Contact Effects in Nuclear Magnetic Resonance Spectra with Lanthanide Shift Reagents

By B. F. G. Johnson, J. Lewis,* P. McArdle, and J. R. Norton
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

Summary With substituted pyridine *N*-oxides and anilines as substrates, increasing contact contributions are observed along the series $Pr(fod)_3$, $Yb(fod)_3$, $Eu(dpm)_3$, $Er(fod)_3$, and $Eu(fod)_3$.

The effects of lanthanide shift reagents[1] have conventionally been attributed to pseudo-contact interactions.[2] Some results are now reported for simple organic π systems which cannot be interpreted on that basis and which are apparently due to contact effects.

Table[a]

		γ-Picoline *N*-oxide[b]		
	α	β	Me	
$Pr(fod)_3$	−10	−3·4	−2·0	
$Yb(fod)_3$	10	2·5	1·3	
$Eu(dpm)_3$	10	2·2	1·0	
$Er(fod)_3$	10	1·2	0·14	
$Eu(fod)_3$	10	−2·0	−5·0	
Calc.[2]	10	3·3	1·7	
		Pyridine *N*-oxide[b]		
	α	β	γ	
$Pr(fod)_3$	−10	−3·1	−3·1	
$Eu(dpm)_3$	10	2·5	2·5	
$Yb(fod)_3$	10	2·2	2·2	
$Eu(fod)_3$	10	−1·4	5·8	
		Aniline[c]		
	o	*m*	*p*	
$Yb(fod)_3$	10	2·8	2·3	
$Pr(fod)_3$	−10	−3·1	−2·7	
$Eu(dpm)_3$	10	2·5	2·7	
$Eu(fod)_3$	10	2·5	3·5	
		$(CO)_3CrPhNH_2$[d]		
$Eu(dpm)_3$	10	2·3	2·3	
$Eu(fod)_3$	10	2·3	2·3	
		Ph(NH)(Me)[c]		
				Me
$Eu(fod)_3$	8·1	1·9	2·0	10
		p-toluidine[b]		
	o	*m*	Me	
$Yb(fod)_3$	10	2·5	1·1	
$Eu(dpm)_3$	10	2·4	0·81	
$Eu(fod)_3$	10	2·2	0·45	

[a] Downfield shifts (at 100 MHz) normalized to largest shift; linear up to 0·8 mol of lanthanide per mol of substrate. [b] Solvent $CDCl_3$. [c] Solvent CS_2. [d] Solvent CD_2Cl_2.

The shift ratios in the Table for pyridine and γ-picoline *N*-oxides in the presence of $Eu(fod)_3$ are especially noteworthy, displaying substantial upfield shifts and disagreeing completely with calculated pseudocontact geometric factor ratios[2] for all reasonable placements of the lanthanide relative to the substrate. On the other hand the pattern observed is quite characteristic of a contact interaction of the type conventionally attributed to spin density in the π system. The change of sign at the *para* position upon methyl substitution is characteristic of such interactions, as is the sign alternation around the pyridine *N*-oxide ring.[3] In fact the shift ratio patterns are similar to those reported for the contact shifts of pyridine *N*-oxides co-ordinated to octahedral nickel(II).[4]

In contrast the results with $Pr(fod)_3$ agree well with calculated geometric factors and reported pseudocontact ratio data.[2] On this basis increasing contact contributions are implied for the series $Pr(fod)_3$, $Yb(fod)_3$, $Eu(dpm)_3$, $Er(fod)_3$, and $Eu(fod)_3$ with the *N*-oxides as substrates.

With aniline and *p*-toluidine contact effects, although smaller, are still clearly present. Again the use of $Eu(fod)_3$ produces the largest contact contribution. More extensive spin delocalization onto substituted anilines has been observed with Ni^{II}.[5] Co-ordination to tricarbonylchromium or the introduction of a methyl substituent on the nitrogen appears to decrease the contact interaction with lanthanide shift reagents.

Contact effects from the presence of lanthanides, while rare, are not unprecedented. Paramagnetic shifts produced by Nd and Pr nitrates and perchlorates in the n.m.r. spectra of substituted pyridines have been ascribed to a mixture of contact and pseudocontact interactions.[6] A number of workers[7–9] employing shift reagents have suggested short-range contact effects to explain deviations of the shifts of nuclei next to the binding site from those predicted by mathematical models for pseudocontact effects. Calculations for such nuclei, however, are very sensitive to minor changes in the geometry assumed.

While the mechanism by which shift reagents produce contact effects is still under investigation, from the above data it appears that these interactions are much larger with stronger Lewis acids such as $Ln(fod)_3$[10] than with $Ln(dpm)_3$ (which produce isotropic shifts largely pseudocontact in origin).[2] It is clear that shift reagent data for strongly binding substrates such as *N*-oxides and amines, with extended π systems, should be used with caution for the purpose of structure elucidation.

(*Received, 2nd March* 1972; *Com.* 349.)

---

[1] (a) C. C. Hinckley, *J. Amer. Chem. Soc.*, 1969, **91**, 5160; (b) J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, 1971, **93**, 641.

[2] W. D. Horrocks, jun., and J. P. Sipe, tert., *J. Amer. Chem. Soc.*, 1971, **93**, 6800, and references therein.

[3] G. A. Webb, Annual Reports on n.m.r. Spectroscopy, ed. E. F. Mooney, Academic Press, London, 1970, vol. 3, p. 211; see, however, W. D. Horrocks, jun., and D. L. Johnston, *Inorg. Chem.*, 1971, **10**, 1835, for calculations suggesting that similar results can be produced by contact effects in σ systems.

[4] R. W. Kluiber and W. D. Horrocks, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 5350.

[5] R. W. Kluiber and W. D. Horrocks, jun., *Inorg. Chem.*, 1967, **6**, 430.

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

[7] J. Briggs, F. A. Hart, G. P. Moss, and E. W. Randall, *Chem. Comm.*, 1971, 364.

[8] P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, 1970, **92**, 5734.

[9] A. M. Grotens, J. Smid, and E. de Boer, *Tetrahedron Letters*, 1971, 4863.

[10] I. Armitage, G. Dunsmore, L. D. Hall, and A. G. Marshall, *Chem. and Ind.*, 1972, 72.