

Figure 2.—The SiH<sub>2</sub> resonance in the <sup>1</sup>H nmr spectrum of 2-(BrSiH<sub>2</sub>)B<sub>5</sub>H<sub>8</sub> at 34° (A), -13° (B), and -85° (C).

(halosilyl)pentaboranes no attempt was made to examine the spectra above 34°.

Electric quadrupole relaxation of a nucleus of  $I = 3/2$  coupled to a nucleus of  $I = 1/2$  has been examined theoretically and experimentally by Bacon, Gillespie, and Quail.<sup>19</sup> These workers have shown that quadrupolar relaxation can produce spectral effects analogous to those observed for the (halosilyl)pentaboranes examined in this study. However, for boron compounds, this effect has been reported only for the <sup>19</sup>F nmr spectra of compounds in which the fluorine atom is directly bonded to the boron atom. The (halosilyl)pentaboranes appear to be the first examples of molecules in which the temperature dependence is observed to affect a two-bond coupling constant between hydrogen and boron.

(19) J. Bacon, R. J. Gillespie, and J. W. Quail, *Can. J. Chem.*, **41**, 3083 (1963).

Evidence to support the interpretation that the splitting of the SiH<sub>2</sub> resonance arises due to coupling with the 2-boron atom and not from coupling to other nuclei in the system was obtained from a heteronuclear spin decoupling, <sup>1</sup>H-<sup>11</sup>B, experiment. Irradiation of the <sup>11</sup>B nuclei at a nominal frequency of 32.1 MHz using a "noise" decoupler while scanning the 100-MHz <sup>1</sup>H spectrum caused the broad doublet resonance to collapse to a sharp singlet of  $\nu_{1/2} = 3$  Hz.

**Deuteration Reactions.**—The deuteration of 2-SiH<sub>3</sub>B<sub>5</sub>H<sub>8</sub> and 2-(ClSiH<sub>2</sub>)B<sub>5</sub>H<sub>8</sub> by DCl-AlCl<sub>3</sub> appears to occur in a manner analogous to that reported for B<sub>5</sub>H<sub>9</sub>.<sup>20</sup> The infrared and <sup>11</sup>B nmr spectra of the 2-silylpentaborane which is recovered and the 2-(chlorosilyl)pentaborane which is formed from the 2-SiH<sub>3</sub>-B<sub>5</sub>H<sub>8</sub>-DCl(AlCl<sub>3</sub>) reaction indicate that specific deuteration at the 1 position of both compounds occurs. Ir absorptions at 1980 cm<sup>-1</sup> for 2-silylpentaborane and 2-(chlorosilyl)pentaborane indicate the presence of deuterium in terminal positions. The collapse of only the upfield doublets to singlets in the <sup>11</sup>B nmr spectra (Figure 1B) suggests that, within experimental error, deuteration has occurred specifically at the 1 position. The presence of deuterium in bridging positions cannot be unambiguously excluded, since both 2-SiH<sub>3</sub>B<sub>5</sub>H<sub>8</sub> and 2-(ClSiH<sub>2</sub>)B<sub>5</sub>H<sub>8</sub> have broad infrared absorptions in the region where bridge-deuterium absorptions are expected to occur.

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(20) T. P. Onak and R. E. Williams, *Inorg. Chem.*, **1**, 106 (1962).

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## Magnetic Resonance Spectra of Tetraborane(10), Pentaborane(11), Hexaborane(10), and Hexaborane(12)

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The 220-MHz <sup>1</sup>H and 70.6-MHz <sup>11</sup>B nmr spectra of B<sub>4</sub>H<sub>10</sub>, B<sub>5</sub>H<sub>11</sub>, B<sub>6</sub>H<sub>10</sub>, and B<sub>6</sub>H<sub>12</sub> have been recorded and confirm the previously accepted structures. Further elucidation of basal and apical signals of B<sub>4</sub>H<sub>10</sub>, B<sub>5</sub>H<sub>11</sub>, and B<sub>6</sub>H<sub>10</sub> was obtained by multiple decoupling experiments at 100 MHz. In the pmr spectra at 51.680 kG two magnetically nonequivalent sets of protons are resolved for the -BH<sub>2</sub> groups of B<sub>4</sub>H<sub>10</sub>, B<sub>5</sub>H<sub>11</sub>, and B<sub>6</sub>H<sub>12</sub>. Distinct bridge resonance signals are found in B<sub>5</sub>H<sub>11</sub>. In addition, the apically attached anomalous proton and the single-bridge proton lying on the symmetry plane display additional fine structure.

### Introduction

Proton magnetic resonance spectra of boron hydrides obtained at lower field strength have proved to be less informative in chemical and structural studies than the

more easily interpreted <sup>11</sup>B nmr spectra.<sup>2</sup> The complexity of the pmr spectra arises from the coupling of each distinct proton with both boron isotopes (80% <sup>11</sup>B,

(2) (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.

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$I = 3/2$  and 20%  $^{10}\text{B}$ ,  $I = 3$ ). In addition, the lack of large chemical shift differences and the broadening of the proton line widths from nuclear quadrupole and normal long-range homonuclear and heteronuclear coupling to boron result in nondistinct, often ambiguous pmr spectra for boron hydrides.

The use of heteronuclear multiple resonance experiments for detailed study of the bridge and terminal hydrogen resonances in polyhedral boranes has previously been reported for pentaborane(9) derivatives.<sup>3</sup> These techniques in conjunction with proton magnetic resonance studies done at higher field than previously attainable now permit the reinterpretation of the nmr spectra of  $\text{B}_4\text{H}_{10}$ ,  $\text{B}_5\text{H}_{11}$ ,  $\text{B}_6\text{H}_{10}$ , and  $\text{B}_6\text{H}_{12}$ . New light is shed on the "classical" problems of interpreting the nmr spectra of  $\text{B}_4\text{H}_{10}$ ,  $\text{B}_5\text{H}_{11}$ , and  $\text{B}_6\text{H}_{10}$  in accordance with their crystallographic structures. In addition, we are now able to correlate pmr spectral features with structural similarities present in the lower boranes.

### Experimental Section

**Materials.**—Tetraborane(10) and pentaborane(11) were prepared by standard synthetic routes. Hexaborane(10) was prepared by reaction of the lithium salt of pentaborane(9) and  $\text{B}_2\text{H}_6$  at  $-78^\circ$  *in vacuo*<sup>4</sup> or by the partial hydrolysis of  $\text{B}_5\text{H}_{12}$ .<sup>5</sup> Hexaborane(12) was obtained from the reaction of  $(\text{CH}_3)_4\text{NB}_3\text{H}_5$  with polyphosphoric acid at room temperature.<sup>6</sup>  $\text{B}_5\text{H}_{11}$ ,  $\text{B}_6\text{H}_{10}$ , and  $\text{B}_6\text{H}_{12}$  were purified with a special low-temperature, high-vacuum distillation column.<sup>7</sup>

**Nuclear Magnetic Resonance.**—Proton spectra were recorded on Varian A-60, HA-100,<sup>8</sup> and HR-220<sup>9</sup> spectrometers. Spectra were referenced to tetramethylsilane ( $\tau$  10.00) as an internal standard. Pmr spectra were run over a  $-26$  to  $+23^\circ$  temperature range using standard HR-220 accessories.

Boron-11 nmr spectra at 70.6 MHz were obtained on an experimental probe built by Mr. A. O. Clouse of Indiana University. Chemical shifts were obtained using an external sample of boron trifluoride diethyl etherate and are referred to  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2 = 0$  ppm.

Decoupled pmr spectra were recorded at CSCLA while irradiating  $^{10}\text{B}$  nuclei at 32.1 MHz employing a Nuclear Magnetic Resonance Specialties Model MD-60 spin decoupler modified for use with the HA-100, together with Hewlett-Packard (Models 200AB and 200CD) and Wavetek (Model 114) wide-range audio oscillators.<sup>3a,b,10</sup> The power settings were extremely sensitive, in particular when more than one oscillator was in use at the same time. In some cases when several oscillators were used to decouple the boron nuclei completely, the resulting resonances were unsymmetrical. This is not considered to be a genuine effect as it was sometimes impossible to balance the power levels completely and eliminate beat and overtone frequencies.

### Results and Discussion

**Tetraborane(10).**—The 220-MHz pmr spectrum of  $\text{B}_4\text{H}_{10}$  (Figure 1) shows a clear resolution of all terminal protons. The  $-\text{BH}_2$  groups appear as two

(3) (a) P. M. Tucker and T. Onak, *J. Amer. Chem. Soc.*, **91**, 6869 (1969); (b) P. M. Tucker, T. Onak, and J. B. Leach, *Inorg. Chem.*, **9**, 1430 (1970).

(4) R. A. Geanangel and S. G. Shore, *J. Amer. Chem. Soc.*, **89**, 6771 (1967).

(5) J. E. Dobson and R. Schaeffer, *Inorg. Chem.*, **7**, 402 (1968).

(6) D. F. Gaines and R. Schaeffer, *ibid.*, **3**, 438 (1964).

(7) J. Dobson and R. Schaeffer, *ibid.*, **9**, 2183 (1970).

(8) The Varian HA-100 at California State College, Los Angeles, Calif., was obtained through Grant GP-8347 from the National Science Foundation.

(9) The HR-220 nmr spectrometers at California Institute of Technology and at Indiana University were available through National Science Foundation Grants GP-8540 and GU-2003, respectively.

(10) J. B. Leach and T. Onak, submitted for publication.

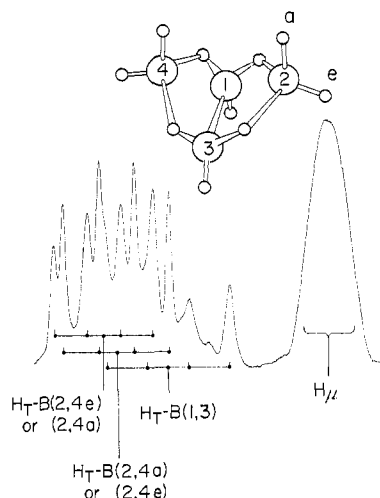


Figure 1.—Proton nmr spectrum of tetraborane(10); 220 MHz.

separate quartets, indicating two sets of magnetically nonequivalent protons. Axial and equatorial sets of protons are consistent with the *endo* and *exo* hydrogens present in the crystalline state.<sup>11</sup> Although these resonances cannot be unambiguously assigned at this time, it is of interest to note that the low-field quartet of the  $-\text{BH}_2$  set exhibits the smaller coupling constant. The 100-MHz decoupled spectrum shown in Figure 2 exhibits the two separate resonances of the  $-\text{BH}_2$  group and the location of these peaks agrees with the chemical shift data obtained from the 220-MHz spectrum. The chemical shift and coupling constant data for tetraborane(10) are summarized in Table I.

TABLE I  
The Proton Magnetic Resonance  
Spectrum of Tetraborane(10)

	$\tau$ , ppm <sup>a</sup>	$J$ , cps
$\text{H}_\mu(1,2,3,4)$	11.38	$>35^b$ $<30^c$
$\text{H}_T\text{-B}(2,4a \text{ or } 2,4e)$	7.74	134
$\text{H}_T\text{-B}(2,4e \text{ or } 2,4a)$	7.54	125
$\text{H}_T\text{-B}(1,3)$	8.66	155

The  $^{11}\text{B}$  Nmr Spectrum of Tetraborane(10)

	$\delta$ , ppm <sup>d</sup>	$J$ , cps	$J_{\text{B-H}}$
B(2,4)	+5.16	132	$\sim 30$
B(1,3)	+41.8	160	$\sim 23$

<sup>a</sup> Values referenced to internal TMS ( $\tau$  10.00) and accurate to  $\pm 0.05$  ppm. <sup>b</sup> B(1 or 3)- $\text{H}_b$  coupling. Partial decoupling of the B(1,3) from the outer envelope of the irradiation frequency used for B(2,4) allows us to quote only the minimum value for this coupling constant. <sup>c</sup> B(2 or 4)- $\text{H}_b$  coupling. Estimated from the width of the peak obtained by irradiation of B(1,3). The individual resonances cannot be seen but an examination of the shape of the broad resonance allows a maximum value to be quoted. <sup>d</sup> Values referenced to external  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  ( $\delta$  0 ppm).

Figure 2c shows the spectrum of  $\text{B}_4\text{H}_{10}$  taken while decoupling the 2- and 4-boron nuclei. It is interesting that the bridge region shows a 1:1:1:1 quartet somewhat complicated by a relaxation effect<sup>12</sup> and partial decoupling by the outer envelope of the wide range audio decoupling frequency. This coupling in the

(11) C. E. Nordman and W. N. Lipscomb, *J. Chem. Phys.*, **21**, 1956 (1953).

(12) M. Suzuki and R. Kubo, *Mol. Phys.*, **7**, 201 (1963).

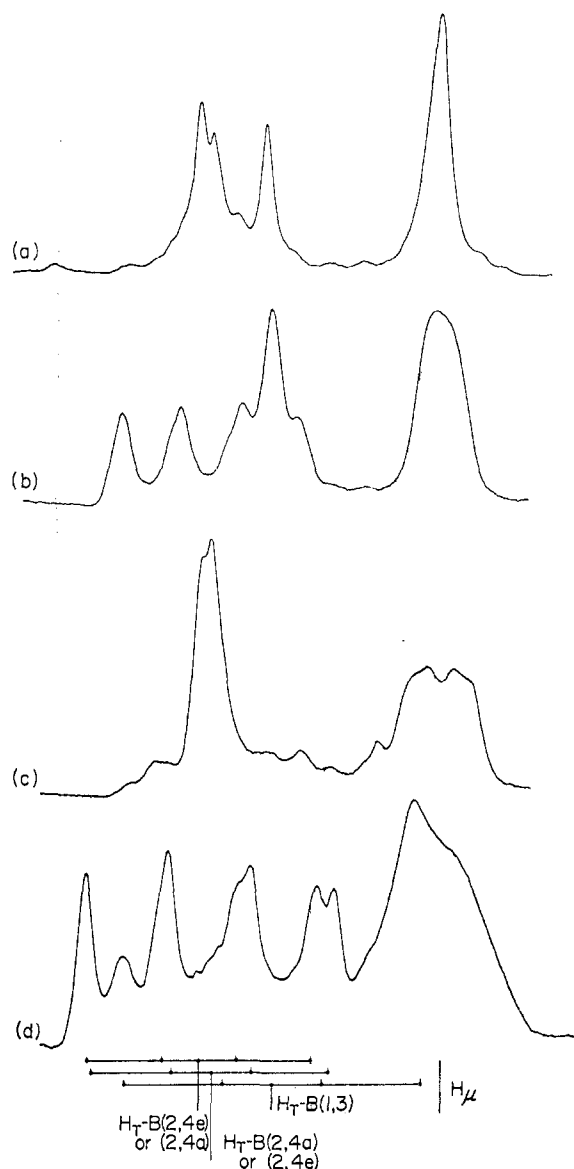


Figure 2.—Proton nmr spectrum of tetraborane(10); 100 MHz: (a) B(1,3) and B(2,4) boron-11 nuclei totally decoupled, (b) B(1,3) boron-11 nuclei decoupled; (c) B(2,4) boron-11 nuclei decoupled; and (d) undecoupled.

bridge region is not resolved when the 1- and 3-boron nuclei are irradiated (Figure 2b), although even here the resonance band width is greater than for the totally decoupled spectrum (Figure 2a) indicating that coupling of a smaller magnitude exists. These results are consistent with previously assigned structural parameters determined by X-ray crystallography where the bridge hydrogens are more closely bonded to the 1- and 3-boron nuclei. Reported values of  $B_1-H_b$  and  $B_2-H_b$  are 1.16 and 1.37 Å, respectively.<sup>13,14</sup> The estimated coupling constants for the bridge region (Table I) are consistent with the values obtained from a calculated spectrum (40 and 29 Hz for B(1 or 3)- $H_b$  and B(2 or 4)- $H_b$ , respectively).<sup>15</sup>

(13) E. B. Moore, R. E. Dickerson, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 209 (1957).

(14) G. S. Pawley, *Acta Crystallogr.*, **20**, 631 (1966).

(15) R. C. Hopkins, J. D. Baldeschwieler, R. Schaeffer, F. N. Tebbe, and A. Norman, *J. Chem. Phys.*, **43**, 975 (1965).

**Pentaborane(11).**—In recent communications<sup>16,17</sup> we presented cursory evidence for the unequivocal assignment of the nuclear magnetic resonance of the anomalous hydrogen in pentaborane(11). The proton spectrum run at 220 MHz clearly indicated a quartet at  $\tau$  8.2 ( $J = 60$  Hz) which was assigned to the apically attached anomalous hydrogen. Heteronuclear boron decoupling experiments at 100 MHz have confirmed this interpretation and are presented in Figure 3. The position of the anomalous bridge hydrogen is readily ascertained from the decoupled spectra shown in Figures 3a and 3b. It should be noted that on decoupling only the basal boron nuclei, shown in Figure 3b, the anomalous hydrogen quartet is clearly resolved. The coupling constant observed under these circumstances is obviously reduced by partial collapse of the quartet resonance, caused by irradiation of the apex boron nucleus from the outer envelope of the wide-range audio oscillator decoupling frequency. Resonance n of this quartet is increased in intensity relative to the other members of the quartet by overlap with the outer low-field resonance of the apex terminal proton quartet. Similarly, resonance m in Figure 3a is a combination of the decoupled apex terminal proton and the 2,4 bridge hydrogen resonances.

The appearance of the anomalous bridge hydrogen at unusually low field compared to the other bridge hydrogens in pentaborane(11) is indicative of a more protonic character than in most bridge (or terminal apical) hydrogens. It is therefore of interest to note molecular orbital calculations by Boer<sup>18</sup> which show the apically attached anomalous hydrogen to carry a positive charge and to be weakly bonded across the long distances to B(2) and B(5).

In addition to the assignment of the apex bridge resonance, the decoupled spectra confirmed the assignment for the basal terminal protons indicated in the 220-MHz spectrum.<sup>16,17</sup> Clearly resolved resonances possessing different chemical shifts and coupling constants are attributable to terminal protons in axial and equatorial configurations on  $-B(2,5)H_2$  groups. As with  $B_5H_{10}$ , the low-field resonance of the  $-BH_2$  set exhibits the smaller coupling constant.

In this regard, comparison of the previously published pmr spectrum of  $B_5H_{11}$ <sup>16</sup> with that of  $^{11}B_5H_{11}$  (98%  $^{11}B$  enriched)<sup>17</sup> is of special interest. The anomalous bridge hydrogen appears to give a better defined quartet in the spectrum of  $B_5H_{11}$  than in the  $^{11}B_5H_{11}$  spectrum. This effect is undoubtedly caused by the presence of  $^{10}B$  in the 2,5 boron positions. The presence of  $^{11}B$  in both positions would result in a secondary septet coupling of each quartet line giving a broad resonance as in the  $^{11}B_5H_{11}$  spectrum. The presence of one  $^{10}B$  in the 2,5 positions (32% probability in  $B_5H_{11}$ ) would result in only a secondary quartet coupling (neglecting the small  $^{10}B$  coupling) arising from the one  $^{11}B$  present,

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

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

(18) P. Boer, Ph.D. Thesis, Harvard University, 1965, University Microfilms, Inc., 65-10682.

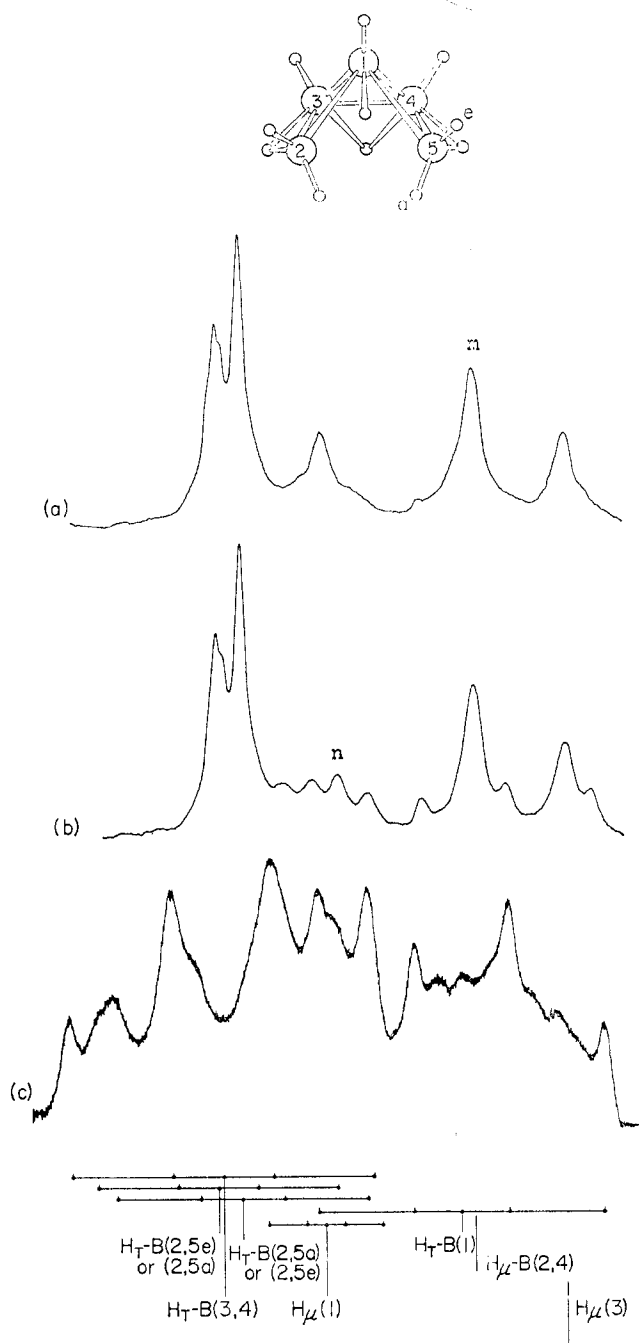


Figure 3.—Proton nmr spectrum of pentaborane(11); 100 MHz: (a) apex and basal boron-11 nuclei totally decoupled, (b) basal boron-11 nuclei decoupled, and (c) undecoupled.

thus producing a sharper quartet for the anomalous proton.

As in earlier studies on pentaborane(9) derivatives,<sup>3a,b</sup> the 100-MHz heteronuclear decoupled spectra and also the higher field strength of the 220-MHz spectra again show their immense value in the resolution of the different bridge hydrogen resonances. Furthermore, the 220-MHz spectrum of  $^{11}\text{B}_5\text{H}_{11}$  clearly shows a septet ( $J = 36$  cps) on the high field bridge proton  $\text{H}_\mu(3)$  corresponding to heteronuclear coupling with  $^{11}\text{B}$  nuclei in the magnetically equivalent 3,4 positions.

The bridging protons  $\text{H}_\mu(2$  or  $4)$  do not lie on a sym-

metry plane; consequently, they give rise to a complex resonance arising from coupling to two nonequivalent boron atoms.<sup>19</sup>

Table II summarizes the chemical shift and coupling constant data for  $\text{B}_5\text{H}_{11}$ . Minor differences from previously reported values<sup>15,16</sup> are the result of a more accurate determination based on comparison of undecoupled and decoupled spectra at various field strengths. It should be noted in particular that the chemical shift of the bridge hydrogen resonance  $\text{H}_\mu(2,4)$  was determined with much greater accuracy from the partially decoupled spectrum (Figure 3b).

TABLE II  
The Proton Magnetic Resonance  
Spectrum of Pentaborane(11)

	$\tau$ , ppm <sup>a</sup>	$J$ , cps
$\text{H}_T\text{-B}(1)$	10.4	152
$\text{H}_T\text{-B}(2,5a$ or $2,5e)$	6.9	135
$\text{H}_T\text{-B}(2,5e$ or $2,5a)$	6.5	127
$\text{H}_T\text{-B}(3,4)$	6.6	160
$\text{H}_\mu(1)$	8.2	~55
$\text{H}_\mu(2,4)$	10.6	...
$\text{H}_\mu(3)$	12.0	36 <sup>b</sup>

The  $^{11}\text{B}$  Nmr Spectrum of Pentaborane(11)

	$\delta$ , ppm	$J$ , cps
$\text{B}(2,5)$	-7.44	132
$\text{B}(3,4)$	-0.47	160
$\text{B}(1)$	+55.2	152

<sup>a</sup>  $\tau$  values relative to internal TMS = 10.0 are considered accurate to  $\pm 0.1$  ppm. <sup>b</sup>  $^{11}\text{B}(3,4)\text{-H}_{\text{bridge}}$  heteronuclear coupling. <sup>c</sup> Measured on  $\text{B}_5\text{H}_{11}$  of 98%  $^{11}\text{B}$  content.

**Hexaborane(10).**—In the past decade much controversy has arisen about the environment of the bridge hydrogen nuclei in hexaborane(10). In a number of studies<sup>20-23</sup> several rapid hydrogen-exchange mechanisms have been put forward to account for the observation of only one basal terminal hydrogen and one bridge hydrogen resonance.

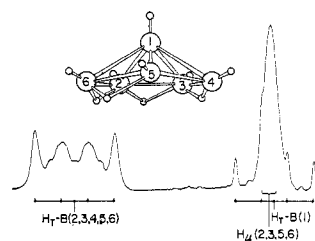


Figure 4.—Proton nmr spectrum of hexaborane(10); 220 MHz.

The 220-MHz spectrum (see Figure 4) does indeed tend to confirm a rapid-bridge hydrogen tautomerism

(19) The symmetry equivalent bridge protons in  $\text{B}_5\text{H}_9$  also give rise to a resonance displaying a poorly resolved septet ( $J = 35$  cps) from  $^{11}\text{B}\text{-H}\text{-}^{11}\text{B}$  coupling. No evidence of this coupling is seen in the 70.6-MHz  $^{11}\text{B}$  nmr spectrum, which simply consists of doublets at +13.7 ppm ( $J = 164$  cps) and +53.7 ppm ( $J = 174$  cps). The pmr spectrum of  $\text{B}_5\text{H}_9$  is discussed in ref 3b.

(20) R. E. Williams, S. G. Gibbins, and I. Shapiro, *J. Chem. Phys.*, **30**, 333 (1959).

(21) R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961).

(22) W. N. Lipscomb, *ibid.*, **11**, 1 (1959).

(23) J. C. Carter and N. L. H. Hock, *J. Amer. Chem. Soc.*, **91**, 589 (1969).

since it is not possible to see a separation of the different basal bridge and terminal protons as might be expected in a static pentagonal-pyramidal structure. Any mechanism for such a tautomerism would have to preserve the integrity of all five terminal B-H units, for an averaging of all nine basal hydrogens is not apparent in the pmr spectra.

Heteronuclear multiple resonance experiments at 100 MHz (see Figure 5) give a sharp single resonance

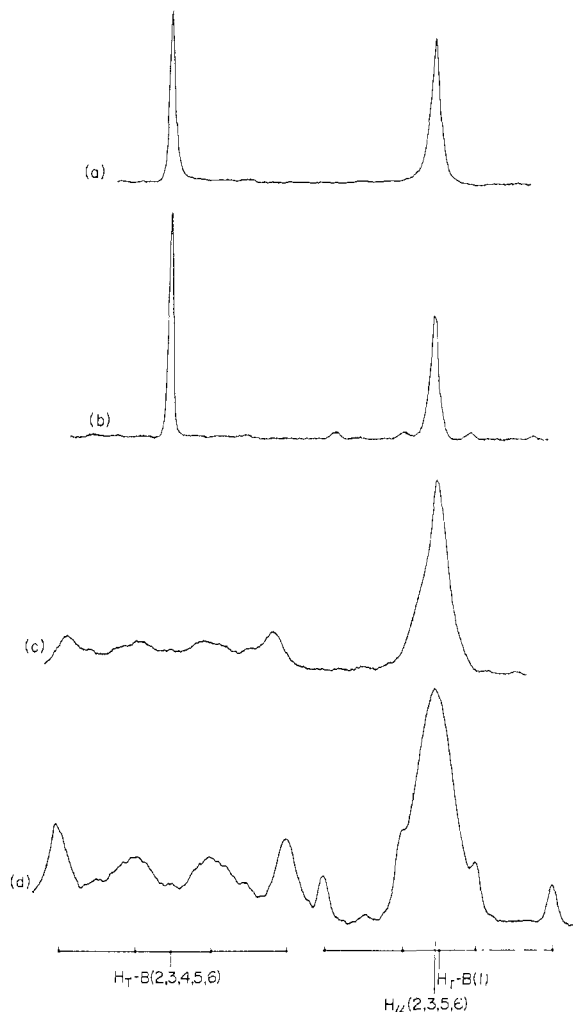


Figure 5.—Proton nmr spectrum of hexaborane(10); 100 MHz: (a) apex and basal boron-11 nuclei totally decoupled, (b) basal boron-11 nuclei decoupled, (c) apex boron-11 nuclei decoupled, and (d) undecoupled.

for the basal terminal hydrogen and a reasonably sharp resonance for the bridge hydrogens. These observations greatly minimize the possibility of coincidental overlap of resonances in a static structure and thus lend additional credence to a tautomeric molecule. The center peaks of the low-field quartet are broadened due to contributions from the underlying septet, and their diminished intensity relative to the outer members of the quartet may be explained by quadrupole relaxation effects.<sup>12</sup> The chemical shift and coupling constant data for hexaborane(10) are summarized in Table III.

**Hexaborane(12).**—Although crystallographic at-

TABLE III  
The Proton Magnetic Resonance  
Spectrum of Hexaborane(10)

	$\tau$ , ppm <sup>a</sup>	$J$ , cps
H <sub>T</sub> -B(2,3,4,5,6) <sup>b</sup>	5.82	158 <sup>c</sup>
H <sub>T</sub> -B(1)	11.22	155
H <sub>μ</sub> (2,3,5,6) <sup>b</sup>	11.10	

The <sup>11</sup>B Nmr Spectrum of Hexaborane(10)

	$\delta$ , ppm	$J$ , cps
B(2,3,4,5,6) <sup>b</sup>	-14.1	158
B(1)	+51.8	155

<sup>a</sup> Values referenced to internal TMS ( $\tau$  10.00) and accurate to  $\pm 0.05$  ppm. <sup>b</sup> Only if a rapid intramolecular bridge hydrogen exchange occurs should all of these be identical. <sup>c</sup> This quartet shows some relaxation effects ( $1 < \alpha < 2.5$ ), as calculated by Suzuki and Kubo.<sup>12</sup>

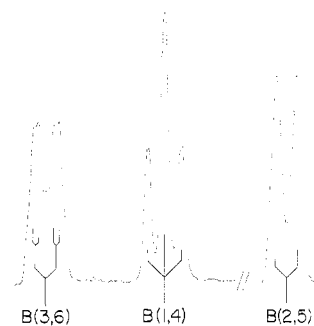


Figure 6.—Boron-11 nmr spectrum of hexaborane(12); 70.6 MHz.

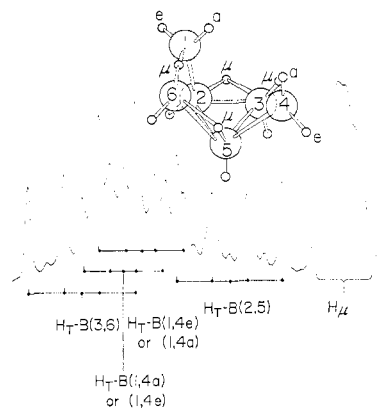


Figure 7.—Proton nmr spectrum of hexaborane(12); 220 MHz.

TABLE IV  
The Proton Magnetic Resonance  
Spectrum of Hexaborane(12)

	$\tau$ , ppm <sup>a</sup>	$J$ , cps
H <sub>T</sub> -B(3,6)	4.9	160
H <sub>T</sub> -B(1,4a or 1,4e)	5.8	120
H <sub>T</sub> -B(1,4e or 1,4a)	6.1	138
H <sub>T</sub> -B(2,5)	7.9	158
H <sub>μ</sub>	10.2	...

The <sup>11</sup>B Nmr Spectrum of Hexaborane(12)

	$\delta$ , ppm	$J$ , cps	$J_{\text{B-H-B}}$ , cps
B(3,6)	-22.6	156	~40
B(1,4)	-7.9	133	...
B(2,5)	+22.6	158	...

<sup>a</sup>  $\tau$  values relative to external TMS and accurate to  $\pm 0.1$  ppm.

tempts to solve the structure of  $B_6H_{12}$  have been unsuccessful,<sup>24</sup> the  $^{11}B$  and  $^1H$  spectra of  $B_6H_{12}$  are in agreement with the structure previously proposed by Gaines and Schaeffer.<sup>6</sup> The 70.6-MHz  $^{11}B$  spectrum (Figure 6) is clearly resolved into a doublet, triplet, and doublet of intensity 2:2:2. The low-field doublet exhibits secondary coupling which probably arises from bridge proton coupling. The pmr spectrum (Figure 7) exhibits the expected axial and equatorial resonances from the  $-BH_2$  groups.

(24) W. N. Lipscomb, private communication.  $B_6H_{12}$  forms a glass at low temperatures and cannot be shocked into the crystalline state.

As with  $B_4H_{10}$  and  $B_5H_{11}$ , the low-field quartet has the smaller coupling constant. Although the bridge resonance is not resolved into two separate resonances as would be expected, its structure indicates that it is not arising from only one type of bridge position.

Chemical shift and coupling constant data for  $B_6H_{12}$  are presented in Table IV.

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## Monocarbon Carboranes. IV.<sup>1</sup> Polyhedral Arsa- and Stibacarbododecaborane(11) Derivatives and Related 11-Atom Cage Fragments

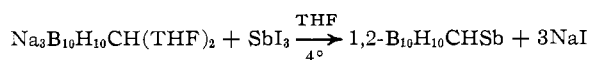
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The syntheses of 1,2-, 1,7-, and 1,12- $B_{10}H_{10}CHAs$  as well as 1,2- and 1,7- $B_{10}H_{10}CHSb$  are discussed. The conversions of the appropriate icosahedral derivative to 7,8- or 7,9- $B_9H_9CHAs^-$ , 7,9- $B_9H_9CHAsCH_3$ , or 7,8- $B_9H_9CHSb^-$  are described. The synthesis and X-ray diffraction study of  $(C_5H_5)_2Co(1,2-B_9H_9CHAs)$  confirm the relative position of the carbon and arsenic atoms in the 1,2-arsacarboranes and show the distorted nature of these derivatives. Dipole moment and nmr data are presented which aid in elucidating the role of the group V atom in these molecules.

### Results and Discussion

**Icosahedral Arsa- and Stibacarboranes.**—Initial attempts to insert an arsenic or antimony atom into the carbollide ion using the experimental procedure developed for 1,2- $B_{10}H_{10}CHP^{1a}$  were unsuccessful. Reaction of arsenic trichloride with  $Na_3B_{10}H_{10}CH(THF)_2$  in tetrahydrofuran (THF) at room temperature produced a 25% yield of sublimable 1,2- $B_{10}H_{10}CHAs$  which has an odor reminiscent of the phosphacarboranes.<sup>1b</sup> Although antimony trichloride reacted in a very exothermic manner with the  $B_{10}H_{10}CH^{3-}$  ion, no 1,2- $B_{10}H_{10}CHSb$  could be isolated. When antimony triiodide was used as the source of antimony and the reaction was run at ice bath temperature, 1,2- $B_{10}H_{10}CHSb$  was obtained in 41% yield by the reaction



The composition of these heteroatom carboranes was determined by their elemental analyses (Table I). Further confirmation of these molecular formulas was

obtained by mass spectral measurement of the parent ion peaks: calcd for  $^{11}B_{10}^{1}H_{11}^{12}C^{75}As$ , 208.1017; found, 208.1010; calcd for  $^{11}B_{10}^{1}H_{11}^{12}C^{123}Sb$ , 256.0833; found, 256.0837.

Thermal isomerization of 1,2- $B_{10}H_{10}CHAs$  in a sealed tube at 495° for 22 hr produced 1,7- $B_{10}H_{10}CHAs$  in moderate yield. Elemental analysis (Table I) and

TABLE I  
ELEMENTAL ANALYSES FOR ARSA- AND STIBACARBORANE DERIVATIVES

Compound	Analyses
1,2- $B_{10}H_{10}CHAs$	Calcd: C, 5.83; H, 5.38 Found: C, 5.78; H, 5.18
1,7- $B_{10}H_{10}CHAs$	Calcd: C, 5.83; H, 5.38 Found: C, 5.82; H, 5.27
$(CH_3)_4N[7,8-B_9H_9CHAs]$	Calcd: C, 22.30; H, 8.56; N, 5.20 Found: C, 22.09; H, 8.60; N, 4.91
$(CH_3)_4N[7,9-B_9H_9CHAs]$	Calcd: C, 22.30; H, 8.56; N, 5.20 Found: C, 21.95; H, 8.49; N, 5.33
7,9- $B_9H_9CHAsCH_3$	Calcd: C, 11.41; H, 6.70 Found: C, 11.51; H, 6.66
1,2- $B_{10}H_{10}CHSb$	Calcd: B, 42.73; Sb, 48.10 Found: B, 42.02; Sb, 48.14
1,7- $B_{10}H_{10}CHSb$	Calcd: C, 4.74; H, 4.38; B, 42.73; Sb, 48.10 Found: C, 5.18; H, 4.28; B, 42.83; Sb, 47.98
$(CH_3)_4N[7,8-B_9H_9CHSb]$	Calcd: C, 18.95; H, 7.32; N, 4.43 Found: C, 18.50; H, 7.52; N, 4.13

(1) (a) For the previous paper in this series, see L. J. Todd, J. L. Little<sup>1</sup> and H. T. Silverstein, *Inorg. Chem.*, **8**, 1698 (1969); (b) for the preliminary communication of this work, see L. J. Todd, A. R. Burke, H. T. Silverstein, J. L. Little, and G. S. Wikholm, *J. Amer. Chem. Soc.*, **91**, 3376 (1969).

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