

QUANTITATION OF THE CHEMICAL SHIFTS INDUCED BY TRIS(DIPIVALOMETHANATO)EUROPIUM III
IN THE PMR SPECTRA OF HYDROXYADAMANTANES AND CYCLOPENTANOL

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Like Wahl and Peterson,¹ we have recently used the NMR shift reagent, tris(dipivalomethanato)europium III $[\text{Eu}(\text{dpm})_3]$,^{2,3} to simplify the spectra of 2-hydroxyadamantane and in addition we have also studied a variety of 1-R-adamantanes ($\text{R} = (\text{CH}_2)_n\text{OH}$, $n = 1, 2, 3$) and cyclopentanol. Wahl and Peterson have reported a lack of linearity between the change in the magnitude of the chemical shift of a proton, upon addition of an equivalent amount of the shift reagent, and the number of bonds intervening between the hydrogen atom and the site of complexation. They attribute the influence of $\text{Eu}(\text{dpm})_3$ to two sources; (a) an effect through bonds, which predominates when only two or three atoms separate the two centres and (b) a direct effect through space, which becomes dominant when more than four bonds are involved. We believe that the direct effect is dominant for all cases and prefer to quantitate the magnitude of the chemical shift change in a different manner.

The quantitation procedure used by Wahl and Peterson involves the measurement of the difference in the chemical shift in the absence and the presence of a molar equivalent of $\text{Eu}(\text{dpm})_3$. One of the main reasons for using this reagent is to simplify spectra and it may not always be possible to assign the chemical shifts for the uncomplexed substrate. In addition, the NMR signals become considerably broadened in the presence of high concentrations of $\text{Eu}(\text{dpm})_3$, leading to some uncertainty in the exact position of the centre. We prefer to interpret the spectrum continually as increasing amounts of $\text{Eu}(\text{dpm})_3$ are added, making use of the sharper nature of the signals, in the presence of lesser quantities of the shift reagent, to facilitate peak assignment.

The chemical shift of a particular hydrogen atom varies linearly with the molar ratio of $\text{Eu}(\text{dpm})_3$ to the substrate for concentrations of shift reagent up to about 180 mg./ml. of CDCl_3 (see Equation 1 and Figure 1). The slope of the lines, which we call "the europium shift parameter \underline{S} ", serves as the measure of quantitation. The curvature observed at higher concentrations, which can be both concave or convex, is probably due to a combination of medium and association effects. The values of \underline{S} for all the hydrogens in the five substrates are listed in Table 1.

As noted previously,¹⁻⁴ the magnitude of the change in the chemical shift, $(\delta_E - \delta)$, is greatest for the hydrogens which are closest to the hydroxyl to which the europium complexes. The observed chemical shift for each $\text{Eu}(\text{dpm})_3$ /substrate ratio is a measure

of the rapid equilibrium between complexed and uncomplexed substrate. Consequently, the average Eu-H separation and not the closest proximity of the europium atom to the hydrogen atom,¹ should be the important factor determining the change in the chemical shift. As an approximate gauge of this separation, we have measured the distance (\underline{r}) between the centre of the hydrogen nucleus and the perimeter of the lone pair of the oxygen of the hydroxyl group,⁵ using Prentice Hall framework molecular models. The values of \underline{r} for each hydrogen are listed in Table 1.

$$(1) \quad \delta_E = \delta + \underline{S} \text{ Eu(dpm)}_3 / \text{substrate}$$

(δ_E and δ (chemical shift in the uncomplexed substrate) are in ppm relative to TMS)

Hinckley³ invokes pseudo-contact shift interactions, involving the inverse cube of the distance from a hydrogen nucleus to the europium atom, to explain the lanthanide-induced paramagnetic shifts. Using our measurement \underline{r} to the oxygen lone-pair perimeter⁵, rather than to the uncertain position of the metal atom, we find a very satisfactory quasi-coulombic relationship between the shift parameter \underline{S} and the inverse square of the separation for most of the hydrogens listed in Table 1 (Figure 2). Only two hydrogens ($S = 15.1, 15.2$) deviate markedly from the plot. In both cases, serious steric interactions with the shift reagent are highly probable and the \underline{r} values are obviously unrealistic.

The absence of a discontinuity in Figure 2 mitigates against a significant contribution arising from transmission through bonds when only a few atoms separate the Eu and H atoms, but accords favourably with the Eu(dpm)_3 exerting its influence through space.

In the more concentrated solutions of Eu(dpm)_3 , it is convenient to use CHCl_3 (in CDCl_3) as a secondary standard, as the broad band of the \underline{t} -butyl hydrogens ($\approx -1\delta$) hinders the use of TMS. As formulated, Equation 1 can be used to relate chemical shift

Figure 1 The relationship between chemical shift and the molar ratio of $\text{Eu}(\text{dpm})_3/\text{substrate}$

$\text{H}_{(n)}$ refer to 1-(2-hydroxyethyl)-adamantane as shown in Table 1

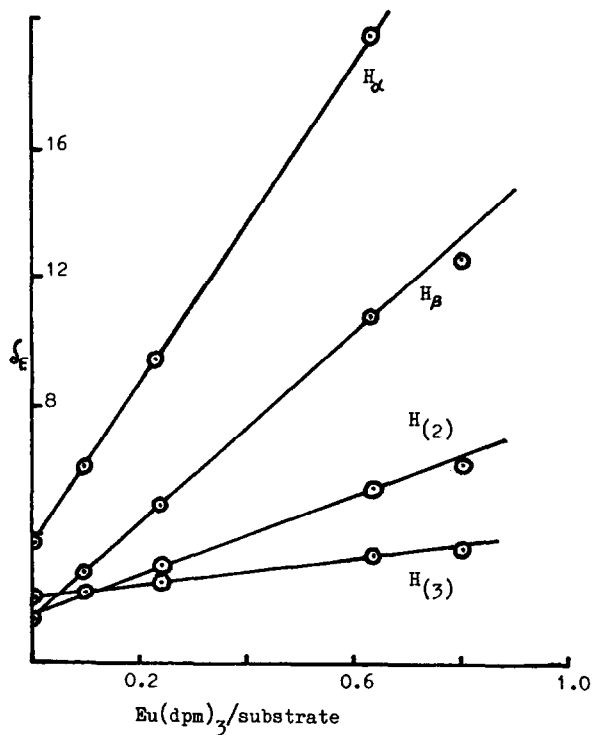
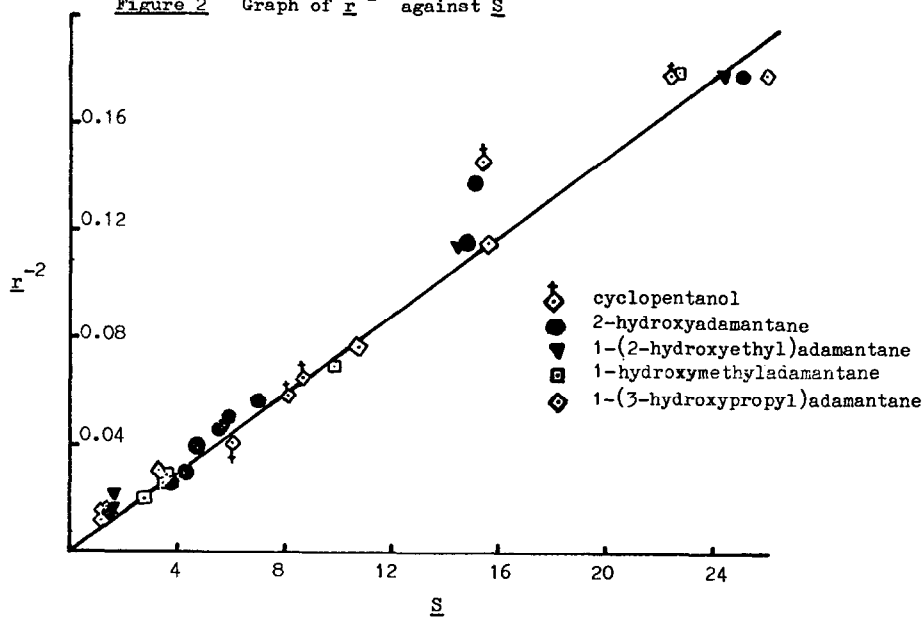


Figure 2 Graph of r^{-2} against S

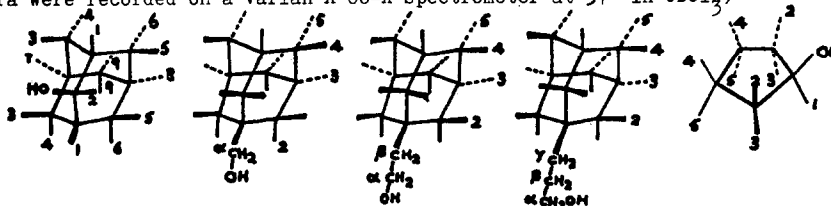


data for NMR spectrometers of varying frequency. In the following paper, an application of the use of the \underline{r} - \underline{S} relationship in the structure elucidation of the $\text{Eu}(\text{dpm})_3$ complex with 2-hydroxy-1-(2-hydroxyethyl)adamantane is outlined.

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Table 1 \underline{S}^a and \underline{r}^b values for hydroxyadamantanes and cyclopentanol

(All spectra were recorded on a Varian A 60-A spectrometer at 37° in CDCl_3)



Hydrogen	\underline{S}	\underline{r}	\underline{S}	\underline{r}	\underline{S}	\underline{r}	\underline{S}	\underline{r}	\underline{S}	\underline{r}
1	14.7	(2.94)							22.3	(2.37)
2	25.0	(2.37)	9.83	(3.75)	5.80	(4.56)	3.43	(5.62)	15.3	(2.62)
3	15.1	(2.69)	3.50	(6.13)	1.85	(6.75)	1.33	(8.06)	8.65	(3.69)
4	7.05	(4.19)	3.60	(5.88)	2.07	(6.49)	^c 1.20	(7.94)	8.05	(3.88)
5	5.58	(4.50)	2.70	(6.95)	1.43	(7.81)	^c 1.20	(9.06)	6.00	(4.88)
6	4.73	(5.00)								
7 or α	5.97	(4.44)	22.6	(2.37)	24.3	(2.37)	25.9	(2.37)		
8 or β	3.75	(5.88)			14.4	(2.95)	15.5	(2.95)		
9 or γ	4.27	(5.75)					10.7	(3.62)		

- a. Europium shift parameter, defined in Equation 1. Errors in values are $\pm 3\%$.
 b. Distance between the hydrogen nucleus and the average position of the europium as approximated by the position of the lone pairs of the oxygen atom of the hydroxyl group (see Reference 5). Errors in values are $\pm 0.06 \text{ \AA}$.
 c. Overall separation too small to distinguish $\text{H}_{(4)}$ and $\text{H}_{(5)}$.

References

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5. For the rigid secondary hydroxyl compounds, complete rotation of the hydroxyl group was assumed. On rotation, the tip of the lone pair orbitals describe a circle. The \underline{r} values were calculated by measuring the distance (in inches, converted to \AA) of the centre of each hydrogen nucleus to the centre of this circle. A similar procedure was used for the side chain substrates, but the orbitals of the hydroxyl group were orientated away from the adamantane to optimise the Eu-adamantane separation.