Aromatic Proton Magnetic Resonances that are not Shifted by $Eu(dpm)_3$

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Summary The failure of the *meta* and *para*-proton magnetic resonances of *cis*-4-t-butyl-1-phenylcyclohexanol to shift in the presence of added $Eu(dpm)_3$ indicates a limit in the precision with which conclusions drawn from shift-reagent analysis can be specified.

RECENT reports[1,2] have described upfield displacements of resonance positions for certain protons in molecules treated with the Lewis-acid lanthanide shift reagent[3] $Eu(dpm)_3$ [tris-(2,2,6,6-tetramethylheptane-3,5-dionato)europium]. The observation of this phenomenon provides an elegant verification for the relationship derived by McConnell and Robertson[4] to describe dipolar (pseudocontact) interactions of paramagnetic centres with magnetically active nuclei,

$$\Delta H_i/H_o = K(3\cos^2\phi_i - 1)/r^3{}_i$$

in that the upfield shift is predicted[2] for $\sim55° < \phi < \sim125°$, independent of the europium–proton distance (r), as found in these molecules.[1,2]

Addition of graduated amounts of $Eu(dpm)_3$ to a solution of *cis*-4-t-butyl-1-phenylcyclohexanol (**1**), which has its hydroxy-group axially disposed, in CCl_4 causes the anticipated, downfield shift of all the proton resonances of (**1**) except those of the *meta*- and *para*-protons of the phenyl group. The gross appearance of these latter signals (see Figure) indicates that they are not separated from each other by the addition of increasing amounts of the shift reagent; simultaneously, the *ortho*-proton signal exhibits evidence of higher-order coupling interactions in its unsymmetrical appearance. Every proton resonance of the *trans*-analogue is shifted downfield by added $Eu(dpm)_3$.

A proton residing at an Eu–O–H angle of *ca.* 55° is predicted to experience neither shielding nor deshielding from the paramagnetic centre.[2] For the *meta*-proton, ϕ is

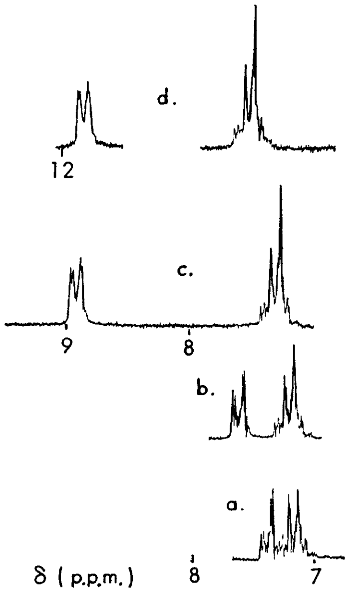

FIGURE. *N.m.r. spectrum of the aromatic protons of* (**1**) *in* CCl_4 *containing* (a) *no*; (b) 0·04; (c)0·18; (d) 0·5 *molar equiv. of* $Eu(dpm)_3$.

only slightly larger than this value, if the usual bond lengths and angles be assumed, whereas, for the *para*-proton, the corresponding angle is somewhat larger, so that small, upfield shifts of different magnitude would be expected for these two sets of signals. At present, the observed behaviour may be rationalized as arising from a modest amount of inexactitude in the McConnell–Robertson relationship, from deviation in the crowded $\mathrm{Eu(dpm)_3}$–(**1**) complex from the cylindrical symmetry that was assumed in the derivation[4] of this expression, from geometric distortion in the Eu–O–C–Ph portion of the $\mathrm{Eu(dpm)_3}$–(**1**) complex, or from some combination of these considerations. A more precise explanation may appear as the understanding of the applications of these shift reagents becomes more sophisticated.

Spectra were recorded on a Varian HA-100 spectrometer at ambient temperature (35°), with internal $\mathrm{Me_4Si}$ (3% v/v) as a lock signal and calibrant. Compound (**1**) and its isomer were provided by Dr. K. D. Berlin.

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