composition of the samples in the vicinity of the coalescence temperature has prohibited verification of this series.[37]

Interconversions involving structure II, *e.g.*, a I $\rightleftarrows$ II process, would depend on the folding motion of the $B_4H_8$ cage along the $B_1$–$B_3$ bond ($B_2$ and $B_4$ moving up and down). This is plausible, but it provides no explanation for the lack of isomers in $F_2HP \cdot B_4H_8$ unless the proposed electrostatic attractions prevent the folding.

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[37] It should also be noted that electrostatic repulsion–attraction forces may be important in the I $\rightleftarrows$ III process. Interaction between protonic P–H and hydridic hydrogens of the tetraborane(8) group could well create "locked" conformation, structure III, for $F_2HP \cdot B_4H_8$. Electrostatic *repulsions* between the $B_4H_8$ cage and X for the ligand might be expected to decrease in the order: $F > (CH_3)_2N > Cl > Br > I$.

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# Magnetic Resonance Spectra of Octaborane(12), Octaborane(18), and 2-[2′-Pentaboran(9)yl]pentaborane(9)

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Proton and boron-11 nmr spectra of $B_8H_{12}$, $B_8H_{18}$, and 2,2′-$(B_5H_8)_2$ obtained at 51.7 kG are presented and discussed in terms of their structural significance.

## Introduction

Until the advent of spectrometers employing superconducting magnets, proton magnetic resonance spectra of boron hydrides have been of only secondary value in structure elucidation.[1] The small range of chemical shifts and consequent overlap of the $^{11}B$–H quartets, as well as the interference from the $^{10}B$–H septets and nuclear quadrapole broadening from both isotopes (80% $^{11}B$, $I = {}^3/_2$; 20% $^{10}B$, $I = 3$), have limited pmr studies to the smaller symmetric hydrides. Recent studies have shown the value of reexamining the pmr spectra of all boron hydrides at higher field strengths.[2–4] In addition to assigning all the proton resonances of $B_4H_{10}$, $B_6H_{10}$, and $B_6H_{12}$, these studies proved that such spectra can differentiate between equatorial and axial $-BH_2$ proton resonances and separate signals arising from magnetically distinct bridge protons. Here we have extended these observations to the pmr spectra of three of the newer boron hydrides.

## Experimental Section

Octaborane(12) and octaborane(18) were prepared by standard synthetic methods.[5,6] The 2-[2′-pentaboran(9)yl]pentaborane(9),[7] 2,2′-$(B_5H_8)_2$, was prepared by reaction of diborane and pentaborane(9) in a hot-cold circulating system.[8] All materials were of normal isotopic distribution (80% $^{11}B$; 20% $^{10}B$) and were purified by standard high-vacuum techniques.

Proton and boron spectra were recorded on a Varian Associates HR-220 spectrometer using standard Varian low-temperature accessories. Proton spectra were referenced to tetramethylsilane ($\delta$ 0.0 ppm) as an external standard.

Boron-11 spectra were frequency swept at 70.6 MHz with a commercially available Varian Associates probe. Chemical shifts were obtained using an external sample of boron trifluoride–diethyl etherate and are referred to $BF_3 \cdot O(C_2H_5)_2 = 0$ ppm. Spectra of $B_8H_{18}$ and 2,2′-$(B_5H_8)_2$ were poorly resolved; however, dilution of these samples with carbon disulfide resulted in pmr spectra of better resolution.

## Results and Discussion

**Octaborane(12).**—The recent suggestion[9] (based on an accidentally overlapped low-field $^{11}B$ nmr spectrum) that liquid $B_8H_{12}$ exists as a mixture of eight tautomers to give apparent $C_{4v}$ symmetry is untenable in light of the high-field spectra presented here (Figure 1). The 220-MHz pmr spectrum of $B_8H_{12}$ (Figure 2) displays, in order of decreasing field strength, *two* nonequivalent bridge resonances, each of intensity 2, two quartets, each of intensity 2, and an interesting quartet with skewed appearance of intensity 4. This low-field quartet arises from the low-field doublet of intensity 4 in the boron-11 spectrum arising from the 3, 5, 6, and 8 boron atoms.[10] The apparent equivalence of these four boron atoms and the attached terminal protons may result either from accidental overlap at the field strengths employed or from a dynamic process occurring in $B_8H_{12}$ which effectively raises the $C_s$ symmetry observed in crystalline $B_8H_{12}$[11] to $C_{2v}$ for liquid $B_8H_{12}$. A dynamic process could consist of rapid tautomerism

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[1] (a) R. Schaeffer, "Progress in Boron Chemistry," Vol. 1, H. Steinberg and A. L. McCloskey, Ed., Macmillan, New York, N. Y., 1964, p 422; (b) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

[2] T. Onak and J. B. Leach, *J. Amer. Chem. Soc.*, **92**, 3513 (1970).

[3] R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *ibid.*, **92**, 3514 (1970).

[4] J. B. Leach, T. Onak, J. Spielman, R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, **9**, 2170 (1970).

[5] J. Dobson, P. C. Keller, and R. Schaeffer, *ibid.*, **7**, 399 (1968).

[6] J. Dobson, D. Gaines, and R. Schaeffer, *J. Amer. Chem. Soc.*, **87**, 4072 (1965).

[7] All boron cage nomenclature and numbering orders are those set forth under the new rules which appeared in *Inorg. Chem.*, **7**, 1945 (1968). Here we prefer the shortened name 2,2′-decaborane(16) or the formulation 2,2′-$(B_5H_8)_2$.

[8] J. Dobson, R. Maruca, and R. Schaeffer, *ibid.*, **9**, 2161 (1970).

[9] R. E. Williams, *ibid.*, **10**, 210 (1971).

[10] The assignments of the $^{11}B$ nmr resonances are supported by 19.3-MHz spectra of labeled $B_8H_{12}$ prepared from $\mu$-4,6,8-$KB_9H_6D_8$: P. C. Keller, unpublished results; P. C. Keller, *Inorg. Chem.*, **9**, 75 (1970).

[11] R. E. Enrione, P. F. Boer, and W. N. Lipscomb, *ibid.*, **3**, 1659 (1964).

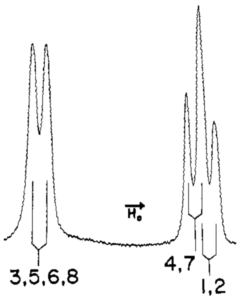

Figure 1.—The 70.6-MHz boron-11 nmr spectrum of octaborane(12) at −23°.

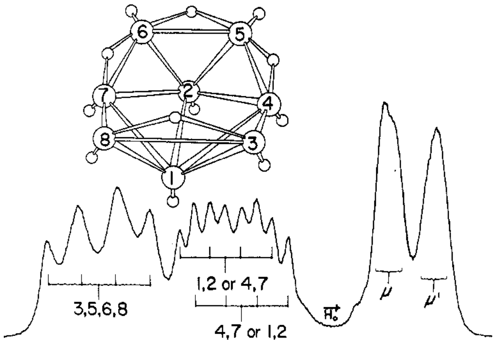

Figure 2.—Structure and 220-MHz proton nmr spectrum of octaborane(12) at −20°.

of two bridge hydrogens between the 3,4 and 4,5 positions and between the 6,7 and 7,8 positions, resulting in $C_{2v}$ symmetry for the $B_8$ skeleton. A mechanism which equilibrates the 3,4 bridge proton to the 4,5 position (or 6,7 to 7,8) and leaves the terminal proton on the 4 (or 7) boron unaffected could occur in a manner similar to that proposed for $B_6H_{10}$;[12] however, we have no labeling or exchange studies to prove or disprove this or other possible mechanisms.

If a dynamic process is occurring in $B_8H_{12}$, it may be possible to observe a static structure at lower temperatures; however, no changes except broadening of individual resonances were effected upon the pmr spectra by cooling $B_8H_{12}$ to −31°, at which temperature the sample froze in the probe. With lower temperatures and suitable solvents, spectra representing $B_8H_{12}$ in the less symmetric $C_s$ state may be observed.

We note that the pmr spectrum of $B_8H_{12}$ is unusual among the boron hydride pmr spectra we have observed, not only for its spectral width (almost 8 ppm) but also for the unusually high-field bridge signal at +3.17 ppm. Chemical shifts, coupling constants, and assignments are given in Table I.

TABLE I

| | δ, ppm | *J*, cps | Intens |
|---|---|---|---|
| Proton Magnetic Resonance Spectrum of Octaborane(12) | | | |
| $H_T$ (3, 5, 6, 8) | −3.93 | 168 | 4.00 |
| $H_T$ (1,2 or 4,7) | −1.18 | 145 | 4.23 |
| $H_T$ (4,7 or 1,2) | −0.83 | 150 | |
| $H_\mu$ | +2.33 | . . . | 3.77 |
| $H_\mu$ | +3.17 | . . . | |
| $^{11}B$ Nmr Spectrum of Octaborane(12) | | | |
| B (3, 5, 6, 8) | −7.50 | 168 | 3.88 |
| B (4,7) | +19.4 | 170 | 4.12 |
| B (1,2) | +22.0 | 175 | |

**Octaborane(18).**—The belt-line fragment model and the bitetraboranyl model (two $B_4H_9$ units bonded at the 2,2′ positions) proposed as probable structures for $B_8H_{18}$ differ only in the placement of two bridge hydrogens.[6] Complete characterization of $B_8H_{18}$ by chemical means has been hindered by the relative scarcity and thermal instability of this hydride; however, the belt-line fragment model is inconsistent with low-temperature X-ray data taken on a disordered crystal.[13]

See Figure 3 for a $^{11}B$ nmr spectrum of $B_8H_{18}$.

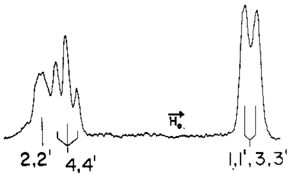

Figure 3.—The 70.6-MHz boron-11 nmr spectrum of octaborane(18) at −21°.

The similarity of the high-field pmr spectra of $B_8H_{18}$ and $B_4H_{10}$ (Figures 4A and 4B, respectively) leads us to favor the bitetraboranyl model for the solution structure of octaborane(18). The $^{11}B$ and pmr spectra (Table II) are assigned by analogy to $B_4H_{10}$.[4,14] Of particular interest are the two low-field quartets, tentatively assigned to the six terminal protons on the 2,2′ and 4,4′ borons. Steric hindrance of bridge protons in a model

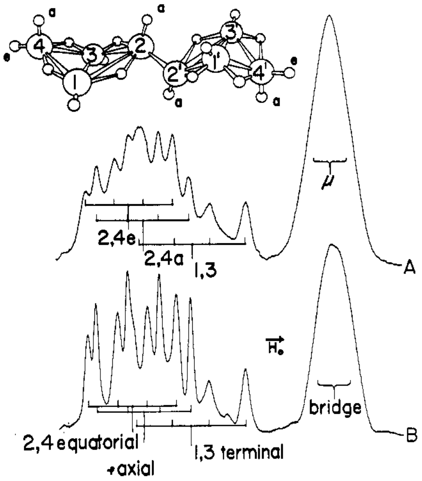

Figure 4.—(A) Proposed structure and 220-MHz proton nmr spectrum of octaborane(18) at 0°. (B) The 220-MHz proton nmr spectrum of tetraborane(10) at −20°.

TABLE II

| | δ, ppm | *J*, cps | Intens |
|---|---|---|---|
| Proton Magnetic Resonance Spectrum of Octaborane(18)[a] | | | |
| $H_T$ (2,4e) | −2.61 | 120 | 10.11 |
| $H_T$ (2,4a) | −2.37 | 130 | |
| $H_T$ (1,3) | −1.40 | 150 | |
| $H_\mu$ | +1.20 | . . . | 7.89 |
| $^{11}B$ Nmr Spectrum of Octaborane(18) | | | |
| B (2,2′)[b] | +1.2 | . . . | 3.77 |
| B (4,4′) | +5.9 | 120 | |
| B (1,1′, 3,3′) | +39.8 | 145 | 4.23 |

[a] In $CS_2$ solution. [b] Half-width 220 Hz.

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[12] J. C. Carter and N. L. H. Mock, *J. Amer. Chem. Soc.*, **91**, 5891 (1969).

[13] H. A. Beall, Ph.D. Thesis, Harvard University, 1966.

[14] Partially relaxed Fourier transform $^{11}B$ nmr spectra at 70.6 MHz of $B_8N_{18}$ show that the downfield resonance (from the 2,2′ borons) is a very broad singlet (half-width ∼220 Hz) and not a doublet as stated in ref 6.

bonded through the 2,2′ axial proton sites suggests that the $B_4H_9$ units are equatorially bonded (see Figure 4). Hence, the protons remaining on the 2,2′ borons are axially bonded. These two protons *and* the two axial protons on the 4,4′ borons comprise the pmr resonance at $\delta$ −2.37 ppm. The quartet of diminished intensity at $\delta$ −2.61 ppm then arises from the *two* remaining equatorial protons on the 4,4′ borons. We note that the equatorial pmr resonance has a smaller coupling constant (120 Hz) and is downfield of the axial pmr resonance (130 Hz). Since this same spectral feature is present for the $-BH_2$ groups in $B_4H_{10}$, $B_5H_{11}$, and $B_6H_{12}$,[4] we tentatively assign each of the lower field $-BH_2$ quartets (with the smaller coupling constants) to the protons lying in the equatorial positions.

**2-[2′-Pentaboran(9)yl]pentaborane(9).**—The formulation of the recently discovered isodecaborane(16)[3,15] as two $B_5H_8$ units boron–boron bonded through the 2,2′ positions is consistent with our boron-11 (Figure 5) and pmr spectra. The pmr spectrum (Figure 6A) consists of two quartets and one bridge resonance, in the ratio 6:2:8, which almost perfectly overlay the pmr spectrum of $B_5H_9$ (Figure 6B). The high-field doublet of intensity 2 in the $^{11}B$ pmr spectrum is easily assigned to the apical borons; however, the low-field peaks must be attributed to the accidental overlap of a 2,2′ boron singlet (intensity 2), a 4,4′ doublet (intensity 2), and a 3,5,3′,5′ doublet of intensity 4. (See Table III for additional spectral data.) Although one might expect the magnetic environment of the 2,2′, 4,4′, and 3,5,3′,5′ borons to differ only slightly from the equivalent positions in $B_5H_9$, other $2-B_5H_8$ derivatives do show distinct splitting of the basal boron signals.[16,17] We are currently applying partially relaxed Fourier transform[18] and artificial line narrowing[19] techniques to this problem. In addition, structural studies on both the 1,2′- and 2,2′-decaborane(16) isomers are under way in this laboratory.

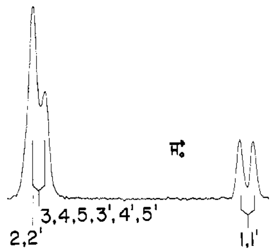

Figure 5.—The 70.6-MHz boron-11 nmr spectrum of 2,2′-decaborane(16) at 16°.

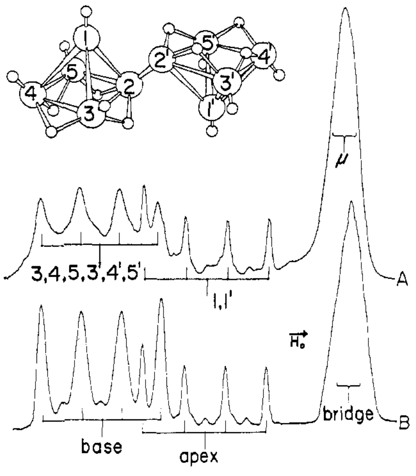

Figure 6.—(A) Proposed structure and 220-MHz proton nmr spectrum of 2,2′-decaborane(16) at 16°. (B) The 220-MHz proton nmr spectrum of pentaborane(9) at 23°.

TABLE III

| | $\delta$, ppm | *J*, cps | Intens |
|---|---|---|---|
| Proton Magnetic Resonance Spectrum of 2,2′-Decaborane(16) | | | |
| $H_T$ (3,4,5,3′,4′,5′) | −2.50 | 162 | 8.22 |
| $H_T$ (1,1′) | −0.47 | 174 | |
| $H_\mu$ | +2.16 | ... | 7.78 |
| $^{11}B$ Nmr Spectrum of 2,2′-Decaborane(16) | | | |
| B (2,2′) | +10.3 | ... | 7.93 |
| B (3,4,5,3′,4′,5′) | +11.3 | 150 | |
| B (1,1′) | +50.0 | 175 | 2.07 |

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(17) T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967).

(18) A. Allerhand, A. O. Clouse, R. R. Rietz, T. Roseberry, and R. Schaeffer, *J. Amer. Chem. Soc.*, in press.

(19) R. Schaeffer, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, No. INOR 52.