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A Proton and Boron-11 NMR Study of Icosaborane Oxide, $B_{20}H_{26}O$

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*Selective ^1H-$\{^{11}B\}$ NMR spectroscopy is a powerful tool for investigating the ^1H spectra of the higher boranes and their derivatives, and is used together with simple-pulse and 'partially relaxed' ^{11}B and ^{11}B-$\{^1H\}$ spectroscopy to assign the ^1H and ^{11}B spectra of icosaborane oxide and to confirm its structure as 6,6'-μ-oxo-bis(*nido*-decaboranyl), $(B_{10}H_{13})_2O$. The observed ^1H shieldings parallel those for the nuclei of the boron atoms to which they are bonded, and also exhibit large changes upon dissolution in aromatic solvents. Boron-11 spin-lattice relaxation times T_1 at 23 °C in $CDCl_3$ solution are also reported and briefly discussed.*

Introduction

The application of ^{11}B NMR spectroscopy has been central in the development of cluster boron hydride chemistry [1, 2], and many techniques such as very high field spectroscopy [3–15], together with ^{11}B-$\{^1H\}$ and ^{11}B-$\{^{11}B\}$ multiple resonance [3, 4, 11, 12, 16, 17], 'partial relaxation' [4, 8, 9], analysis of relaxation rates [18], line-narrowing [5, 7, 8, 10] and deuterium substitution [3–7] have been used to assign the ^{11}B spectra of known boranes and their derivatives, and to elucidate the structures of unknown ones. By contrast, the ^1H NMR behaviour of the higher boranes and their derivatives remains essentially uninvestigated, principally because of spectral complexity. In general, each proton resonance is at least a quartet of very broad lines arising from electron-mediated spin–spin coupling and scalar relaxation associated with ^{11}B (natural abundance 80%; spin quantum number $I = 3/2$), with additional lines arising from the presence of ^{10}B (natural abundance 20%; $I = 3$). It is therefore often difficult to analyse the ^1H NMR spectrum of even a relatively small borane which will typically be a non-degenerate combination of many such multiplets. Thus, although the assignment of the ^1H spectrum of the important C_{2v} boron hydride, *nido*-decaborane, $B_{10}H_{14}$, was established some 15 years ago by a simulation technique [19] and subsequently confirmed by high-field spectrometry together with specific deuteration [20], the ^1H spectra of its many (less symmetric) derivatives remain unexamined. We have now found that selective ^1H-$\{^{11}B\}$ double resonance NMR spectroscopy is a powerful tool for the investigation of these ^1H spectra, and report here as a preliminary example the results of ^{11}B, ^{11}B-$\{^1H\}$ and, in particular, selective ^1H-$\{^{11}B\}$ NMR experiments on icosaborane oxide, $B_{20}H_{26}O$ [21]. These establish and assign the ^1H chemical shifts, and confirm the previous tentative conclusion [22] that the structure is that of 6,6'-bis-(*nido*-decaboranyl) oxide, $(B_{10}H_{13})_2O$.

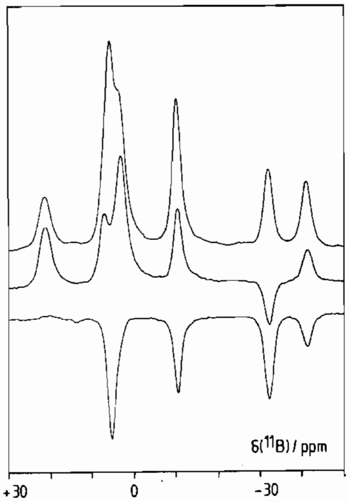
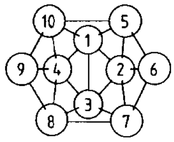


Fig. 1. Normal (upper trace) and 'partially relaxed' (lower traces) 32 MHz ^{11}B-$\{^1H$(broad band)$\}$ NMR spectra of $B_{20}H_{26}O$ in $CDCl_3$ solution at 23 °C. These clearly differentiate the resonances at +7.2, +5.6, and +3.0 ppm.

Results and Discussion

Reasonable chemical deduction and the method of preparation suggest that $B_{20}H_{26}O$ is a bis(*nido*-decaboranyl) oxide, $(B_{10}H_{13})_2O$ [21, 22]. A projection of the *nido*-decaboranyl deltahedral skeleton is given in (I).



(I)

In unsubstituted *nido*-decaborane, $B_{10}H_{14}$, there are terminal hydrogen atoms on each boron atom, and there are bridging hydrogen atoms in the (5, 6), (6, 7), (8, 9) and (9, 10) positions. The 32 MHz ^{11}B-{^{1}H-(broad band)} NMR spectrum of $B_{20}H_{26}O$ is a 1:1:2:5:1 pattern (Fig. 1, uppermost trace), with some asymmetry of the peak with relative intensity 5. 'Partially relaxed' spectra [8] obtained using the 180°–τ–90° pulse sequence showed that the latter peak consisted of 3 resonances (Fig. 1, lower traces), for which the relative 'completely relaxed' intensities I_∞ were estimated using the expression $I_\tau = I_\infty[1 - 2\exp(-\tau/T_1)]$. The 1:1:2:2:2:1:1 intensity pattern thus established (Table I) is consistent with either 2- or 6-substitution on *nido*-decaborane, and consideration of the known [12] assignments for the 2- and 6-halogenodecaboranes $B_{10}H_{13}X$ indicates 6-substitution. The signs of the substituent chemical shifts [12] are as those for 6-chlorodecaborane, but their magnitudes are greater, as expected from the greater inductive effects of the oxygen atom. Consistent with this structural conclusion, the resonance at $\delta(^{11}B)$ = +21.8 ppm ascribed to the B(6) nucleus is a singlet in the absence of ^{1}H decoupling, whereas all the other ^{11}B resonances are doublets arising from couplings $^{1}J(^{11}B\text{-}^{1}H)$ = *ca.* 150 Hz. The oxygen linkage is therefore in the 6,6′ position, which confirms the previous conclusions [21, 22] based on chemical evidence and lower resolution ^{11}B NMR spectroscopy.

The 180°–τ–90° pulse-sequence experiments also yielded values for the spin–lattice relaxation times T_1 for the quadrupolar ^{11}B nuclei, and these are given in Table I for a solution in $CDCl_3$ at 23 °C. T_1 for a quadrupolar nucleus depends on the electric field gradient at the nucleus and on the rotational correlation time τ_c. In principle therefore T_1 measurements offer an insight into either or both of these factors. However, since $B_{20}H_{26}O$ is a very asymmetric rotor the molecular (including intramolecular) motion will be anisotropic and thus the effective τ_c will vary substantially throughout the molecule. The significance of the relative T_1 values is therefore difficult to assess. However, it is of interest that those for the oxygen-substituted B(6) and equivalent unsubstituted B(9) positions are very similar, and also that the low value for B(4) compared to that for B(2) may imply that B(4) lies very close to a principal rotational axis, possibly that associated with rotation about the oxygen–B(6) bond.

The 100 MHz ^{1}H NMR spectra of $B_{20}H_{26}O$ are complex (Fig. 2), but simplify considerably upon high power simultaneous broad-band irradiation at

TABLE I. Proton and Boron-11 NMR Data for $B_{20}H_{26}O$ at 23 °C.

Assignment	$\delta(^{11}B)(CDCl_3)^{a}$	$\delta(^{11}B)(C_6D_6)^{a}$	Relative Intensity	$T_1(^{11}B)(CDCl_3)/ms^{b}$	$^{1}J(^{11}B\text{-}^{1}H)/Hz$	$\delta(^{1}H)(CDCl_3)^{c}$	$\delta(^{1}H)(C_6D_6)^{c}$	Relative Intensity	$\Delta\sigma(B_{20}H_{26}O)^{d}$	$\Delta\sigma(B_{10}H_{14})^{d}$	$\delta(^{1}H)(B_{10}H_{14})(CDCl_3)^{c}$
6	+21.8	+22.1	1	6.8	–	–	–	–	–	+0.39	+3.85
9	+7.2^{e}	+8.0^{e}	1	7.8	145 ± 10	+3.91	+3.48	1	+0.43		
1, 3	+5.6^{e}	+5.6^{e}	2	17.1	145 ± 10	+3.29^{e} ^{f}	+3.70	2	−0.41^{g}	−0.40	+3.69
8, 10	+3.0^{e}	+2.4^{e}	2	7.3	145 ± 10	+3.17^{e}	+3.20	2	−0.03^{h}	+0.04	+3.13
5, 7	−10.7	−10.9	2	10.2	150 ± 10	+2.45	+2.56	2	−0.11		
2	−33.2	−33.1	1	32.8	155 ± 10	+1.34	+1.70	1	−0.36	−0.41	+0.65
4	−42.5	−42.4	1	11.3	155 ± 10	+0.32	+0.71	1	−0.39		
μ-(5,6) & (6,7)	–	–	–	–	–	−0.45^{i}	−0.83^{i}	2	+0.38	+0.69	−2.14
μ-(8,9) & (9, 10)	–	–	–	–	–	−1.72^{j}	−2.35^{j}	2	+0.63		

[a] In ppm ± 0.4 to high frequency of $[BF_3(OEt_2)]$. [b] ±15%; the ratio of T_1 values is more accurate than this. [c] In ppm ± 0.02 to high frequency of internal $SiMe_4$. [d] Change in nuclear *shielding* on dissolution in C_6D_6 rather than $CDCl_3$. [e] Overlapping resonances in both ^{11}B and ^{1}H spectra separable by 'partially relaxed' spectroscopy. [f] Both ^{11}B and ^{1}H resonances too close for the selective ^{1}H-{^{11}B} results to be conclusive. [g] May be −0.53 (see footnote f). [h] May be +0.09 (see footnote f). [i] Assignment tentative; based on apparent selective sharpening when 2,6 or 5,7 ^{11}B resonance positions irradiated. [j] Assignment tentative; based on apparent selective sharpening when 4,9 and 8,10 ^{11}B resonance positions irradiated.

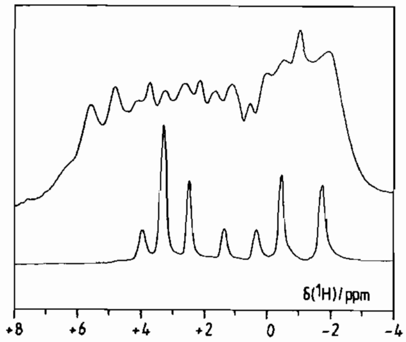


Fig. 2. Normal (upper trace) and, at reduced spectrometer gain, ^{11}B-decoupled (lower trace) 100 MHz ^{1}H NMR spectra of $B_{20}H_{26}O$ in $CDCl_3$ solution at 23 °C.

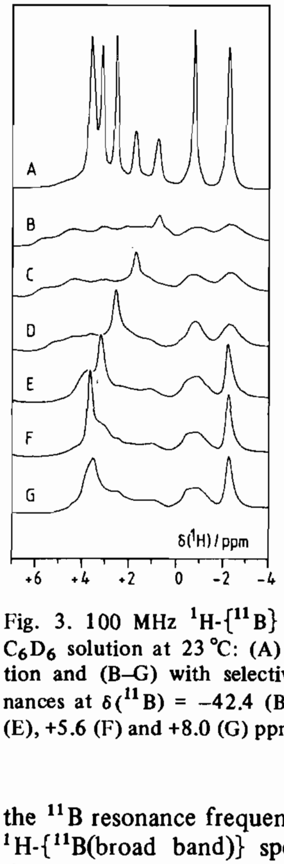


Fig. 3. 100 MHz ^{1}H-{^{11}B} NMR spectra of $B_{20}H_{26}O$ in C_6D_6 solution at 23 °C: (A) with 'broad band' ^{11}B irradiation and (B–G) with selective decoupling of the ^{11}B resonances at $\delta(^{11}B)$ = −42.4 (B), −33.1 (C), −10.9 (D), +2.4 (E), +5.6 (F) and +8.0 (G) ppm.

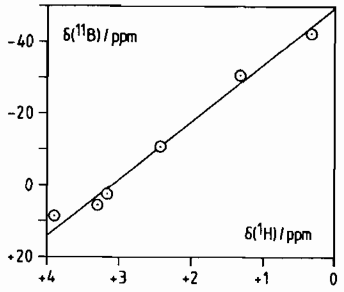


Fig. 4. Plot of $\delta(^{11}B)$ *versus* $\delta(^1H)$ for $B_{20}H_{26}O$ in $CDCl_3$ solution at 23 °C; slope = *ca.* 16.

the ^{11}B resonance frequencies (Figs. 2 and 3). In the ^{1}H-{^{11}B(broad band)} spectra the multiplicities of the compound peaks at $\delta(^1H)$ *ca.* 3.2 ($CDCl_3$ solution) and 3.6 ppm (C_6D_6 solution) and the chemical shifts of their components were again readily obtained using the 'partially relaxed' technique (Table I). The two resonances of relative intensity 2 at extreme low frequency (*i.e.* 'high field') are reasonably ascribed [2] to the bridging hydrogen atoms and the correspondence between the ^{11}B and ^{1}H resonance lines for the remaining protons was established by selective ^{1}H-{^{11}B} experiments using unmodulated ^{11}B frequencies and smaller irradiation power levels than were required for complete ^{11}B decoupling (Fig. 3). In these experiments the selective decoupling of the proton resonances at $\delta(^1H)$ = +3.70, +3.48 and +3.20 ppm associated with the ^{11}B resonances at $\delta(^{11}B)$ = +5.6, +8.0 and +2.4 ppm respectively (C_6D_6 solution) is of particular interest since the effective resolution of the *boron-11* spectrum by observation of the *proton* spectrum with selective ^{11}B decoupling was greater than that achieved by direct observation of the ^{11}B spectrum itself (Fig. 1) at the same field strength. By contrast, the relative assignments of the two well-separated resonances of the bridging protons in the (5, 6) (6, 7) and (8, 9) (9, 10) positions was not certain, since each was associated with two ^{11}B resonance positions and it was difficult to establish any differential sharpenings and distinguish them from off-resonance effects.

These results are summarized in Table I. The most striking feature about the measured shieldings of the terminal protons is their correlation with the nuclear shieldings of the boron atoms to which they are attached (Fig. 4). This behaviour is consistent with many of the hypotheses regarding diamagnetic and 'paramagnetic' shielding in deltahedral boron hydride cages, but unfortunately it is difficult to see how it can distinguish between them. Also interesting are the large solvent effects on dissolution in the aromatic solvent C_6D_6, and it is convenient to note at this point that the previously reported [20] (1, 3) and (6, 9) proton chemical shift assignments for *nido*-decaborane in C_6D_6 solution are incorrect and should be interchanged. For $B_{20}H_{26}O$ and $B_{10}H_{14}$ the changes in proton shielding $\Delta\sigma$ upon replacement of $CDCl_3$ as solvent by C_6D_6 are also given in the Table; the magnitudes and signs of $\Delta\sigma$ are similar for both compounds indicating that the electronegative substituent does not stabilize any transient aromatic π-complex to any appreciably greater extent.

Experimental

Icosaborane oxide, $B_{20}H_{26}O$, was prepared from $[B_{10}H_{12}(SMe_2)_2]$ and H_2SO_4 as described in the literature [21]. The pulsed (Fourier transform) NMR experiments were carried out on saturated solutions using a JEOL FX-100 instrument. Chemical shifts are quoted to high frequency (low field) of the reference standards $BF_3 \cdot Et_2O$ (^{11}B) and $SiMe_4$ (^1H). 'Partially relaxed' (PRFT [8]) spectra were obtained using the 180°–τ–90° pulse sequence; 180° and 90° pulse-widths measured for the samples used were 32 and 16 μs respectively for ^{11}B at 32 MHz and 26 and 13 μs respectively for ^1H at 100 MHz. Boron-11 T_1 values were obtained using semi-logarithmic plots for the isolated resonances, and from an estimation of τ_{null} values for the overlapping resonances; this latter method was calibrated against the semi-logarithmic plot method using the isolated resonances. Within experimental error, the T_1 values obtained in the ^{11}B-{^1H(broad band)} and in undecoupled ^{11}B experiments were identical.

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