Proton Broad-line N.m.r. Study of $[^2H_6]$Dimethoxy$[^{11}B]$borane

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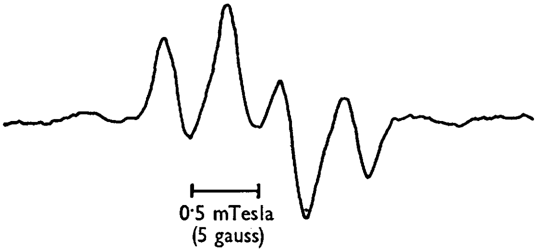
As part of a broad-line n.m.r. study of a variety of hydride derivatives[1,2] we have investigated the proton spectrum of $H^{11}B(OCD_3)_2$. Since this compound is one of the few examples of a monomeric (at least in the gas phase), non-electron-deficient boron hydride derivative, determination of the boron–hydrogen distance was of particular interest. Further, the spectrum itself affords a particularly clear example of the fine structure which may arise in the broad-line powder spectra of two-spin systems when intermolecular broadening effects are minimal.

Since we wished to investigate the magnetic interaction of the hydridic hydrogen with the ^{11}B nucleus, it was necessary to use samples containing essentially pure ^{11}B and to introduce fully-deuterated methyl groups into the molecule. The material used in this study was prepared from isotopically-enriched diborane (boron content 97—98% ^{11}B) and $[^2H_3]$methyl alcohol (isotopic purity $\geqslant$99%) by the procedure of Burg and Schlesinger.[3] Samples were characterized by vapour-phase molecular weight [found: 80·8; calculated for $H^{11}B(OCD_3)_2$: 80·1] and measurement of hydrogen liberated on hydrolysis (101·5% of theoretical). No diborane or $[^2H_9]$trimethoxyborane could be detected in the infrared spectrum. Broad-line spectra were obtained at a frequency of 29·95 MHz using a conventional spectrometer[4] over a temperature range from the melting point (−131° c)[3] to −180° c. The second moment (21·90 ± 1·0 G^2) and the line separations were essentially unchanged over this range. A typical proton spectrum of the polycrystalline hydride, taken at −169° c, is shown in the Figure.

As in the cases of $HMn(CO)_5$[1] and $HCo(CO)_4$,[2] which have been investigated in this laboratory, the spectrum of $H^{11}B(OCD_3)_2$ may be interpreted in terms of a magnetically isolated two-spin system. The spectrum shows four lines arising from the intramolecular dipolar coupling of the proton with the ^{11}B nucleus ($I = 3/2$). For the polycrystalline samples, the observed resonance is of course an envelope which includes contributions averaged over all orientations of the B–H bond with respect to the external field direction, from perpendicular to parallel. The occurrence of four distinct and rather narrow lines provides strong evidence that interactions other than intramolecular B–H coupling are relatively insignificant. On the assumption that the four principal lines are attributable to protons in the "perpendicular" orientation, the separation, $\Xi_\perp$, of the outer pair is given by: $r_{BH} = [2\gamma_B\hbar I_B/\Xi_\perp]^{1/3}$ where r_{BH} is the boron–hydrogen bond length, $I_B (= 3/2)$ is the ^{11}B nuclear spin, and γ_B is the ^{11}B magnetogyric ratio. In addition to the four main lines, the spectrum shows at the extremes an inflection which arises from molecules with the B–H axis parallel (or nearly so) to the external field direction. The separation, $\Xi_\parallel$, of these lines is related to the B–H bond distance: $r_{BH} = [4\gamma_B\hbar I_B/\Xi_\parallel]^{1/3}$. The measured values of $\Xi_\perp$ and $\Xi_\parallel$ lead to an average value of 1·24 ± 0·1 Å for r_{BH}.[5]



FIGURE

Proton magnetic resonance spectrum of polycrystalline $H^{11}B(OCD_3)_2$ *at* 29·95 *MHz.*

Using the Van Vleck formula[6] for the second moment of the proton resonance in a polycrystalline solid and considering only directly-bonded B–H interactions, agreement with the experimentally determined second moment is obtained for $r_{BH} = 1·25 \pm 0·05$ Å.

The B–H bond length measured here is identical within experimental error to that obtained by Ford and Richards[7] for the borohydride ion (1·255 ± 0·02 Å). It may be compared with values for terminal B–H bond lengths in the boron hydrides and $OCBH_3$, which average about 1·19 Å.[8] It is interesting to note that dimethoxyborane is monomeric in the gas phase, suggesting that the boron hybridization is approximately sp^2. If this hybridization persists in the solid, the B–H bond length might have been expected to be somewhat shorter than in BH_4^- where hybridization is sp^3. It is thus possible that the bond length in dimethoxyborane reflects the influence of intramolecular π-bonding or of association in the solid phase. It is to be noted, however, that association, if any, must almost certainly involve O–B dative bonding, since the fine structure in the proton spectrum is inconsistent with a symmetric singly- or doubly-hydrogen-bridged structure.

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[1] T. C. Farrar, W. Ryan, A. Davison, and J. W. Faller, *J. Amer. Chem. Soc.*, 1966, **88**, 184.

[2] T. C. Farrar, F. E. Brinckman, T. D. Coyle, A. Davison, and J. W. Faller, to be published.

[3] A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1933, **55**, 4020.

[4] H. S. Gutowsky, L. H. Meyer, and R. E. McClure, *Rev. Sci. Instr.*, 1953, **24**, 644.

[5] The value of r_{BH} determined from line separations is somewhat less accurate than the value determined from the second moment, but provides a confirmation of the latter. The larger error limits associated with the values obtained from the maxima in the spectrum reflect the uncertainty in associating these precisely with the "perpendicular" and "parallel" contributions to the resonance curve. The observation of the "parallel" contribution at the extremes of the spectrum is highly important, since this contributes significantly to the experimental second moment. A detailed discussion of the resonance line shapes in this and similar compounds will appear in a subsequent publication.

[6] J. H. Van Vleck, *Phys. Rev.*, 1948, **74**, 1168.

[7] P. Ford and R. E. Richards, *Discuss. Faraday Soc.*, 1955, **19**, 193.

[8] *Chem. Soc. Special Publ. No.* 18, Supplement.