. From these results and the experimental results in the previous sections,

Table V. Eu(DPM)$_3$ Induced Shift Parameters, S Values, of α-, β- and γ-Protons of α-Substituted Propane Derivatives

Substituent	Chemical shift (ppm)			S value		
	α	β	γ	α	β	γ
NH_2	2.66	1.48	0.93	23.5	13.5	8.5
OH	3.60	1.60	0.94	9.5	5.0	3.5
CN	2.25	1.65	1.05	2.5	2.0	1.0
NO_2	4.32	2.00	1.00	0	0	0

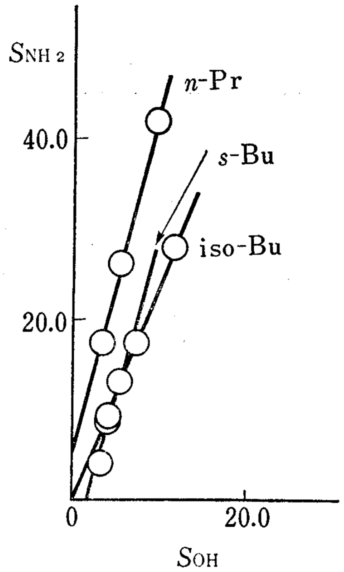

Fig. 6. Correlations between Shift Parameters, S Values, of Aliphatic Amines, S_{NH_2}, and Those of Aliphatic Alcohols, S_{OH}, with Same Alkyl Residues

we can conclude that the S value is a measure of the steric strain energy of the metal–ligand addition reaction.

α-Substituted Propane Derivatives

The H-1 chemical shifts and S values of various α-substituted propane derivatives ($MeCH_2CH_2R$: R=NH_2, OH, CN, NO_2) are summarized in Table V. Linear relations were observed between their S values, as shown in Fig. 7. As the $\Delta\Delta E_R$ of n-propyl groups are ~0.0, the slopes observed in Fig. 7 represent the relative weights of equilibrium of the coordination reactions. The following empirical equations were deduced from the linear relations between log S and the substituent constants, σ_i.⁷⁾ (*cf.* Fig. 8).

$$S_\alpha = 14.0e^{-8.05\sigma_i} \quad S_\beta = 11.9e^{-6.20\sigma_i} \quad S_\gamma = 10.7e^{-5.06\sigma_i}$$

Introducing the condition $\Delta E_i = C.\ \sigma_i$, where C=a collection of constants, the above equations can be written as follows:

$$S_\alpha = 14.0e^{-8.05\Delta E_i/C} \quad S_\beta = 11.9e^{-6.20\Delta E_i/C}$$

$$S_\gamma = 10.7e^{-5.06\Delta E_i/C}$$

The substituent constant σ_i and the corresponding energy ΔE_i are measures of the contributions of the field effect —the electrostatic interaction through space between the shift reagent and the ligand molecule — and manifest the σ-charge delocalization. These trends are supported by the σ-delocalization mechanism, and are expressed best by an electrostatic potential model, where the magnitude of the shift decreases with the reciprocal of the distance between the coordination site and the metal ion.

β-Substituted Ethanol Derivatives

Based on the above considerations, the steric strain energies of the β-substituted ethanol series RCH_2CH_2OH (R=NMe_2, OMe, Me, H, Cl, Br, Ph, CN) are assumed to be negligible. The H-1 chemical shifts and the induced shift parameters are summarized in Table VI. As shown in Fig. 9a, the H-1 chemical shifts of the α positions are linearly related with the substituent constants σ_i, whereas those of the β-positions are regular, except with a substituent group without a magnetic anisotropy effect, and the S values are related roughly exponentially with σ_i (*cf.* Fig. 9b).

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7) Y. Yukawa and Y. Tsuno, *Nippon Kagaku Zasshi*, **86**, 873 (1965).

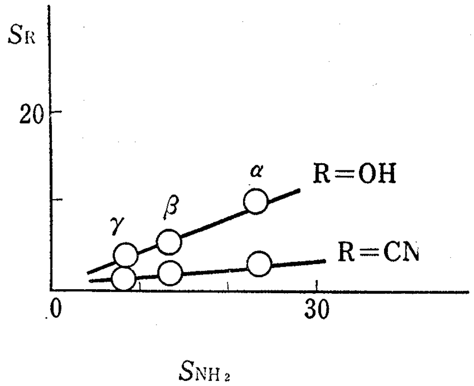

Fig. 7. Correlations between S Values of α-, β- and γ-H of Propyl Alcohol and Butyronitril and Those of Propylamine

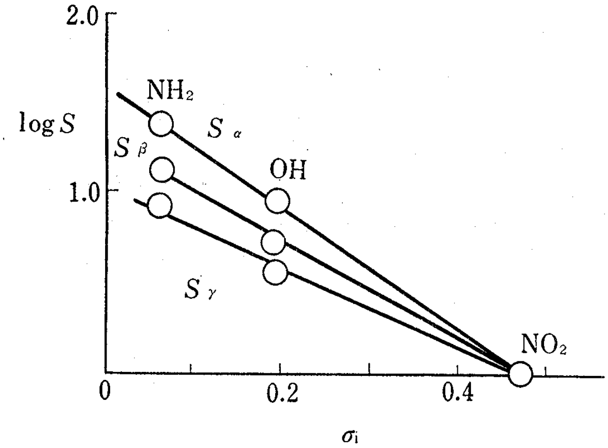

Fig. 8. Correlations between log S of α-, β- and γ-H of α-Substituted Propane Derivatives and Substituent Constants, σ_i

TABLE VI. Chemical Shifts and $Eu(DPM)_3$ Induced Shift Parameters, S Values, of α- and β-Protons of β-Substituted Ethanol Derivatives

Substituent	Chemical shift (ppm)		S value	
	α	β	α	β
Me	3.55	1.54	9.5	5.0
NMe_2	3.59	2.41	5.5	5.5
OMe	3.63	3.52	4.5	3.5
Br	3.90	3.50	4.0	2.5
Cl	3.83	3.65	16.0	8.5
CN	3.83	2.53	4.5	3.0
Ph	3.80	2.80	7.0	4.5
H	3.70	1.20	7.5	4.0

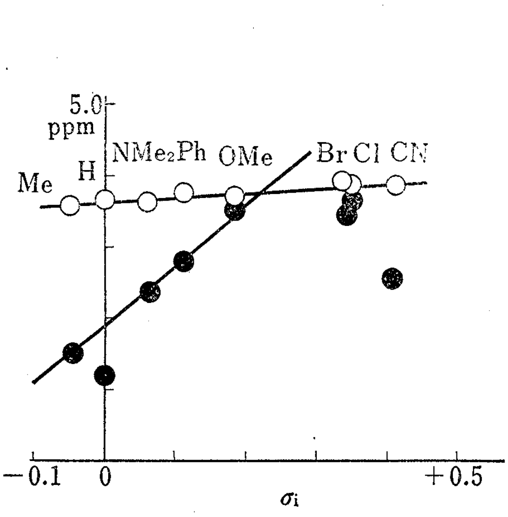

Fig. 9-a. Correlations between α- and β-H Chemical Shifts of β-Substituted Ethanol Derivatives and Substituent Constants, (○: α-H, ●: β-H) Ph=phenyl

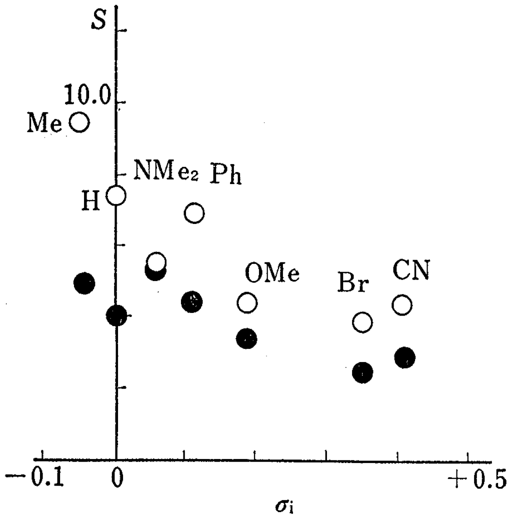

Fig. 9-b. Correlations between S Values of α- and β-H of β-Substituted Ethanol Derivatives and Substituent Constants, (○: α-H, ●: β-H) Ph=phenyl

Conclusion

The induced paramagnetic shift parameters, S values, due to $Eu(DPM)_3$ of aliphatic amines and alcohols with a varieties of steric conditions, but similar electronic conditions were expressed by the equation, $S=A.\,e^{-B\Delta E}$, where $\Delta\,E$=a steric strain energy term. A contribution from the field effect or delocalization effect of the sigma charge densities is highly probable for the aliphatic series with similar steric but variable electronic conditions. These results provide interesting information on the origin of the so-called pseudocontact effect due to the lanthanide shift reagent.