# A Ready Method of Assignment for ^{13}C Nuclear Magnetic Resonance Spectra: The Complete Assignment of the ^{13}C Spectrum of Borneol

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Summary Paramagnetic shifts induced in the ^{13}C n.m.r. spectrum of borneol by tris-(2,2,6,6-tetramethylheptane-dionato)praseodymium, Pr(tmhd)$_3$, have been used in a total assignment; these shifts and those induced by the corresponding europium and terbium complexes agree well with values calculated on the basis that their origin is of a pseudo-contact nature.

THE study of natural-abundance ^{13}C n.m.r. spectra has been hindered by the lack of a ready method of spectral assignment. Since broad-band decoupling of protons is commonly used, assignment has usually rested on semi-empirical knowledge of chemical shift values, on off-centre double resonance, or on deuteriation studies. For larger molecules, a full assignment is often extremely difficult.

(I)
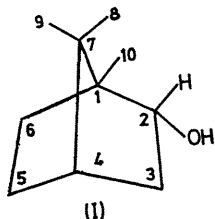
We have reported that shifts induced in the ^1H n.m.r. spectrum of borneol (I) by Pr(tmhd)$_3$[2] may be used for its complete assignment. The shifts agree well with values calculated on the basis of a pseudo-contact interaction [equation (1)].

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

where χ is the O–Pr–H internuclear angle and r is the corresponding Pr–H distance.

positions and assignments are shown in the Table. Assignments were obtained by comparison of experimental shift values with those predicted by calculation. Calculation was by substitution of the appropriate values of χ and r for each carbon atom in turn into the expression $(3\cos^2\chi - 1)r^{-3}$.[1] Values of χ (the O–Pr–C internuclear angle) and r (the Pr–C internuclear distance) were obtained by direct measurement of a Dreiding model of borneol co-ordinated to praseodymium in the configuration previously described.[1] A best mean-squares fit of the experimental and theoretical values gave a standard deviation of 2·7% and alone sufficed to assign all resonances, except that the predicted paramagnetic shift values of C-4 and C-5 were equal by chance and their observed shifts were in fact equal. The ^{13}C resonance positions of the carbon atoms of the norbornane framework have previously been reported[3] and these assignments agree with ours; the remaining methyl resonances C_8, C_9, and C_{10} have not previously been assigned.

A number of points of general interest seem to arise. The method of assignment, like its ^1H counterpart, should be of general application to those compounds containing oxygen or nitrogen lone pairs. A *provisional* and not entirely reliable assignment may be obtained in the case of monodentate compounds by using the r^{-3} value alone and ignoring the angular dependence. For compounds containing potentially bidentate donors a geometric factor involving two angular variables is needed. In the case of poly(monodentate) molecules, it would be necessary to use a weighted mean of the shifts expected for the various modes of co-ordination with the lanthanide.

These results provide confirmation that the mechanism is of a pseudo-contact nature. Not only are the ^{13}C para-magnetic shifts predictable on this basis, but the constant K_C† for best fit of this ^{13}C data is 1·16K_H where K_H is the corresponding constant for the proton spectra. As the expression for the value of $\Delta H/H$ is independent of the nuclear magnetic moment on a pseudo-contact basis

^{13}C *N.m.r. spectra of borneol*

Carbon	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8[a]	C-9[a]	C-10
Chemical shift[b]	−49·5	−76·8	−39·0	−45·4	−28·4	−26·1	−48·0	−18·8	−20·3	−13·4
Pr shift[c]	33·5	87·8	37·3	19·7	19·7	29·8	17·6	10·6	10·1	25·0
$K_C(3\cos^2\chi - 1)r^{-3d}$	33·1	74·6	37·3	20·3	20·5	28·0	18·0	11·8	10·2	22·2
Eu shift[c]	−14·0	−60·8	−21·8	−10·6	−12·3	−20·6	−9·5	−6·7	−5·0	−15·1
Tb shift[c,e]	182	—	171	91	91	125	85	51	51	108

[a] These two assignments might possibly be interchanged.   [b] δ-value in p.p.m. downfield from Me$_4$Si.   [c] Expressed as (δ-value for 1 : 1 mole ratio of [Ln(tmhd)$_3$] : borneol) minus (δ-value for borneol alone.)   Praesodymium shifts are to high field.   [d] K_C selected to allow direct comparison with observed shifts.   [e] Measured in dilute solution only; considerable broadening present.

We now report lanthanide-induced shifts in the ^{13}C spectrum of borneol. Solutions of borneol in carbon tetrachloride containing Me$_4$Si as an internal ^{13}C standard and hexafluorobenzene as an internal heteronuclear lock and from 0 to 0·1M proportions of Pr(tmhd)$_3$ afforded ^{13}C Fourier n.m.r. spectra at 22·628 MHz. The resonance

[equation (1)], ^1H and ^{13}C paramagnetic shifts should be identical after allowance for the geometrical factor $(3\cos^2\chi - 1)r^{-3}$, *i.e.* K_C should equal K_H. We regard the observed K_C/K_H ratio of 1·16 as fairly satisfactory agreement. A contact mechanism would be expected to show the effect of differing spin densities on linked C and H

† From the expression $\Delta H/H = K_C(3\cos^2\chi - 1)r^{-3}$.[1] We now write K_H instead of K.

atoms; the value of the K_C/K_H ratio and the observed dependence on the geometrical factor mark the mechanism as pseudo-contact. Contact effects may however be present in a π-bonded framework and there is some evidence for the occurrence of such effects in pyridine complexes of lanthanides.[4,5] The 18% discrepancy between predicted and experimental values of $\Delta H/H$ for C_2 might also be partially caused by electron delocalisation.

Shifts produced by $Eu(tmhd)_3$[6] may equally well be used in this assignment; the resulting $\Delta H/H$ values are given in the Table. The Pr:Eu shift ratio is 1·8 and the Tb:Eu ratio is 8·6. The Eu spectra show no significant broadening and the Pr spectra very little, but the Tb peaks broaden considerably.

The spectra were obtained by means of a Brüker HFX-90 spectrometer using the Fourier transform technique. Data were accumulated in 1024 scans at a dwell time of 200 μs per point and stored in 4096 channels; power spectra, $v^2 + u^2$, were observed in 2048 channels.

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