An *Up*field ^{1}H Nuclear Magnetic Resonance Shift Induced by Tris(dipivalomethanato)europium

By T. H. SIDDALL, III

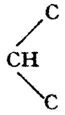
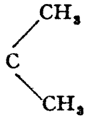
(Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122)

Summary The n.m.r. shift reagent tris(dipivalomethanato)-europium shifts *up*field one of the β-methyl doublets of 2,6-di-2-propylacetanilide.

THERE have now been several reports[1–3] on the use of $Eu(dpm)_3$ (I) as a reagent to enhance n.m.r. shifts in polar organic molecules. These shifts have always been reported as *down*field with respect to signal positions in the organic molecule by itself. It has been suggested that these shifts may serve as quantitative indicators of the distance between the europium ion and the resonating nucleus. I report an instance of failure of the shift–$1/r^3$ relationship, not just with respect to magnitude, but with respect to sign.

Shift data are given in the Table for 0·4 M-2,6-di-2-propylacetanilide (II) plus 0·4M-(I) at 35° in $CDCl_3$. (I thank Ethyl Corporation for a sample of 2,6-di-2-propylaniline.) This amide, (II), exhibits isomerism, due to slow rotation around the carbonyl–nitrogen bond. Rotation around the nitrogen–benzene-ring bond is also slow on the n.m.r. time-scale in both isomers. Rotation around this bond becomes rapid above −60° in the *endo*-isomer (benzene ring *cis* to the carbonyl oxygen) but remains slow in the *exo*-isomer (benzene *trans* to oxygen) to above 75°.[4] At room temperature this leads to two complete sets of signals, one for each isomer, with a further doubling of the β-methyl signals of the 2-propyl groups of the *exo*-isomer.

Signal shifts (p.p.m.)

$CH_3C(O)$					
endo	*exo*	*endo*	*exo*	*endo*	*exo*
3·3	9·4	3·1	4·1	0·91	1·74[a] +0·27[a]

[a] Decoupling shows these to be coupled to the same methine proton.

The *up*field shift of one of the β-methyl doublets in the *exo*-isomer persists under all conditions examined. These included lowering the temperature to −50° (shift = + 0·89; signals became very broad below −50°), varying the concentrations of (I) and (II), and the shift is even greater in the corresponding isobutyramide (IV) (+0·4 at 35°). As a sidelight,the presence of (I) changes the isomer ratio of (II). For 0·4M-(II) alone this ratio is 2/1, *endo/exo*; with 0·4M-(I) present, the ratio become 1/2, *endo/exo*.

Complexing, *per se*, with a lanthanide tris(dipivalomethanate) does not produce the observed effect. In the presence of tris(dipivalomethanato)lanthanum the β-methyl signals are partly obscured by the t-butyl signal. However, no β-methyl signal is shifted more than about 0·1 p.p.m. The isomer ratio again was changed to about 1/2, *endo/exo*.

A possible explanation for the upfield shifts for (II) and (IV) would be a substantial alternation of geometry in the interactions of these compounds with (I) as compared to the interactions of planar steroids with (I).[1,2] With such an alteration the dependence of shift on angle could become important enough to change the sign of the shift.[5] An alternative explanation based on a change in relative magnitudes of the magnetic susceptibility tensors seems unlikely. For Eu^{III} these relative magnitudes are dictated in all environments by the dominance of off-diagonal (in J_z) matrix elements for the Zeeman effect. There can be no diagonal elements for the ground manifold ($^7F_0$). Boltzmann factors reduce any contribution from the diagonal elements for the excited manifolds. The opposite sign of the shift for tris(dipivalomethanato)praseodymium as a shift reagent[6] reflects the possibilities inherent in the ground ($^3H_4$) manifold. The energies of the nine possible crystal-field levels within this manifold and also the admixture of J_z values in the eigenvector for each level are all quite sensitive to environment.[7]

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