Temperature and Concentration Dependence of the Paramagnetic Induced Shifts in Proton Magnetic Spectroscopy

By L. TOMIĆ, ZDENKO MAJERSKI, M. TOMIĆ, and D. E. SUNKO*
(*"Rudjer Bošković" Institute, Zagreb, Yugoslavia*)

Summary The paramagnetic induced proton shifts of alcohols are strongly affected by temperature and by absolute concentrations of both the alcohol and tris-(dipivalomethanato)praseodymium(III), Pr(DPM)$_3$.

THE paramagnetic rare-earth complexes, tris(dipivalomethanato)europium(III)[1-5] and tris(dipivalomethanato)-praseodymium(III)[6] [Eu(DPM)$_3$ and Pr(DPM)$_3$], have been shown to be strong n.m.r. shift reagents which largely simplify complex spectra of compounds containing lone-pair functionalities. These complexes associate with, for example, the hydroxy-group of alcohols inducing selective paramagnetic shifts of proton signals through pseudocontact[1,3,4,5c] proton–metal interactions.†

It was reasonable to assume that not only structure and conformation of the compound bearing lone-pair functionalities should influence the induced chemical shifts. Recently Demarco *et al.*[3a] with Eu(DPM)$_3$ and *cis*-4-t-butylcyclohexanol have demonstrated that each proton signal is shifted linearly to lower field with increasing complex concentration, the change in chemical shift being larger for protons closer to the europium atom associated with the hydroxy-group.

In our studies of paramagnetic induced shifts in n.m.r. spectra of cyclopropylmethanols we used Pr(DPM)$_3$‡ since this complex shows shifts in the opposite direction three times larger than the europium complex.[6] Figure 1 shows n.m.r. spectra of cyclopropylmethanol and (1-methylcyclopropyl)methanol in the presence of Pr(DPM)$_3$. The spectra were assigned by inspection of the corresponding Dreiding models taking into account probable coupling constants and the mathematic expression for pseudocontact shifts.[8]

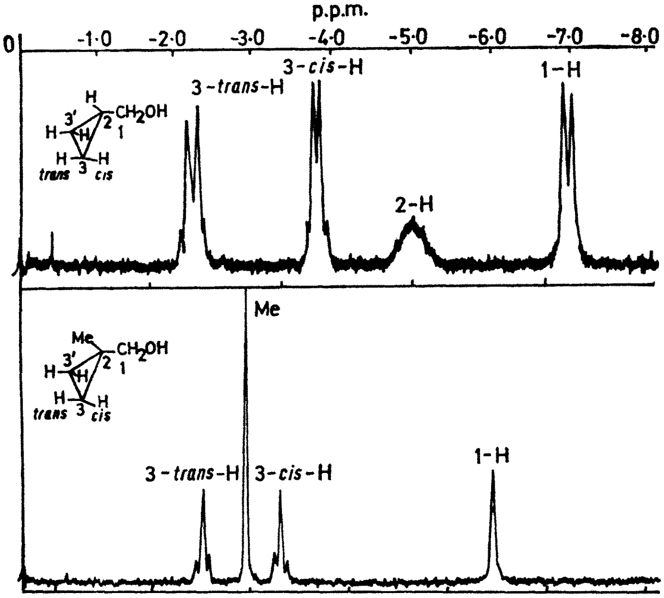

FIGURE 1. *Pr(DPM)$_3$-induced n.m.r. spectra of cyclopropylmethanol and (1-methylcyclopropyl)methanol* [0·2M-ROH, 0·05M-Pr(DPM)$_3$ *in* CCl$_4$].

Change in the concentration of Pr(DPM)$_3$ affected the upfield shifts in a similar manner to that observed for the downfield shifts with Eu(DPM)$_3$[3a] (see *e.g.* Figure 2B). Concentrations of Pr(DPM)$_3$ greater than 0·05M induced considerable broadening of the signal for protons close to the site of co-ordination, probably owing to reduced spin–lattice relaxation time near the paramagnetic centre.[9] However, factors other than concentration also strongly affect the position of the proton resonance signal. The addition of a small amount of the same alcohol, or other compounds bearing lone-pair functionalities, shifts all the signals downfield (towards tetramethylsilane), thus decreasing the effect of the added complex (Figure 2D—F). The exact position of the proton signals depends upon the absolute concentrations of the solute and the lanthanide complex, rather than upon their ratio. Dilution also shifts the signals downfield (Figure 2C). A change of solvent from CCl$_4$ to CS$_2$§ is essentially without effect.

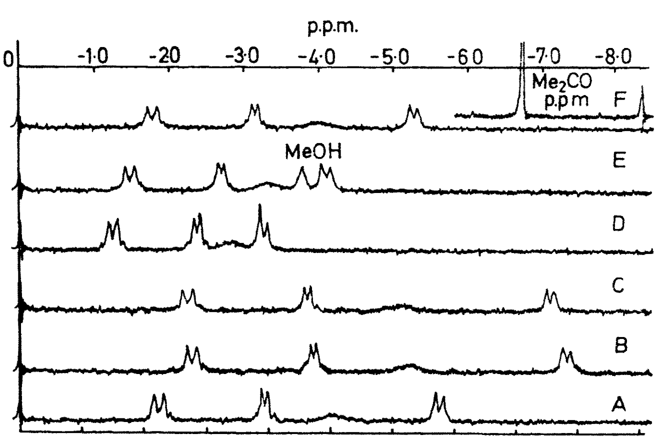

FIGURE 2. *Dependence of* Pr(DPM)$_3$*-induced shifts of cyclopropylmethanol* (**1**) *proton signals upon concentration of* (**1**), Pr(DPM)$_3$, *and "impurities."* A, (**1**) 0·2M, Pr(DPM)$_3$ 0·05M *in* CCl$_4$; B, A + ca. 5 *mg* Pr(DPM)$_3$; C, B + ca. 0·1 *ml* CCl$_4$; D, C + ca. 10 *mg of* (**1**); E, B + ca. 5 *mg* MeOH; F, B + ca. 10 *mg* Me$_2$CO.

Shifts induced by Pr(DPM)$_3$ are very sensitive and inversely proportional to temperature as might be expected on a theoretical basis.[8] This shifting is reversible and a

---

† The contact interactions may be important only in the case of α-protons.[1,3a,4]

‡ Spectra were recorded on a Varian A-60A spectrometer. Pr(DPM)$_3$ was prepared by a published procedure.[7]

§ Carbon disulphide might be a superior solvent for low temperature investigations due to its low melting point (−110·8°) and good solubility of Pr(DPM)$_3$.

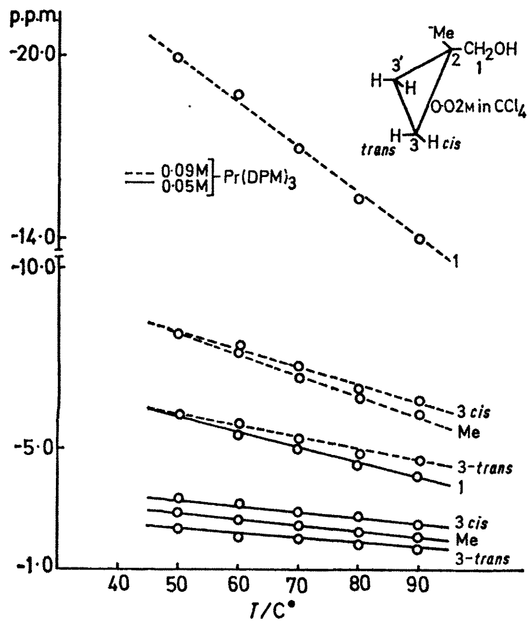

FIGURE 3. *Temperature and concentration dependence of induced proton shifts for different protons in (1-methylcyclopropyl)methanol.*

good linearity was observed over the temperature range of 50—90° (Figure 3). Analogous patterns were observed with 1-methylcyclobutanol and n-pentanol. However, the slopes are dissimilar for different protons and always larger for protons closer to the co-ordination site. Some of the lines (*e.g.* for methyl and 3-*cis*-protons) even intersect at around only 40 °C. Since the slopes for different protons are not parallel, the same behaviour is to be expected for other protons at other temperatures. This probably indicates a temperature-dependent change of the relative positions of the corresponding protons and the rare-earth metal. However, at higher concentrations of $Pr(DPM)_3$ the slopes are considerably larger, particularly for protons closer to the co-ordination site. Studies of paramagnetic induced chemical shifts should therefore always take into account their strong temperature and concentration dependence.

Our results further support Wahl and Peterson's[4] suggestion that a rapid (on the n.m.r. scale) equilibrium exists between a labile complex of the paramagnetic complex with the Lewis base (*e.g.* alcohol) and unassociated solutes. In other words, the shifted spectrum represents a time-averaged spectrum of the free and complexed solute.[6]

(*Received, April* 1*st*, 1971; *Com.* 479.)

[1] C. C. Hinckley, *J. Amer. Chem. Soc.*, 1969, **91**, 5160.

[2] J. K. M. Sanders and D. H. Williams, *Chem. Comm.*, 1970, 422.

[3] P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, (a) 1970, **92**, 5734; (b) 1970, **92**, 5737.

[4] G. H. Wahl, jun. and M. R. Peterson, jun., *Chem. Comm.*, 1970, 1167.

[5] (a) K. J. Liska, A. F. Fentiman, jun., and R. L. Foltz, *Tetrahedron Letters*, 1970, 4657; (b) L. H. Keith, *ibid.*, 1971, 3; (c) R. R. Fraser and Y. Y. Wigfield, *Chem. Comm.*, 1970, 1471; (d) G. M. Whitesides and J. San Filippo, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 6611.

[6] (a) J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Staniforth, *Chem. Comm.*, 1970, 749; (b) J. Briggs, F. A. Hart, and G. P. Moss, *ibid.*, p. 1506.

[7] K. J. Eisentraut and R. E. Sievers, *J. Amer. Chem. Soc.*, 1965, **87**, 5254.

[8] D. R. Eaton and W. D. Phillips, "N.m.r. of Paramagnetic Molecules," in "Advances in Magnetic Resonance," Vol. 1, Academic Press, New York, 1965, p. 103; H. J. Keller and K. E. Schwarzhans, *Angew. Chem. Internat. Edn.*, 1970, **9**, 196.

[9] L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1969, 2nd edn., p. 9.