The Application of Lanthanide-induced Shifts to the Complete Analysis of the Borneol Nuclear Magnetic Resonance Spectrum

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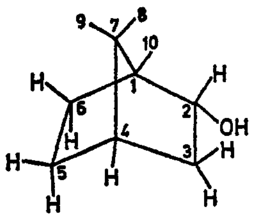
Summary Paramagnetic shifts induced in the n.m.r. spectrum of borneol by tris-(2,2,6,6-tetramethylheptane-3,5-dionato)praseodymium [Pr(tmhd)$_3$] have been used to evaluate all chemical shifts and coupling constants; the paramagnetic shifts agree well with calculated values.

WE have reported[1] that [Pr(tmhd)$_3$] shifts the n.m.r. signals of many organic compounds to higher field. This work, and the related studies[2,3] with [Eu(tmhd)$_3$] on shifts to lower field, used substrates having conformational flexibility. Although it was shown[2] that the shifts were predominantly of a pseudo-contact nature, precise calculations were not possible. The rigid stereochemistry of borneol (I) permits the construction of a much more accurate model so that the expected paramagnetic shifts may be calculated.



(I)

Spectra of CCl$_4$ solutions containing 0, 0·08, 0·16, 0·30, and 0·33 mole of [Pr(tmhd)$_3$] per mole of borneol were obtained at 100 MHz. Each signal could be followed in these spectra and the shift to higher field was for all signals directly proportional to the mole fraction of complex present. Hence the chemical shift of each proton in the second-order 100 MHz spectrum of pure borneol could be calculated. The shifted spectrum represents a time-averaged spectrum of the free and complexed borneol.

The pseudo-contact shift is given[4] by

$$\Delta H/H = \{f(g_{\parallel}, g_{\perp}, J)\}\, \frac{(3\cos^2\chi - 1)}{3kTr^3}$$

where χ is the O–Pr–proton internuclear angle and r is the corresponding Pr–proton distance. Effective uniaxial symmetry is assumed. Hence, for a particular orientation of the borneol molecule in its adduct with [Pr(tmhd)$_3$], the pseudo-contact shift of any proton is directly proportional to $(3\cos^2\chi - 1)r^{-3}$. This orientation may be defined in terms of the Pr–O internuclear distance, the Pr–O–(C-2) angle and the Pr–O–(C-2)–2-H dihedral angle. Inspection of a Dreiding model and other considerations suggested initial values for these parameters, namely 2·6 Å, 109°, and 33°, respectively. Using these numbers, a set of values of $(3\cos^2\chi - 1)r^{-3}$ was obtained for all protons. Comparison with the observed paramagnetic shifts now enabled a complete assignment to be made after consideration of probable coupling constants.

These assignments were confirmed and more accurate values of chemical shifts and coupling constants were obtained by first-order analysis of the spectrum of borneol obtained at 220 MHz (Tables 1 and 2). Further confirmation was provided by direct comparison of this spectrum with a 200 MHz spectrum of a solution containing 0·012 moles of [Pr(tmhd)$_3$] per mole of borneol. Decoupling experiments on the parent spectrum at 100MHz, and, more easily, on the shifted spectra at 100 and at 60 MHz were also confirmatory. The protons 2-H and 4-H have previously been assigned[5] by deuteriation studies.

The calculated values of $(3\cos^2\chi - 1)r^{-3}$ were further refined by a reiterative procedure to make the proportionality with the observed shifts as constant as possible. The standard deviation of the initial model was ±27%, which was improved to ±5·8% in the final model (Table 1) where Pr–O = 3·0 Å, Pr–O–(C-2) = 126° and the dihedral angle Pr–O–(C-2)–(2-H) = 25°. It is significant that these parameters appear to correspond with an orientation of the borneol molecule which has minimal intramolecular steric interactions with the other ligands. The Pr–O bond length of 3·0 Å remains, after correction for the lanthanide contraction, somewhat greater than similar bond lengths determined by *X*-ray crystallography; thus the H_2O ligand in [$Yb(CH_3COCHCOCH_3)_3H_2O$] has Yb–O = 2·34 Å.[6]

TABLE 1

^{1}H *n.m.r. spectra of* CCl_4 *solutions of borneol* (I) *in the presence of* [Pr(tmhd)$_3$]

Proton	*exo*-2-H	*exo*-3-H	*endo*-3-H	4-H	*exo*-5-H	*endo*-5-H	*exo*-6-H	*endo*-6-H	8-Me[a]	9-Me[a]	10-Me
Chemical shift[b]	6·10	7·80	9·08	8·42	8·30	8·77	8·88	7·97	9·14	9·15	9·18
Paramagnetic shift[c]	45·0	16·6	34·2	10·1	10·5	16·0	15·7	35·6	7·78	8·01	17·8
$K(3\cos^2\chi - 1)r^{-3}$[d]	49·0[e]	15·8	30·2	9·84	11·0	16·1	16·0	38·7	7·84	7·88	16·5

[a] These two assignments might possibly be interchanged.
[b] τ-value from 220 MHz spectrum.
[c] Expressed as (τ-value for 1 : 1 mole ratio [Pr(tmhd)$_3$] : borneol) minus (τ-value for borneol alone).
[d] *K* selected to allow direct comparison with observed shifts.
[e] This value compares well with the observed value, although the *exo*-2-H proton was excluded from configurational calculations on account of possible contact effects.

TABLE 2

Coupling constants (Hz) of borneol ^{1}H *n.m.r. spectrum; all other couplings* < 1 *Hz*

	exo-3-H	*endo*-3-H	4-H	*exo*-5-H	*endo*-5-H	*exo*-6-H	*endo*-6-H
exo-2-H	9·8	3·4				1·8	
exo-3-H		13·3	4·8	3·4			
4-H				4·8			
exo-5-H					12·9	8·8	3·7
endo-5-H						4·5	9·1
exo-6-H							12·9

The shifts to lower field caused by [Eu(tmhd)$_3$] are roughly proportional to each corresponding [Pr(tmhd)$_3$] shift. However, in detail it is clear that there is a change in orientation of the borneol in the complex as well as the expected smaller Eu–O distance.[7] Preliminary results from an analysis of the [Pr(tmhd)$_3$] shifts of cedrol[7] indicate that the geometry of co-ordination of the hydroxyl group is not identical with that of borneol. Hence it is probably necessary to determine the position of the lanthanide atom for each new substrate.

The strong dependence of the paramagnetic shift upon χ as well as upon r is especially noteworthy. This contrasts with previous work[2] and should especially be noted in the interpretation of shifted spectra, particularly in the assignment of protons having small values of r.

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