

Figure 18-5. ^{11}B nmr spectrum of B_4H_{10} at 15.1 MHz. Chemical shifts relative to $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$. The fine structure in the high-field doublet arises from extensive ^{11}B —H spin coupling, which is not explained by a simple first-order scheme. [After R. C. Hopkins, J. D. Baldeschwieler, R. Schaeffer, F. N. Tebbe, and A. D. Norman, *J. Chem. Phys.*, 43, 975 (1965).]

of the interconnections between atoms; from it you can gain some idea of the gross geometry of the molecule.

The Topological Approach to Boron Hydride Structure: the *styx* Numbers.²⁰ In all neutral boron hydrides, hydroborate anions, or carboranes, each boron has at least one H (or other substituent) attached by a normal two-electron σ bond. Lipscomb proposed that, in addition to these, there could be three-center B—H—B bonds (labeled *s* in Figure 18-6; cf. B_2H_6 in Chapter 5), closed and/or open three-center B—B—B bonds (both labeled *t*), additional B—H_{terminal} bonds (labeled *x*) and B—B two-center bonds (labeled *y*). Subsequent theoretical studies have shown that open B—B bonds need not be considered.²¹ However, it is apparent that three-center bonds of some type are necessary to account for boron hydride bonding because each B—H unit at a polyhedral vertex can supply three orbitals but only two electrons to the framework. Consequently, relative to the “octet” concept, each boron is responsible for a “bonding electron deficiency” of one electron; and the molecule would be “deficient” by one electron per boron if only two-center bonds were formed. How-

²¹E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, 92, 3847 (1970).

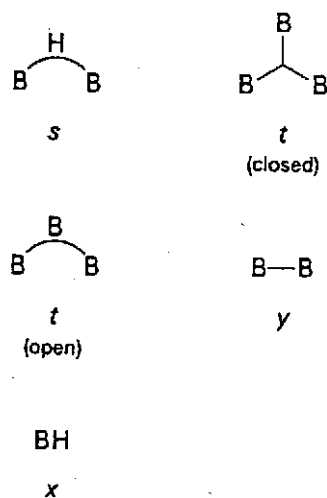


Figure 18-6. Topological representations of the localized interactions commonly found in the boranes.

ever, if one three-center bond (holding two electrons) is formed per boron, the "bonding electron deficiency" in the boron hydride is eliminated. For example, in B_2H_6 there are 12 valence electrons and 14 valence orbitals; therefore, two three-center BHB bridges are formed in addition to two extra two-center B—H bonds. In an even more extreme case, B_6H_{10} has 28 valence electrons and 34 valence orbitals. Its 14 pairs can be accommodated in eight two-center bonds (BH and BB) and six three-center bonds (BHB and BBB).

Utilizing the concept of localized, three-center BBB and BHB bonds, in addition to two-center BB and additional BH bonds, it is possible to describe the topology of the boron hydrides. The relationship between the formula of the boron hydride $(BH)_pH_q$ and the number and kinds of bonds in the molecule is described by simple equations of balance:²²

(i) *Three-center orbital balance.*

$$p = s + t$$

(18-

As stated above, the "electron deficiency" in a boron hydride is eliminated if one three-center bond is formed per boron atom. Therefore, the sum of the number of three-center BHB bonds (s) and the number of three-center BBB bonds (t) must equal the number of BH units (p).

(ii) *Hydrogen balance.*

$$q = s + x$$

(18-

It is assumed that each boron has at least one "terminal" hydrogen attached. Therefore, the remaining hydrogen atoms, q , must be divided between bridges (s) and additional B—H terminal bonds (x).

(iii) *Electron balance.*

no. of electron pairs = no. of bonds

$$p + (q/2) = s + t + y + x$$

(18-3

or more simply [by substitution of (i) and (ii)]

$$y = \frac{1}{2}(s - x)$$

(18-4

This rule arises from the fact that each of the p (BH) groups can contribute two electrons or one pair to the framework, and each of the additional q hydrogens can contribute one electron or half of a pair. All of these electron pairs must then be used in bonding, the total number of bond pairs being $s + t + y + x$.

With this set of equations relating the formula of a boron hydride to the types of bonds formed, the topology of a boron hydride may be described in terms of the so-called *styx* number. For example, consider the simplest possible case, diborane, $B_2H_6 = (BH)_2H_4$.

²² You are reminded of the equations developed in Chapter 2 that allowed the allocation of the valence electrons in a molecule ($= V$) to σ bonds, π bonds, and lone pairs. Here we present equations that relate the number of valence electrons to the different types of σ bonds that can form.

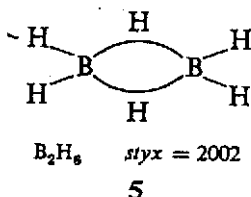
Step a. For diborane, $p = 2$ and $q = 4$.

Step b. In general, s , the number of BHB bridges, must always be >0 and $\geq x$ but $\leq q$.²³ Furthermore, s must be $\geq q/2$.²⁴ That is, s must have values in a range from $q/2$ to q . For diborane, $q = 4$ and $2 \leq s \leq 4$, so $s = 2, 3$, or 4 .

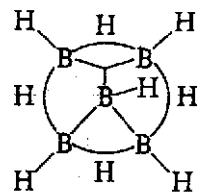
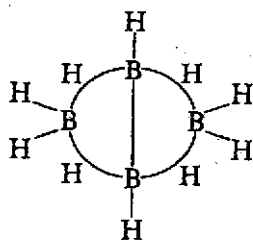
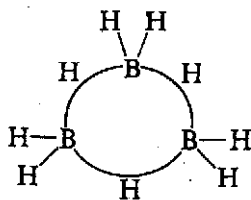
Step c. As a result of the three possible values for s , there are three sets of solutions for the values of s , t , y , and x (called the *styx* numbers).

s	t	y	x
2	0	0	2
3	-1	1	1
4	-2	2	0

Only the first of these three solutions is physically reasonable, since the latter two involve negative parameters. From your knowledge of the diborane structure, the *styx* number 2002 is, of course, seen to be correct; that is, there are two BHB bridges ($= s$), no three-center BBB bonds ($= t$) or two-center BB bonds ($= y$), and two B—H terminal bonds in addition to those already assumed.

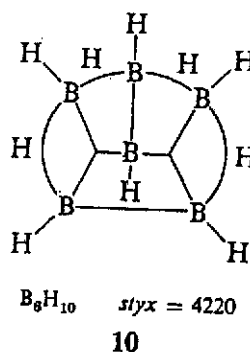
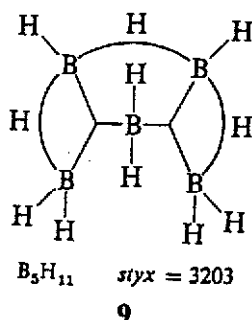


Other boron hydrides with their *styx* numbers are pictured below. You might note at this point that there are four variables (s , t , y , and x) but only three independent equations relating them, so you can arrive only at sets of possible *styx* numbers (defined by the range $q/2 \leq s \leq q$). However, by applying the empirical rules given in Study Question 3 (where they are applied to tetraborane), reasonable topologies may be predicted, and it is these that are shown.



²³The statement that $s \leq q$ is true because the additional q H's form BHB bridges ($= s$) and/or additional terminal BH bonds ($= x$). From equation 18-2, you see that the number of BHB bridges cannot exceed the number of additional H's. The statement that $s \geq x$ follows from equation 18-4, since y cannot be negative (i.e., $y \geq 0$).

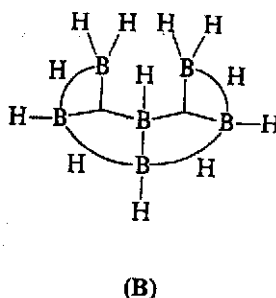
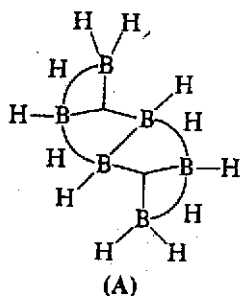
²⁴This statement is derived as follows: Since $p + (q/2) = (q - x) + t + y + x$, then $p = t + y + (q/2)$. From equation 18-1, $(s + t) = t + y + (q/2)$, so $y = s - (q/2)$, and $s = (q/2) + y$.



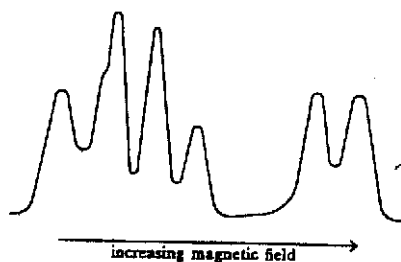
STUDY QUESTIONS

- Derive the *styx* number for B_3H_9 (6) and show that it is the only one possible. On a sketch of 6 show to which parts of the molecule each of the *styx* letters applies.
- B_3H_9 (6) and B_3H_7 are thought to be kinetically unstable intermediates in the pyrolysis of diborane. They may arise according to the reaction

$$B_2H_6 + BH_3 \rightarrow B_3H_9 \rightarrow B_3H_7 + H_2$$
 - Derive the possible sets of *styx* numbers for B_3H_7 .
 - Draw the structure corresponding to each *styx* number.
 - If you have drawn two or more structures, which is the most reasonable and why?
- There are usually several *styx* numbers for a given boron hydride, and therefore several possible topologies. In order to choose among the several possibilities, empirical rules have been developed and are given as follows:
 - All known boron hydrides have at least a two-fold element of symmetry, so it is assumed that any new hydride probably would have at least a plane, center, or two-fold axis of symmetry. Low symmetry appears to provide centers of reactivity.
 - Only one terminal hydrogen, and no bridging hydrogen, may be attached to a boron that is bound to five neighboring borons. This restricts BHB bridges and BH_2 groups to the open edges of boron frameworks.
 - If a boron is bound to four other boron atoms, it will probably not make use of more than one BHB bridge.
 - A boron atom that is bound to only two other boron atoms will be involved in at least one BHB bridge.
 - Derive the different *styx* numbers possible for B_4H_{10} .
 - Draw the structure corresponding to each *styx* number.
 - On the basis of the rules above, choose the most likely structure.
- Although B_6H_{10} was known from Alfred Stock's work (see page 983), B_6H_{12} was only recently isolated, the compound having been synthesized by the reaction of $B_3H_8^-$ with polyphosphoric acid.
 - Derive the possible sets of *styx* numbers.
 - To which *styx* numbers do the two structures below correspond?



- c) B_6H_{12} is thermally unstable, so structural information comes from the low temperature ^{11}B nmr spectrum that is sketched below. Note that there is no spin coupling between ^{11}B and bridging H; only $B-H_{\text{terminal}}$ spin coupling is seen.



The spectrum consists of two doublets of equal intensity and a triplet. Identify these parts of the spectrum. How many different types of boron atoms are there in B_6H_{12} ? How many borons are bound to just one terminal H and how many to two terminal H's? Of the two topologies possible for B_6H_{12} drawn in part (b), which is the more likely? For a recent spectrum, see J. B. Leach, *et al.*, *Inorg. Chem.*, 9, 2170 (1970).]

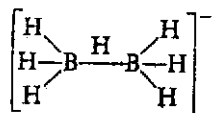
5. It is also possible to derive structures for anionic boron hydrides such as $B_2H_7^-$ by modifying the *styx* equations to take the charge into account. For a molecule of the general formula $[(BH)_pH_{q+c}]^{c-}$, the new equations are:

$$x = q + c - s$$

$$t = p + c - s$$

$$y = \frac{1}{2}(s - 3c - x)$$

For example, for $B_2H_7^-$, the structure of which is given below, $p = 2$, $q = 6$ (note that $q + c = 5$, and so $q = 6$ since $c = -1$), $c = -1$, $x = 4$, $s = 1$, $t = 0$, and $y = 0$.



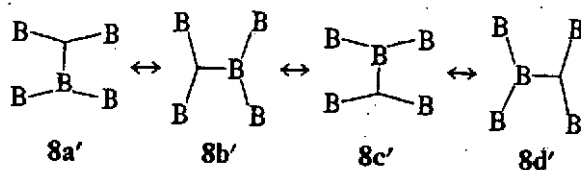
- Derive the sets of *styx* numbers for $B_3H_8^-$, and sketch a structure based on each *styx* number.
- Derive *styx* numbers and structures for $B_3H_{11}^{2-}$ (see also Study Question 6).
- The nmr spectra of some simple BH anions were recently reported [see S. G. Shore, *et al.*, *J. Amer. Chem. Soc.*, 97, 5395 (1975)], among them $B_4H_9^-$. Derive a reasonable structure for this anion.

Molecular Orbital Concepts. Pentaborane(9), B_5H_9 or $(BH)_5H_4$, is a *nido*-borane. As such, it illustrates the variety of problems with which you are confronted when considering boranes wherein at least one boron atom is formally "connected" to more than three other boron atoms.

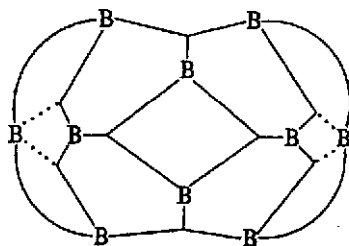
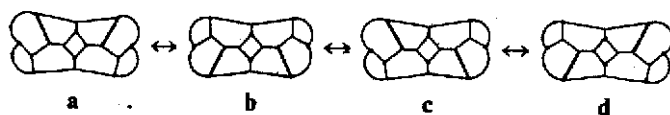
The most common *nido*-boranes are B_5H_9 , B_6H_{10} [$= (BH)_6H_4$], and $B_{10}H_{14}$ [$= (BH)_{10}H_4$]. As illustrated on page 989 and in Figure 18-4, *nido*-boranes all have the general formula $(BH)_pH_4$ (*i.e.*, $q = 4$) and all of the q hydrogens are used to stitch up the open, non-triangular face of the borane with BHB bridges. Further, the compounds all have one or more "apical" (or non-facial) boron atoms that are formally connected to four or five other boron atoms, in addition to forming a terminal B—H bond. Since each apical boron has only three atomic or hybrid orbitals remaining to be used in framework bonding (one orbital having been used to form a

terminal BH bond), each apical boron must be involved in at least one three-center BBB bond. In fact, it can be shown that, for neutral *nido*-boranes of general formula $(\text{BH})_p\text{H}_4$, the number of three-center BBB bonds ($= t$) must be $p - 4$.²⁵ Therefore, for the *nido*-boranes being considered, $t = 1$ for B_5H_9 , $t = 2$ for B_6H_{10} , and $t = 6$ for $\text{B}_{10}\text{H}_{14}$.

Based on the analysis above, pentaborane(9) must have the topology depicted by structure 8'. However, this is not the final answer, since it is clear from the x-ray structural studies on this molecule that all of the $\text{B}_{\text{apical}}-\text{B}_{\text{edge}}$ distances are equal (Figure 18-4). The only way to rationalize this is to recognize that 8 is only one of four possible canonical resonance structures (8a-8d) for the 4120 topology of B_5H_9 . Since electron delocalization often confers special kinetic and/or thermodynamic stability (*cf.* benzene), B_5H_9 should be a "stable" molecule, as indeed it is. (We shall explore the question of reactivity very shortly.)



The fact that $\text{B}_{10}\text{H}_{14}$ must have more three-center bonds ($p = s + t = 10$) than pentaborane(9) means that it may have numerous canonical structures. In fact, Lipscomb has calculated that there will be 24 topologically allowed valence structures if open three-center BBB bonds are not considered.²⁶ Four of the 24 possible resonance structures are shown below as a through d, while the last structure best conveys the picture of decaborane bonding that has been derived from localized molecular orbital calculations (see discussion of such calculations at the end of Chapter 4).^{27,28}



To avoid the problem of writing out numerous resonance structures to describe the bonding in the more symmetrical boranes (*closo* and *nido* compounds), it is clear that molecular orbital theory presents a distinct advantage. Therefore, we turn now to a molecular orbital treatment of pentaborane(9).

²⁵ This statement is derived as follows: Since, in general, $q/2 \leq s \leq q$, then s must be 2, 3, or 4 when $q = 4$. However, in *nido*-boranes, all extra q H's are used in BHB bridges, so $x = 0$; since $q = s + x$, then q must equal $s = 4$. Since $t = p - s$ (equation 18-1), t must equal $p - 4$.

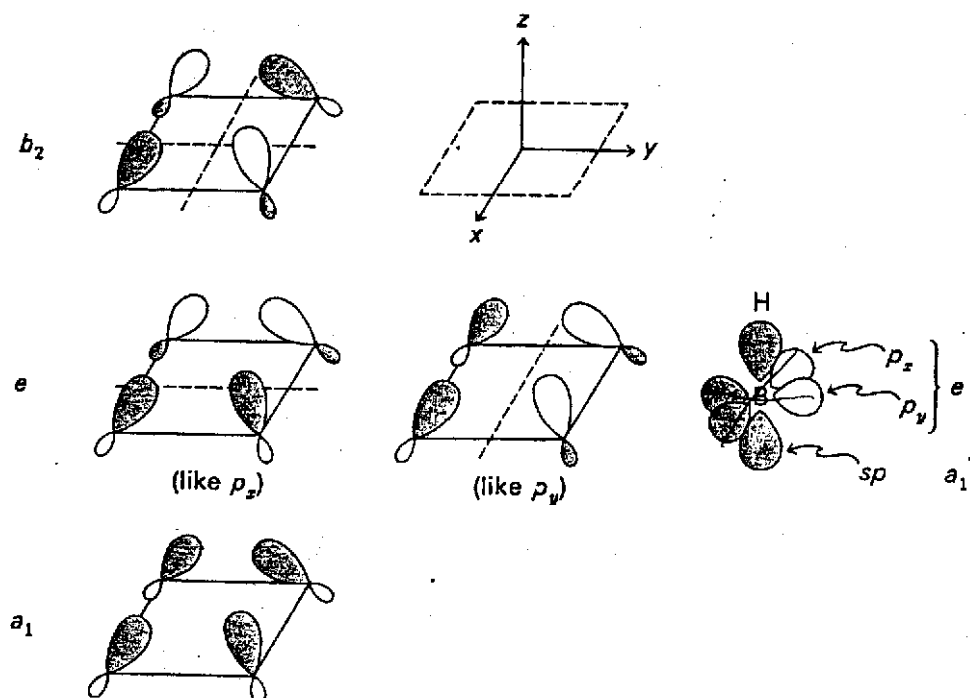
²⁶ See ref. 13.

²⁷ E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **94**, 4467 (1972).

²⁸ W. N. Lipscomb, *Pure and Appl. Chem.*, **29**, 493 (1972). This paper presents a summary of the theoretical work done by Lipscomb and his students.

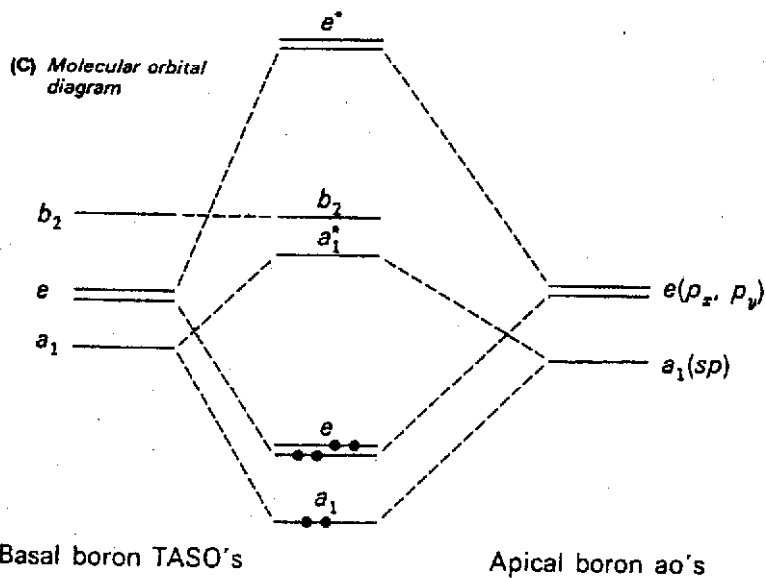
Applying the techniques learned in Chapter 4, you first seek sets of symmetry-related atoms. In the case of B_5H_9 (C_{4v} symmetry), there are two symmetry-related sets of boron atoms: the four basal borons and the apical boron. The basal boron atoms define a set of " σ " TASO's as shown in Figure 18-7(A)²⁹ (cf. Figure 4-15 and Table 4-1); the apical boron atom will utilize the orbitals in Figure 18-7(B). The next step is to decide which of the central atom ao's (the apical boron in this case) will have

²⁹These are shown as " sp " hao's following Chapter 4, p. 163, item 2.



(A) Basal boron TASO's

(B) Apical boron ao's



B_5 framework mo's

Figure 18-7. Formation of B_5H_9 framework molecular orbitals from basal boron TASO's and apical boron ao's.

non-zero overlaps with the TASO's, and to form bonding and anti-bonding mo's accordingly. The molecular orbital diagram that results is shown in Figure 18-7(C). The six electrons remaining after allowing for five B—H_{terminal} pairs and four BHB pairs just fill the cage or framework bonding molecular orbitals and give the required diamagnetic molecule.

In addition to pentaborane(9),³⁰ detailed molecular orbital calculations have been carried out for the majority of the neutral boron hydrides,^{31,32} and the following general conclusions can be drawn:

- There is little or no evidence for open, three-center BBB bonding.
- Apical boron atoms carry more negative charge than others. (As seen below, such borons are therefore more susceptible to electrophilic attack.)
- A characteristic of BHB bridge units is that there is very little electron density along a line connecting the two boron atoms.

Synthesis and Reactivity of the Neutral Boron Hydrides^{33,34}

Since the neutral boranes are polyhedral fragments, it might be supposed that they can be synthesized from the appropriate polyhedral species. However, nothing could be further from the truth; with a few exceptions, the neutral boranes are in fact synthesized from smaller boranes. Indeed, the best way to synthesize B₄H₁₀, B₅H₉, B₅H₁₁, and B₁₀H₁₄ is to pyrolyze diborane under carefully controlled conditions, and the fact that such an approach is feasible becomes clearer if we organize the borane family somewhat differently than we have done thus far.

Up to this point the general borane formula has been used in the form B_pH_{p+q}.

³⁰ See ref. 21.

³¹ See ref. 28.

³² W. N. Lipscomb, *Acc. Chem. Res.*, 6, 257 (1973).

³³ R. W. Parry and M. K. Walter, "The Boron Hydrides," in "Preparative Inorganic Reactions," Vol. 5, W. L. Jolly, ed., Interscience Publishers, New York (1968).

³⁴ A potentially powerful topological approach to the systematization of boron hydride chemistry is given by R. W. Rudolph and D. A. Thompson, *Inorg. Chem.*, 13, 2779 (1974).

TABLE 18-2
THE NEUTRAL BORANES WRITTEN
ACCORDING TO THE GENERAL
FORMULATIONS (BH)_pH_q AND (BH)_n(BH₃)_z.
Unknown boranes are indicated by *.

<i>n</i>	<i>q</i> = 2, <i>x</i> = 1	<i>Nido</i> <i>q</i> = 4, <i>x</i> = 2	<i>Arachno</i> <i>q</i> = 6, <i>x</i> = 3
0	BH ₃	B ₂ H ₆ (BH ₃) ₂	B ₃ H ₉ [*] (BH ₃) ₃
1		B ₃ H ₇ [*] (BH)(BH ₃) ₂	B ₄ H ₁₀ (BH)(BH ₃) ₃
2		B ₄ H ₈ [*] (BH) ₂ (BH ₃) ₂	B ₅ H ₁₁ (BH) ₂ (BH ₃) ₃
3		B ₅ H ₉ [*] (BH) ₃ (BH ₃) ₂	B ₆ H ₁₂ (BH) ₃ (BH ₃) ₃
4		B ₆ H ₁₀ [*] (BH) ₄ (BH ₃) ₂	B ₇ H ₁₃ [*] (BH) ₄ (BH ₃) ₃
5		B ₇ H ₁₁ [*] (BH) ₅ (BH ₃) ₂	B ₈ H ₁₄ (BH) ₅ (BH ₃) ₃
6		B ₈ H ₁₂ [*] (BH) ₆ (BH ₃) ₂	B ₉ H ₁₅ (BH) ₆ (BH ₃) ₃
7		B ₉ H ₁₃ [*] (BH) ₇ (BH ₃) ₂	B ₁₀ H ₁₆ (BH) ₇ (BH ₃) ₃
8		B ₁₀ H ₁₄ [*] (BH) ₈ (BH ₃) ₂	B ₁₁ H ₁₇ (BH) ₈ (BH ₃) ₃

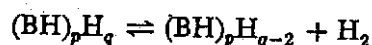
This was done to clarify the prediction of numbers of different σ bonds and topologies. However, the chemical relationships between boranes may be seen better if we combine the B_nH_{p+q} formulation with another general formula $(BH)_n(BH_3)_x$, where n can assume values from 0 through 10, and $x = 1, 2$, or 3.³⁵ In Table 18-2 the known (and some unknown) boranes through B_{11} are listed according to their n , q , and x numbers. The usefulness of this tabular form becomes apparent when it is recognized that it shows that two boranes may be interconverted, or higher boranes made from simpler ones, by the application of one or more of the following reactions in the proper sequence:³⁶

(A) Gain or loss of BH_3 . Used to convert a borane of a given n and x to a borane of the same n but different x .

(B) Gain or loss of H_2 . Used to convert a borane of a given n and x to one of the next higher or lower n and x . Can be thought of in terms of the reaction $BH_3 \rightleftharpoons BH + H_2$. Thus,

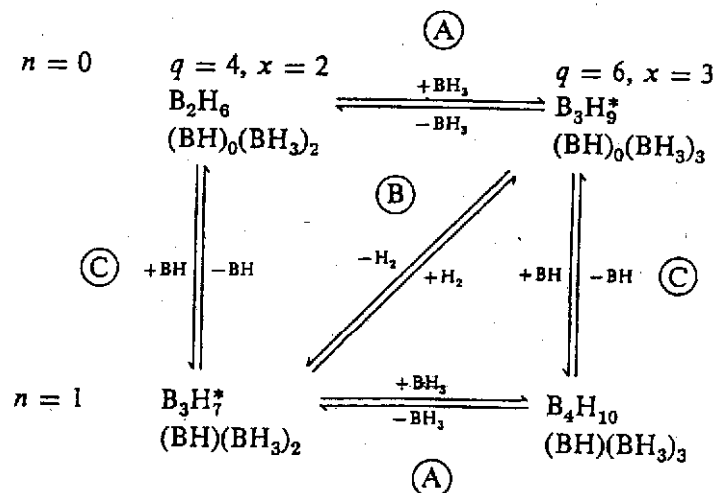


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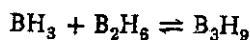
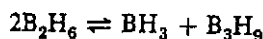


(C) Gain or loss of a BH unit. Used to convert a borane of a given n and x to a borane of higher n but the same x . Can also be thought of as occurring by the hypothetical reaction $BH_3 \rightarrow BH + H_2$.

These reactions are illustrated by a portion of Table 18-2 reproduced below.



The interrelations between boranes have been recognized for some time, and a great deal of effort has gone into writing reaction routes for the production of higher boranes from the simpler ones. However, as Parry and Walter have commented, "Up to the present time [i.e., 1968] such studies have frequently generated more heat than light."³⁷ One of the latest schemes linking diborane to B_3 , B_4 , and B_5 boranes incorporates the ideas noted above in addition to several important experimental facts.³⁸

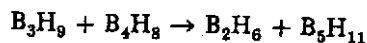
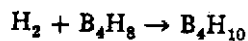
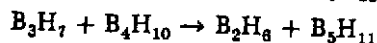
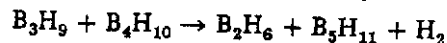
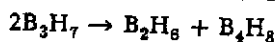
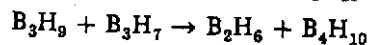
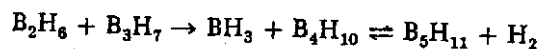
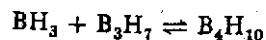
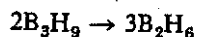
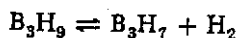


³⁵ See ref. 6.

³⁶ See ref. 33.

³⁷ See ref. 33.

³⁸ L. H. Long, *J. Inorg. Nucl. Chem.*, 32, 1097 (1970); *Prog. Inorg. Chem.*, 15, 1 (1972).



The enthalpy change for the dissociation of B_2H_6 into two BH_3 moieties is now thought to be about 35.5 kcal.³⁹ Since the activation energy for the recombination of 2BH_3 's to give B_2H_6 is approximately zero,⁴⁰ the activation energy for the dissociation of diborane must also be about 35 kcal. As this seems an excessively high activation energy for the first step in the decomposition process, the alternative bimolecular reaction of two diborane molecules to give BH_3 and B_3H_9 has been suggested. Triborane(9) is also formed in the second reaction, so that the sum of the first two processes is $3\text{B}_2\text{H}_6 \rightarrow 2\text{B}_3\text{H}_9$. This agrees with the experimental observation that the rate of disappearance of diborane is 3/2 order in diborane. The third reaction generates still another reactive intermediate, B_3H_7 , and the scheme continues on to the formation of B_4H_{10} , B_5H_{11} , and B_6H_{12} using basically reaction types (A), (B), and (C). The intermediates BH_3 , B_3H_7 , and B_3H_9 are important to all of the steps in the scheme, and their great reactivity is indicated by the fact that they have never been isolated or characterized as the simple boranes (although all are known in the form of adducts with Lewis bases).

Tetraborane(10) may be prepared in several ways, but perhaps the most effective on a larger scale is the pyrolysis of diborane.^{41,42} This is usually done in a "hot-cold" reactor such as that illustrated in Figure 18-8. The diborane is first admitted to the evacuated reactor and is frozen onto the outer walls by immersing the reactor in liquid nitrogen (-196°C). The liquid nitrogen is then removed and replaced by a

³⁹D. A. Dixon, I. M. Pepperberg, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **96**, 1325 (1974).

⁴⁰G. W. Mappes, S. A. Fridmann, and T. P. Fehlner, *J. Phys. Chem.*, **74**, 3307 (1970).

⁴¹See ref. 33.

⁴²M. J. Klein, B. C. Harrison, and I. J. Solomon, *J. Amer. Chem. Soc.*, **80**, 4149 (1958).

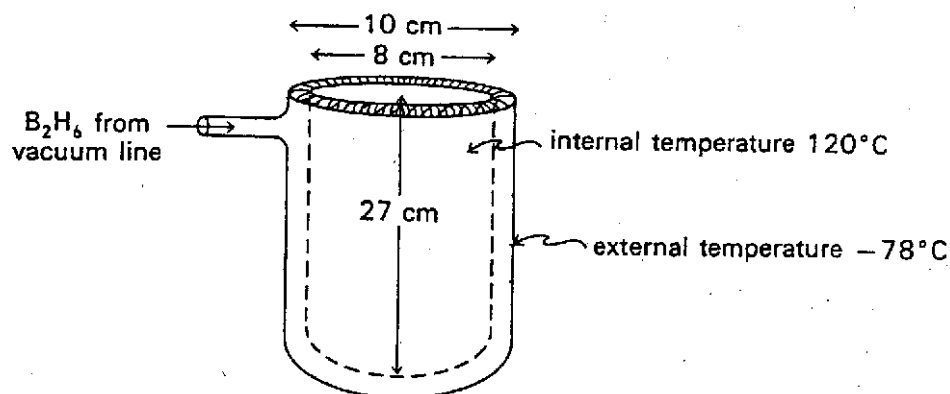


Figure 18-8. A "hot-cold" reactor for the pyrolytic condensation of B_2H_6 to B_4H_{10} .