Contact and Pseudo-contact Lanthanide-induced Shifts in the Nuclear Magnetic Resonance Spectrum of Quinoline

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Contact shifts produced by trisdipivaloylmethanatogadolinium [Gd(dpm)$_3$] are used to analyse the observed ^{1}H and ^{13}C lanthanide-induced shifts of quinoline with Ln(dpm)$_3$ complexes (Ln = Pr, Nd, Eu, Dy, Ho, Er, and Yb). The analysis gives varying contact and pseudo-contact contributions for the lanthanides, the former depending on $\langle S_z \rangle$ and the degree of covalency of the Ln–N bond, and the latter in agreement with theory.

LANTHANIDE shift reagents (l.s.r.) can be used in n.m.r. spectroscopy at three levels of precision: spectral simplification, assignment, and determination of molecular geometry. Simplification by increasing chemical shift differences is the least precise and most common use,[1] and in this application europium l.s.r. seem to be preferred because of their favourable shift to broadening ratios and the downfield shifts (l.i.s.) they induce. Assignment of nuclear resonances and calculation of exact substrate conformation from relative l.i.s. values depend increasingly on knowledge of the l.s.r.–substrate geometry, and the degree to which the l.i.s. are pseudo-contact and obey some geometric relationship such as the McConnell–Robertson equation.[2] Contact contributions to the l.i.s. will cause difficulties in these more exact applications, first because the l.i.s. of the nuclei will perhaps not be in the same order as the geometric terms and secondly because the fixing of the l.s.r.–substrate geometry depends most critically on the

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l.i.s. of nuclei closest to the site of complexation and these nuclei will usually have the largest contact interaction. The predominantly pseudo-contact nature of ^{1}H l.i.s. has been inferred for numerous systems[1] although contact contributions have been invoked to explain anomalies in the l.i.s. of protons close to the site of complexation, and the presence of considerable contact shift has been suggested for the l.i.s. of pyridine *N*-oxides and anilines.[3] ^{14}N and ^{31}P spectra also show contact interaction[4,5] and although the ^{13}C lines of borneol[6] and isoborneol[7] have been assigned on a pseudo-contact basis from the l.i.s. due to Pr and Eu l.s.r. respectively, the ^{13}C l.i.s. of other substrates with the same l.s.r. show gross deviations from pseudo-contact behaviour.[8-10]

The relative pseudo-contact shifts due to lanthanide (Ln^{3+}) ions are known from theory,[11] and the observed contact shifts, induced in the ^{17}O resonance of water by Ln^{3+} ions,[12] correlate well with calculated values of $\langle S_z \rangle$.[13] If these known parameters can be used in the trisdipivaloylmethanatolanthanide [$Ln(dpm)_3$] series, as has been shown at least for the pseudo-contact shifts,[14] the l.s.r. producing the smallest proportion of contact shift could be easily predicted to be Yb.

TABLE 1

Observed [a] l.i.s. (p.p.m.) for $Ln(dpm)_3$–quinoline

	Pr	Nd	Eu	Gd	Dy	Ho	Er	Yb
C-2	−99·5	−55·0	90·0	76	−558	−152	196	139
C-3	−27·5	−9·0	6·0	−27	−251	−86·5	56·5	50·0
C-4	−25·0	−12·5	22·0	14	−169	−48·5	65·0	44·5
C-5	−15·5	−7·0	7·5	0	−123	−42·0	37·5	28·5
C-6	−11·0	−5·5	7·0	0	−101	−32·0	32·5	23·0
C-7	−18·5	−12·0	14·0	9	−126	−38·0	48·0	28·0
C-8	−54·0	−30·0	46·0	29	−374	−109	137	83·0
C-8a	−71·5	−33·5	44·0	−11	−601	−208	178	144
C-4a	−20·0	−2·5	−2·5	−49	−277	−98·0	59·5	57·5
H-2	−53·5	−22·0	24·5	*b*	−465	−123	112	74·0
H-3	−16·0	−7·0	8·0	*b*	−135	−39·5	37·0	27·5
H-4	−13·5	−5·5	7·5	*b*	−112	−33·0	34·5	25·0
H-5	−9·0	−4·5	5·5	*b*	−84·0	−29·5	27·0	20·0
H-6	−7·5	−4·0	4·5	*b*	−60·5	−21·0	27·0	13·5
H-7	−7·0	−4·0	4·0	*b*	−77·0	−23·5	22·5	13·5
H-8	−44·5	−22·0	22·0	*b*	−423	−136	147	74·0

[a] Positive downfield. [b] Not observed.

The system $Ln(dpm)_3$–quinoline has been examined with Ln = Pr, Nd, Eu, Dy, Ho, Er, and Yb and the l.i.s. for all ^{1}H and ^{13}C nuclei obtained. In addition the ^{13}C l.i.s. for $Gd(dpm)_3$ have been measured. The substrate quinoline was chosen because aromatic amines may be expected to show substantial contact shifts and since ^{13}C and ^{1}H assignments are available.[15,16] The rigidity and planarity of the molecule simplifies certain geometric problems while the lack of further symmetry and the overall shape of the molecule gives a large number of measurements for nuclei with angle and distance co-ordinates such that, in principle the fixing of the $Ln(dpm)_3$–quinoline geometry should be unambiguous.

^{1}H L.i.s. of quinoline by $Eu(dpm)_3$,[17-20] $Pr(dpm)_3$,[19] and $Yb(dpm)_3$[21] have already been the subject of a number of communications. The inclusion here of further ^{1}H l.i.s. for these three shift reagents is justified in that our analysis treats both ^{1}H and ^{13}C l.i.s. and it is essential that they be measured under the same conditions.

RESULTS

The values in Table 1 have been obtained by linearly extrapolating observed shifts to a 1 : 1 ratio of $Ln(dpm)_3$–substrate. The accuracy of peak measurement (at best ±0·5 Hz) depends on the degree of line broadening which is in general greater for the more shifted peaks. The estimated errors vary from ±5 to ±20% for the greatest and least shifted peaks respectively.

The ^{13}C l.i.s. were measured with ease and probably greater accuracy than the ^{1}H values which were obtained

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by first-order analysis. The ^{13}C l.i.s. for **Gd**(dpm)$_3$ are of lower accuracy than those for the other l.s.r., especially for nuclei such as C-8a where severe broadening accompanies small *shift*. The equations of Solomon and Bloembergen for the effect of paramagnetic species on relaxation times [22,23] show that the broadening of ^1H spectra will be **15·8** times greater than for ^{13}C. We were unable to detect any shift in ^1H lines with Gd(dpm)$_3$ before the spectrum was obliterated.

The Gd(dpm)$_3$ l.i.s. are taken to be contact in origin as have previously the Gd^{3+} shifts in an analysis of the Ln^{3+} ^{17}O and ^1H shifts of water.[12b] The presence of contact contribution to the ^{13}C l.i.s. of the other Ln(dpm)$_3$ complexes is particularly evident for lanthanides from the first half of the series which produce certain shift ratios which cannot be accounted for by geometric differences.[8]

THEORY

These obvious contact contributions must be considered in any attempt to analyse the l.i.s. in the Ln(dpm)$_3$–quinoline system. The observed shift of a nucleus i induced by a l.s.r. (Ln) can be expressed by equation (1)

$$S_i^{\mathrm{Ln}} = C^{\mathrm{Ln}}D_i + P^{\mathrm{Ln}}G_i \qquad (1)$$

with G_i the geometric factor $(3\cos^2\theta_i - 1)r_i^{-3}$ relative to C-2 ($G_{\text{C-2}} \equiv 1{\cdot}0$), r_i the length of the vector joining Ln to the i^{th} nucleus, and θ_i the angle between this vector and the Ln–N bond. This simple way of obtaining the angle parameter has been shown to be valid.[24,25] C^{Ln} and P^{Ln} are measures of the contact and pseudo-contact contributions respectively, of a particular lanthanide and D_i the relative spin density at nucleus i ($D_{\text{C-2}} \equiv -1{\cdot}0$). The P^{Ln} values are expected to be proportional to the factors calculated by Bleaney [11] if either the complexes are axially symmetric or the Ln–N bond has the same orientation with respect to the tensor axes throughout the series. The C^{Ln} values will depend on $\langle S_z \rangle$, and the degree of covalency in the Ln–N bond. The assumption in fitting the l.i.s. to equations (1), that G_i and D_i are the same for each Ln(dpm)$_3$–quinoline system, will be discussed later.

The unknowns C^{Ln}, P^{Ln}, D_i, and G_i were obtained, using an iterative computer program, from the ^1H and ^{13}C l.i.s. The geometric factors G_i were calculated from the Cartesian co-ordinates of Ln with respect to the substrate in a co-ordinate system with the xy-plane coinciding with the plane of the quinoline molecule, the origin at N, the positive y-axis passing through C-4, and the carbocyclic ring in the positive quadrant. The atomic co-ordinates for the quinoline molecule were derived from standard bond lengths and bond angles. The method for fixing the Ln position is similar to that reported by ApSimon and Beierbeck,[26] but the additional contact parameters are also considered.

One further parameter had to be fixed in the system of linear equations derived from equation (1). The method employed was to vary one P^{Ln} until the output values of the relative carbon spin densities D_i were closest to those observed with Gd(dpm)$_3$. Table 2 gives the best agreement achieved between computed D_i and observed Gd ratios.

TABLE 2

	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-8a	C-4a
D_i	−1·00	0·44	−0·04	0·10	0·04	−0·11	−0·40	−0·02	0·60
Gd	−1·00	0·36	−0·18	0·0	0·0	−0·12	−0·38	0·14	0·64

An example [Eu(dpm)$_3$] of the calculated shifts is given in Table 3, and the results for the other lanthanides may be derived from these data by scaling the contact and pseudo-contact shifts by the appropriate values of C^{Ln} and P^{Ln} (Table 4) relative to Eu. The final Ln co-ordinates were $x = -0{\cdot}13$ and $y = -3{\cdot}87$ Å.

TABLE 3

Calculated shifts (p.p.m.) for the Eu(dpm)$_3$–quinoline system

	Calc.	Obs. − calc.	Contact	Pseudo-contact
C-2	84·5	5·5	39·8	44·7
C-3	4·0	2·0	−17·6	21·6
C-4	18·9	3·1	1·4	17·4
C-5	7·9	−0·4	−4·0	11·9
C-6	7·4	−0·4	−1·7	9·1
C-7	15·4	−1·4	4·4	11·0
C-8	46·5	−0·5	15·9	30·6
C-8a	44·2	−0·2	0·8	43·4
C-4a	−2·1	−0·4	−23·5	21·4
H-2	23·6	0·9	−13·3	36·9
H-3	7·2	0·8	−6·4	13·6
H-4	7·2	0·3	−3·8	11·0
H-5	5·4	0·2	−3·0	8·3
H-6	5·3	−0·8	0·0	5·3
H-7	5·5	−1·5	1·6	3·9
H-8	26·5	−4·5	−8·3	34·8

TABLE 4

	C^{Ln}	P^{Ln}	$\langle S_z \rangle$ [a]	$\dfrac{\sum^{i}\lvert C^{\mathrm{Ln}}D_i\rvert}{\sum^{i}\lvert S^{i}_{\mathrm{obs}}\rvert}$
Pr	23·0	−68·8	3·0	0·17
Nd	21·8	−33·6	4·5	0·34
Eu	−39·7	44·7	−10·7	0·46
Dy	16·5	−536	−28·5	0·02
Ho	−9·1	−163	−22·6	0·03
Er	−43·1	168	−15·4	0·13
Yb	−18·4	115	−2·6	0·08

[a] From ref. 13.

DISCUSSION

The geometry converged on is similar to that previously obtained from ^1H data,[17,18] with 3·87 Å for the Ln–N distance and the Ln atom displaced slightly away from the carbocyclic ring as might be expected on steric grounds.

The values of P^{Ln} agree considerably better with those calculated by Bleaney [11] (Figure 1) than previous experimental data,[14] supporting the assumption of identical geometries for all the Ln(dpm)$_3$–quinoline systems. The straight line in Figure 1 was obtained by a regression analysis and gives a correlation coefficient of 0·996.

The average difference between observed and calculated shifts was 9%, which is similar to the estimated experimental accuracy. Not too much significance can be attached to values of C^{Ln} for lanthanides where the contact shift makes only a small contribution to the total shift (Dy, Ho, and Yb). Nevertheless the signs of C^{Ln} are the same as the signs of $\langle S_z \rangle^{\mathrm{Ln}}$ except for Dy. The relative magnitudes of C^{Ln} and $\langle S_z \rangle^{\mathrm{Ln}}$ are different indicating that the latter parameter alone does not

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govern the relative magnitudes of the contact shifts in the Ln(dpm)$_3$ series. When the ratio $(C : \langle S_z \rangle)^{\text{Ln}}$ is plotted against the ionic radii of Ln^{3+} (Figure 2), a moderately smooth curve results with a minimum in the region of Dy, Ho. The minimum may be illusory because of the inaccuracy in C^{Yb}, but the evidence for a downward trend towards Dy, Ho is clear. Boeyens[27] has interpreted similar curves for various properties of Ln(dpm)$_3$ complexes in terms of the bonding properties and we believe that Figure 2 represents the relative degree of covalency in the Ln–N bond. The decrease in contact shift is yet another consequence of the smaller ionic radii of the later lanthanides which can be considered to make Ln less accessible to covalent bonding from the substrate. This interpretation does not invalidate the assumption of constant geometry for the Ln(dpm)$_3$–quinoline systems since pseudo-contact shifts are not very sensitive to small variations in geometry[28] while as little as 1% of covalent character will give observable contact interaction.[29]

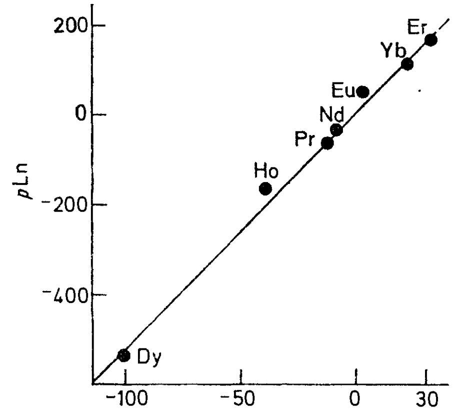

FIGURE 1 Plot of P^{Ln} against theoretical[11] pseudo-contact values

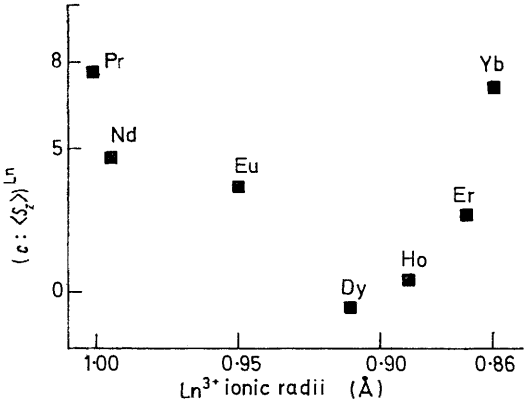

FIGURE 2 Plot of $(C : \langle S_z \rangle)^{\text{Ln}}$ against ionic radius of Ln^{3+}

Relative spin densities at all nuclei have been assumed to be the same in Ln(dpm)$_3$–quinoline systems and at carbon nuclei fixed as closely as possible to those observed with Gd(dpm)$_3$. This assumption is implicit in quantum mechanical calculations of spin densities induced by paramagnetic metals[30] and seems reasonable in view of the similarities in the orbitals available on the lanthanides. The relative spin densities induced by Gd(dpm)$_3$ and Ni(acac)$_2$[30] on quinoline nuclei are different in several respects but a similar alternation of signs is found in the heterocyclic ring.

The analysis predicts contact shifts for the protons. These have all the same sign except for H-7 where the value is small enough to be of no real significance. The sign of the relative spin densities on the protons and their regular decrease with the number of intervening bonds agrees with theoretical calculations on the naphthyl radical[30] (ρ_{H1s}) (Table 5). A serious discrepancy exists for H-8 only, the proton closest to the Ln position. It is obvious (Table 3) that a small increase in contact shift will cause H-3 to have a smaller l.i.s. than H-4 which is the most striking evidence for ^{1}H contact shifts in the spectra of pyridine *N*-oxides.[3]

TABLE 5

	H-2	H-3	H-4	H-5	H-6	H-7	H-8
D_i	1·00	0·48	0·29	0·24	0·00	−0·12	0·64
ρ_{H1s}	1·00	0·28	0·25	0·18	−0·02	0·03	0·00

The problem throughout is the fixing of the lanthanide position in the presence of contact shift. The analysis of the l.i.s. for all lanthanides together is attractive since sufficient experimental data are available to give results with the assumptions made. There are, however, problems in handling small contributions to large shifts, and other uncertainties in the calculation such as the correct form of the geometric factor, its application to mobile complexes,[31] and the importance of quadrupole terms.[32] It is instructive, therefore to inspect the observed l.i.s. for deviations from pseudo-contact behaviour. Calculation of the usual geometric term for a range of positions of the Ln atom (Ln 2·5—4·0 Å, $\text{Ln-}\overset{\wedge}{\text{N}}\text{-C-4}$ 170—190°) gave a range of geometric ratios. Certain calculated ranges are so great that they encompass all observed shift ratios, but other ranges are quite small. One of the least sensitive is C-4 : H-4 (1·77—1·56 with the above range of geometry), which is also an experimentally accurate ratio. The experimental deviations from this range are in the order Eu > Nd > Pr, Er, Ho > Dy > Yb. A similar sequence is obtained considering the relative contributions from contact interactions to the total observed shift for each lanthanide as shown in the last column of Table 4.

Another interesting observation is the relative magnitudes of the C-2 and C-8a l.i.s. This seems to be determined by the relative signs of $\langle S_z \rangle$ and the pseudo-contact shift (Table 4) since when these signs are the

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same (Dy, Ho) C-2 has the smaller absolute shift, but for the other lanthanides C-2 has the greater shift, except in the case of Yb where they are the same within experimental error.

Conclusions.—The analysis of the quinoline l.i.s. shows that l.s.r. from the first half of the lanthanide series give the larger contact shifts and that Eu(dpm)$_3$ gives the largest of all. Proof that the order of contact shifts found here is general and must await further experiments with other substrates, but we do agree with other authors [5,28] that Yb(dpm)$_3$ for downfield shifts, and Dy(dpm)$_3$ or Ho(dpm)$_3$ for upfield shifts should be used in the more precise applications of shift reagents.

EXPERIMENTAL

The Ln(dpm)$_3$ complexes were prepared by the method of Eisentraut and Sievers,[33] purified by vacuum sublimation, and stored under vacuum over P_2O_5. Elemental C and H analyses were satisfactory and spark source mass spectrography showed no significant metallic contaminants except in the case of the Er complex which contained some Eu.

^{1}H and ^{13}C spectra were obtained using Varian HA-100 and XL-100-FT spectrometers. A solution of quinoline (1·2M) in CDCl$_3$ was used for all experiments. ^{13}C L.i.s. were obtained by the addition of three equal quantities of Ln(dpm)$_3$ to quinoline solution (2·5 ml). The maximum Ln(dpm)$_3$–quinoline mole ratio was 1 : 10 in the case of the reagents giving smaller shifts and the presence of La(dpm)$_3$ at this mole ratio gave no detectable shifts. Plots of ^{13}C l.i.s. against mole ratio were linear, but back extrapolated to a small positive value of mole ratio for zero shift. After the final addition a portion of the sample was run for its ^{1}H spectrum. The shifts of resonances which could be immediately assigned were used to scale the ^{1}H shift ratios to obtain absolute values of ^{1}H shifts. These ^{1}H shift ratios were obtained by dilution of sample with stock quinoline solution.

Much less Gd(dpm)$_3$ could be employed and the final mole ratio in the ^{13}C experiments was 1 : 81. With this the shift of C-2 was 21 Hz. Numerous mole ratios up to this value were employed to check the consistency of the shift ratios.

[3/1940 *Received*, 21*st September*, 1973]

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