Lanthanide-induced Shifts in Nuclear Magnetic Resonance Spectroscopy. Shifts to High Field

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Summary Tris-(2,2,6,6-tetramethylheptane-3,5-dionato)-praseodymium, [Pr(tmhd)$_3$], induces shifts in ^{1}H n.m.r. spectra which are of opposite sign to, and much larger than, those reported for [Eu(tmhd)$_3$].

N.M.R. SPECTRA may usually be obtained from complexes of paramagnetic lanthanide ions with organic ligands.[1-3] Such spectra commonly show paramagnetic shifts, mainly of dipolar (pseudo-contact) origin, of between 0 and 20 p.p.m. This principle has been applied by Hinckley[4] to the weak association between tris-(2,2,6,6-tetramethylheptane-3,5-dionato)europium, [Eu (Bu^{t}CO·CH·COBu^t)$_3$],[5] and cholesterol (the complex being used as its bis-pyridine adduct). Large low-field shifts were produced in the cholesterol spectrum, which were approximately proportional to r^{-3} (r = Eu-H distance) and hence yield structural information in addition to simplifying the spectrum. Further examples of simplified spectra, those of n-hexanol and benzyl alcohol, have been reported more recently and the omission of pyridine (which tends to block co-ordination of the substrate) has been recommended.[6]

We report that praseodymium complexes show shifts which, compared with corresponding europium compounds are usually reversed in direction and about triple in magnitude.[2] Hence we find that [Pr(tmhd)$_3$][5] added to a CCl$_4$ solution of n-pentanol induces the pentanol spectrum to become first order but with all peaks greatly shifted to high field (Figure). The capability of producing shifts in either direction at will, by use of the Pr or Eu complex, must greatly increase the utility of the method. By this means, a specific peak lying under an envelope otherwise composed of relatively unaffected peaks of 'distant' protons may be

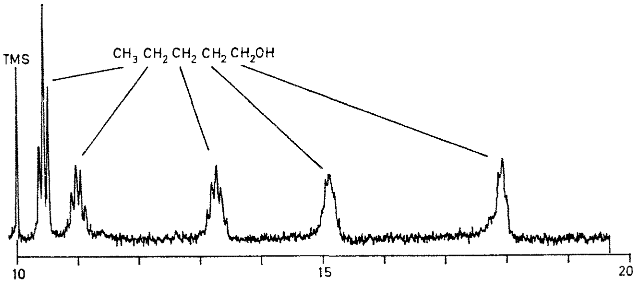

FIGURE. 100 *MHz* ^{1}H *n.m.r. spectrum of n-pentanol* (0·22 M) *and* Pr(tmhd)$_3$ (0·053 M); CCl$_4$ *solution*, τ *units, internal* Me$_4$Si *standard.*

moved out from that side of the envelope to which it lies nearest, or to whichever side is clear of other resonances. Thus a 0·27 M-solution of cholesterol in CCl_4, 0·10 M in $[Pr(tmhd)_3]$, shows the 10-methyl resonance in a clear region at τ 11·88, a 2·90 p.p.m. high field shift (instead of remaining within the methylene envelope[4]), while the 13-methyl resonance (τ 9·90) is now well separated from the C-21 (τ 9·14, doublet) and C-26, 27 methyl resonances (τ 9·17, doublet) instead of being shifted back upon them.

The relative sign and magnitude of the shifts produced by different lanthanides (which depend on the appropriate *g*-tensor) are illustrated by the proton resonance shifts of acetonitrile solutions of the new series of complexes $M(ClO_4)_3\{OP(NMe_2)_3\}_4$ (p.p.m. to high field, relative to the diamagnetic La complex) Ce, −1·5; Pr, −3·0; Nd, −1·15; Sm, −0·27; Eu, 1·33; Gd, not observed; Tb, −19·2; Dy, not observed; Ho, −17·0; Er, 4·4; Tm, 6·9; Yb, 6·66; Lu, 0. The resonances of the Pr complex in this and other[2,7] series are the sharpest of those of like sign.

It is suggested[4] that lanthanide complexes other than $[Eu(tmhd)_3]$ will probably act as shift reagents. We believe this possibility to be limited, as $[M(tmhd)_3]$ are unusual lanthanide compounds in having a co-ordination number of only six (thus allowing co-ordination by the substrate); in being soluble in non-polar solvents; in being stereochemically rigid, in giving an adduct having a highly anisotropic *g*-tensor, and in showing minimal interfering proton resonances. The combination of these properties must indeed be rare. We find, for example, that $Pr(NO_3)_3(OPPh_3)_3$, $Pr(ClO_4)_3\{OP(NMe_2)_3\}_4$, $Eu(NO_3)_3(OAsPh_3)_4$, $Ce(NCS)_3(OPPh_3)_4$, and lanthanide perchlorates induce shifts in added alcohols and ketones which are very small, only *ca.* 0·5 p.p.m. for an α-proton in $CDCl_3$ solution.

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