The Contact-term Contributions to Lanthanide-induced ^{13}C Paramagnetic Shifts in Acridine, Quinoline, and Isoquinoline

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^{1}H and ^{13}C paramagnetic shifts induced by Eu(DPM)$_3$ and Pr(DPM)$_3$ in acridine, quinoline, and isoquinoline in CCl$_4$ are observed. It has been found that, while the ^{1}H shifts can be interpreted solely in terms of a pseudo-contact interaction, there is a much larger contact-term contribution to ^{13}C shifts induced by Eu(DPM)$_3$ than by Pr(DPM)$_3$ in these compounds; this contribution to the ^{13}C shifts cannot be explained by a simple combination of σ- and π-contact terms.

Since the discovery by Hinckley[1] that the dipyridine adduct of europium(III) tris(dipivalomethanate), Eu(DPM)$_3$, produces large and stereo-specific chemical shifts in the NMR spectrum of cholesterol, numerous communications reporting work with lanthanide-shift reagents of this type have appeared. While the action of these shift reagents is generally attributed to a through-space dipolar interaction,[2,3] it has recently been reported that abnormal shift values are observed for atoms (^{14}N) co-ordinated to the lanthanide ion[4] and for ^{13}C and ^{1}H nuclei close to the co-ordinating atom in some aliphatic compounds.[5] Johnson *et al.* have reported that abnormal relative ^{1}H shift patterns are observed for substituted pyridine *N*-oxides and anilines with some lanthanide complexes, and that the shift patterns for these substrates with Eu(FOD)$_3$ are characteristic of a contact interaction attributed to the π-spin density.[6] For pyridine derivatives, several workers have observed ^{1}H shifts induced by Ln(DPM)$_3$ and Ln(FOD)$_3$ (Ln=lanthanide ion).[3,7-9] These shifts were interpreted approximately in terms of a pseudo-contact interaction by all these authors[3,7,8] except for Mackie *et al.*,[9] who showed that a contact mechanism made the major contribution to the observed shifts induced by Eu(DPM)$_3$ in γ-picoline. The large ^{1}H isotropic shifts observed in the complexes of Pr^{3+} and Nd^{3+} (nitrates and perchlorates) with some pyridine derivatives were interpreted as originating from both contact and pseudo-contact terms of nearly equal magnitudes, but of opposite signs.[10] Also for quinoline, the observed ^{1}H shifts induced by some lanthanide chelates, Ln(DPM)$_3$, could be explained approximately by a pseudo-contact term.[7,11] Huber *et al.* tentatively took account of the contact-term contribution through π-bonding by using the Hückel spin distribution of the quinoline anion radical; they obtained better predicted values, but the agreement was not good.[11]

On the other hand, we have previously reported that the observed ^{13}C paramagnetic shifts induced by two lanthanide chelates, Ln(DPM)$_3$ and Ln(FOD)$_3$, in pyridine and β-picoline include a large contact term which does not arise through π-bonding.[8] Thus, further data on the ^{13}C shifts are required for the interpretation of a spin-delocalization mechanism in such a system. We wish to report here on the ^{13}C shifts induced by Eu(DPM)$_3$ and Pr(DPM)$_3$ in acridine, quinoline, and isoquinoline, discussing the contact-shift patterns in these ligand compounds.

Experimental

Quinoline and isoquinoline were purified by vacuum distillation, and acridine, by recrystallization from ethanol. CCl$_4$ was used as the solvent. Eu(DPM)$_3$ and Pr(DPM)$_3$ were obtained from Dojindo Co., Ltd., Research Laboratories, and were dried before use. 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.* 1.1 M in acridine and *ca.* 1.4 M in quinoline and isoquinoline for ^{13}C, and *ca.* 0.6 M for ^{1}H. The amount of the lanthanide complex was continuously varied up to a complex-substrate molar ratio of 0.2.

The ^{13}C spectra were recorded at 22.63 MHz with a Hitachi R-22 spectrometer with an R-228 proton wide-band decoupler and an A-1600A signal-averaging analyzer at a probe temperature of 35 °C, and the ^{1}H spectra, with a Hitachi R-20A spectrometer at 60 MHz at a probe temperature of 34 °C, both spectrometers operating in the frequency-swept mode.

Results and Discussion

The observed ^{1}H and ^{13}C shifts for these compounds

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[1] C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

[2] Sometimes referred to as a pseudo-contact interaction.

[3] W. DeW. Horrocks, Jr., J. P. Sipe, III, *J. Amer. Chem. Soc.*, **93**, 6800 (1971).

[4] It is considered that a large contact-term contribution is included in the lanthanide-induced shift of the ^{14}N resonance of pyridine, from the experimental fact that a shift ratio S(Yb)/S(Eu) in the ^{14}N resonance[20] disagrees largely with those in the proton resonances in pyridine.[7]

[5] J. Briggs, F. A. Hart, G. P. Moss, and E. W. Randall, *Chem. Commun.*, **1971**, 364; J. Briggs, F. A. Hart, and G. P. Moss, *ibid.*, **1970**, 1506; R. J. Cushley, D. R. Anderson, and S. R. Lipsky, *ibid.*, **1972**, 636; M. Kainosho, K. Ajisaka, and K. Tori, *Chem. Lett.*, **1972**, 1061.

[6] B. F. G. Johnson, J. Lewis, P. McArdle, and J. R. Norton, *Chem. Commun.*, **1972**, 535.

[7] J. Reuben and J. S. Leigh, Jr., *J. Amer. Chem. Soc.*, **94**, 2789 (1972).

[8] M. Hirayama, E. Edakawa, and Y. Hanyu, *Chem. Commun.*, **1972**, 1343.

[9] R. K. Mackie and T. M. Shepherd, *Org. Magn. Resonance*, **4**, 557 (1972).

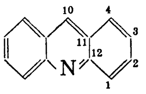
[10] E. R. Birnbaum and T. Moeller, *J. Amer. Chem. Soc.*, **91**, 7274 (1969).

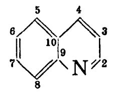
[11] H. Huber and C. Pascual, *Helv. Chim. Acta*, **54**, 913 (1971).

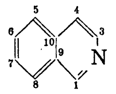
Table 1. COMPARISONS OF THE OBSERVED LANTHANIDE-INDUCED SHIFTS AND THE PSEUDO-CONTACT CONTRIBUTIONS

Compound	Position	S_{obsd} (Eu)[a]	S_{obsd} (Pr)[a]	$\dfrac{S_{\text{obsd}}\ (\text{Eu})}{S_{\text{obsd}}\ (\text{Pr})}$	S_{pcs} (Eu)[c]	S_{pcs} (Pr)[c]
Acridine	1H	−20.1	+56.1	−0.36	−20.91	+55.38
	2H	− 3.1	+ 6.5	−0.48	− 1.51	+ 6.75
	3H	− 3.1	+ 6.5	−0.48	− 2.52	+ 6.75
	4H	− 4.3	+ 8.8	−0.49	− 4.16	+ 9.59
	10H	− 6.2	+ 9.3	−0.67	− 5.42	+12.07
	1C	−40.7	+47.0	−0.87	−16.88	+37.28
	2C	− 6.0	+ 8.5	−0.71	− 5.67	+14.91
	3C	− 4.8	+ 8.0	−0.60	− 4.54	+10.65
	4C	−12.2	+13.5	−0.90	− 6.05	+13.14
	10C	−18.7	+13.0	−1.44	−11.47	+17.75
	11C	+ 2.3	+13.0	+0.18	−10.84	+22.01
	12C	−38.0	+49.5	−0.77	−23.06	+43.67
Quinoline	2H	−27.0	+61.6	−0.44	−25.68	+57.25
	3H	− 8.1	+18.2	−0.45	− 9.84	+21.94
	4H	− 8.6	+14.2	−0.61	− 7.92	+17.65
	5H	− 6.2	+ 9.8	−0.63	− 6.02	+13.42
	6H	− 4.5	+ 8.4	−0.54	− 3.84	+ 8.57
	7H	− 3.2	+ 8.4	−0.38	− 2.63	+ 5.86
	8H	−23.1	+52.6	−0.44	−24.19	+53.93
	2C	−85.0	+94.0	−0.90	−31.12	+69.40
	3C	− 5.5	+27.3	−0.20	−15.64	+34.87
	4C	−21 0	+24.7	−0.85	−12.47	+27.79
	5C	− 8.5	+16.0	−0.53	− 8.55	+19.05
	6C	− 8.5	+11.3	−0.75	− 6.61	+14.73
	7C	−15.0	+20.7	−0.72	− 8.25	+18.40
	8C	−45.0	+54.0	−0.83	−22.78	+50.78
	9C	−39.5	+70.7	−0.56	−31.12	+69.40
	10C	+ 2.5	+33.0[b]	+0.08[b]	−15.64	+34.87
Isoquinoline	1H	−39.5	+72.3	−0.55	−41.02	+71.01
	3H	−43.7	+71.6	−0.61	−41.02	+71.01
	4H	−14.0	+25.4	−0.55	−15.71	+27.19
	5H	− 8.8	+14.1	−0.62	− 8.76	+15.16
	6H	− 5.2	+ 8.6	−0.60	− 5.60	+ 9.69
	7H	− 5.2	+ 8.6	−0.60	− 5.41	+ 9.36
	8H	− 8.8	+14.1	−0.62	− 9.94	+17.14
	1C	−93.6	+102.5	−0.91	−60.46	+104.67
	3C	−80.5	+99.8	−0.81	−60.46	+104.67
	4C	+ 1.7	+27.5	+0.06	−26.65	+46.13
	5C	− 4.7	+10.7	−0.44	−11.28	+19.52
	6C	−11.0	+10.4	−1.06	− 8.06	+13.95
	7C	− 1.7	+ 9.4	−0.18	− 8.25	+14.28
	8C	−11.0	+12.6	−0.87	−13.38	+23.16
	9C	+10.9	+22.8	+0.48	−26.65	+46.13
	10C	−29.0	+25.2	−1.15	−21.73	+37.62

a) S is the lanthanide-induced shift in ppm obtained by linear extrapolation to a complex-substrate ratio of 1.0. Negative signs designate shifts to lower field.
b) The large errors may be involved in these values, owing to the weak intensities of spectral lines.
c) The pseudo-contact contributions.







are listed in Table 1.[12] The spectral assignments made by Pugmire *et al.*[13] were used here, those for ^{1}H being quite consistent with those made from the observed splitting patterns. On the assumption that

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[12] In the course of this work, ^{13}C lanthanide-induced shift data for quinoline have been reported, which are quite similar to our data. See, A. A. Chalmers and K. G. R. Pachler, *Tetrahedron Lett.*, **1972**, 4033.

[13] R. J. Pugmire, D. M. Grant, M. J. Robins, and R. K. Robins, *J. Amer. Chem. Soc.*, **91**, 6381 (1969).

the geometries of the adducts of Eu(DPM)$_3$ and Pr(DPM)$_3$ are identical, the $S_{\rm obsd}$(Eu)/$S_{\rm obsd}$(Pr) ratio should be constant over all the positions in a ligand substrate if both $S_{\rm obsd}$(Eu) and $S_{\rm obsd}$(Pr) arise only from a pseudo-contact interaction. Table 1 shows that while the ratios for ^{1}H are approximately constant, those for ^{13}C are quite variable, and, furthermore, that the shifts of ^{13}C in the β-position to nitrogen (β-^{13}C) induced by Eu(DPM)$_3$ are positive in all three substrates (they are negative, but very small in the 3 position of quinoline). Thus, it is apparent from the present data that the contact-term contributions to the ^{1}H shifts by both Eu(DPM)$_3$ and Pr(DPM)$_3$ are very small, while those to the ^{13}C shifts are much larger when affected by Eu(DPM)$_3$ than by Pr(DPM)$_3$; this is consistent with the result for pyridine[8] with respect to the dependence of the contact-term contribution on a lanthanide chelate.

It has been recently found that this kind of lanthanide chelate adduct is not axially symmetric;[14] consequently, information is not obtainable concerning the location of its principal magnetic axis.[15] Therefore, the use of the so-called geometric factor $(3\cos^2\theta-1)/r^3$ in the calculation of pseudo-contact shifts, as is commonly done, is essentially inappropriate.[16] However, in the present estimation of a relative pseudo-contact term, this approximation is adopted, because such an approximation of an axial symmetry has successfully been used for a number of systems by many workers. Calculations done while changing the N–Eu(Pr) distance led to a good agreement of the relative geometric factors (R) with the relative observed ^{1}H shifts obtained with both Pr(DPM)$_3$ and Eu(DPM)$_3$ at 4.5 Å[17] for acridine, at 3.6 Å for quinoline, and at 3.0 Å for isoquinoline.[18] For ^{13}C, the agreement is, however, not good, particularly with Eu(DPM)$_3$. These results substantiate the above expectation that ^{1}H shifts can be approximately explained only with a pseudo-contact interaction.[19] Therefore, a proportionality constant (A) fitting $S_{\rm pcs}(^1{\rm H})=A\times R$ to $S_{\rm obsd}(^1{\rm H})$, was calculated by the least-squares technique. On the reasonable assumption that $S_{\rm obsd}=S_{\rm pcs}+S_{\rm cs}$, the $S_{\rm cs}$ values for ^{1}H and ^{13}C were estimated as the differences in the $S_{\rm obsd}$ values and the $S_{\rm pcs}$ values calculated by using the A values. Hence, the $S_{\rm cs}$ values for ^{1}H should be small. The calculated results are listed in Table 2 only for Eu(DPM)$_3$ for a reason to be given below.

TABLE 2. COMPARISONS OF THE CONTACT CONTRIBUTIONS AND THE RELATIVE CALCULATED CONTACT TERMS

Compound	Position	$S_{\rm CS}$ (Eu)[a]	R_π[b]	R'_π[c]	R_σ[d]
Acridine	1H	+0.82	+0.18	+0.16	
	2H	−1.59	+0.18	+0.07	
	3H	−0.58	−0.14	−0.04	
	4H	−0.14	+0.29	+0.15	
	10H	−0.78	+0.62	+0.25	
	1C	−23.82	−1.00	−1.00	
	2C	−0.33	−0.99	−0.16	
	3C	−0.26	+2.01	+0.74	
	4C	−6.15	−2.17	−0.96	
	10C	−7.23	−3.87	−1.49	
	11C	+13.14	+1.92	+0.63	
	12C	−14.94	+1.93	+1.66	
Quinoline	2H	−1.32	+1.00	+0.07	−1.39
	3H	+1.74	+0.03	+0.06	−0.39
	4H	−0.68	+2.31	+0.34	−0.35
	5H	−0.18	+1.51	+0.32	−0.25
	6H	−0.66	+0.10	+0.10	+0.03
	7H	−0.57	+0.49	+0.08	−0.04
	8H	+1.09	+1.15	+0.34	-0.00_3
	2C	−53.88	+1.00	+1.00	+1.00
	3C	+10.14	+7.79	+0.56	−2.09
	4C	−8.53	−15.12	−2.09	+0.50
	5C	+0.05	−10.00	−1.90	−0.06
	6C	−1.89	+4.09	+0.30	−0.13
	7C	−6.75	+0.01	+0.57	+0.19
	8C	−22.22	−6.46	−2.02	−0.98
	9C	−8.38	+7.90	+1.91	+0.39
	10C	+18.14	+10.72	+1.91	−1.52
Isoquinoline	1H	+1.52	+0.26	+0.27	−1.11
	3H	−2.68	−0.02	+0.06	−0.97
	4H	+1.71	+0.16	+0.32	−0.31
	5H	−0.04	+0.14	+0.30	+0.02
	6H	+0.40	+0.07	+0.10	−0.02
	7H	+0.21	0	+0.03	−0.04
	8H	+1.14	+0.20	+0.30	−0.03
	1C	−33.14	−1.00	−1.00	+1.00
	3C	−20.04	+0.71	+0.22	+0.54
	4C	+28.35	−1.11	−1.95	−1.21
	5C	+6.58	−0.77	−1.71	−0.22
	6C	−2.94	−0.10	+0.14	+0.12
	7C	+6.55	+0.65	+0.74	−0.18
	8C	+2.38	−1.33	−1.91	−0.04
	9C	+37.55	+1.26	+1.55	−1.59
	10C	−7.27	+0.77	+1.57	+0.27

a) The contact contributions, $S_{\rm obsd}-S_{\rm pcs}$.
b) The relative π-contact terms estimated from a spin-density distribution of the anion radical.
c) The relative π-contact terms estimated from a spin-density distribution of the cation radical.
d) The relative σ-contact terms, Ref. 21.

Since the $S_{\rm cs}$ values of ^{13}C induced by Pr(DPM)$_3$ are relatively small, these magnitudes are extremely sensitive to even small variations in A and to the molecular geometry of the ligand substrate; consequently,

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[14] W. DeW. Horrocks, Jr., J. P. Sipe, III, and J. R. Luber, *ibid.*, **93**, 5258 (1971); R. E. Cramer and K. Seff, *Chem. Commun.*, **1972**, 400.

[15] C. L. Honeybourne, *Tetrahedron Lett.*, **1972**, 1095.

[16] G. N. La Mar, W. DeW. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964).

[17] For Eu(DPM)$_3$, a further better agreement was obtained with 3.8 Å.

[18] This Ln–N distance for quinoline is approximately equal to those by Reuben *et al.* and Huber *et al.*, and that for isoquinoline is also quite similar to that by Huber *et al.*

[19] Such a lack of the contact contribution in ^{1}H shifts is consistent with the results due to Reuben *et al.*[7] and Huber *et al.*,[11] but is inconsistent with the consideration on the γ-picoline–Eu(DPM)$_3$ system due to Mackie *et al.*[9] This may be attributed to that they have not taken account of the difference of a pseudo-contact shift contribution between γ-picoline and 2,4,6-trimethylpyridine arising from the difference of N–Eu distances based on steric hindrance. Relatively large contact shifts observed by Birnbaum *et al.* for some lanthanide complexes may be ascribed to a very short Ln–N distance.[10]

the intrinsic pattern of ^{13}C contact shifts was difficult to identify for the three ligand compounds. However, those induced by Eu(DPM)$_3$ are not greatly dependent on these parameters; hence, a pattern mode with marked features was commonly found for the three ligands; the patterns are downfield for α- and γ-^{13}C, and for the ^{13}C nearest to the Eu ion in the adjacent ring, and upfield for β-^{13}C, the contact-term contributions being comparatively small in the other positions. The spin-density distributions obtained from these contact shift patterns are shown in Fig. 1. It can thus be assumed from the sign alternation in the pyridine ring that a negative spin induced by the Eu ion onto the nitrogen atom is transmitted through σ-bonds by means of a spin-polarization mechanism. Although this assumption is consistent with the observed large upfield shift of the ^{14}N resonance line induced by Eu(DPM)$_3$,[20] the sign alternation is opposite to that observed for the quinoline- and isoquinoline–Ni(AcAc)$_2$ systems, where the σ-contact shift term has already been shown to be the main contributor to the paramagnetic shifts.[21] Furthermore, the large positive spin density at C-1 in acridine and C-8 in quinoline cannot yet be reasonably explained.

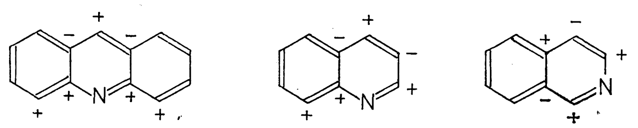

Fig. 1. The spin-density distributions induced by Eu(DPM)$_3$.

Then, assuming that the contact shift term arises only through π-bonds (S_π), the relative π-contact terms (R_π) were tentatively estimated. First, the hyperfine splitting constants, a^{C} and a^{H}, were calculated from McLachlan's spin distribution[22] in the anion radicals of these compounds by using the approximation that the bonding orbital formed between an f-orbital on Eu containing an unpaired electron and a π^*-MO of a ligand substrate may be regarded as the π^*-MO itself. The following values for σ-π interaction parameters in the McConnell and the Karplus-Fraenkel equations[23] were used:

$Q_{\mathrm{CH}}^{\mathrm{H}} = -23.0$ G in the equation, $a^{\mathrm{H}} = Q_{\mathrm{CH}}^{\mathrm{H}} \rho_{\mathrm{C}}^{\pi}$;

$Q_{\mathrm{CN}}^{\mathrm{C}} = 4.0$ G, $Q_{\mathrm{NC}}^{\mathrm{C}} = -20.5$ G,[24] and the generally-used values for S^{C}, $Q_{\mathrm{CC'}}^{\mathrm{C}}$, $Q_{\mathrm{C'C}}^{\mathrm{C}}$, and $Q_{\mathrm{CH}}^{\mathrm{C}}$ in the equation,

$$a^{\mathrm{C}} = (S^{\mathrm{C}} + \sum_i Q_{\mathrm{CX}_i}^{\mathrm{C}}) \rho^{\pi} + \sum_i Q_{\mathrm{X}_i\mathrm{C}}^{\mathrm{C}} \rho_i^{\pi}.$$

Secondly, the R_π values were estimated from the contact-shift equation and the relation $\gamma_{\mathrm{H}}/\gamma_{\mathrm{C}} = ca.\ 4$. The calculated results are listed in Table 2. An attempt was also made to estimate the ^{13}C shifts from the spin-density distribution of the cation radical (Table 2). It is apparent from Table 2 that the ^{13}C contact shifts can be explained neither by a π-contact interaction nor by a suitable combination of σ- and π-contact terms. Although the spin-transfer mechanism is still under investigation, together with the diamagnetic induction effect, we assume that a positive spin induced directly by the Eu ion to α-^{13}C and the ^{13}C nearest to the Eu ion contributes to the ^{13}C paramagentic shift induced by Eu(DPM)$_3$.

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[20] M. Witanowski, L. Stefaniak, H. Januszewski, and Z. W. Wolkowski, *Tetrahedron Lett.*, **1971**, 1653.

[21] I. Morishima, K. Okada, and T. Yonezawa, *J. Amer. Chem. Soc.*, **94**, 1425 (1972).

[22] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

[23] M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

[24] A. H. Maki and E. W. Stone, *ibid.*, **39**, 1653 (1963).