Tetrahedron Letters No. 30, pp. 2817-2820, 1971. Pergamon Press. Printed in Great Britain.

TRIS(DIPIVALOYLMETHANATO)EUROPIUM^{III} INDUCED PMR SHIFTS OF CYCLIC KETONES

P. Kristiansen and T. Ledaal

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway.

(Received in UK 2 June 1971; accepted in UK for publication 24 June 1971)

Since the introduction of a lanthanide NMR shift reagent a couple of years ago[1], such reagents have become of great interest, and their usefulness are currently being illustrated by new important applications[2-8].

In the present investigation $Eu(DPM)_3$ was used as a PMR shift reagent on a series of homologous cyclic ketones, for which preferred individual conformations had previously been indicated[9,10]. The induced shifts are given in Table 1. The measuring conditions were kept as constant as possible, and as all homologs are assumed to form adducts with $Eu(DPM)_3$ of the same type, the data should allow comparison. However, in order to avoid any influence of unknown variations, we shall consider relative values for the different protons within the same compound. The $Eu(DPM)_3$ induced shifts are supposed to be mainly of the pseudo contact type[11]. The pseudo contact shift, Δ_p, can be expressed by the relationship

$$(1): \quad \Delta_p = K \frac{3\cos^2\phi - 1}{r_i^{\,3}} \quad ^{12} .$$

K is a constant for a given complex, r_i is the distance between the Eu atom and a proton H_i, and ϕ is the angle between the Eu - H_i and the Eu - O directions. As K is the same for different protons within the same molecule, the relative shifts become a function of distances and angles only.

Table 1

Compound	Eu(DPM)$_3$ induced shifts of the different protons in Hz					
	alpha	beta	gamma	delta	epsilon	others
Cyclopentanone	456	165				
cyclohexanone	402	165	124			
cycloheptanone	432	183	126			
cyclooctanone	497	247	167	255		
cyclononanone	410	251	185	168		
cyclodecanone	467	305	219	(219)	(219)	
cycloundecanone	329	237	178	147	113	
cyclododecanone	320	215	200	107	78	78
cyclotridecanone	296	211	127	92	63	63
cyclotetradecanone	396	279	195	116	74	74
cyclopentadecanone	321	228	135	78	46	46

Provided the relationship (1) holds, the induced shifts should vary appreciably with variations in the angle ϕ. However, such shifts seem often, to a good approximation, to depend only on the distance r_i. This is of course the case when $3\cos^2\phi - 1 = 1$, and may be when the protons are symmetrically arranged relative to the symmetry axis of the Eu(DPM)$_3$ complex. The simplified relationship (2): $r_i/r_j = \sqrt{\Delta p_j/\Delta p_i}$ was tested on a model molecule of known structure, i.e. adamantanone. The angle C-O-Eu was assumed equal to 109° and the Eu-O distance 2.80 A. This is the oxygen-metal distance found by Dahl and Groth[13] in a cyclononanone-HgCl$_2$ complex. As Eu^{3+} and Hg^{2+} have the same empirical ionic radius and the ligand is a cyclic ketone in each case, the distance may be nearly correct. (The assumed angle and calculated distance for a similar Pr(DPM)$_3$ complex were 109° and 3.0 A, respectively[14]). The induced shifts, calculated distances, and distances measured on a Dreiding model are given in Table 2. As can be seen the correlation with equation (2) is good. Aside from uncertainties in measurements of ca one per cent, the calculated values are from 0 to 4 per cent too low.

Table 2

Hydrogen atoms	Induced shifts	Calculated r_i	r_i measured on model
alpha	480 Hz	(4.28 A)	4.28 A
beta"syn"	242 "	5.36 "	5.36 "
beta"anti"	161 "	6.16 "	6.28 "
gamma	129 "	6.64 "	6.84 "
delta	107 "	7.08 "	7.36 "

(The too low values are for protons pointing away from the adamantanone carbonyl group, *i.e.* protons situated in the anisotropy deshielding zone of this group. Assuming an increase in anisotropy deshielding caused by the Eu-complex of 10, 12, and 14 Hz for the beta "anti", gamma, and delta protons respectively the fit seems complete. However, in order to get a common K for all the adamantanone protons, one would have to assume an increase in inductive effects as well, of ca 55, 25, 10, and 8 Hz for the alpha, beta, gamma, and delta protons respectively. This makes $r_i^3 \cdot \Delta_p$ net = K = 33 600, where Δ_p net = Δ_p observed $-(\Delta_i + \Delta_a)$. The terms in the parenthesis are the assumed increase in inductive and anisotropy deshielding effect of the carbonyl group due to adduct formation with the Eu-complex).

Results obtained for adamantanone may not without caution be used on flexible molecules like the simple cyclic ketones. The corresponding distances may for flexible molecules be mean values of various conformations, and even if one single conformation exists in the complex, the uncomplexed molecule may be different. However, within one and the same complex the relative induced shifts may still correspond to mean relative distances being compatible with only one single or a given mixture of few distinct conformations. A computer programme may be useful in the search for such conformations. PMR measurements should preferably be performed with wide and systematic variation of concentrations and temperature.

This preliminary investigation seems to indicate similar conformational features of the cyclic ketones as found by other means[9,10]. The high relative induced shifts for the delta protons in the 8-ring ketone reflects the short transannular distance between just these protons and the carbonyl group. Relative induced shifts for the 14-ring ketone seem only compatible with one single conformation with maximum anti bonds and minimum empty space inside the ring. For the 5-, 6-, and 7-ring ketones calculated and measured distances were in good accordance with a half chair, a flattened chair and a slightly twisted chair conformation respectively.

Experimental.

The samples were prepared in the following way: $4 \cdot 10^{-4}$ mole of tris(dipivaloylmethanato)-europium^{III} (0.2186 g) and $8 \cdot 10^{-4}$ mole of the cyclic ketone in question was dissolved in 5 ml carbontetrachloride, and the spectrum was run on a Varian A 60 A apparatus. For the fourteen membered ring and for adamantanone the europium complex was added until the induced shifts became sufficiently large, without weighing of the sample.

Proton assignments were based on observed splitting patterns and confirmed by decoupling at 100 MHz.

References.

1) C.C. Hinckley, J. Am. Chem. Soc. 91, 5160 (1969).

2) J.K.M. Sanders and D.H. Williams, J. Am. Chem. Soc. 93, 641 (1971), and references cited therein.

3) R. v.Ammon, R.D. Fischer and B. Kanellakopulos, Chem. Ber. 104, 1072 (1971).

4) D.G. Buckley, G.H. Green, E. Ritchie and W.C. Taylor, Chem. and Ind., 298 (1971).

5) L.H. Keith, Tetrahedron Letters, 3, 1971.

6) K.K. Andersen and J.J. Vebel, Tetrahedron Letters, 5253, 1970.

7) S.G. Levine and R.E. Hicks, Tetrahedron Letters, 311, 1971.

8) K. Tori, Y. Yoshimura and R. Muneyuki, Tetrahedron Letters, 333, 1971.

9) T. Ledaal, Tetrahedron Letters, 4397, 1967.

10) T. Ledaal, Tetrahedron Letters, 651, 1968.

11) E.R. Birnbaum and T. Moeller, J. Am. Chem. Soc. 91, 7274 (1969).

12) H.M. McConnell and R.E. Robertson, J. Chem. Phys. 29, 1361 (1958).

13) S. Dahl and P. Groth, Acta Chem. Scand. In press.

14) J. Briggs, F.A. Hart and G.P. Moss, Chem. Comm., 1506, 1970.