Tetrahedron Letters No. 21, pp. 1819-1820, 1971. Pergamon Press. Printed in Great Britain.

UPFIELD AND DOWNFIELD SHIFTS IN THE NUCLEAR MAGNETIC RESONANCE SPECTRUM OF A TRIS(DIPIVALOMETHANATO)EUROPIUM(III) COMPLEX[1]

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(Received in USA 12 April 1971; received in UK for publication 21 April 1971)

Since their introduction[2] the nmr shift reagents, tris(dipivalomethanato)europium(III) and tris(dipivalomethanato)praseodymium(III), have experienced immediate and marked popularity. The obvious utility of the technique is demonstrated by the number of structural problems which have been solved via its use.[3-6]

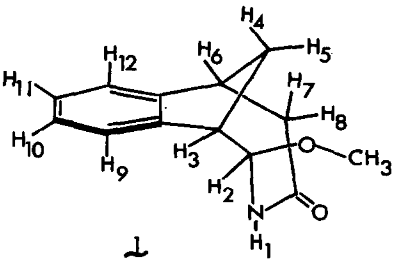
The induced shift has recently been shown to be essentially pseudocontact in nature[7,8] and, for axially symmetric complexes, should be governed by the equation of McConnell and Robertson[9]

$$\Delta H_i/H_p = K(3\ \cos^2 \phi_i - 1)/r_i^3$$

Although angle dependence has been considered in at least one case[7] it has usually been assumed that the 3 $\cos^2 \phi$ term will be of little importance and that it is a reasonable approximation to assume that the chemical shift difference, Δ_{Eu}[10], is essentially only Eu - H distance dependent.[2,8]

In the course of a photochemical investigation we[12] isolated a product, **1**, whose nmr spectrum was difficult to interpret due to coincidences in the chemical shifts of a number of its protons. Treatment of **1** with Eu(DPM)$_3$ caused chemical shift changes sufficient to allow the analysis of the proton spin-spin couplings on a first order basis. Decoupling experiments confirmed the proton assignments and the structure of **1**.

	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	$H_{10,11}$	H_{12}	O-CH$_3$
δ	6.87	4.23	3.53	2.40	2.40	3.21	2.87	2.87	7.20	7.20	7.20	3.29
Δ_{Eu}	-13.0	-2.54	-2.38	-2.76	-3.86	-4.39	-10.7	-14.0	-1.03	-1.58	-4.0	+1.81



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All of the ring protons of 1 show the expected negative Δ_{Eu} values[11] but, exceptionally, the Δ_{Eu} of the -O-CH_3 protons is positive i.e. we observe *upfield* and *downfield* shifts in the Eu(DPM)$_3$ complex of the same molecule. Similar results are obtained with Pr(DPM)$_3$ i.e. the ring protons are shifted *upfield* but the -O-CH_3 protons are shifted *downfield*.

We believe that this is due to the particular geometry of 1 and is a clear example of the importance of the angle dependence term in the equation of McConnell and Robertson. Care should be used in the interpretation of future results obtained with these shift reagents especially in cases where bridged or folded molecules are involved. We expect that additional examples of this phenomenon will appear in the literature shortly.[14]

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(10) Where $\Delta_{Eu} = \delta CDCl_3 - \delta^{n=1}_{Eu(DPM)_3}$ and n is the molar ratio of Eu(DPM)$_3$ to substrate.[11]

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(12) Experiments resulting in the formation of 1 will be reported elsewhere. The structure of 1 is consistent with its nmr, ir and analytical data. P.H. Mazzocchi and H.J. Tamburin, unpublished results.

(13) Nmr experiments were carried out on either a Varian A-60-D or a Hitachi R-20A instrument.

(14) M.R. Willcott has obtained similar results, see: M.R. Willcott, Abstracts, 12th Experimental NMR Conference, Gainesville, Florida, February 18-20.