Shifts Induced by Tris(dipivalomethanato)lanthanides in ^{19}F Nuclear Magnetic Resonance Spectroscopy

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Summary Comparative studies of the effects of lanthanide-(dpm) chelates on the ^1H and ^{19}F n.m.r. spectra show that the shifts caused by the reagents have a dipolar origin; Dy(dpm)$_3$ is shown to be the preferred high-field shift reagent and Yb(dpm)$_3$ the best low-field reagent.

Chemical shifts induced by lanthanide chelates have been studied in ^1H, ^{13}C, ^{14}N, and ^{31}P n.m.r.[1–4] The resonating nuclei, commonly encountered in organic compounds, fall into two classes: those (*e.g.* ^1H, ^{13}C, and ^{19}F) which are primarily subject to distance dependent pseudocontact shifts of dipolar origin, and those like ^{14}N, ^{15}N, and ^{31}P which carry lone pair electrons and interact with the co-ordinating ion by a predominating contact mechanism.[5]

We report shifts induced in ^{19}F n.m.r. of 2,4,6-trifluoroaniline by rare earth dipivalomethanates and compare them with ^1H n.m.r. results in aniline. Our results (see Table) provide evidence of a common pseudocontact mechanism for shifts in ^1H and ^{19}F n.m.r., a comparable shift scale being obtained for both nuclei.† The shift ratio of *ortho* to *para* substituents varies from 4·1 to 5·2 over the entire series in both cases and this suggests similar geometrical interaction models.

Table

Effect of lanthanide(dpm) chelates on ^{19}F *and* ^1H *n.m.r. Spectra of 2,4,6-trifluoroaniline and aniline.*

	2,4,6-Trifluoroaniline		Aniline			
	ortho	*para*	*ortho*	*meta*[c]	*para*	NH_2
La[b]	0	0	−0·2	0	0	−1·0
Pr	+28	+7	+25·3	+7·6	+6·2	+120
Nd	+9	+2	+9·0	+2·0	+1·8	+43
Sm	small positive value		+1·7	+1·5	+0·4	+6·5
Eu	−26	−6	−22·0	−5·7	−5·2	−110
Dy	+197	+38	+151·0	+41·0	+32·0	+800
Ho	+95	+20	+66·0	+17·4	+12·3	+300
Er	−48	−11	−44·5	−10·8	−9·3	−230
Yb	−55	−12	−46·8	−13·0	−9·5	−220

[a] Values in p.p.m., extrapolated to equimolar ratio of shift reagent to solute, for four different concentrations up to 0·5—0·6 molar equivalents. Accuracy ±5%. Experimental conditions: ^1H, 10% CCl_4 solutions at 60 MHz, 33 °C, (Me_4Si); ^{19}F, 10% ($CDCl_3$ and $CFCl_3$) at 56·4 MHz, 32 °C. Increasing field direction taken as positive. [b] With La, Ce, and Gd the chelate is inactive, within experimental error. The paramagnetic shifts reported here may therefore be regarded relative to the adduct with La(dpm)$_3$ (referee's suggestion). [c] Induced shifts for *meta* proton and NH_2 signals are comparable in trifluoroaniline but reduced by a factor of 1·5 ± 0·2.

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† A somewhat different scale is obtained for 1-fluoropyridine, probably due to specific interaction between fluorine and ligands in the chelate.

The best shift reagents in terms of shift magnitude, line-broadening,[6,7] solubility, and price are Dy(dpm)$_3$ for high-field shifts, and Yb(dpm)$_3$ for low-field shifts. Although the mechanisms involved are totally different this conclusion, which we have drawn previously for ^{14}N,[3] also applies to nuclei participating in the two types of interaction mentioned.‡

However ^{19}F spectra are generally simple to interpret and rarely need to be expanded. The use of shift reagents is also limited by the electronegativity of fluorine which considerably lowers the basicity of potential co-ordination sites. For example, no shift was apparent with n-perfluorobutylamine or polyfluorinated alcohols. This disadvantage does not apply to aqueous solutions if anions, such as carboxylates, are studied using appropriate lanthanide derivatives.[8]

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‡ Tb(dpm)$_3$ and Tm(dpm)$_3$, which may be of comparable interest (see ref. 6 for a survey of lanthanide dpm chelates in proton n.m.r.) were not included in our studies.

[1] For example: J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, 1971, **93**, 641 and references therein; C. Beauté, Z. W. Wolkowski, J. P. Merda, and D. Lelandais, *Tetrahedron Letters*, 1971, 2473 and references therein.

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[3] M. Witanowski, L. Stefaniak, H. Januszewski, and Z. W. Wolkowski, *Tetrahedron Letters*, 1971, 1653; *Chem. Comm.*, 1971, 1573.

[4] J. K. M. Sanders and D. H. Williams, *Tetrahedron Letters*, 1971, 2813; R. Craig Taylor and D. B. Walters, *ibid.*, 1972, 63.

[5] It is possible to give a satisfactory theoretical interpretation of the general effect of lanthanide chelates in ^{14}N n.m.r. R. M. Golding, personal communication.

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