

Figure 1. Proton nmr spectrum (220 MHz) and ball and stick model of  $B_5H_{11}$ .

that this hydrogen is bonded somewhat strongly to the apex boron atom and also bonded weakly, but perhaps equally, to boron atoms 2 and 5. The boron nmr data<sup>2-4</sup> suggest that the bonding of this hydrogen to any of the mentioned boron atoms is rather weak, for no direct coupling is observed. To add to this perplexity, no direct observation of this anomalous hydrogen in the proton nmr has heretofore been confirmed. This can be attributed to the labyrinth of overlapping resonances at the field strengths previously used, thus not allowing for a transpicuous assignment.<sup>2-5</sup>

From both the 220-MHz proton nmr spectrum (Figure 1) and decoupling experiments at 100 MHz we have been successful in locating the resonance of this anomalous proton. The quartet of resonances located at  $\tau$  8.2 can be collapsed by double-resonance experiments affecting the apex boron only. Preferential irradiation of the basal borons in triple-resonance studies sharpens the other assigned bridge resonances at  $\tau$  10.4 and 12.0.<sup>6</sup> From these observations and also from the coupling constant,  $J_{H-B(1)} = 60$  Hz, for the resonance at  $\tau$  8.2, the position for the anomalous hydrogen can be unambiguously assigned. The apparent stronger coupling of this hydrogen to the apex boron atom than to the basal boron atoms is consistent with the relative bond distances suggested by the X-ray studies.<sup>1</sup> The magnitude of the coupling constant is somewhat higher than is found for bridge hydrogens (usually *ca.* 30–40 Hz) in the boron hydrides and considerably smaller than that found for terminal hydrogens at apically situated borons (usually *ca.* 170–180 Hz). Following this comparison, the moot question of categorizing the nature of this anomalous hydrogen within the context of these previously known bonding types is left up to the catechism of the reader.

The chemical shift of the anomalous hydrogen is unusually low when compared to the other bridge hydrogens in pentaborane(11) or when compared to bridge

(2) R. Schaeffer, J. N. Shoolery, and R. Jones, *J. Amer. Chem. Soc.*, **79**, 4606 (1957).

(3) R. E. Williams, S. G. Gibbins, and I. Shapiro, *J. Chem. Phys.*, **30**, 320 (1959).

(4) R. E. Williams, F. J. Gerhart, and E. Pier, *Inorg. Chem.*, **4**, 1239 (1965).

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(6) The details of the irradiation experiments will be published at a later date.

hydrogens in other boron hydrides. It is also at significantly lower field than other apically bonded terminal hydrogens in other pyramidal boron hydrides.<sup>7</sup> Any simple explanation of this shift is subject to some degree of imputation; however, we would like to suggest that the low-field appearance of this resonance may indicate a higher amount of protonic character than in most bridge (or terminal apical) hydrogens. It is to be noted that in previous structures assigned to pentaborane(11) this hydrogen is depicted in a fashion so as to suggest a localization of two of the six electrons bonding the apex boron to the basal boron framework. By assigning a high measure of protonic character to this hydrogen, the partially relinquished pair of electrons may be better able to stabilize the framework through extensive delocalization analogous to that observed for related pyramidal systems.<sup>8</sup>

**Acknowledgment.** This work was supported, in part, by a grant from the Office of Naval Research. The HR-220 nmr instrument was available at California Institute of Technology through a grant by the National Science Foundation, No. GP-8540. The HA-100 nmr instrument at CCLA was available through a grant by the National Science Foundation, No. GP-8347.

(7) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

(8) D. Marynick and T. Onak, *J. Chem. Soc., A*, 1797 (1969).

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Received March 12, 1970

## The 220-MHz Proton Resonance Spectra of the Volatile Boron Hydrides

Sir:

We have recently obtained 220-MHz pmr spectra of  $B_4H_{10}$ ,  $B_5H_9$ ,  $B_5H_{11}$ ,  $B_6H_{10}$ ,  $B_6H_{12}$ ,  $B_8H_{12}$ ,  $B_8H_{18}$ ,  $n-B_9H_{15}$ ,  $i-B_{10}H_{16}$ ,  $^{10}B_4H_{10}$ ,  $^{11}B_4H_{10}$ ,  $^{11}B_5H_{11}$ , and  $n-B_9H_{10}D_5$ . New features are resolved at this frequency which greatly enhance the value of pmr for structural studies in the boron hydride field. In contrast to spectra observed at lower fields, the 220-MHz spectra can, in favorable cases, resolve bridge regions into separated peaks corresponding to structurally nonequivalent bridging protons. For example, in Figure 1 the bridge region of  $^{11}B_5H_{11}$  is resolved into two peaks of ratio 2:1. Assignment of the bridging protons is confirmed not only by the relative intensity of the peaks, but also by the appearance of fine structure on the peak at highest field, corresponding to splitting into a septet ( $J = 36$  cps) of relative intensity 1:2:3:4:3:2:1 by the 3,4 boron atoms.<sup>1</sup> This  $^{11}B-^1H-^{11}B$  bridge coupling is confirmed in the 70.58-MHz spectrum<sup>2</sup> (Figure 2) of  $^{11}B_5H_{11}$ , where a splitting of 36 cps is clearly observed on the doublet arising from the 3,4 boron atoms. Furthermore, the "unique terminal" proton is clearly visible,

(1) All boron cage nomenclature and numbering orders are those set forth under the new rules which appeared in *Inorg. Chem.*, **7**, 1945 (1968).

(2) The  $^{11}B$  spectra of the above compounds were obtained with an experimental 70.58-MHz probe built by Mr. A. O. Clouse of this laboratory.

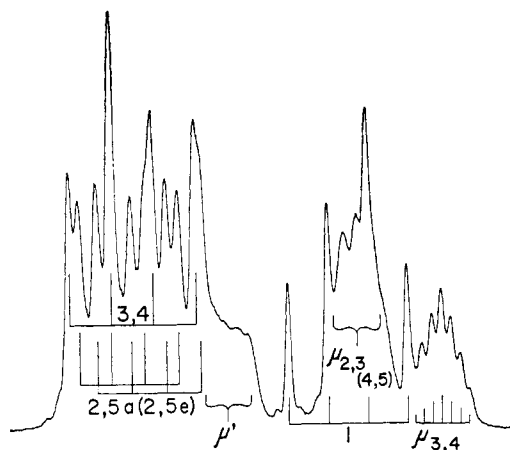


Figure 1.  $^1\text{H}$  spectrum (220 MHz) of  $^{11}\text{B}_5\text{H}_{11}$  containing 98%  $^{11}\text{B}$ . The spectrum of normal isotopic content contains similar features but is less informative.

at  $\delta - 2.09$  ppm, as a separate broad multiplet of intensity one.

A second new feature that appears in the higher field pmr studies is the resolution of peaks attributed to  $-\text{BH}_2$  groups into magnetically nonequivalent sets of equatorial and axial protons. Although we are as yet unable to conclusively assign the two resonances, they display both different coupling constants and a chemical shift difference. We note that the lower field absorption of the  $-\text{BH}_2$  set displays the smaller coupling constant (see Table I).

Table I

	$\delta$ , ppm	$J$ , cps
220-MHz Proton Magnetic Resonance		
2,5e or a	-3.91 <sup>a</sup>	127
3,4	-3.82	160
2,5e or a	-3.47	135
$\mu'$	-2.09	
1	-0.23	153
Bridge 2,3(4,5)	+0.46	
Bridge 3,4	+1.64	36 <sup>b</sup>
70.58-MHz Boron-11 Magnetic Resonance		
2,5	-7.44 <sup>c</sup>	132
3,4	-0.47	160
		36 <sup>b</sup>
1	+55.25	152

<sup>a</sup> Relative to TMS. <sup>b</sup> Boron-11-bridge proton coupling. <sup>c</sup> Relative to  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ .

Features similar to the above appear in the spectra of  $\text{B}_4\text{H}_{10}$ ,  $\text{B}_5\text{H}_9$ ,  $\text{B}_6\text{H}_{12}$ ,  $\text{B}_8\text{H}_{12}$ ,  $\text{B}_8\text{H}_{18}$ , and  $n\text{-B}_9\text{H}_{15}$ . In addition, we have noted unusually shaped low-field quartets in the pmr spectra of  $\text{B}_6\text{H}_{10}$  and  $\text{B}_8\text{H}_{12}$ , but we cannot easily explain their skewed appearance at this time.

Finally, we are able to make gross structural inferences based on the general appearance of the pmr spectra. The pmr spectrum of  $\text{B}_8\text{H}_{18}$  can nearly be superimposed on that of  $\text{B}_4\text{H}_{10}$  except for the low-field quartet of the  $-\text{BH}_2$  set, which has diminished intensity. This decrease in intensity and the presence of only one symmetric bridge proton resonance lead us to discount the beltline fragment model and to favor the bitetra-

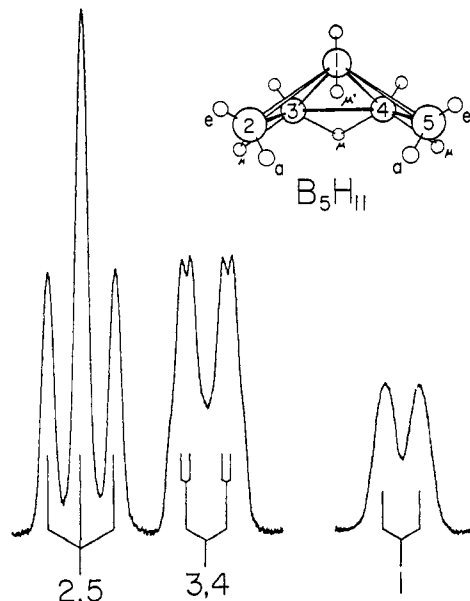


Figure 2.  $^{11}\text{B}$  spectrum of (70.58 MHz)  $^{11}\text{B}_5\text{H}_{11}$ .

bornyl structure (two  $\text{B}_4\text{H}_9$  units joined with a boron-boron bond at the 2,2' positions).<sup>3</sup> Also striking is the pmr spectrum of the recently discovered isodecaborane (16),<sup>4</sup> whose two quartets and symmetric bridge resonance in the ratio 6:2:8 almost perfectly overlay the pmr spectrum of  $\text{B}_5\text{H}_9$ . The formulation of this molecule as two  $\text{B}_5\text{H}_9$  units boron-boron bonded through the 2,2' positions is also supported by the 2:6:2 singlet, doublet, doublet pattern resolved in the 70.58-MHz  $^{11}\text{B}$  nmr spectrum.

Reproductions of these spectra with complete tables of chemical shifts, coupling constants, and assignments will appear in full detail elsewhere.

**Acknowledgments.** The authors gratefully acknowledge the support of the National Science Foundation (Grant No. GP-4944). We are also indebted to Mr. A. O. Clouse for invaluable assistance in obtaining the  $^1\text{H}$  and  $^{11}\text{B}$  nmr spectra.

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Received March 29, 1970

### Catalysis of Symmetry-Restricted Reactions by Transition Metal Compounds. The Valence Isomerization of Cubane

Sir:

The subject of this communication is our discovery that certain transition metal compounds, notably of rhodium(I), are powerful catalysts for the valence isomerizations of cubane and its derivatives<sup>1</sup> to the corresponding *syn*-tricyclooctadienes, according to eq 1 and 2. We also wish to report some observations

(1) P. E. Eaton and T. W. Cole, Jr., *J. Amer. Chem. Soc.*, **86**, 962, 3157 (1964). Rearrangement of the cubane compounds under the conditions of our experiments in the absence of a catalyst was negligible.