Quantitative Estimates of π-Contact-term Contributions to the Lanthanide-induced Paramagnetic ^{1}H Shifts in Aniline and *m*-Toluidine

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The paramagnetic proton chemical shifts induced by a series of Ln(FOD)$_3$(Ln=Pr, Eu, Dy, Ho, Er, and Yb) were observed for aniline and *m*-toluidine in CCl$_4$. In an attempt to separate the pseudo-contact(pcs) and contact shift(cs) contributions, the spin-density distributions of the π-cation radicals or the Ni(AcAc)$_2$-induced shifts were used for the cs pattern in a molecule, as well as the geometric factors for the pcs pattern. The appropriate regions of the two geometric parameters were determined by the computer-search method for the least-squares fits of the observed to the calculated shifts. Thus, the intramolecular average value of the ratio of cs-to-pcs contributions was evaluated. The variation in this ratio with an Ln ion corresponds relatively well to that of the theoretical ratio, $|\langle S_z\rangle/|\delta||$, where $\langle S_z\rangle$ has been calculated by Golding *et al.* and where δ is the relative pcs predicted by Bleaney *et al.*

There have been a number of reports showing that the contribution of the contact shift(cs) to the lanthanide-induced shifts(LIS's) may be considerable for protons as well as for ^{13}C and ^{31}P. However, most of the discussions of cs contributions have been qualitative.[1] It has recently been reported in studies of the temperature dependence of LIS's that the term proportional to $1/T$ can be separated from the term depending on $1/T^2$ on the basis of Bleaney's theory[2] and that it leads to the cs contribution for all the complexes except for those of Eu^{3+} and Sm^{3+}.[3] With a correction for the temperature effect on the equilibrium between an Ln complex(Ln=lanthanide metal) and a substrate, this method may be valuable for the determination of the cs contribution. On the other hand, the determination of the molecular structure and the conformation analysis due to the use of LIS have been made in terms of a computer search for the best fit of the calculated geometric factors to the observed paramagentic shifts.[4] These searches are based on the fact that a true pattern of pseudo-contact shifts(pcs) can be calculated if a ligand molecule includes several or more nuclei having only pcs almost entirely. Therefore, these searches are limited to the σ-compounds, in which there is a cs contribution only in some atoms close to a coordinating atom. In such a molecule, the σ-cs contribution can be calculated as the difference between the observed shift and pcs.[5] However, for aromatic molecules with cs at almost all atoms, the above procedure cannot be applied, and a relative cs(a cs pattern) in a molecule is required for a quantitative separation of the two contributions. Three possible sources of cs pattern are: (1) Gd(III)-induced shifts,[6] (2) Ni(AcAc)$_2$-induced shifts(NIS's), and (3) a theoretically estimated pattern. While (1) may not be used for ^{1}H because of the long T_1 of the electron spin,[7] an attempt has been made to use (2)[8] or (3). The results from (3) seem to be unsatisfactory.[9]

In a previous paper,[10] our procedure for estimating the cs contribution has been outlined. This report will describe in detail an attempt at separation by using the cs patterns obtained from a π-spin density distribution of a cation radical and NIS for both aniline and *m*-toluidine. In the present study, the agreement factor, R,[11] between the observed and calculated shifts was satisfactorily small for the adducts with all the Ln(FOD)$_3$* substances used here. In order to check the validity of our procedure for the separation of the two contributions, the relative cs contribution thus evaluated was compared to the $\langle S_z\rangle$ value reported by Golding *et al.*[12] for the six Ln chelates studied here, and a comparatively good correspondence was thus obtained. The separated pcs contribution led to a good linear relation to the relative value of Bleaney's pcs.[2]

Experimental

Aniline and *m*-toluidine were purified by vacuum distillation from zinc dust and were dried over barium oxide in the dark. CCl$_4$(Spectro grade) was used as the solvent without further purification. The Ln(FOD)$_3$ complexes were prepared according to the method of Springer, Jr., Meek and Sievers,[13] except for the Pr, Eu, and Yb complexes, which were obtained commercially. Particular care was taken for all the substrates used to ensure anhydrous conditions, since the observed shifts are very sensitive to traces of moisture. The solutions were *ca.* 0.5 M in the substrates. The amount of Ln(FOD)$_3$ or Ni(AcAc)$_2$ was continuously varied up to a Ln(FOD)$_3$- or Ni(AcAc)$_2$-substrate molar ratio of about 0.2. The NMR spectra were recorded with a Hitachi R-20A spectrometer at 60 MHz at a probe temperature of 34 °C, operating in the frequency-swept mode, using TMS as the internal standard.

Results and Discussion

In many lanthanide shift experiments, it has become customary to consider only one step of equilibrium with a sufficiently rapid exchange:

$$L + A \rightleftharpoons LA \qquad K_1 = \frac{[LA]}{[A]\cdot[L]} \tag{1}$$

and to use the shift characteristic of a 1 : 1 adduct (δ_1) obtained from the linear extrapolation of $[L_0]/[A_0] = R_L$ to 1, on the basis of the idea that the observed shift is approximately equal to $R_L\cdot\delta_1$ if $R_L \ll 1$ and $K_1 \gg 1$, where A and L are a substrate and an Ln chelate respectively, and where $[L_0]$ and $[A_0]$ are the total concentrations of L and A. However, it was recently found in low-temperature experiments that two mole-

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* FOD=1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl octane-4,6-dione.

cules of $(CH_3)_2SO$ coordinate to $Eu(FOD)_3$ in CD_2Cl_2.[14] Also, considering a second equilibrium for the *n*-hexyl amine–$Eu(FOD)_3$ system in $CDCl_3$,

$$LA + A \rightleftharpoons LA_2 \qquad K_2 = \frac{[LA_2]}{[LA][A]} \tag{2}$$

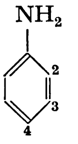
an attempt has been made to determine K_1, K_2, δ_1, and the shift characteristic of a 1 : 2 adduct (δ_2) from the least-squares fits.[15]

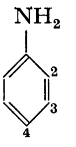
In the present investigation, δ_2 is assumed to be approximately equal to δ_1 in magnitude;[16] consequently, if $K_1 \gg 1$ and $R_L \ll 1$, the observed LIS (S) is formulated as Eq. (3):

$$S = \delta_1 \cdot R_L \frac{1+2K_2 \cdot [A_0]}{1+K_2 \cdot [A_0]} \tag{3}$$

K_1 may be expected to be sufficiently large. Actually, we obtained an apparent linearity between the observed shifts and R_L at sufficiently low values of R_L in all the systems investigated in this work. The shift value

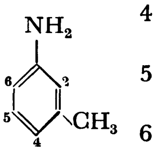
Table 1. The observed lanthanide-induced shifts and the separation of calculated shifts to cs and pcs contributions for aniline[a)]

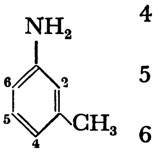
		Pr			Eu			Dy		
	Position	S_{obsd}[b)]	S_{calcd}[c)]		S_{obsd}[b)]	S_{calcd}[c)]		S_{obsd}	S_{calcd}[c)]	
			S_{pcs}	S_{cs}		S_{pcs}	S_{cs}		S_{pcs}	S_{cs}
	2	22.33	21.88 21.92	0.40 0.43	−16.07	−14.58 −14.44	−1.48 −1.59	185.0	185.55 186.43	−0.94 −1.00
	3	6.90	7.06 7.07	−0.15 −0.17	−4.00	−4.56 −4.66	0.56 0.65	62.3	62.03 61.81	0.36 0.41
	4	5.97	5.53 5.54	0.45 0.43	−5.23	−3.55 −3.65	−1.69 −1.59	47.8	48.95 48.70	−1.08 −1.00
	χ	46—50° 46—50°	d)		43—47° 45—50°	d)		49—54° 49—54°	d)	
	A	1729±69 1732±69			−1157±47 −1146±51			14576±578 14559±599		
	B	0.398±0.017[e)] 0.428±0.020			−1.480±0.031[e)] −1.589±0.026			−0.920±0.182[e)] −0.993±0.140		
	$\frac{\Sigma\vert S_{cs}\vert}{\Sigma\vert S_{pcs}\vert}$	0.024±0.001 0.026±0.001			0.137±0.003 0.146±0.003			0.007±0.002 0.007±0.001		

		Ho			Er			Yb		
	Position	S_{obsd}	S_{calcd}[c)]		S_{obsd}	S_{calcd}[c)]		S_{obsd}	S_{calcd}[c)]	
			S_{pcs}	S_{cs}		S_{pcs}	S_{cs}		S_{pcs}	S_{cs}
	2	60.84	61.78 62.06	−1.09 −1.16	−49.14	−47.31 −47.20	−1.72 −1.85	−30.83	−30.48 −30.33	−0.40 −0.43
	3	20.31	19.93 19.82	0.41 0.47	−14.60	−15.27 −15.37	0.65 0.76	−9.69	−9.83 −9.88	0.15 0.18
	4	14.35	15.61 15.50	−1.24 −1.16	−13.89	−11.96 −12.07	−1.96 −1.85	−8.17	−7.70 −7.75	−0.46 −0.43
	χ	46—49° 45—49°	d)		46—50° 47—51°	d)		46—50° 47—51°	d)	
	A	4900±175 4911±195			−3739±149 −3724±149			−2409±96 −2394±96		
	B	−1.077±0.062[e)] −1.156±0.066			−1.716±0.039[e)] −1.841±0.051			−0.403±0.025[e)] −0.430±0.025		
	$\frac{\Sigma\vert S_{cs}\vert}{\Sigma\vert S_{pcs}\vert}$	0.023±0.001 0.024±0.001			0.048±0.001 0.052±0.001			0.018±0.001 0.019±0.001		

a) All the S values are given in ppm. The observed shifts were corrected for CFS's observed with $La(FOD)_3$. The values in the second line are those calculated by using NIS as R_{cs}. Negative signs designate shifts to lower field. b) The data reported by M. Kainosho *et al.*, 12th NMR Symposium, 1973, Abstract, p. 107. c) The values giving rise to the minimum of R with $r_N = 2.7$ Å. d) The regions of some quantities on the restriction of R to less than 1% with a range of 2.6—2.8 Å for r_N. e) The sign of B coincides with that of the electron spin introduced into the ligand molecule.

TABLE 2. THE OBSERVED LANTHANIDE-INDUCED SHIFTS AND THE SEPARATION OF CALCULATED SHIFTS TO CS AND PCS CONTRIBUTIONS FOR *m*-TOLUIDINE a)

Position	Pr			Eu			Dy		
	S_{obsd}	S_{calcd} b)		S_{obsd}	S_{calcd} b)		S_{obsd}	S_{calcd} b)	
		S_{pcs}	S_{cs}		S_{pcs}	S_{cs}		S_{pcs}	S_{cs}
2	25.63	25.08 25.14	0.21 0.19	−15.53	−13.86 −13.75	−1.32 −1.38	227.2	222.50 224.26	−2.70 −3.08
 4	6.97	6.02 6.03	0.24 0.19	−5.17	−3.32 −3.39	−1.50 −1.38	59.6	56.89 56.68	−3.08 −3.08
5	8.29	7.75 7.77	−0.08 −0.08	−3.92	−4.28 −4.35	0.49 0.56	80.2	72.47 72.35	1.00 1.24
6	25.14	25.08 25.14	0.20 0.19	−14.83	−13.86 −13.75	−1.29 −1.38	214.4	222.50 224.26	−2.63 −3.08
CH_3	4.27	4.81 4.82	0.08 0.07	−2.94	−2.66 −2.73	−0.53 −0.49	39.4	46.37 46.05	−1.08 −1.09
χ	42—46° 42—46°		e)	42—46° 43—49°		e)	46—52° 46—52°		f)
A	1994±74 1999±76			1102±43 1090±53			17576±797 17873±1076		
B	0.220±0.067 c) 0.193±0.053			−1.322±0.015 c) −1.387±0.016			−2.660±0.716 c) −3.284±0.673		
$\frac{\sum\lvert S_{cs}\rvert}{\sum\lvert S_{pcs}\rvert}$	0.013±0.004 0.010±0.002			0.135±0.001 0.138±0.000$_5$			0.017±0.005 0.020±0.004		

Position	Ho			Er			Yb		
	S_{obsd}	S_{calcd} b)		S_{obsd}	S_{calcd} b)		S_{obsd}	S_{calcd} b)	
		S_{pcs}	S_{cs}		S_{pcs}	S_{cs}		S_{pcs}	S_{cs}
2	97.5	96.97 96.85	−2.99 −3.40	−59.2	−57.55 −57.34	−1.67 −1.71	−35.03	−34.58 −34.62	−0.07 −0.05
 4	22.5	24.75 24.76	−3.40 −3.40	−17.6	−14.55 −14.66	−1.90 −1.71	−8.56	−8.05 −8.05	−0.08 −0.05
5	34.5	31.53 31.55	1.10 1.37	−18.8	−18.57 −18.68	0.62 0.69	−10.82	−10.43 −10.44	0.03 0.02
6	90.0	96.79 96.85	−2.91 −3.40	−59.2	−57.55 −57.34	−1.63 −1.71	−34.39	−34.58 −34.62	−0.07 −0.05
CH_3	17.5	20.17 20.19	−1.20 −1.20	−11.4	−11.82 −11.95	−0.67 −0.60	−5.92	−6.38 −6.39	−0.03 −0.02
χ	47—52° 46—52°		f)	45—52° 45—53°		d)	39—45° 39—45°		d)
A	7613±307 7645±340			4533±223 4529±243			2760±129 2763±132		
B	−3.035±0.265 c) −3.382±0.323			−1.674±0.189 c) −1.729±0.167			−0.078±0.149 c) −0.062±0.133		
$\frac{\sum\lvert S_{cs}\rvert}{\sum\lvert S_{pcs}\rvert}$	0.044±0.004 0.047±0.005			0.040±0.005 0.041±0.004			0.004±0.004 0.004±0.004		

a), b), and c): See Footnotes a), c), and e) in Table 1, respectively. d) Values on the restriction of R to less than 3%. e) Values on the restriction of R to less than 3.5%. f) Values on the restriction of R to less than 4.5%.

obtained from the linear extrapolation of R_L to 1 is $\delta_1(1+2K_2[A_0])/(1+K_2[A_0])$; K_2 value is required in estimating the magnitude of δ_1. However, since the relative shift values are adequate for the estimation of the intramolecular ratio of the cs and pcs contributions, we used $\delta_1(1+2K_2[A_0])/(1+K_2[A_0])$ as S_{obs}. The S_{obs} values were corrected for the diamagnetic shifts due to complex formation (CFS's),1e) by using shifts induced by $La(FOD)_3$ in CCl_4; they are listed in Tables 1 and 2 for aniline and *m*-toluidine respectively, with Ln(FOD)$_3$ (Ln=Pr, Eu, Dy, Ho, Er, and Yb). It has been presumed that the geometry of such an adduct does not vary widely with an Ln ion. From this point of view, the variation in the S_{obs} ratios with an Ln ion seen in Tables 1 and 2 clearly shows the existence of a cs contribution.

Our procedure for separating the two contributions is as follows: At first, the calculated shift is taken as $S_{cal}=S_{pcs}+S_{cs}=A\cdot R_{pcs}+B\cdot R_{cs}$, where R_{pcs} is the geometric factor; R_{cs}, the cs relative to the 2 position, and A and B, the proportionarity constants. With the R_{pcs} and R_{cs} patterns in a molecule obtained by appropriate methods, the A and B values are determined by the least-squares technique and lead to S_{cal}. In order to assess the correspondence between S_{cal} and S_{obs}, the agreement factor, R,[11] is used as a good criterion. The dependence of R on the two geometric parameters χ and r_N (Fig. 1) required for determining R_{pcs} is conveniently displayed using contour lines on a map projection. Appropriate combinations of χ and r_N values are chosen, based on the mode of minimizing the R values in the contour plot, and on the validity of the molecular structure. From the amounts of S_{cs} and S_{pcs} corresponding to these values, the average intramolecular cs contribution to the pcs contribution, $\sum|S_{cs}|/\sum|S_{pcs}|$, is calculated. Here, if $K_2[A_0]\gg 1$, $S_{cs}/2$ and $S_{pcs}/2$ are the separated shifts corresponding to the δ_1 value.

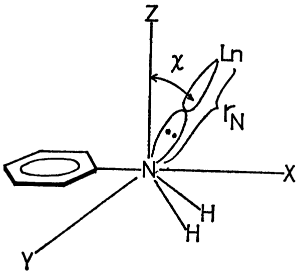


Fig. 1. Geometric parameters in the aniline adduct of Ln(FOD)$_3$.

McConnell-Robertson's equation[19] for axial symmetry was used in evaluating R_{pcs}, because, for such an adduct of the lanthanide chelate, this relation has been successfully used to interpret the dipolar shifts. Thus, the geometric factors were calculated with varying amounts of two geometric parameters, χ and r_N in the chemically reasonable ranges of 20—60°[20] and 2.0—4.0 Å respectively (Fig. 1). Here, since the Ln–N vector was assumed to be co-linear with a principal magnetic axis,[21] the rotation about the N–Ln bond did not need to be considered. The effect of rotation about the N–C bond was not introduced into the pcs calculations, because the N-lone pair orbital could be expected to conjugate with the π-MO of the ring to a great extent. For CH$_3$ protons, R_{pcs} was averaged over those values calculated for each 10° of rotation about the C–CH$_3$ bond.

Since the spin induced into the N-lone pair orbital may be expected to be delocalized predominantly through the π-bonds,[22] an approximate π-spin density distribution obtained by McLachlan's method[23] was used for the calculation of R_{cs}. There are four possible R_{cs} patterns occurring from the α- and β-spins in the highest occupied π-MO [h.o(α) and h.o(β)] and from the α- and β-spins in the lowest vacant π-MO [l.v(α) and l.v(β)]. It was found from a preliminary comparison of S_{obs} and S_{cal} that only the R_{cs} due to the h.o is effective in correcting the R_{pcs} pattern. This corresponds well to the fact that the h.o is symmetric to the molecular axis and can interact strongly with an AO of the metal ion. Furthermore, this preliminary testing suggested that the electron spin introduced into the h.o has a sign opposite to that of some Ln ions. For example, the h.o(β) is particularly excellent in explaining the observed relation, $|S(\beta\mathrm{H})|<|S(\gamma\mathrm{H})|$, for the aniline adduct of Eu(FOD)$_3$. Then, an intramolecular R_{cs} pattern was calculated from the π-spin density distribution of the cation radical[24] (ρ_c^π) of each substrate and was applied to all the Ln complexes (Table 3). The map projection of R for the aniline adduct is very similar in mode for all the Ln ions used here and does not reveal a single smooth minimum in R, an example with Eu(FOD)$_3$ being shown in Fig. 2(a). However, a very deep valley in R passes through a structurally favorable region in the map and, besides, varies in shape almost not at all with an Ln ion. This suggests that the π-approximation for R_{cs} is valid; further, that there seems to be no large variation in the geometry of an adduct with an Ln ion. Also, with the R_{cs} due to NIS's (Table 3), contour plots were produced for all the Ln ions, which are very similar in pattern to one another and, further, to those formed with ρ_c^π and which include sufficiently small values of R. The map projection prepared from the Ho(FOD)$_3$-induced shifts is shown in Fig. 2(b). This leads us to conclude that the amount of S_{cs} may by considerably smaller than that of S_{pcs}. Then, by reference to the N–Ln distance in the Eu(DPM)$_3$-(Pyridine)$_2$ crystal, 2.65 Å,[25] the range of 2.6—2.8 Å was adopted as a reasonable one, and by restricting the limit of R to 1%, a reasonable area on the map was determined (Fig. 2). A possible range of $\sum|S_{cs}|/\sum|S_{pcs}|$ corresponding to this area was then evaluated, where $\sum|S_{cs}|/\sum|S_{pcs}|$ is the average value of the cs contribution relative to that of pcs in a molecule.

Table 3. The intramolecular relative cs[a)]

Compound	Position	$R_{cs}(\rho_c^\pi)$[b)]	R_{cs}(NIS)[c)]
Aniline	2	1.000	1.000
	3	−0.377	−0.410
	4	1.139	1.000
m-Toluidine	2	1.000	1.000
	4	1.138	1.000
	5	−0.370	−0.402
	6	0.974	1.000
	CH$_3$	0.401	0.354

a) See Tables 1 and 2 on the positions. b) ρ_c^π represents the spin density distribution of α spin in the h. o (h. o(α)). Q_{CH}^{H} and $Q_{CCH_3}^{H}$ were taken as −24.0 and 27.0 gauss, respectively. c) NIS's were observed in our laboratory, but are essentially those reported in Ref. 22.

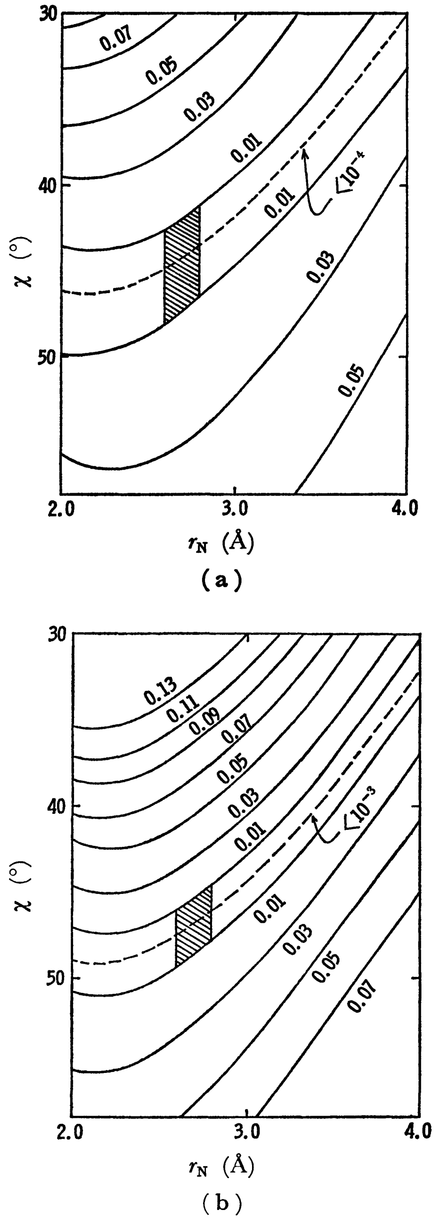


Fig. 2. Contour plots of R for the aniline adduct of Eu(FOD)$_3$ calculated by using ρ_c^π as R_{cs} (a), and of Ho(FOD)$_3$ calculated by using NIS as R_{cs} (b). Shaded parts indicate those chosen to determine a possible range of the magnitudes of S_{cs}.

The results with all the Ln(FOD)$_3$ substances are shown in Table 1, along with the ranges of χ, where the magnitudes of S_{cs} and S_{pcs} are those giving rise to the minimum of R with r_N=2.7 Å. In all the systems, the agreement between S_{obs} and S_{cal} is sufficiently good and the χ values fall within the range of 40—55°. When the limit of R can be extended to the 5% level, with the range of r_N held constant, the corresponding region of χ is fairly much expanded, but $\sum|S_{cs}|/\sum|S_{pcs}|$ does not vary so widely, except with Dy(FOD)$_3$.

Next, in order to check the above results, on the assumption of the K_2 being independent of the Ln ion, attempts were made at examining the relation of the A value to the relative pcs by Bleaney *et al.*[2] and that of the B value to $\langle S_z \rangle$ by Golding *et al.*[12] As is shown in Fig. 3, the linearity for the former is fairly good, consequently, one may consider that the above assumption regarding K_2 is acceptable. For the latter comparison, a good correspondence was obtained, as may be seen from Fig. 4, except for the values with Ho and Dy(FOD)$_3$. If a large expansion of the limit of R to 0.07 is allowable, and if the resulting decrease in χ to about 35° is not particularly noticable, for these two chelates the values of B calculated by using ρ_c^π can be improved to some extent, as may be seen

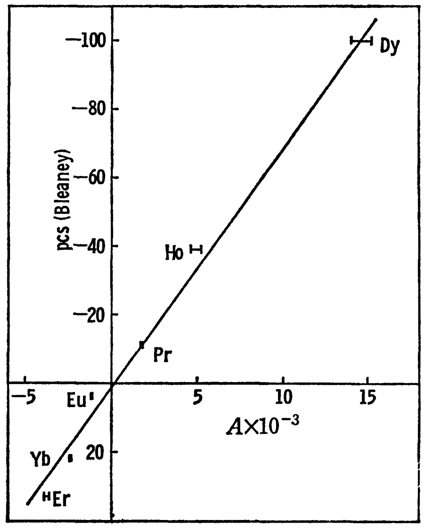


Fig. 3. Comparisons of A values for aniline (Table 1) to Bleaney's relative pcs, where A values were calculated by using ρ_c^π as R_{cs}. This figure is almost equal to that obtained with NIS as R_{cs}.

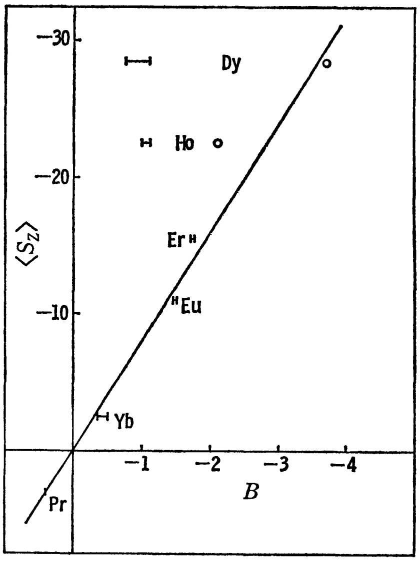
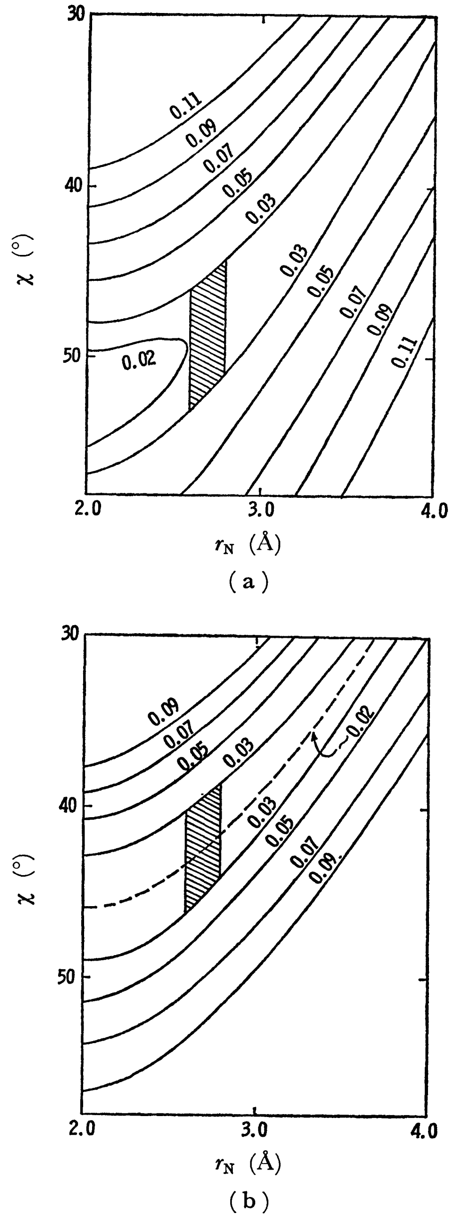


Fig. 4. Comparisons of B values for aniline (Table 1) to Golding's $\langle S_z \rangle$, where B values were calculated by using ρ_c^π as R_{cs}. This figure is similar in pattern to that with NIS as R_{cs}. (See the text) The circles show B values obtained from the expansion of allowed limit of R to 0.07.

○ (Dy): r_N=2.7 Å, χ=35°, R=0.07
○ (Ho): r_N=2.4 Å, χ=34°, R=0.07



(a)

(b)

Fig. 5. Contour plots of R for the m-toluidine adduct of Eu(FOD)$_3$ calculated by using ρ_c^π as R_{cs} (a), and of Yb(FOD)$_3$ calculated by using NIS as R_{cs} (b). Shaded parts indicate those chosen to determine a possible range of the magnitudes of S_{cs}.

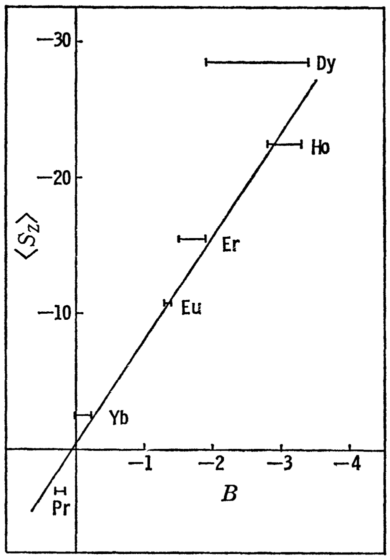


Fig. 6. Comparisons of B values for m-toluidine (Table 2) to Golding's $\langle S_z \rangle$, where B values were calculated by using ρ_c^π as R_{cs}. This figure is almost equal to that with NIS as R_{cs}.

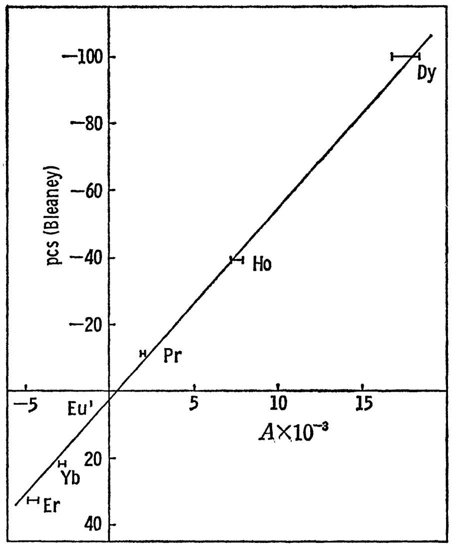


Fig. 7. Comparisons of A values for m-toluidine (Table 2) to Bleaney's relative pcs, where A values were calculated by using ρ_c^π as R_{cs}. This figure is almost equal to that with NIS as R_{cs}.

from Fig. 4, but those due to NIS's cannot be largely altered under such conditions.

The same treatments of m-toluidine adducts of Ln(FOD)$_3$ using the R_{cs} values from both ρ_c^π and NIS led to satisfactorily small values of R, though not with a valley in R so steep as in aniline, in the contour plot. We then discussed with setting the limit of R at a level between 3.0 and 4.5%. Some examples of the contour plots are shown in Fig. 5. The linear relation of the cs term to $\langle S_z \rangle$ is better than that in aniline, as is shown in Fig. 6, as is that of the pcs term to Bleaney's theoretical one (Fig. 7). Furthermore, the $\sum|S_{cs}|/\sum|S_{pcs}|$ ratios are compared with the theoretical ratios of $|\langle S_z \rangle|/|\text{pcs}|$ (Bleaney) in Fig. 8. The results for aniline are inferior to those for m-toluidine, corresponding to the comparison made separately for cs and pcs.

Thus, it may be considered that the present attempt has been roughly successful in determining the intramolecular ratio of cs and pcs contributions. However, these results may be fairly much affected by the combined inaccuracies introduced by the several assumptions and approximations included. In order to make a more accurate estimate of the cs contribution, the following investigations are in progress: (1) the variation in the angle between the Ln–N vector and the principal magnetic axis in the adduct is introduced to the computer program, and the rotation about the

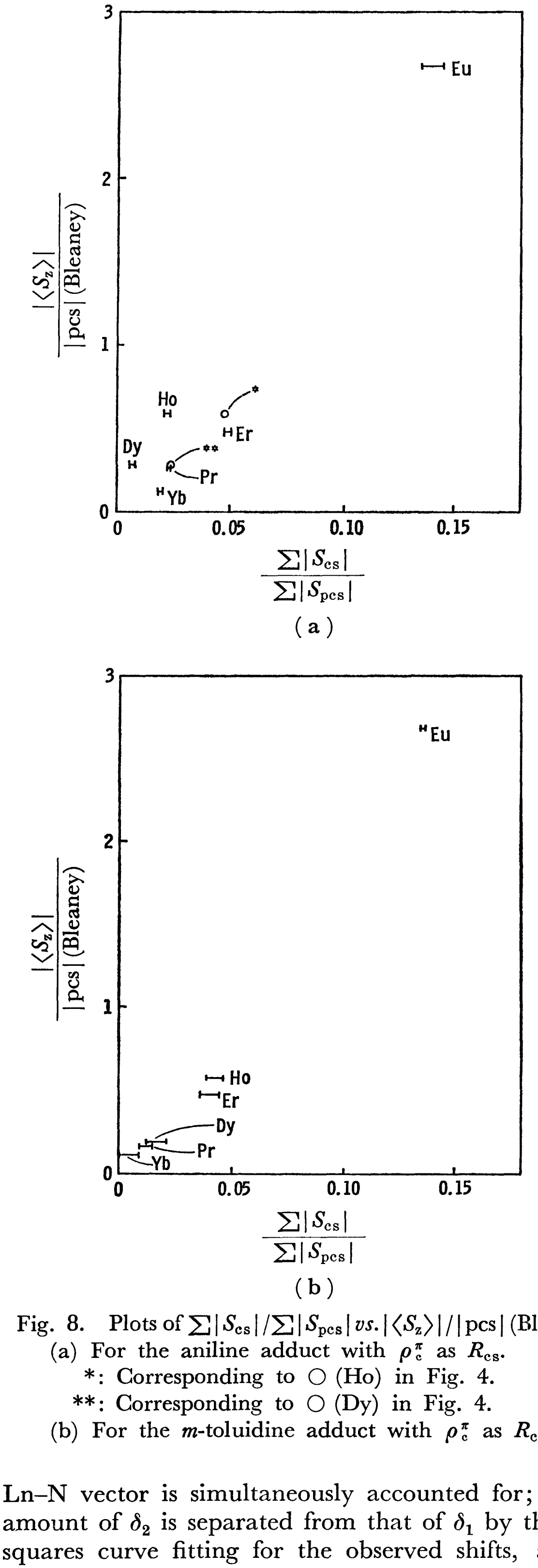


Fig. 8. Plots of $\sum|S_{cs}|/\sum|S_{pcs}|$ *vs.* $|\langle S_z\rangle|/|\mathrm{pcs}|$ (Bleaney).
(a) For the aniline adduct with ρ_c^{π} as R_{cs}.
*: Corresponding to ○ (Ho) in Fig. 4.
**: Corresponding to ○ (Dy) in Fig. 4.
(b) For the *m*-toluidine adduct with ρ_c^{π} as R_{cs}.

Ln–N vector is simultaneously accounted for; (2) the amount of δ_2 is separated from that of δ_1 by the least-squares curve fitting for the observed shifts, and (3) a σ-cs term is added to the R_{cs} pattern.

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16) As this work was in progress, it was reported by Shapiro *et al.* that δ_2 is fairly smaller than δ_1 in the cyclohexanone- and cyclohexanol-Eu(FOD)$_3$ systems in CCl$_4$.[17] The combination of this finding and that of the *n*-hexyl amine-Eu(FOD)$_3$ system in CDCl$_3$[15] indicates that both the difference in magnitude between δ_1 and δ_2 in each position in the molecule and the difference in the intramolecular ratio of δ_2 from that of δ_1 vary considerably with the substrate. Consequently, it may be considered that our present findings regarding cs contributions, as described in the last part in the text, are not very reliable. However, if K_2 is large, the shift value obtained from the linear extrapolation of the initial slope, R_L, to 1.0 is approximately two times δ_2, as was indicated by Shapiro *et al.*[18] From this point of view, the cs contributions estimated here are possibly those on δ_2, if the K_2 can be expected to be as large as that (~14) in the *n*-hexyl amine-Eu(FOD)$_3$ system dealt with in Ref. 15.

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20) The calculation of R while varying χ from 0° to 90°

using a suitable range of r_N values showed that only the region of 20—60° in χ is needed for all the Ln ions. This suggests that the χ is slightly larger than that in the Ni(AcAc)$_2$-or Co(AcAc)$_2$-aniline adduct,[22] probably because of the steric hindrance and a different complexation.

[21] The shift study on the Eu(DPM)$_3$-3-picoline system by Cramer *et al.* at low temperatures has shown that, when the $(3\cos^2\theta-1)/r^3$ term for axial symmetry is used in the calculation of dipolar shifts at room temperature, the effect of restricted rotation about the Eu–N bond should be accounted for, since the Eu–N vector may not accord with the magnetic axis. However, since the angle between the Eu–N vector and the effective magnetic axis may be expected to be very small,[5a] we roughly regard this angle as zero in the present study. See R. E. Cramer and R. Dubois, *Chem. Commun.*, **1973**, 939.

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