

# Lanthanide-induced Shifts in the Carbon-13 Nuclear Magnetic Resonance Spectra of Ketones

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**Summary** Contact contributions can be significant to the  $\text{Eu}(\text{dpm})_3$ - and  $\text{Pr}(\text{dpm})_3$ -induced shifts of  $\alpha$ -carbon atoms in the  $^{13}\text{C}$  n.m.r. spectra of ketones:  $\text{Yb}(\text{dpm})_3$  is an excellent shift reagent for  $^{13}\text{C}$  n.m.r. structural studies.

THE usefulness of lanthanide shift reagents for quantitative structural studies relies upon the assumption that the induced n.m.r. shifts are pseudo-contact in origin.<sup>1</sup> For induced proton shifts, this assumption seems largely to be justified.<sup>2</sup> Lanthanide-induced contact shifts have been observed in the  $^{13}\text{C}$  spectra of amines,<sup>3,4</sup> pyridines,<sup>5</sup> and alcohols.<sup>6</sup> Our data for some ketones are given in Figure 1. For the carbonyl carbon atoms, the values given in parentheses are those directly obtained from additions of the paramagnetic shift reagents. However, a parallel series of experiments was carried out using  $\text{La}(\text{dpm})_3$  to obtain the "complex-formation shift" in the absence of the paramagnetic shift.<sup>7,8</sup> The complex-formation shift was important for the carbonyl carbons (but negligible for all other carbons). The relevant values for the carbonyl carbons are therefore those which do not appear in parentheses, and these were obtained by correcting the parenthetical values for the complex-formation shift.

To be able to calculate the  $^{13}\text{C}$  pseudo-contact shifts for 4-*t*-butylcyclohexanone (5), we have determined the proton lanthanide-induced shifts (Table 1) and used the data for  $\text{Pr}(\text{dpm})_3$  (assuming the proton shifts to be exclusively pseudo-contact in origin) to determine the position of the Pr ion. This was accomplished using a computer program,<sup>9</sup> and using the usual geometric dependence [ $\text{shift} \propto (3 \cos^2 \theta - 1)/r^3$ ] for pseudo-contact shifts; in the absence of an X-ray crystal structure for (5), we have used the Cartesian co-ordinates described by Tai and Allinger.<sup>10</sup> The precision of the data did not allow unique location of the Pr ion. Acceptable solutions were found in the ranges  $R$  3–4 Å,  $\phi$  80–90°,  $\psi$  130–150° and 210–230° (Figure 2) with the metal ion's symmetry axis along the direction of the Pr–O axis. Thus complexation seems to occur into the oxygen atom's lone pair orbitals, and not along the axis of the C–O  $\sigma$ -bond.

TABLE 1.

Proton lanthanide-induced shifts for (5)<sup>a</sup>

	H-2 <sub>eq</sub>	H-2 <sub>ax</sub>	H-3 <sub>eq</sub>	H-3 <sub>ax</sub>	H-4 <sub>ax</sub>	Bu <sup>t</sup>
$\text{Eu}(\text{dpm})_3$	19.0	15.9	4.7			1.7
$\text{Pr}(\text{dpm})_3$	-26.7	-20.1	-7.2	-11.3	-7.6	-2.1
$\text{Yb}(\text{dpm})_3$	53.4	41.4	16.2			5.2

<sup>a</sup> Determined as for  $^{13}\text{C}$  shifts using *ca.* 1.7 M solutions in  $\text{CCl}_4$ : $\text{C}_6\text{H}_6$  (3:1) on a Perkin Elmer R 32 B spectrometer.

The calculated pseudo-contact  $^{13}\text{C}$  shifts based on the 'best' metal position from the proton data are given in Table 2.

Comparison of the predicted  $^{13}\text{C}$  pseudo-contact shifts and the observed values for (5) (Figure 1) indicates that although contact contributions to the observed carbonyl carbon shifts may be significant for  $\text{Eu}(\text{dpm})_3$  and  $\text{Pr}(\text{dpm})_3$ , the pseudo-contact shift accounts for a very large proportion of the total observed shift. The relatively small variation in the Eu/Pr shift ratio [–0.73 to –0.79 in (1)–(5)] for the carbonyl carbons of all five ketones also supports the

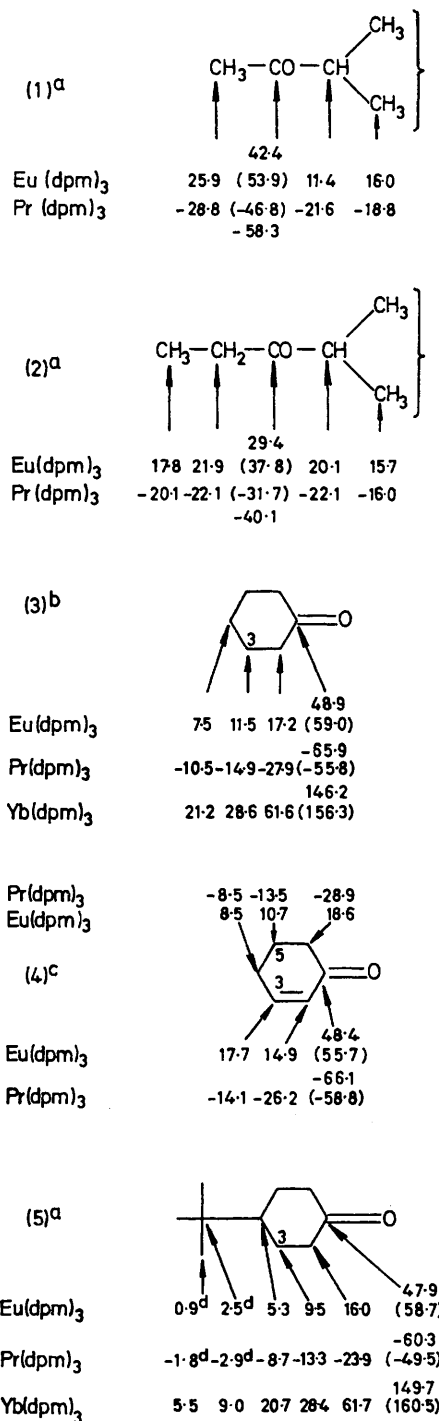


FIGURE 1.  $^{13}\text{C}$  Lanthanide-induced shifts determined on a Varian XL-100 spectrometer by sequential addition of shift reagent to substrate solution in the presence of  $\text{Cr}(\text{acac})_3$  (*ca.* 0.06M) and linear least-squares extrapolation to molar ratios.

<sup>a</sup> Solutions *ca.* 2M in  $\text{CCl}_4$ : $\text{C}_6\text{H}_6$  (3:1). <sup>b</sup> Solutions *ca.* 2M in  $\text{CCl}_4$ : $\text{C}_6\text{H}_6$  (5:1). <sup>c</sup> Solutions *ca.* 3M in  $\text{CCl}_4$ : $\text{CHCl}_3$  (4:1) <sup>d</sup> These values are much less precise ( $\pm 0.3$ ) than the other data owing to (i) signal overlap with the shift reagent ligand and (ii) the relatively small shifts.

conclusion that in all cases the pseudo-contact shifts are dominant. Neglect of the complex formation shifts would have led to different conclusions.

TABLE 2.

Predicted  $^{13}\text{C}$  lanthanide-induced shifts for (5)<sup>a</sup>

	C-4	C-3	C-2	C-1
Eu(dpm) <sub>3</sub>	.. 7.6	9.8	22.8	51.1
Pr(dpm) <sub>3</sub>	.. -10.7	-13.8	-32.0	-71.8
Yb(dpm) <sub>3</sub>	.. 21.4	27.6	64.0	143.5

<sup>a</sup> These predictions assume effective axial symmetry in the complex.

For the carbon atoms adjacent to the carbonyl group of (5) ( $\alpha$ -carbon atoms), the shifts observed for Eu(dpm)<sub>3</sub> and Pr(dpm)<sub>3</sub> are appreciably less than the calculated values. The conclusion that contact contributions can be important in determining  $\alpha$ -carbon shifts is supported by the relatively large variation in Eu/Pr shift ratios observed for the  $\alpha$ -carbons of (1). For  $sp^3$  carbons more distant from the carbonyl groups of the cyclic ketones (3)—(5), the observed shifts are consistent with those expected from a pseudo-contact mechanism. Contact contributions are observed for the C-2 and C-3 shifts in cyclohexenone (4) (Eu/Pr shift ratios of -0.57 and -1.25, respectively).

Our most important observation in the present work is the excellent agreement between the  $^{13}\text{C}$  calculated pseudo-contact shifts for (5) as a substrate for Yb(dpm)<sub>3</sub> (Table 2)

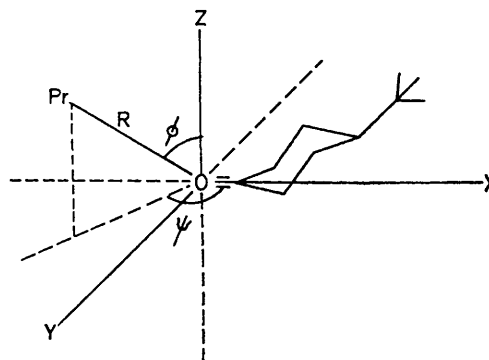


FIGURE 2.

and the observed values (Figure 1). Thus Yb(dpm)<sub>3</sub> is an excellent shift reagent for  $^{13}\text{C}$  spectra since (i) contact contributions are minimised and (ii) the observed shifts are large.<sup>11</sup>

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<sup>1</sup> E. DeBoer and H. van Willigen, *Progr. N.M.R. Spectroscopy*, 1967, **2**, 111

<sup>2</sup> See, for example, J. K. M. Sanders and D. H. Williams, *Nature*, 1972, **240**, 385; for an exception, see B. F. G. Johnson, J. Lewis, P. McArdle, and J. R. Norton, *J.C.S. Chem. Comm.*, 1972, 535.

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<sup>8</sup> K. Tori and Y. Yoshimura, *Tetrahedron Letters*, 1973, 3127.

<sup>9</sup> Program "METALSEARCH" provided by L. O. Ford, Laboratory of Molecular Biophysics, University of Oxford, and modified by us for use with an I.B.M. 370 computer.

<sup>10</sup> J. C. Tai and N. L. Allinger, *J. Amer. Chem. Soc.*, 1966, **88**, 2179; the Y and Z co-ordinates and the co-ordinates for equatorial and axial substituents at C-4 have been interchanged.

<sup>11</sup> See also O. A. Gansow, P. A. Loeffler, R. E. Davis, M. R. Willcott, and R. E. Lenkinski, *J. Amer. Chem. Soc.*, 1973, **95**, 3389.