On the Mechanism of Deshielding of the Tris(dipivalomethanato)europium Nuclear Magnetic Resonance Shift Reagent

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Summary Application of the tris(dipivalomethanato)-europium, [Eu(dpm)$_3$], n.m.r. shift reagent to adamantan-1- and -2-ol provides evidence that the mechanism of deshielding involves *both* interaction through space and through bonds.

SANDERS AND WILLIAMS[1] have recently reported on the preparation of an n.m.r. shift reagent, [Eu(dpm)$_3$], which has properties superior to those of the dipyridine adduct of Eu(dpm)$_3$ mentioned earlier by Hinckley.[2] In both these reports, observed chemical shift effects (where they could be confidently assigned) do not allow a clear distinction to be made between an effect of the europium complex through space or through chemical bonds. For example, of the more than thirty different types of hydrogens in cholesterol, only eight could be distinguished through application of the shift reagent[2] and of these only one was out of the order predicted based on the number of intervening bonds. The effects observed in the examples reported by Sanders and Williams[1] also correlate well with the number of bonds separating europium and the hydrogen studied. We report our results using Sanders and Williams' reagent on adamantan-1- and -2-ol.†

The n.m.r. spectrum of adamantan-1-ol (I)[3] has several very closely spaced absorptions. However, in a CDCl$_3$ solution [0·6 M in (I) and 0·4 M in Eu(dpm)$_3$] absorptions due to four different hydrogens on carbon are clearly visible. The signal for the OH proton could not be observed and was assumed to be at very low field[1] (see Table 1).

TABLE 1

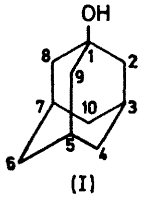
Effect of Eu(dpm)$_3$ *on the* 60 *MHz n.m.r. spectrum of adamantan-1-ol* (I)

Hydrogen(s)	d_{Eu-H}(Å)	No. of intervening bonds (Eu–H)	$\Delta\omega$(Hz)[a]
2,8,9 (6H)	2·77	4	268
4,6,10-*cis* (3H)	4·82	6	87
3,5,7 (3H)	5·03	5	81
4,6,10-*trans* (3H)	6·34	6	66

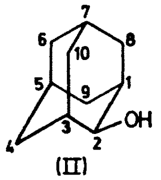
[a] Produced by a 0·4:0·6 mole ratio of Eu(dpm)$_3$ and (I) in CDCl$_3$.

The isomeric adamantan-2-ol (II) is considerably less symmetric and contains nine different types of hydrogens (2-H; 1,3-H; 8,10-*cis*-H; 7-H; 8,10-*trans*-H; 4,9-*cis*-H; 4,9-*trans*-H; 5-H; 6-H) in addition to the OH proton. Its normal n.m.r. spectrum is similarly uninformative.[4] However, solutions of (II) in CDCl$_3$ with varying proportions of the reagent reveal all nine different hydrogens (including two geminal methylene AB pairs!) (see Table 2).

Of greatest interest is the relative magnitude of the deshielding of the various hydrogens on the carbon skeleton. 2-H, as might be expected[1,2] since it is on the same carbon as oxygen, is most affected. However, the hydrogens at positions 8 and 10 which are *cis*-diaxial with respect to the OH are affected more than those at positions 1 and 3, even though the latter are separated by only four bonds from a europium atom that might associate at oxygen,[1] while the former are separated by five. Similar "inversions" of the effect occur when comparing 4,9-*cis*-H with 7-H, and 5-H with 6-H.



(I)



(II)

TABLE 2

Effect of Eu(dpm)$_3$ *on the* 60 *MHz n.m.r. spectrum of adamantan-2-ol* (II)

Hydrogen(s)	d_{Eu-H}(Å)	No. of intervening bonds (Eu–H)	$\Delta\omega$(Hz)[a]
2 (1H)	3·26	3	>1500
8,10-*cis* (2H)	1·53	5	900
1,3 (2H)	2·77	4	870
8,10-*trans* (2H)	3·16	5	449
7 (1H)	3·18	6	413
4,9-*cis* (2H)	5·03	5	391
4,9-*trans* (2H)	5·14	5	341
6 (2H)	5·16	7	320
5 (1H)	6·34	6	298

[a] Produced by a 1 : 1 mole ratio of Eu(dpm)$_3$ and (II) in CDCl$_3$.

Further evidence for the importance of the interaction through space may be seen by comparing 8,10-*cis*- and -*trans*-H and 4,9-*cis*- and -*trans*-H. All are separated from the europium by five bonds but their $\Delta\omega$'s range from 341 to 900 Hz. Several other examples of this may be seen in Tables 1 and 2.

A rationalization of these data is possible if it is assumed that the europium reagent forms a labile complex with the alcohol. Assuming also an oxygen–europium bond distance equivalent to the sum of the two covalent radii, an approximate C–O–Eu angle of 115° and allowing rotation about the C–O bond, distances of closest approach of the europium with each of the various hydrogen atoms (d_{Eu-H}) may be calculated.[5] Thus, the europium may approach much closer to the axial hydrogens (8,10-*cis*) than to the tertiary (1,3) hydrogens. The other two "inversions" are similarly explained, as is the analogous situation in the spectrum of (I) (*i.e.*, 4,6,10-*cis*-H *vs.* 3,5,7-H).

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† Samples of pure adamantan-1- and -2-ol were prepared by standard methods and their physical and chemical properties matched literature values.

We suggest that the shift reagent exhibits its effect by establishment of a rapid (on the n.m.r. time scale) equilibrium between a labile complex of Eu(dpm)$_3$ with a Lewis base [*e.g.*, (I) or (II)] and unassociated solutes. Furthermore, it is likely that this labile complex contributes very significantly to the observed shift through at least two mechanisms, through bonds and through space. The former is more important when only two or three bonds separate hydrogen and europium [*e.g.*, OH, and 2-H in (II)]. The latter effect becomes dominant when four or more bonds are involved if close approach of europium and hydrogen is likely. This explanation is in accord with all recently published observations of the various lanthanide reagents.[1,2,6] The reagent may thus become useful for the assignment of stereochemistry in complex structures, complementing other techniques such as the Nuclear Overhauser Effect (NOE).[7]

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[3] R. C. Fort, jun., and P. von R. Schleyer, *J. Org. Chem.*, 1965, **30**, 789.

[4] F. W. van Deursen and P. K. Korver, *Tetrahedron Letters*, 1967, 3923.

[5] Program COORD. Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana. Program number 136, donated by M. J. S. Dewar and N. C. Baird.

[6] J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Staniforth, *Chem. Comm.*, 1970, 749.

[7] A review of applications of the NOE in Organic Chemistry has recently appeared: P. D. Kennewell, *J. Chem. Educ.*, 1970, **47**, 278.