

LANTHANIDE INDUCED PMR SHIFTS OF CYCLIC KETONES
A COMPARISON OF Pr(DPM)₃ AND Eu(DPM)₃ AS SHIFT REAGENTS

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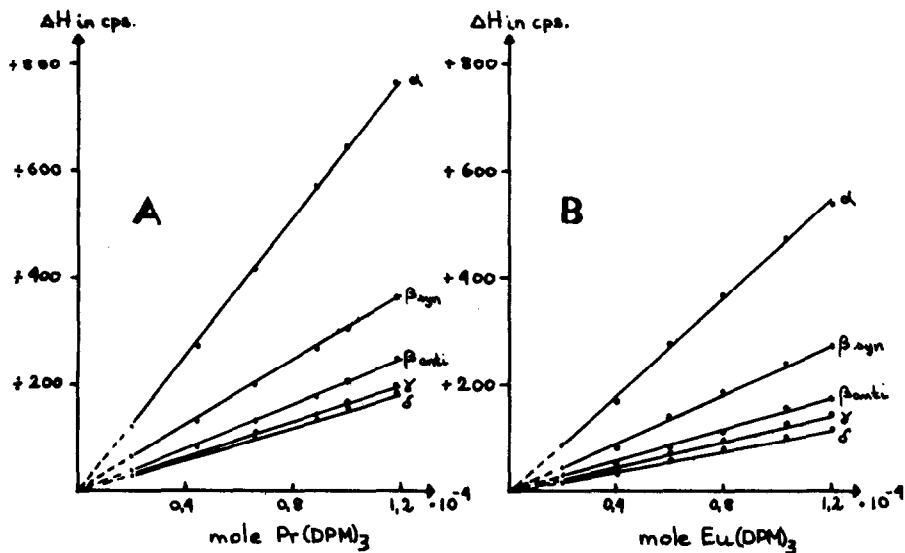
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The generally most useful and also complementary PMR shift reagents seem to be Eu(DPM)₃ and Pr(DPM)₃¹. Until now applications of the former dominates the literature, and relatively little have been published on Pr(DPM)₃²⁻⁶. Strictly comparable data of quantitative character are also lacking.

Recently the present authors gave some results obtained with Eu(DPM)₃ on cyclic ketones⁷, and we now report on comparable results obtained with Pr(DPM)₃ as shift reagent. Measurements have been made on a complete series of homologous cyclic ketones with from 5 to 15 ring carbon atoms. For comparable quantitative measurements adamantanone has been used as a standard cyclic ketone and an ideal model molecule. As seen from curves A and B below, both shift reagents showed strictly linear relationships for induced shifts to molar ratios at constant concentration and temperature.

As standard conditions for all further measurements were used a shift reagent /ketone mole ratio of 0.5, a ketone concentration of $2 \cdot 10^{-4}$, and a temperature of ca. 37 °C. Carbon tetrachloride was used as solvent with TMS as an internal standard, and the spectra were run on a Varian A 60 A apparatus.



In Table 1 are given observed and relative induced shifts at standard conditions with $\text{Pr}(\text{DPM})_3$ and $\text{Eu}(\text{DPM})_3$ as shift reagents on adamantanone.

Table 1

Shift reagent	Induced shifts for adamantanone protons					Relative shifts			
	α	β "syn"	β "anti"	γ	δ	α/β "syn"	α/β "anti"	α/γ	α/δ
$\text{Pr}(\text{DPM})_3$	-645	-307	-207	-163	-156	2.12	3.14	3.96	4.15
$\text{Eu}(\text{DPM})_3$	472	239	153	127	105	1.98	3.08	3.72	4.50
$\Delta\text{Pr}/\Delta\text{Eu}$	1.37	1.28	1.35	1.28	1.48	1.07	1.02	1.06	0.92

If one assumes the same geometry for the two complexes, and that all induced shifts are governed by the same laws, the relative shifts Δ_i/Δ_j for corresponding hydrogens should be the same for both shift reagents. From the right bottom column of Table 1 this is seen not strictly to be the case. If different contact shifts⁸ exists, it should mainly influence the alpha hydrogens by

causing too large shifts with the Eu- and too small shifts with the Pr-complex. As the $\Delta\text{Pr}/\Delta\text{Eu}$ ratio is not abnormally low for the alpha hydrogens, absence of a contact shift is indicated.

By making use of the relationship $r_i/r_j \approx \sqrt{\Delta H_j/\Delta H_i}$ and setting r_α equal to 4.28 Å as measured on a model, one gets the results given in Table 2.

Table 2

Shift reagent	Distances between lanthanide atom and adamantanone hydrogens					
	r_α	$r_{\beta\text{"syn"}}$	$r_{\beta\text{"anti"}}$	r_γ	r_δ	
Pr(DPM) ₃	(4.28)	5.48	6.25	6.76	6.89	calculated
Eu(DPM) ₃	(4.28)	5.35	6.21	6.63	7.06	calculated
	4.28	5.36	6.28	6.84	7.36	measured on a model

The discrepancies between calculated and measured values may be within the limits of error except perhaps for r_δ .

In order to make the product $\Delta H_i \cdot r_i^3$ equal to a common constant for all the adamantanone hydrogens, one may have to take differences in angles into account, i.e. to use the "more exact" relationship $\Delta H_i = K \frac{3 \cos^2 \phi_i - 1}{r_i^3}$

The angles should then be defined as the angles between the lanthanide/hydrogen directions and the symmetry axis of the actual complex. If the angles are defined relative to the lanthanide/adamantanone oxygen direction, the discrepancies become greater by using the angle relationship. Another way of making K equal for all the adamantanone hydrogens, as indeed it should be, is to assume that the complexation causes changes in the inductive and anisotropy effects of the adamantanone carbonyl group. This means that the observed induced shifts, $\Delta H_{\text{obs.}}$, are equal to $\Delta H_{\text{net}} + \Delta_I + \Delta_A$, where the two last terms stand for the above mentioned changes. For adamantanone with Eu(DPM)₃, and using the same corrections as in our previous report, we find the same constant $K \approx r^3 \cdot \Delta H_{\text{net}} \approx 33600$. With Pr(DPM)₃ as shift reagent, it is sufficient to assume that the deshielding adamantanone carbonyl group anisotropy on $\beta_{\text{"anti"}}$, γ and δ hydrogens are changed to small shielding effects by complexation.

A total assumed change of 13, 13 and 24 Hz for the β_{anti} , γ and δ hydrogens, results in a common K equal to ca 47500 i.e. $K_{\text{Pr}}/K_{\text{Eu}} \approx 1.4$.

In Table 3 are given $\text{Pr}(\text{DPM})_3$ induced shifts for the different protons of $\text{C}_5 - \text{C}_{15}$ ring ketones together with relative shifts $\Delta\text{Pr}/\Delta\text{Eu}$.

Table 3

Compound Cyclo-	Induced shifts in Hz and relative shifts for the protons					
	α	β	γ	δ	ϵ	
-pentanone	-521, 1.14	-223, 1.35				
-hexanone	-544, 1.36	-237, 1.43	-185, 1.49			
-heptanone	-567, 1.31	-245, 1.34	-166, 1.33			
-octanone	-545, 1.10	-292, 1.18	-182, 1.09	-271, 1.06		
-nonanone	-565, 1.37	-381, 1.52	-284, 1.53	-224, 1.33		
-decanone	-446, 0.96	-335, 1.10	-234, 1.07	-224, 1.02	-215, 0.98	
-undecanone	-423, 1.29	-358, 1.51	-254, 1.36	-213, 1.45	-158, 1.40	
-dodecanone	-386, 1.21	-296, 1.39	-285, 1.42	-151, 1.41	-89, 1.14	
-tridecanone	-400, 1.35	-321, 1.52	-234, 1.84	-144, 1.56	-86, 1.36	
-tetradecanone	-407, 1.03	-330, 1.18	-226, 1.16	-138, 1.19	-79, 1.07	
-pentadecanone	-469, 1.46	-389, 1.70	-240, 1.78	-142, 1.82	-79, 1.72	

The most striking facts are the strongly individual shifts for each ring size, with great variations as well as general trends. The alpha protons are drastically less shifted for the 10-ring and higher ketones than for the lower members. The shift ratios $\Delta\text{Pr}/\Delta\text{Eu}$ are abnormally low and very similar for the 8-, 10- and 14- ring ketones, and especially high for tridecanone and pentadecanone. Upward from the 7-ring ketone there are marked alternations in relative shifts, with high values for odd- and low values for even-membered rings. The mean value of all shift ratios is ca. 1.35 or the same as for the adamantanone protons. However, the variations in shift ratios are ca $\pm 30\%$ compared with less than 10% for the stiff adamantanone molecule. All taken together no contact shift is indicated. The correlation factor between mean distances calculated from $\text{Pr}(\text{DPM})_3$ and $\text{Eu}(\text{DPM})_3$ induced shifts is in the range 0.97 - 0.99 for the majority of distances. The lowest correlation factor is 0.90 for the distances of beta protons in cyclotridecanone.

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