Proton Magnetic Resonance Studies of Cyclic Compounds. Part X.[1] The Spectrum and Conformation of *trans*-Decahydroquinoline co-ordinated to Tris(dipivaloylmethanato)europium

By **H. Booth** * and **D. V. Griffiths**, Department of Chemistry, University of Nottingham, Nottingham

The ^1H n.m.r. spectrum of *trans*-decahydroquinoline, simplified to a near-first-order situation by the addition of tris(dipivaloylmethanato)europium, is in complete agreement with a twin-chair conformation for the molecule, and decoupling experiments allowed confident assignment of every signal. Graphs of induced shifts, for each proton, plotted against the molar ratio of $Eu(dpm)_3$ to *trans*-decahydroquinoline, were linear only up to a ratio of *ca.* 0·3. A full quantitative treatment yielded a value of 12 l mol^{-1} for the equilibrium (or binding) constant, at 31 °C, in the reaction of the base with the lanthanide.

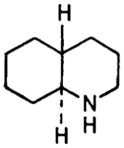
THE preferred conformation of many molecules in solution has been deduced from their proton magnetic resonance spectra. For some molecules, however, the conformational information obtained is severely limited by the complexity of the spectrum. Thus the spectrum[2] of *trans*-decahydroquinoline (1), measured at 220 MHz in $CDCl_3$, shows a broad envelope at high field (δ 0·8—2·0), accounting for no less than 16 of the 19 protons. Three one-proton signals, which occur at δ 3·05 (doublet, *J* 12 Hz), 2·65 (triplet, *J* 12 Hz, each part a doublet, *J* 4 Hz), and 2·09 (ill-defined triplet) were assigned to H(2*eq*), H(2*ax*), and H(8a) respectively, in the twin-chair conformation (2). However, it was clear that more refined techniques would be needed to establish every detail of conformation (2). The advent of the lanthanide

---

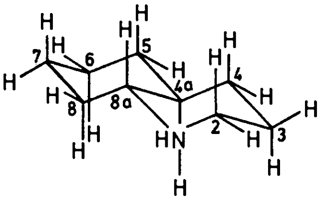
[1] Part IX, H. Booth and J. H. Little, *J.C.S. Perkin II*, 1972, 1846.

[2] H. Booth and A. H. Bostock, *J.C.S. Perkin II*, 1972, 615.

' shift reagents ',[3-5] an example of which is tris(dipivaloylmethanato)europium, offered a chance to simplify the spectrum of (1). These reagents form complexes with those compounds (donors) which contain atoms having unshared electron pairs. The ^1H shifts in the donor molecule undergo very large changes as a consequence of the unpaired electron of the lanthanide atom, the largest changes occurring for those protons which are closest in space to the lanthanide atom. In spite of some assumptions to the contrary, it seems unlikely that the donor molecule is ever fully complexed and thus the observed ^1H shifts are inevitably weighted averages of the ^1H shifts in the complexed donor, and those in the donor remaining uncomplexed. It follows, too, that any quantitative treatment must take into account the existence of a temperature-dependent equilibrium constant.



(1)



(2)

The addition of tris(dipivaloylmethanato)europium, $Eu(dpm)_3$ to a solution of *trans*-decahydroquinoline in $CDCl_3$ produced low-field shifts for all protons. A solution containing $Eu(dpm)_3$ and *trans*-decahydroquinoline in the molar ratio of 1·533 : 1 gave a 100 MHz spectrum which included 11 well separated low-field signals: a broad N–H singlet, 4 doublets, 4 quartets, and 2 triplets, all splittings being 10—12 Hz, since $|J_{gem}| \simeq |J_{aa}| \simeq$ 10—12 Hz (Figure 1, N–H not shown). A second-order pattern at high field became of the first order (3 quartets, 3 doublets) at 220 MHz.

The difficult task of making assignments was accomplished through the ten decoupling experiments (100 MHz) summarised in Figure 1. A vertical arrow establishes the irradiated signal, whilst vertical lines point to the signal(s) which is simplified by the loss of one coupling of 10—12 Hz. The two triplets B and C must be due to H(2*ax*) and H(8a). In experiment (a), irradiation of B caused doublet A (equatorial) to collapse to a singlet. Therefore B must have a geminal partner; therefore B is due to H(2*ax*), A is due to H(2*eq*), and triplet C must be due to H(8a). The remaining assignments follow logically from experiments (b)—(j), and all assignments are listed in Table 1. Next we investigated the quantitative aspects associated with the spectrum of *trans*-decahydroquinoline produced by successive additions of $Eu(dpm)_3$. Quantitative work with lanthanide shift reagents, co-ordinated with a given donor, have produced correlations of two types: (i) a graph of the induced shift, for a given proton, plotted against the ratio of molar concentrations of $Eu(dpm)_3$ to donor, gives a straight line, for ratios of up to *ca.* 0·5. Although some authors have drawn straight-line graphs for measurements up to a molar ratio of 1·0, it is clear from published graphs that the linearity does not, in fact, extend to such a high molar ratio.[6] (ii) The magnitude of induced shifts, for different protons, decreases with increasing distance of the proton from the lanthanide ion. In other words, the gradients of the plots in (i) for different protons, can be correlated with the distance of the proton from the europium atom, the steepest plots occurring for protons closest to the europium. If the induced shifts are due to pseudocontact shifts, basic theory[7] indicates that the shift should be proportional to r^{-3}, where r is the distance from the proton to the europium ion, and has an angular dependence of the form $(3 \cos^2\theta - 1)$, where θ is the angle between the principal axis of the complex and the vector from the europium to the proton. The first correlation (i) concerned us most, since extrapolation of the straight-line plots, for a particular proton, to zero molar ratio, gives the chemical shift of the proton in the uncomplexed donor molecule. It should, therefore, be possible to obtain the chemical shifts of those protons which give hidden signals in the spectrum of the donor molecule itself. In addition, it was of interest to determine the equilibrium constant for the reaction of the donor with the lanthanide complex.

TABLE 1

^1H shifts (δ values, p.p.m. from Me_4Si) in *trans*-decahydroquinoline complexed to tris(dipivaloylmethanato)-europium ($CDCl_3$ solution, molar ratio 1 : 1·533)

Proton	Shift	Proton	Shift
2*eq*	24·19	6*eq*	*a*
2*ax*	19·78	6*ax*	5·33
3*eq*	6·05	7*eq*	*a*
3*ax*	11·01	7*ax*	*a*
4*eq*	7·35	8*eq*	16·32
4*ax*	8·18	8*ax*	15·15
5*eq*	4·86	8a	18·24
5*ax*	5·86	4a	12·76

N–H at about 45·36

[a] Impossible to measure accurately.

Preliminary investigations encountered difficulties when solutions were prepared with a high molar ratio of $Eu(dpm)_3$ to *trans*-decahydroquinoline, consistent with sufficient *trans*-decahydroquinoline to give a useful ^1H n.m.r. spectrum. Such solutions usually contained

---

[3] C. C. Hinckley, *J. Amer. Chem. Soc.*, 1969, **91**, 5160; J. K. M. Sanders and D. H. Williams, *Chem. Comm.*, 1970, 422.

[4] J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, 1971, **93**, 641.

[5] I. Armitage and L. D. Hall, *Canad. J. Chem.*, 1971, **49**, 2770, and references therein.

[6] K. E. Stensio and U. Åhlin, *Tetrahedron Letters*, 1971, 4729; H. van Brederode and W. G. B. Huysmans, *ibid*, 1971, 1695; A. F. Cockerill and D. M. Rackham, *ibid.*, 1970, 5149.

[7] H. M. McConnel and R. E. Robertson, *J. Chem. Phys.*, 1958, **29**, 1361.

suspended solid or, alternatively, they deposited solid very soon after preparation. The precipitated solid was of unknown constitution and had to be filtered off to allow well-resolved spectra to be obtained. As a result, it was impossible, by direct weighing of each component, to prepare solutions of known, high molar ratios of $Eu(dpm)_3$ to *trans*-decahydroquinoline. The difficulty was overcome in the following way. A solution was prepared, of minimum volume for spectroscopic purposes, containing only just sufficient *trans*-decahydroquinoline in $CDCl_3$ to give a useful ^1H n.m.r. spectrum. The solution was saturated with $Eu(dpm)_3$ and then filtered directly into an n.m.r. sample tube, giving a solution of high (but unknown) molar ratio of $Eu(dpm)_3$ to *trans*-decahydroquinoline. The method of analysis of this solution is described later. The ^1H n.m.r. spectrum of this solution was determined. To the solution was added, successively, equal aliquot portions of a standard solution of *trans*-decahydroquinoline, in $CDCl_3$, the spectrum being determined after each addition. To accommodate the increase in volume, a special n.m.r. tube was constructed, consisting of a normal tube with the open end fused to an overflow bulb. Additions of *trans*-decahydroquinoline were made directly into this tube.

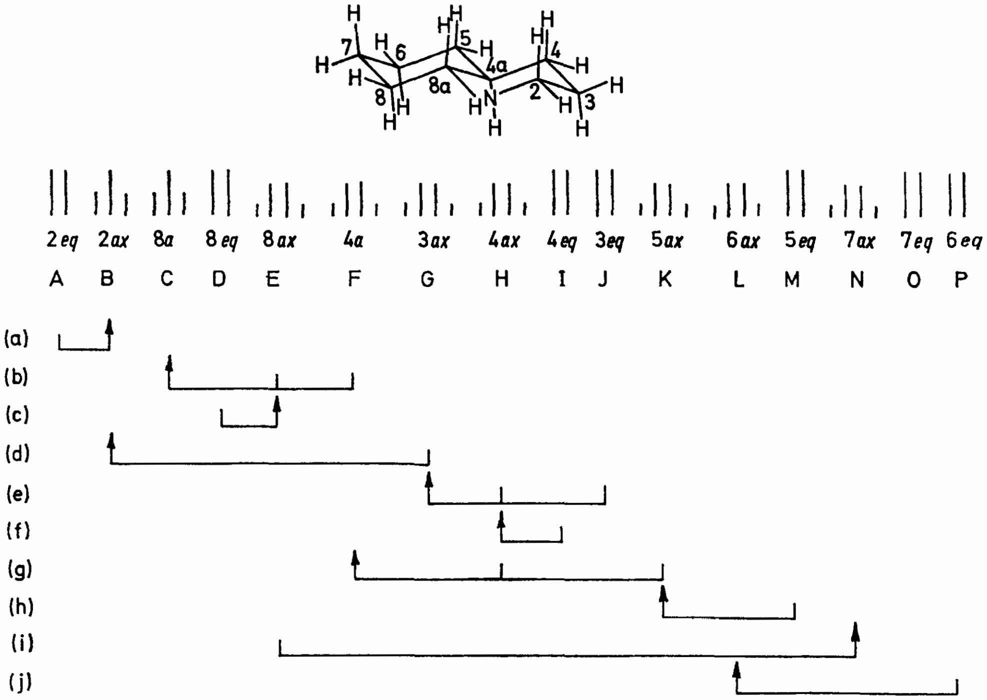


FIGURE 1 Summary of double irradiation experiments; vertical arrow, irradiated signal; vertical line, observed signal(s)

Theory of Complexing.—Basic equation. Let Eu stand for $Eu(dpm)_3$ and D for donor (*trans*-decahydroquinoline). Let mole fraction of D initially present

$$D + Eu \rightleftharpoons D,Eu \qquad (1)$$

be x, and mole fraction of Eu initially present be $(1 - x)$. Let there be y moles of D,Eu present at equilibrium. Then there are $(x - y)$ moles of D and $(1 - x - y)$ moles of Eu at equilibrium. Concentrations being expressed as mole fractions, the equilibrium constant K is given by equation (2). Applying the boundary

$$K = y(1 - y)/[(x - y)(1 - x - y)] \qquad (2)$$

condition, $y = 0$ when $x = 0$, we obtain equation (3).

$$y = \tfrac{1}{2}\left[1 - \sqrt{\left(1 - \frac{4Kx(1 - x)}{1 + K}\right)}\right] \qquad (3)$$

Let the chemical shifts of a given proton in uncomplexed D and in fully complexed D be δ_D and $\delta_{D,Eu}$ respectively. Then δ_{obs} = observed shift of the proton, is given by (4) and $\delta_{Ind.}$ = induced shift, by equation (5). Substitution for y in (1) gives equation (6) which is the basic

$$\delta_{obs.} = \frac{x - y}{x} \cdot \delta_D + \frac{y}{x} \cdot \delta_{D,Eu} \qquad (4)$$

$$\delta_{Ind.} = \frac{y}{x} \cdot \delta_{D,Eu} \qquad (5)$$

$$\delta_{Ind.} = \frac{1}{2x}\left[1 - \sqrt{\left(1 - \frac{4Kx(1 - x)}{1 + K}\right)}\right] \delta_{D,Eu} \qquad (6)$$

equation connecting the induced shift of the proton with the mole fractions of D and Eu.

Determination of $\delta_{D,Eu}$. The determination of $\delta_{D,Eu}$ is only possible after an assumption has been made. We assume that complete complexing of Eu occurs at a low ratio of [Eu] to [D], *i.e.*, when $(1 - x) \ll x$. Under these conditions, $y = (1 - x)$ and therefore we obtain equation (7). Thus a plot of $\delta_{\mathrm{Ind.}}$ (for a given proton)

$$\delta_{\mathrm{Ind.}} = \frac{(1-x)}{x}\,\delta_{\mathrm{D,Eu}} \qquad (7)$$

against $(1-x)/x$ should give a straight line for low values of $(1-x)/x$. This was found to be the case, and details for H(2*eq*) are listed in Table 2. The slope of the plot gave $\delta_{\mathrm{D,Eu}}$ for H(2*eq*) as 28·105 p.p.m. The standard solutions required for the determinations of Table 2 were obtained by direct weighing of components, since precipitation does not occur at low molar ratios.

TABLE 2

Variation of induced shift (δ value, p.p.m. from Me_4Si) of H(2*eq*) in *trans*-decahydroquinoline with molar ratio of $Eu(dpm)_3$ to *trans*-decahydroquinoline

Induced shift	Molar ratio
1·533	0·0575
1·624	0·0717
2·538	0·0908
2·514	0·1096
2·656	0·1137
3·694	0·1503
3·736	0·1527
4·310	0·1852
4·979	0·1877
5·975	0·2428
8·279	0·3212

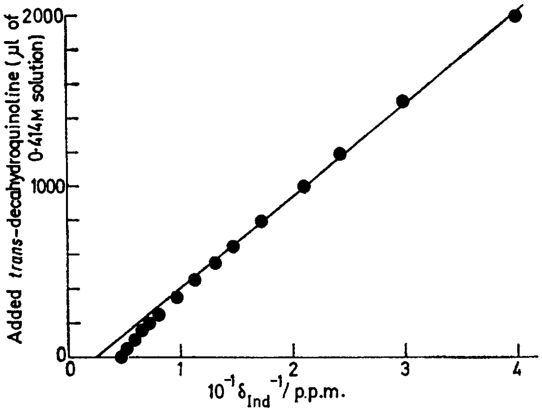


FIGURE 2 Variation of induced shift of H(2*eq*) with number of moles of *trans*-decahydroquinoline added to a $Eu(dpm)_3$–*trans*-decahydroquinoline mixture

Determination of x *and* (1 — x) *for high molar ratios of* (1 — x) *to* x. The remaining problem was the determination of t_0 and Eu_0, these being the number of moles of *trans*-decahydroquinoline and of $Eu(dpm)_3$, respectively, in the original filtered solution. Let t be the number of moles of *trans*-decahydroquinoline added to this solution before determinations of chemical shifts.

Rewriting of equation (7) gives equation (8). Substitution of $(t_0 + t)$ for x, and Eu_0 for $(1-x)$, gives (9).

$$\frac{1}{\delta_{\mathrm{Ind.}}} = \frac{x}{(1-x)}\cdot\frac{1}{\delta_{\mathrm{D,Eu}}} \qquad (8)$$

$$\frac{1}{\delta_{\mathrm{Ind.}}} = \frac{t_0}{Eu_0\cdot\delta_{\mathrm{D,Eu}}} + \frac{t}{Eu_0\cdot\delta_{\mathrm{D,Eu}}} \qquad (9)$$

When the reciprocal of $\delta_{\mathrm{Ind.}}$ was plotted against t (Figure 2), a straight line was obtained for high values of t [low ratios $(1-x):x$], thus justifying our assumption that complete complexing occurs under these conditions. The slope of the straight-line portion gave $(Eu_0\cdot\delta_{\mathrm{D,Eu}})^{-1}$ and hence Eu_0. The intercept gave $t_0(Eu_0\cdot\delta_{\mathrm{D,Eu}})^{-1}$ and hence t_0. Eu_0, t_0, and t being known, the molar ratios were available for each shift determination. For low molar ratios, the values obtained by this procedure agreed well with those obtained by direct weighting.

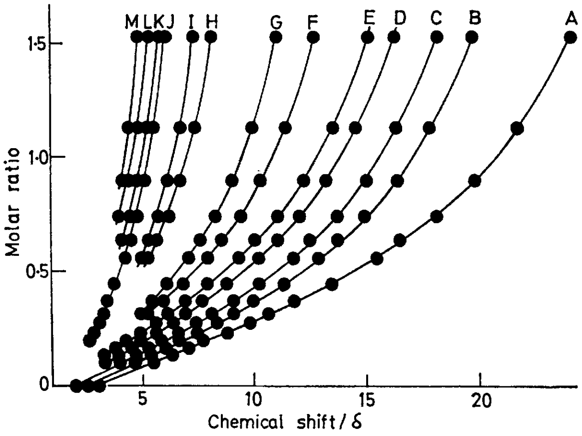


FIGURE 3 The dependence of the chemical shift of protons in *trans*-decahydroquinoline on the molar ratio of $Eu(dpm)_3$ to *trans*-decahydroquinoline. Letters A, B, *etc.* correlate with those in Figure 1

Determination of K. Finally, the molar ratio $(1-x):x$ was plotted against the induced shift $\delta_{\mathrm{Ind.}}$ for each proton in the molecule (Figure 3). The points for H(2*eq*) are also shown in Figure 4. Next, by use of equation (2), values of $\delta_{\mathrm{Ind.}}$ for H(2*eq*) were calculated for each value of x and with various values of the binding constant K. Curves of $(1-x)/x$ against $\delta_{\mathrm{Ind.}}$ for each value of K, were plotted by computer until a good match was obtained with the experimental points (Figure 4). The best fit was obtained with the binding constant $K = 12$ l mol⁻¹. Interestingly, this value

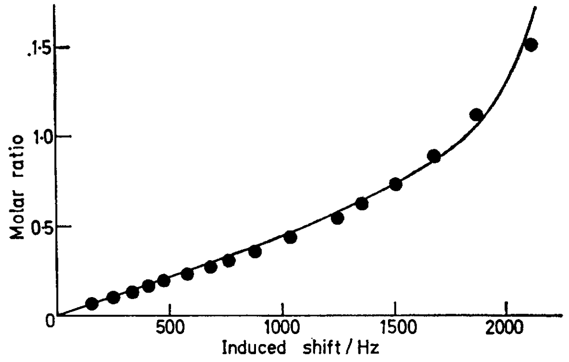


FIGURE 4 The dependence of induced shift of H(2*eq*) on molar ratio of $Eu(dpm)_3$ to *trans*-decahydroquinoline. Points: by experiment. Curve: calculated for a binding constant of 12 l mol⁻¹

is close to that determined by Armitage and Hall[8] for the complexing of n-propylamine with Eu(dpm)$_3$.

Finally Figure 3 shows that a satisfactory extrapolation of the curves to a molar ratio of zero is only possible for those signals clearly visible at low molar ratios of Eu(dpm)$_3$ to *trans*-decahydroquinoline.

EXPERIMENTAL

trans-*Decahydroquinoline*.—A commercial sample (Koch-Light) was freshly sublimed before use.

Tris(dipivaloylmethanato)europium.—The solid obtained by the literature method[9] was sublimed at 180 °C and 0·05 mmHg before use.

Spectra were measured on Varian HA-100 and Varian HR-220 spectrometers.

We thank the S.R.C. for a Studentship (to D. V. G.).

[2/1391 *Received, 4th August*, 1972]

---

[8] I. Armitage, G. Dunsmore, L. D. Hall, and A. G. Marshall, *Chem. Comm.*, 1971, 1281.

[9] K. J. Eisentraut and R. E. Sievers, *J. Amer. Chem. Soc.*, 1965, **87**, 5254.