Contact Term Contribution to Lanthanide-induced ^{13}C Nuclear Magnetic Resonance Shifts in Pyridine and β-Picoline

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Summary There is a large contact term contribution to ^{13}C paramagnetic shifts induced by $Eu(dpm)_3$, $Pr(dpm)_3$, and $Eu(fod)_3$ in pyridine and β-picoline; this contribution may not be due mainly to spin delocalization through π-bonds.

ALTHOUGH it is generally accepted that paramagnetic shifts induced by some lanthanide complexes are mainly due to pseudo-contact interaction,[1] it has been recently reported that abnormal shift values are observed for atoms (^{14}N), co-ordinated to the lanthanide ion[2] and for ^{13}C or ^{1}H nuclei close to the co-ordinating atom in some aliphatic compounds.[3] 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 π-spin density.[4] For pyridine derivatives, the observed shifts induced by $La(dpm)_3$ (La = Pr, Eu, and Yb) could be interpreted approximately in terms of a pseudo-contact interaction only by using a distance between nitrogen and lanthanide ion of 4 Å.[5] Huber *et al.* tentatively took account of the contact term contribution through π-bonding by using the Hückel spin distribution of quinoline anion radical, to obtain better predicted values,[6] but the agreement is not good.

We report here observed ^{13}C paramagnetic shifts induced by $Eu(dpm)_3$, $Pr(dpm)_3$, and $Eu(fod)_3$ for pyridine and β-picoline, and discuss the contact term contribution.

The observed ^{1}H and ^{13}C shifts for pyridine and β-picoline are shown in Table 1 with the related pseudo-contact shifts calculated from the geometric factor $(3\cos^2\theta - 1)/r^3$. Although the observed relative shifts for ^{1}H can be explained with the pseudo-contact term only by using a value of r_N(the nitrogen–lanthanide distance) of 3·00 Å,[5] those for ^{13}C disagree completely with the values predicted on this basis. With $Eu(dpm)_3$ and $Eu(fod)_3$, the large upfield shift component is clearly included in the β-^{13}C resonance. These results thus show the existence of a much larger contact term contribution for ^{13}C than for ^{1}H. The agreement between the observed relative shifts with those calculated using only the pseudo-contact term for ^{1}H is presumably not co-incidental, and so the other term is not required. The most suitable values for K in the equation $S_{pcs} = (3\cos^2\theta - 1)/r^3 \times K$ for pyridine are 594, 1776, and 880 with $Eu(dpm)_3$, $Pr(dpm)_3$, and $Eu(fod)_3$ respectively. The S_{pcs} values for ^{13}C calculated using $K = 594$ are shown in Table 2.

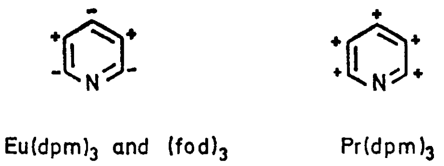

FIGURE. S_{cs} *patterns for* ^{13}C.

Observed S values for pyridine obtained with $Eu(dpm)_3$ in $CHCl_3$ (or $CDCl_3$) are used to discuss the ^{13}C contact term in detail. The contribution to the lanthanide-induced shift other than that from the pseudo-contact term may be considered to be only that due to the contact term (S_{cs}) (see Table 2). Assuming that S_{cs} arises only through π-bonds (S_{π}), the hyperfine coupling constants a^{C} and a^{H}

$$S = S_{pcs} + S_{cs}$$

were estimated from McLachlan's spin distribution[7] in the pyridine anion radical by using the approximation that the bonding orbital formed between an *f*-orbital on Eu containing an unpaired electron and a π*-MO of pyridine may be regarded as a π*-MO itself. The following values for σ–π interaction parameters in the McConnell and the Karplus–Fraenkel equation[8] were used.

$Q^{H}_{CH} = -23{\cdot}0$ G in the equation $a^{H} = Q^{H}_{CH}\ \rho^{\pi}_{C}$, $Q^{C}_{CN} = 4{\cdot}0$ G and $Q^{C}_{NC} = -20{\cdot}5$ G;[9] Q^{C} values for C and H, and C and C are given by

$$a^{C} = (S^{C} + \sum_{i} Q^{C}_{CX(i)})\ \rho^{\pi} + \sum_{i} Q^{C}_{X(i)C}\ \rho_{i}^{\pi}$$

TABLE 1. *Observed paramagnetic shifts, S*[a]

		Pyridine		
		α	β	γ
Eu(dpm)$_3$	^{13}C	−67·5	+ 3·5	−23·0
	^{1}H	−12·16	− 4·46	− 3·86
Pr(dpm)$_3$	^{13}C	+93·5	+25·8	+25·8
	^{1}H	+35·3	+12·7	+10·6
Eu(fod)$_3$	^{13}C	−43·5	+14·5	−11·0
	^{1}H	−18·0	− 6·25	− 6·10
Calc.[b]	^{13}C	1·00	0·42	0·34
	^{1}H	1·00	0·36	0·30

		β-Picoline			
		α	β	γ	β-Me
Eu(dpm)$_3$	^{13}C	−78·3 −75·3	− 4·7 − 3·8	−26·6	− 8·9
	^{1}H	−17·5	− 6·1	− 5·8	− 4·0
Pr(dpm)$_3$	^{13}C	+86·5 +79·5	+22·6 +21·8	+25·9	+ 9·7
	^{1}H	+38·6	+14·0	+11·2	+ 8·6
Calc.[b]	^{13}C	1·00	0·42	0·34	0·21
	^{1}H	1·00	0·36	0·30	0·22

[a] *S* is the lanthanide-induced shift in p.p.m. obtained by linear extrapolation to a complex–substrate ratio of 1·0. Negative signs designate shifts to lower field. ^{13}C spectra were recorded at 22·63 MHz with a Hitachi R-22 spectrometer with a R-228 proton wide band decoupler and a A-1600A signal averaging analyser, and ^{1}H spectra with a Hitachi R-20A spectrometer at 60 MHz, both spectrometers operating in the frequency-swept mode. Solutions were *ca.* 2·0M for ^{13}C and *ca.* 0·5M for ^{1}H. The amount of lanthanide complex was continuously varied up to a complex–substrate molar ratio of 0·2. $CHCl_3$ was the solvent for ^{13}C and $CDCl_3$ for ^{1}H.
[b] Geometric factors relative to the α-position.

TABLE 2. *Contact term contribution in the* Eu(dpm)$_3$*–pyridine system*

	S_{obs}[a]	$(3\cos^2\theta - 1)/r^3$	S_{pcs}[b]	S_{cs}[c]	S_π	a^C or a^H (in G)
α-H	−12·16	0·02045	−12·15	− 0·01	+ 3·00B	− 3·00
β-H	− 4·46	0·00742	− 4·41	− 0·05	− 0·32B	+ 0·32
γ-H	− 3·86	0·00615	− 3·65	− 0·21	+ 9·66B	− 9·66
α-C	−67·5	0·03032	−18·01	−49·49	+14·56B	− 3·64
β-C	+ 3·5	0·01274	− 7·57	+11·07	+32·64B	− 8·16
γ-C	−23·0	0·01036	− 6·15	−16·85	−61·60B	+15·40

[a] Observed shifts. [b] Pseudo-contact term using $K = 594$ and $r_N = 3{\cdot}00$ °A. [c] $S_{obs} - S_{pcs}$.

From the contact shift equation and the relation γ_H/γ_C = *ca.* 4, the π-contact term is $-a^H{\cdot}B$ for ^{1}H and $-4a^C{\cdot}B$ for ^{13}C, where *B* is a constant. Comparison of S_{cs} with the S_π values for ^{1}H in Table 2 shows that the limiting *B* value is *ca.* 0·1 at most, and, therefore, S_π for ^{13}C is $-0{\cdot}4\ a^C$. The π-contact contribution for ^{13}C would thus be very small, even if it were present at all, and may be due mainly to another spin transfer mechanism which affects ^{13}C much more than ^{1}H. The shift patterns due to this effect with Eu(dpm)$_3$ and Eu(fod)$_3$ are downfield for α- and γ-^{13}C and up field for β-^{13}C (Figure). The sign alternation is opposite to that observed for the Ni(acac)$_2$–pyridine system where the σ-contact term has already been shown to be the main contributor to the paramagnetic shift.[10] S_{cs} values for ^{13}C in the Pr(dpm)$_3$–pyridine system are positive for all positions

Although the spin-transfer mechanism is still under investigation, we assume that a positive spin induced directly at α-^{13}C by Eu contributes to the ^{13}C paramagnetic shifts induced by Eu(dpm)$_3$ and Eu(fod)$_3$.

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