RECENT STUDIES OF THE BORON HYDRIDES

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I. Introduction

Of the monumental early work by Stock on the boron hydrides, so ably summarized by him in his Baker Lectures (*68*), Sidgwick (*65a*) remarks that "All statements about the boron hydrides earlier than 1912, when Stock began to work upon them, are untrue." In a remarkable series of studies, Stock characterized B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$ and gave tentative evidence for a dodecaborane and possibly an additional hexaborane. The fact that it was over twenty years before an additional boron hydride (B_9H_{15}) was well characterized is only one of many tributes that can be made to the thoroughness of Stock's chemical researches.

The systematic principles of boron hydride structures and chemistry are the principal subjects of the present review. There are several reasons why these principles became clear such a long time after the discovery of these compounds: (a) most of the compounds must be handled in grease-free vacuum line systems; (b) some of the boron hydrides are unstable at ordinary temperatures, explosive on contact with air, and toxic; (c) the structures are based on principles, still incompletely developed, of electron-deficient compounds; and (d) location of the hydrogen atoms is a crucial part of the structure determinations, unlike the situation in hydrocarbons, and had to be done for the most part in X-ray diffraction studies of single crystals grown at low temperatures.

The present review will be restricted to the boron hydrides themselves and their relatively simple substitution derivatives. Even the closely related, and very important, borohydrides are not reviewed and are mentioned here only insofar as they are relevant to the boron hydrides. Also, in order to restrict the review to manageable dimensions, I have omitted references to nearly all of the early structure investigations and early systematic valence theories now generally believed to be incorrect, and to claims made for the existence of new compounds when the evidence seems to be not sufficiently extensive or convincing.

The several sections of this review include the structures, the valence theory of known structures with emphasis on the charge distribution, the nuclear resonance studies of hydrides, derivatives and related compounds, the topological extension of the valence theory and its use in making predictions, and finally some brief remarks on the interconversions of the hydrides.

II. The Boron Hydride Structures

The various times when a given structure is guessed correctly, given some support from experiment, convincingly proved by experiment, and understood, are rarely the same. An attempt to establish the latter three objectives has been made (*37, 18*) for B_2H_6, $B_{10}H_{14}$, B_5H_9, B_4H_{10}, and B_5H_{11} in chronological order. Later studies have established the structure (*17, 16*) of B_9H_{15} and the structure (*16, 44, 23*) of B_6H_{10}.[1] The certainty with which these structures are known results from spectroscopic techniques for B_2H_6, and from X-ray diffraction studies of single crystals for all of the other hydrides; but independent though not conclusive evidence exists for the structures from concurrent electron diffraction studies of B_5H_9 and B_4H_{10} and from subsequent electron diffraction studies of B_2H_6 and $B_{10}H_{14}$; also, a microwave study of B_5H_9 and several recent nuclear magnetic resonance studies, to be described in Section IV, have now appeared.

The structures and significant details of the molecular geometry are summarized in Figs. 1 to 7. Since the previous summary, the full microwave study of B_5H_9 has appeared (*27*). The slightly low X-ray

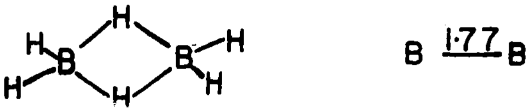

FIG. 1. The B_2H_6 structure. Electron diffraction parameters are B-B = 1.77 Å, B-H = 1.19 Å, B-H (bridge) = 1.33 Å, ∠ HBH = 121.5°.

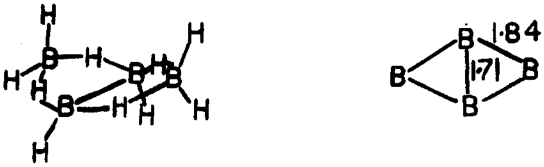

FIG. 2. The B_4H_{10} structure. Revised parameters are taken from the recent reinvestigation (*60*) of the X-ray data. Electron diffraction values of B-H (terminal) = 1.19 Å, and for B-H (bridge), 1.33 and 1.43 Å are chosen; the X-ray study established that the bridge H's are closer to the central borons.

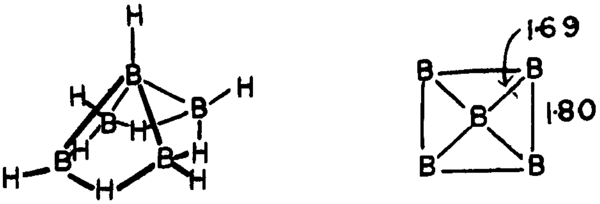

FIG. 3. The B_5H_9 structure. Interatomic distances, 1.69 Å and 1.80 Å are taken from the microwave study (*27*).

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[1] "What I tell you three times is true" (*12*).

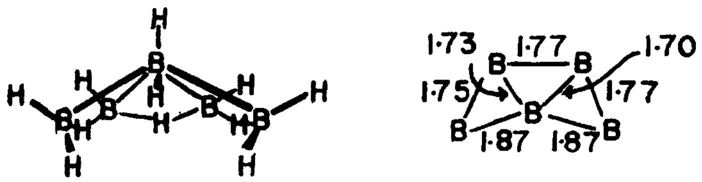


FIG. 4. The B_5H_{11} structure, with revised X-ray parameters (*50*) not averaged over the apparent molecular symmetry plane.

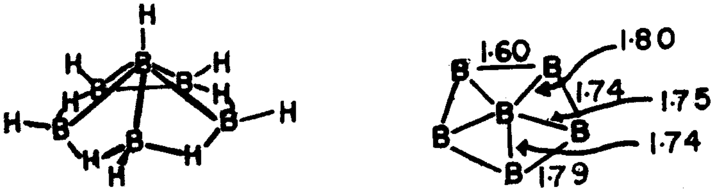


FIG. 5. The B_6H_{10} molecule. The unusually short B-B distance of 1.60 Å has a standard deviation of ± 0.01 Å in the X-ray study.

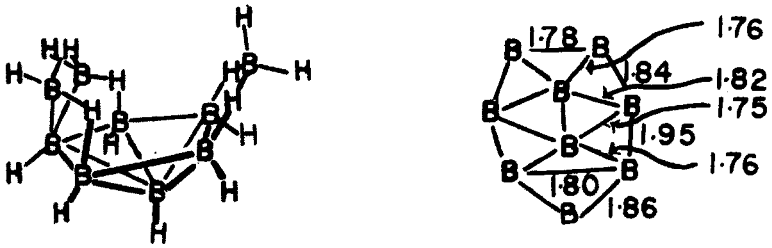


FIG. 6. The B_9H_{15} structure (*16*).

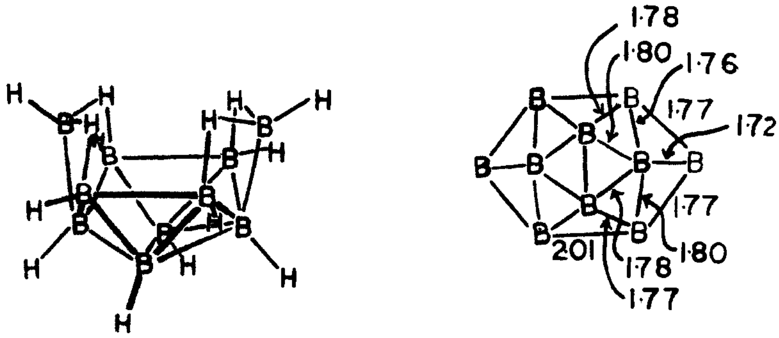


FIG. 7. The $B_{10}H_{14}$ structure. Parameters are from the reinvestigation (*50*) of the original data and have not been averaged over the presumed C_{2v} molecular symmetry.

values of the B-B distances in the X-ray study of B_5H_9 have been shown (*38*) to be caused by a torsional motion of the molecule in the crystal, but the probable errors previously assigned do include the revised values. A reinvestigation (*50*) of the X-ray data for B_4H_{10}, B_5H_{11}, and $B_{10}H_{14}$ has led to slightly revised distances, as shown in the figures and discussed in Section III on valence theory. The position of the unique hydrogen in the apparent symmetry plane of the B_5H_{11} molecule improved in this revision to a distance of 1.09 Å from the central, apex B, and to distances of 1.77 and 1.68Å (±0.19 Å) from the two outer boron atoms.

The B-H distances in the X-ray diffraction studies are not listed here. They not only have large probable errors, but also have recently been shown (*23*) to be very sensitive to the choice of X-ray scattering curves for boron. The electron diffraction values for B-H distances, although they have large probable errors, are not subject to large systematic errors, and hence are probably fairly reliable for B_2H_6 and B_4H_{10}. There is some theoretical evidence (*37*) that the B-H distances should increase slightly as the H/B ratio decreases, but this effect has not been tested. The same theoretical discussion has predicted the direction of asymmetry of the hydrogen bridges.

The remarkable geometrical similarities of these hydrides is very striking and will become more so as the valence theory is developed. Superposition of the "ball and stick" type of molecular models on one another brings out the diborane type of geometry in the open parts of these molecules, and is very suggestive of the kinds of hybridization that may be chosen for convenience about the boron atoms.

III. The Valence Theory

A. ELECTRON DEFICIENCY

The theory of valence of these structures is of interest for several reasons. The hydrides themselves have an unusual set of formulas, and one might hope that a theory would correlate these and predict other members of the series. But more important, because these hydrides are "electron deficient" in the sense that there are more orbitals than electrons, one might hope that their electronic and geometrical structures will aid in the understanding of the large number of intermetallic compounds, and of the border line between metals and nonmetals. This interpretative problem is comparatively simpler for boron, which uses only the 2*s* and the three 2*p* orbitals, and hydrogen, which uses only the 1*s* orbital, in the approximation discussed here. This approximation is fairly good in the smaller hydrides but may need some modification in the larger hydrides and infinite solids.

In saturated hydrocarbons, for example, C_2H_6, each carbon supplies four orbitals and each hydrogen supplies one. Bonds are formed by overlapping of one of the four tetrahedral sp^3 orbitals of carbon with either the 1*s* orbital of hydrogen to form a C-H bond, or another sp^3 orbital of carbon to form a C-C bond. When the total number of electrons exceeds the number of available atomic orbitals, as in NH_3 or N_2H_4, excess pairs occur in hybrid orbitals. In these compounds the chemist writes chemical bonds, and unshared pairs if necessary, and regards the orbitals as filled if each element of the first row has an octet of electrons and if hydrogen has two electrons.

Now in B_2H_6 there are only 12 electrons for 14 orbitals. Any molecule in which the number of valence orbitals exceeds the number of valence electrons we shall call electron deficient. But the chemist's intuition tells him that a polyatomic molecule with unfilled valence orbitals should not exist for long. If such a molecule were formed, it should adopt a new geometry capable of description in terms of closed shells. Such a description is indeed possible for B_2H_6, and extension of the principles to the higher boron hydrides is also possible. The chemical generalization is an electron-pair three-center bond, which can be regarded as a localized molecular orbital extending over three atomic nuclei with no change of sign of its wave function in the region between the nuclei. This description is a simple extension of an ordinary electron-pair bond, which can be regarded as a localized two-center orbital extending over two atomic nuclei with no change in the sign of its wave function between the nuclei.

B. The Three-Center Bond

The usual hybrid orbitals for boron in its better-known chemistry are tetrahedral (e.g., BH_4^-) or trigonal (e.g., BF_3). We shall start our description with these hybrids and with the 1*s* orbital of hydrogen (Fig.

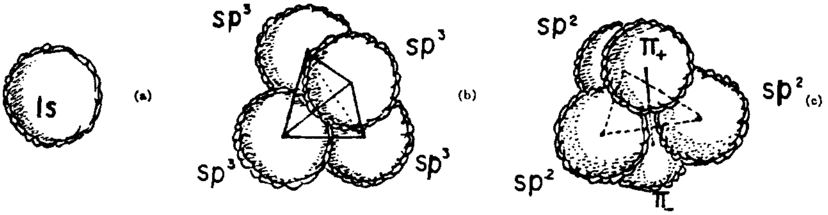


FIG. 8. (a) The spherically symmetrical 1*s* orbital for H; (b) tetrahedral hybrid orbitals for B; (c) trigonal hybrid orbitals for B, showing the π-orbital extending above and below the plane of the sp^3 hybrids (*41*).

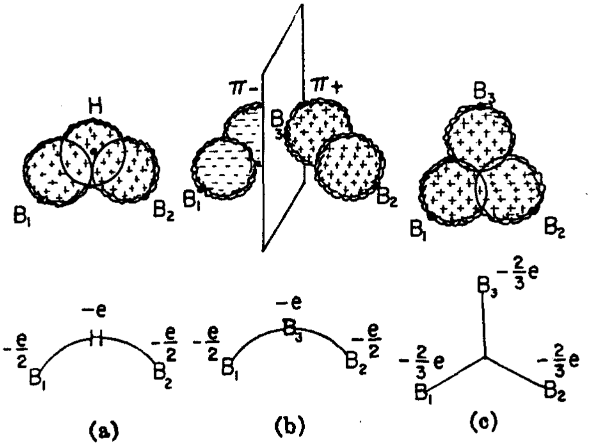


FIG. 9. Examples of three-center bonds (*41*). Boron orbitals from B_1 and B_2, and from B_3 of (c) may be sp^2 or sp^3. The simplest LCAO calculations distribute the bonding electron pair equally among the three atoms of the central three-center bond in (c), and place $-e$ on H or on B_3 of the open three-center bonds, (a) or (b).

8). Then we may form the types of three-center bonds shown in Fig. 9. Intermediate types also may occur.

The results of a simple LCAO discussion (*18*), in which the molecular orbital is formulated as a linear combination, $a_1\psi_A + a_2\psi_B + a_3\psi_C$, from the atomic orbitals ψ_A, ψ_B, and ψ_C of atoms A, B and C, respectively, yield only one lowest energy state for reasonable assumptions of the geometries and interaction parameters. Thus for the ground state, only a single electron pair is required. The detailed discussion (*18*) will not be repeated here but the results are summarized in Fig. 10. As an example, however, consider the bonding level of the open three-center bond where overlap is neglected. Symmetry requires that ψ_A and ψ_C enter equally, and normalization requires that the sum of squares of coefficients shall be unity. Hence the form of this orbital must be

$$\psi = a(\psi_A + \psi_C) + \sqrt{1 - 2a^2}\,\psi_B.$$

Now neglect the interaction between the nonadjacent pair ψ_A and ψ_C, and call $\int\psi_A H\psi_B d\tau = \int\psi_B H\psi_A d\tau = \int\psi_C H\psi_B d\tau = \int\psi_B H\psi_C d\tau = \beta$, and $\int\psi_A H\psi_A d\tau = \int\psi_B H\psi_B d\tau = \int\psi_C H\psi_C d\tau = H_0$. Then the energy $E = \int\psi H\psi d\tau$ becomes

$$E = H_0 + 4a\sqrt{1 - 2a^2}\,\beta.$$

The energy minimum can be found by setting $dE/da = 0$, from which we find $a = \frac{1}{2}$, so that $E = H_0 + \sqrt{2}\,\beta$, and therefore

$$\psi = \frac{1}{2}\psi_A + \frac{1}{\sqrt{2}}\psi_B + \frac{1}{2}\psi_C.$$

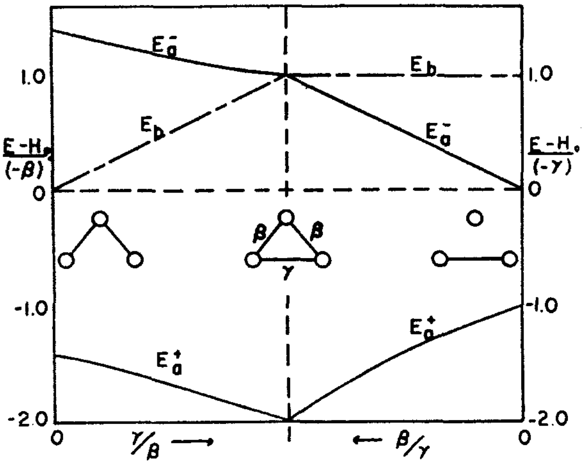


FIG. 10. Results of simplified LCAO discussion of the three-center orbital (*41*). Orthogonality of the AO's and constancy of the Coulomb integrals have been assumed. The ratio of resonance integrals $\gamma/\beta = 0$ corresponds to an open three-center bond, that for $\gamma/\beta = 1$ to a central three-center bond, and that for $\beta/\gamma = 0$ to an ordinary electron-pair bond. The lowest energy states is E^+_a.

A simplified interpretation of the ψ^2's as probability functions then places the electron pair with probability ¼ on atoms *A* and *C*, and ½ on atom *B* in the open three-center bond (Fig. 9).

We now outline two approaches to a description of valence in the boron hydrides. The first employs three-center bonds. This particular kind of localized molecular orbital seems most suitable for the smaller, more open hydrides. Its use in the more complex hydrides will require delocalization of the bonding electrons either by a molecular orbital modification or a resonance description. The second approach is simply that of molecular orbitals, which is particularly effective in the more condensed and symmetrical hydrides. These approaches merge as the discussion becomes more complete. It is an important result that filled orbital descriptions are obtainable for the known boron hydrides. Also some remarks about charge distribution in the boron hydrides are possible. But the incompleteness of this valence theory in this nontopological form is indicated by the lack of a large number of unknown hydrides, whose existence would be consistent with these assumptions.

C. DIBORANE

The molecular geometry and three-center bonding scheme (*45*, *18*) for B_2H_6 are shown in Fig. 11. If we assume that two of the sp^3 hybrid orbitals of boron have maxima directed toward the singly bonded hydro-

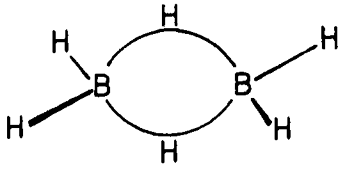


FIG. 11. Bonding in B_2H_6 (*41*).

gen atoms with ∠ HBH = 121.5°, then the equivalent (*14*) hybrid orbitals in the three-center bond should make an angle $H_bBH_b = 102°$. The observed value of this angle is 97°, in excellent agreement, considering the experimental uncertainties, and the possibility of bent bonds.

Although the atoms are neutral in this simplified valence theory, there is experimental evidence from a study of the proton magnetic resonance spectrum (*53*) that the two bridge protons are more negative than are the four terminal protons. Such differences in the diamagnetic shielding have not yet been put on a satisfactory quantitative basis. However, a thorough theoretical study of the molecular orbitals, in a complete LCAOSCF discussion of the 4-electron problem involving the bridge hydrogen atoms and the boron orbitals directed toward them, indicates (*21*) that the bridge protons have about $-0.2e$ excess charge, a result confirmed by a more extensive study (*75*). A recent study of the infrared vibrational intensities indicates a large change in electric moment as the bridge hydrogens move toward the same boron and a small change when a terminal hydrogen moves (*63*). In our discussion of the more complex boron hydrides, we shall make some use of these indications of charge distribution about bridge and terminal hydrogen atoms in discussions of their dipole moments (Section III E).

Comparison of the bonding in diborane and ethylene is illuminating. In the usual description, each C atom of ethylene has planar sp^2 orbitals, two directed toward H and the third directed toward the other C atom. Overlap of the two sp^2 orbitals directed toward each other, and of the remaining π-orbital normal to the plane of sp^2 hybridization with the corresponding orbitals of the other C atom, give the two molecular orbitals of the double bond. If we call these molecular orbitals ψ_σ and ψ_π, we may then form equivalent orbitals $\chi_1 = \psi_\sigma + \psi_\pi$, and $\chi_2 = \psi_\sigma - \psi_\pi$, without altering the description of the ground state or of the molecular wave function. But if we remember that ψ_σ has the same sign above and below the plane of the molecule, while ψ_π changes sign in this molecular plane, we then observe that χ_1 is almost completely above the molecular plane, and χ_2 is almost completely below this plane (Fig. 12). The equivalent molecular orbital, χ_1, for example, can be thought of as being formed from two atomic approximately sp^3 hybrids, one from each C atom. This

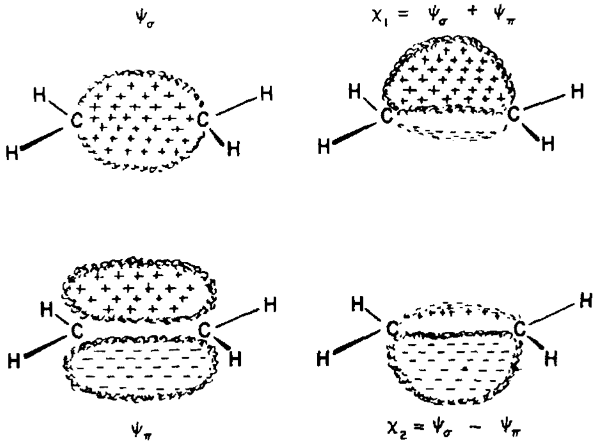


FIG. 12. Equivalent orbitals in the ground state of ethylene (*41*).

two-center orbital can be thought of as an electron-pair bond. In order to obtain the three-center electron-pair bond in B_2H_6, one has only to superimpose the 1*s* orbital of hydrogen and replace C by B. Thus the general appearance of the orbitals is not greatly changed, and, in particular, the symmetry properties and number of nodes remains exactly the same in C_2H_6 and B_2H_6.

D. HIGHER HYDRIDES

The use of three-center bonds in describing bonding in the higher hydrides has been discussed in some detail (*18*) and hence only a brief summary is given here with a few modifications.

As a first illustration of the procedure, consider B_4H_{10} (Fig. 13). Electron-pair bonds to six hydrogen atoms, and three-center bonds to the four bridge hydrogens, employ ten electron pairs out of the total of eleven. These ten pairs also use up all of the hydrogen orbitals and all but two of the boron orbitals, one on each B_I. Thus we have one electron pair for two boron orbitals which are directed toward each other and hence form a single electron-pair bond between atoms B_I.

As a second illustration, consider B_5H_{11}. Bonds to the eight terminal hydrogen atoms and to the three bridge hydrogen atoms require all but two electron pairs and use up all but six boron orbitals. Hence, we must form two three-center bonds to utilize the remaining two electron pairs in these six orbitals; and the two methods of doing so, consistent with the molecular plane of symmetry, are shown in Fig. 13.

Similarly for framework bonds, B_6H_{10} is required to have two three-center bonds and two two-center bonds, B_9H_{15} is required to have four

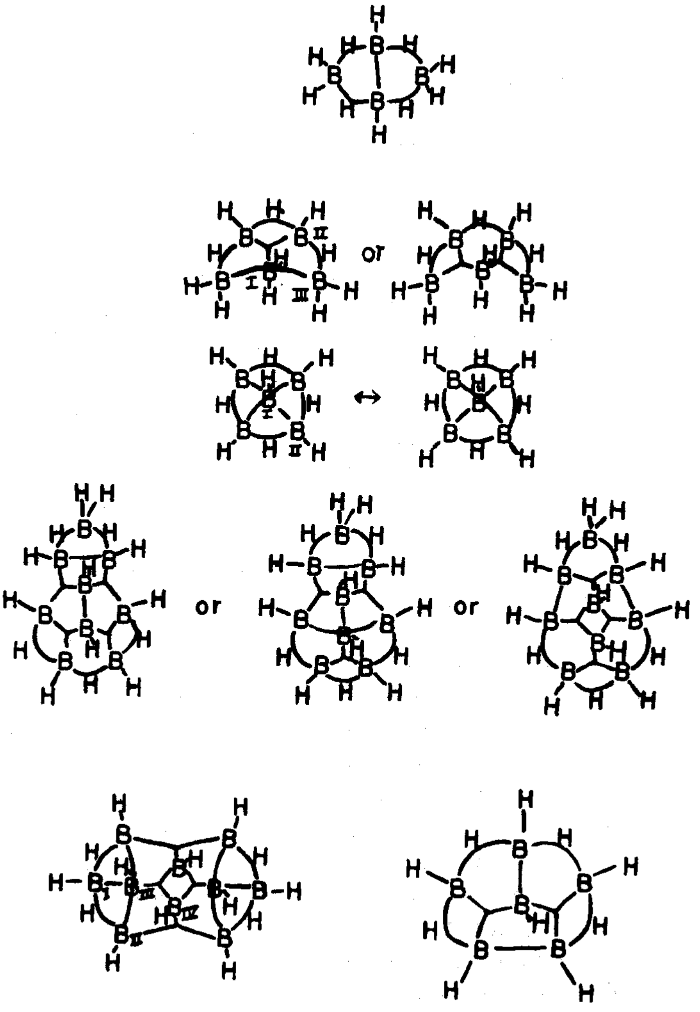


FIG. 13. A topological valence bond description of the known higher hydrides of boron. Resonance hybrids are indicated by the symbol ↔. If the bonding geometry at each boron atom is recognized as tetrahedral or trigonal, the correct three-dimensional structures can be realized.

three-center bonds and two two-center bonds, and $B_{10}H_{14}$ must have six three-center bonds and two two-center bonds. Except for B_5H_9, for which a more general approach is more informative, these bonds can be drawn consistent with the molecular symmetry (Fig. 13). Invariably the simplest method of arriving at the appropriate hybrid orbitals for the boron atoms is to start from the bridge hydrogen regions where the directions of hybrid orbitals are most clear, and then work toward the inner parts of the molecule.

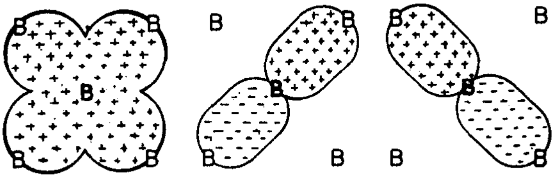
As a prediction, consider B_3H_9, a reaction intermediate. This molecule has nine electron pairs, all of which would be required for bonds to terminal hydrogen or to bridge hydrogen atoms. The most satisfactory model has three BH_2 groups linked by bridge hydrogen atoms.

E. MOLECULAR ORBITALS

Useful as the three-center bond concept is in forming a common basis for describing the known boron hydrides in terms of filled orbitals, and in making some predictions, it seems clear that the electrons in the more complex and symmetrical boron hydrides must be much more delocalized. Consider the three-center bond approximation in B_5H_9, in which three electron pairs are left to fill molecular orbitals from seven boron orbitals after all bonds to H have been formed. We would then expect one three-center bond and two two-center bonds. The resulting bonds (Fig. 13) indicate that the apex boron atom B_I forms three electron-pair bonds (one to H and two to B_{II}) and one open three-center bond to two other boron atoms. Now, if we divide the electron pairs equally and use the simplest LCAO approach (Fig. 9) for the charge distribution in the open three-center bond, we find that the apex boron atom has a net charge of -1, and hence the four other boron atoms have a charge of $+\frac{1}{4}$. This result, which comes from the assumption (*18*) of constant single-electron Coulomb integrals, will evidently be modified if variation of the magnitudes of these integrals is allowed. An attempt to introduce this variation into the ordinary secular equation method with the use of Moffitt's linear relation (*49*) between the Coulomb integral and the number of electrons on the atom in question has been made by Eberhardt, Crawford, and Lipscomb (*18*). The net result has been to reduce the total formal charges on these atoms by a factor of about two, and hence to obtain dipole moments in rough agreement with experiment, assuming that the excess charge is centered on the atoms in question.

A more detailed consideration (*39*) of the charge distribution in the hybrid orbitals about boron atoms in B_5H_9 and B_5H_{11} indicates that the excess charge centered on the atoms in question probably needs to be reduced somewhat further in order for the expected dipole moment value to approach more closely the experimental value. The qualitative charge distribution for B_5H_9 is as follows: Assume, as the bridge-hydrogen geometry around B_{II} (Fig. 13) suggests, that the hybridization is tetrahedral. The two boron orbitals of each B_{II} atom directed toward the bridge protons are deficient in electrons, compared with the other two B_{II} orbitals which are directed toward, respectively, the terminal hydrogen and B_I. This situation can be thought of as arising from the relative deficiency of electrons in the boron orbitals of the three-center bonds involving bridge hydrogens, as compared with the electron pair in the bond toward the terminal hydrogen or the framework electrons in the bond toward B_{II}. This relative deficiency has been shown (*39*) to be almost independent of hybridization about the apex boron atom, B_I, and can be attributed to the unbalance of the relatively large atomic moments in hybrid orbitals about B_{II}. Then, if we assume neutral hydrogen atoms and neutral boron atoms, the resulting dipole moment of B_5H_9 would be about 6 Debyes, where the negative end of the molecule is toward the apex. As the first correction to this argument, one would anticipate that the bridge hydrogens carry a slight excess of negative charge (*64*). If we then place about $-0.1e$ on each bridge hydrogen, this calculated value will be in reasonably good agreement with the experimental value (*28*) of 2.13 Debyes. As a second correction, the apex boron atom probably does carry a small negative charge, relative to the basal boron atoms, and quite possibly the bridge hydrogens carry slightly more than $-0.1e$ of negative charge. Further corrections would include a discussion of electron correlation effects, usually of importance in charge distribution; but the higher hydrides have yet to be studied theoretically in this much detail. A similar unpublished analysis of charge distribution in B_4H_{10} by C. W. Kern and W. N. Lipscomb has led to a value of < 2 Debyes in reasonable agreement with the as yet unpublished value of 0.6 Debyes observed by J. R. Weaver, C. W. Heitech, and R. W. Parry.

The symmetry characteristics of the filled molecular orbitals (*18*) of B_5H_9 are similar in some respects to those of benzene. The orbital of lowest energy does not change sign throughout the molecule, and can be thought of as a five-center orbital. The orbitals of next lowest energy change sign at the apex boron atom and each has one node which corresponds to the node in the apex boron "π" orbitals perpendicular to the symmetry axis of the molecule. These three orbitals take up the six



(a) (b) (c)

FIG. 14. Topological representation of the lowest framework orbital (a) in B_5H_9, and the doubly degenerate pair, (b) and (c). Six bonding electrons go into these three orbitals (*41*).

bonding electrons (Fig. 14) in agreement with the Pauli exclusion principle. This molecular orbital description is certainly the most natural one and the relation between this description and the three-center bond description has been discussed in detail (*18*).

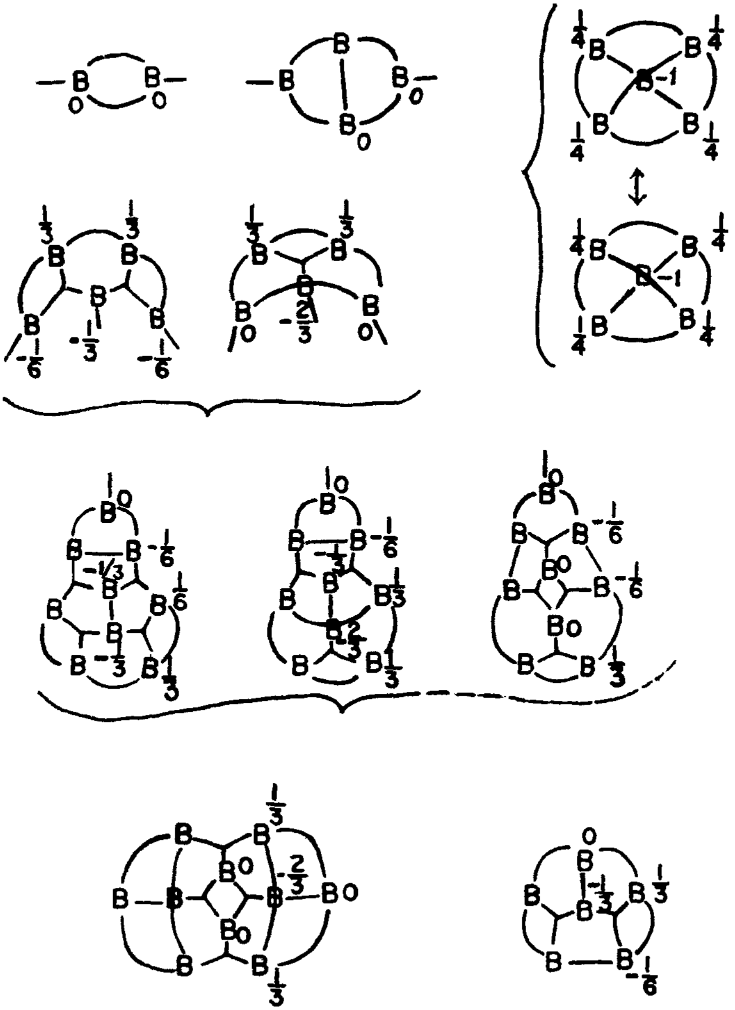


FIG. 15. First approximation to the charge distribution in the known boron hydrides. The abbreviated notation omits all terminal hydrogens except when a BH_2 group is present. These results are obtained when the bond charge distribution in Fig. 9 is applied to the structures in Fig. 13. The third valence structure for B_9H_{15} (extreme right) correlates relatively poorly with the observed bond distances and with the other hydride structures. Charges in B_5H_9 are averaged over the resonance hybrid.

Discussion of the orbitals in the more complex hydrides, for example, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$, follows similar lines but their symmetries are lower and hence there are more parameters in the molecular orbitals. The results are similar to those for B_5H_9, however, and the resulting charge distributions appear in general to place the negative end of the molecule as a whole at or near the apex, away from the bridge hydrogen atoms. As in B_5H_9, the dipole moments can be thought of as arising from the atomic moments about boron atoms, if one chooses to discuss atoms in terms of hybridization.

The results of the simplest three-center bond discussion of charge distribution in the boron hydrides are of some interest in connection with electrophilic substitution, and hence are summarized here for the known hydrides (Fig. 15). These charge distributions are more detailed than those given (*39*) by a free-electron model of charge distribution in a hemisphere or hemispherical shell, but both of these treatments agree in a general way. Negative charge tends to concentrate in the inner regions of the molecule because the wave functions vanish toward the exposed regions. If one superimposes this general effect on the LCAO results shown in Fig. 15, one may well expect that the two outer borons attached to bridge hydrogens in $B_{10}H_{14}$ would be more positive than the innermost pair of borons. If one adds the further conclusion that the bridge hydrogens carry about $-0.1e$ to $-0.2e$ of charge, these two outermost borons, labelled with 0 excess charge in Fig. 15, would become even more positive. It then becomes difficult to say whether this outer pair of borons or the next inner group of four equivalent borons is the more positive. On the other hand, the identity of the most negative pair of borons in $B_{10}H_{14}$ is reasonably certainly that shown in Fig. 15, as has been confirmed by experiments described in Section IV.

IV. Nuclear Resonance (NMR) Studies of the Boranes, Substituted Boranes, and Related Compounds

The recent applications of both H and B^{11} resonance techniques to the boron hydrides and related compounds has led to the confirmation of some of the structures, elucidation of many of the substituted structures, and an impressive amount of detail about the charge distribution in these molecules and ions.

A. BH_4^-

The alkali borohydrides contain the tetrahedral BH_4^- ion, as has been established by the early infrared work of Price (*56*) and powder-diffraction study by Soldate (*67*). A confirmation of the tetrahedral structure was obtained by high-resolution NMR techniques by Ogg (*53*) who also studied B_2H_6 by this method. A study of the second moment of the comparatively broad proton resonance in the solid alkali borohydrides (*19*) has led to the B-H distance of $1.25_5 \pm 0.02$ Å, which is distinctly greater than one might extrapolate from the well-known distances of 1.092 Å in CH_4 and 1.035 Å in NH_4^+. This effect of the negative charge in expanding the hydrogen and boron orbitals is discussed in Section IV C in relation to internal exchange in some of the negative hydride ions.

B. $Al(BH_4)_3$

The trigonal, planar arrangement of 3B about a central Al has been established in an electron-diffraction study (*6, 66, 4*) which succeeded in disproving the correct hydrogen arrangement, later established from the infrared spectrum (*56*). The remarkable nuclear resonance (Al^{27}, B^{11}, and H) spectra (*54*) produces a time equivalence of the protons in each BH_4 group by a tunnelling type of mechanism. In this process, collapse of the hydrogen fine structure of the B^{11} resonance does not occur but rather all H's become equivalent so that the quintet of relative intensities 1, 4, 6, 4, 1 is produced by interaction of four equivalent H's with the B^{11} spectrum. The hydrogen resonance is broad. The temperature independence of these spectra and the non-collapse of the H fine structure argue strongly for this internal rearrangement, as opposed to some dissociation type of equilibrium.

C. $B_3H_8^-$

The B^{11} resonance (*55*) of a solution of NaB_3H_8 (*25*) in ether or D_2O yields an apparent septet with observed relative intensities of 1.0:3.5:6.3:7.8:6.3:3.5:1.0. The equality of spacings is very striking, but agreement is poor with the ratios 1:6:15:20:15:6:1 expected for a septet resulting from a group of six H atoms. However, if all B's are equivalent, and all B's see all eight H atoms, the relative intensities of the nonet are 0.1:0.9:3.2:6.4:8.0:6.4:3.2:0.9:0.1. The two very weak outer lines are predicted to be one-eighth of the intensity of the weakest members of the septet, and hence are presumably lost in the background. The proton resonance is broad, as is the case in $Al(BH_4)_3$. A static model in agreement with the observations seems impossible, and hence this author has suggested a model in which the electronic structure remains nearly invariant and internal exchange takes place as in $Al(BH_4)_3$. The two possible structures shown in Fig. 16 are both derivable from the predicted B_3H_9 structure by removal of either a bridge or terminal proton. Presumably this type of internal exchange is facilitated by negative charge

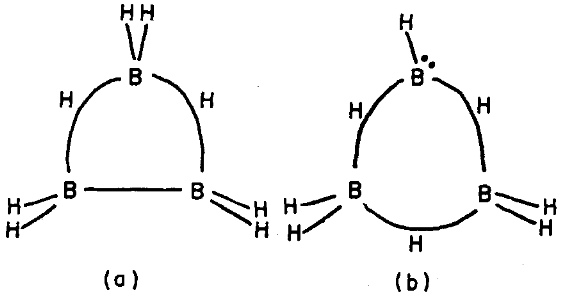


FIG. 16. Possible $B_3H_8^-$ structures. Preference for structure (a) is suggested by the valence theory.

transfer toward the boron and hydrogen by the Al in $Al(BH_4)_3$ and by the negative charge in the ions. The resulting expansion of the interatomic distances, similar to that observed in BH_4^-, probably makes this internal exchange much more likely in these compounds than in the hydrides themselves.

D. B_3H_7 ADDITION COMPOUNDS

An X-ray diffraction study (*52*) of $(CH_3)_3NB_3H_7$, and the preparation (*26*) and preliminary B^{11} resonance study (*55*) of $(C_2H_5)_2O \cdot B_3H_7$ have been reported. The crystallographic evidence that the molecule has a three-fold axis, and the somewhat rapid fall-off of intensities with increasing angle of scattering, together with the valence-theoretical observation that a single hydrogen on the three-fold axis will be nonbonding to the B_3 molecular orbitals, have led to the suggestion (*23*) of a disordered crystal structure, in which there is a vacant orbital available for formation of a single bond to the lone pair of NH_3 or $N(CH_3)_3$ (Fig. 17a).

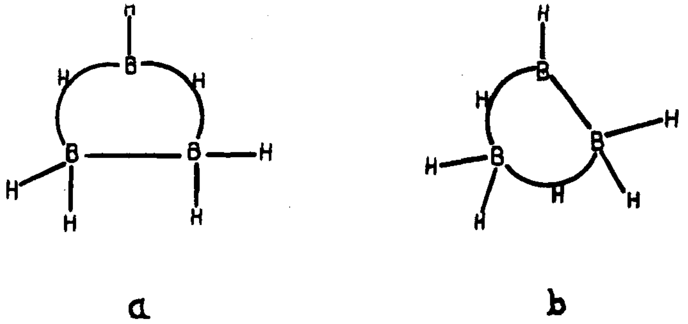


FIG. 17. Possible B_3H_7 structures. The B atom at the top has a vacant orbital. Formal charges are +1 and +½ on the apex B atoms of (a) and (b), respectively.

The B^{11} resonance in $(C_2H_5)_2O \cdot B_3H_7$ is apparently a symmetrical sextet which, on the grounds of a similar argument to that given in Section IV C above for $B_3H_8^-$, is very probably the more intense group of an octet with theoretical line ratios of $\frac{1}{7}$:1:3:5:5:3:1:$\frac{1}{7}$. Again, the two outermost lines are presumably lost in the background. If so, we can expect internal exchange in B_3H_7-ether complexes, partly because of transfer of negative charge toward the B_3H_7. These etherates were first prepared by Edwards and co-workers (*26*).

In $B_3H_7 \cdot NH_3$ a crystal disorder similar to that found in $B_3H_7 \cdot N(CH_3)_3$ has been observed (*51*) above about −16°C. Nevertheless, C. E. Nordman and co-workers have obtained ordered single crystals of the low temperature form, and in an excellent and detailed X-ray diffraction study have shown that the B_3H_7 residue shown in Fig. 17(b) is joined to the NH_3 by a single bond to the boron atom having a vacant orbital. It may, of course, not be correct to deduce the structure of the isolated B_3H_7 molecule from these results, but the structure of Fig. 17(b) has, in fact, a more favorable charge distribution than that of Fig. 17(a). Note that addition of H^- to the vacant orbital of either of these possible B_3H_7 structures gives the $B_3H_8^-$ ion of Fig. 16(a).

E. B_2H_6

The several NMR studies (*32, 53, 64*) of diborane confirm the bridge structure. In general, among all of the boron hydrides, the bridge hydrogens tend to show H resonance at higher fields than the terminal hydrogens. This result is striking confirmation of the type of charge distribution expected on chemical grounds and predicted from molecular orbital theory (*21*). The detail with which the NMR spectrum can be analyzed is shown by Schoolery (*64*) especially in the case of B_2H_6. In this compound and in the higher hydrides, it has proved possible to simplify the observed NMR spectra very greatly by "nuclear stirring" techniques, in which a given nucleus (e.g., B^{11}) is induced to undergo many transitions during an observation. Under these circumstances, a neighboring nucleus sees only the average over these orientations, and the fine structure due to the nucleus being "stirred" collapses to a single line.

F. B_4H_{10}

The NMR spectrum has been run (*32*).

G. B_5H_9

The use of B^{11} "stirring" techniques (7) has not only confirmed (*64*) the tetragonal pyramidal structure including the ratio of bridge to terminal hydrogens, but has further indicated that the apex boron atom shows resonance at a higher field than the basal borons. This result agrees with the simplified valence theory of this compound, in which the apex boron is the more negative. Somewhat improved spectra obtained later *(61)* confirm these results. The hydrogen resonance *(64)* indicates that the apical hydrogen atom is slightly more negative than the basal terminal hydrogens, but not so negative as the bridge hydrogens.

H. B_5H_{11}

The H and B^{11} resonances have been analyzed *(61)* to assign the most negative boron (type I, apex) of the valence theory to the boron resonance at highest field. In the B^{11}-saturated hydrogen NMR spectrum, the peaks reading from low to high field are said to be of approximate relative intensities of 6:1:3:1. Schaeffer, Schoolery, and Jones *(61)* assign the six terminal H, except the apex H, to the large peak; then the terminal apex H to the next peak, the three bridge hydrogens to the next peak, and the unique hydrogen on the apex boron atom to the single peak at highest field. They emphasize the lack of certainty about this assignment, and further investigation is desirable by a combination of NMR, infrared, and isotopic exchange techniques. In particular the relative peak weights may be 6:1:2:2, the bridge hydrogens may not all give peaks at the same place since two of the hydrogen bridges are probably unsymmetrical *(37)*, and the unique hydrogen may not be so greatly different from the other terminal hydrogens that it should show resonance at the highest field.

The position of the unique hydrogen almost in the basal plane of the four boron atoms has been reinvestigated twice *(50)* since the original structure study *(36)*. Among all of the boron hydrides, this is the only extra hydrogen attached to a boron atom connected to more than two other boron atoms. The valency rules would be somewhat simpler if this hydrogen were a bridge hydrogen, and a satisfactory structure can be drawn in such a case *(23)*, although the hydrogen arrangement does not have the symmetry of the boron arrangement. However, a very recent unpublished reinvestigation by Dr. M. G. Rossmann and myself of these X-ray diffraction data by the least-squares method, in which all atoms have been assigned different temperature factors, indicated no randomness in the hydrogen positions; and hence it is still very likely that this unique hydrogen lies in the apparent symmetry plane of the molecule and that the published structure is correct.

I. B_6H_{10}

Preliminary H resonance results on a somewhat small sample *(58)* are in better agreement with the hydrogen arrangement established *(16,* *23*) by X-ray diffraction than with the alternative arrangement suggested earlier (*40, 41*) on the basis of valence theory. The presence of four bridge hydrogens rather than three thus receives some support from the NMR data, but some caution is appropriate in interpreting these NMR results in a molecule of low symmetry.

J. $B_{10}H_{14}$

The low symmetry of $B_{10}H_{14}$ does not readily permit a complete assignment of all peaks to specific boron or hydrogen atoms. Two assignments, however, are reasonably certain. That there are four bridge hydrogens is indicated by the H resonance peak at highest field (*64, 61*) which, relative to those peaks at lower field, has the correct relative integrated intensity. Also, the B^{11} resonance shows a doublet at high field which is no doubt due to the two equivalent borons of type III (Fig. 13) split by the terminal hydrogens on each. This latter assignment is predicted by the charge distribution and strongly supported by the results described below (Section IV L) for $B_{10}H_{12}I_2$. The doubt that one must have about the remaining assignments will probably be removed as additional isotopic or otherwise substituted boron hydrides are studied by NMR techniques.

K. $B_{10}H_{13}^-$

The $B_{10}H_{14}$ molecule in 50% ethanol-water behaves (*20*) as a strong monoprotic acid. The second ionization constant has a pK > 10, out of range of the studies made so far. The doubled peak at high field in the B^{11} NMR spectrum shows that the initial stages of ionization do not involve the III, III′ hydrogen atoms (*58*). Infrared spectra of deuterium-hydrogen exchange of $B_{10}D_{14}$ indicate (*20, 24*) that the four bridge hydrogens exchange first, followed by further exchange or internal rearrangement involving at least four of the terminal hydrogen positions. There is also some as yet unpublished (*20*) infrared evidence suggesting a BH_2 group in $B_{10}H_{13}^-$, and possible structures for this ion are discussed in Section VII.

L. $B_{10}H_{12}I_2$

The assignment of substitution of I in $B_{10}H_{12}I_2$ to the III, III′ positions is based on a determination (*59*) of the intramolecular I . . . I distance by projection methods from X-ray diffraction data. The observed distance of 6.25 Å compares favorably with that expected from the known molecular structure. If the B-H results of Kasper, Lucht, and Harker (*30*) are extrapolated to an expected B-I distance, the result is 5.92 Å for the III, III′ substitution, and 7.28 Å and 7.56 Å for the other possibilities. If the further refinement of the $B_{10}H_{14}$ structure by Moore, Dickerson, and Lipscomb (*50*) is used, III, III′ substitution predicts a distance of 6.21 Å, in somewhat better agreement with the observed value. The other possible positions lead to predictions of 7.88 Å and 7.60 Å, and hence are rejected as possibilities. In view of the importance of this structure determination in the following argument, the location in some future study of the boron framework in the X-ray diffraction study would be important as confirmatory evidence of the position of substitution.

The B^{11} resonance study (*62*) of $B_{10}H_{12}I_2$ establishes that the I atoms are substituted on the two B's giving B^{11} peaks at highest field. It is important that in this and the following B^{11} resonance studies of substituted boron hydrides, the positions of boron resonances are but little shifted from their relative positions in the pure hydrides. This discovery has made the field of substituted boron hydrides easily studied by NMR techniques, and should lead to the identification of presently unassigned resonance peaks in the pure hydrides themselves and provide a basis for studies of internal exchange reactions. Thus, we can expect more detailed analyses of the charge distributions in both the hydrides and their substitution products to appear in the near future.

This identification of the I substitution at the III, III′ positions in $B_{10}H_{12}I_2$ leads also, upon comparison with the charge distribution in $B_{10}H_{14}$, to the idea that the dominating mechanism of substitution is electrophilic attack of the halogen atom, as was predicted earlier (*40, 41*). Perhaps this is true in a majority of cases, but the existence of two different $B_{10}H_{13}I$'s leads one to the caution that other processes may be involved, perhaps a competing reaction by the same or a different mechanism (*58*).

M. $B_{10}H_{13}I$ (MP, 116°) AND $B_{10}H_{13}Br$ (MP, 105°)

The H and B^{11} resonance spectra indicate (*62*) that substitution takes place in both of these compounds on the boron giving resonance at highest field. By the arguments given in Section IV L, this is the boron atom of type III.

N. $B_{10}H_{13}I$ (MP, 72°)

The H and B^{11} resonance spectra show clearly that the doublet at highest field is unaffected, and hence that substitution does not occur at the III position. A detailed argument (*58*) suggests that II substitution has taken place and that the previously published assignment (*61*) of the unresolved peaks in $B_{10}H_{14}$ itself needs to be revised. An investigation of this structure by X-ray diffraction methods is needed.

O. B_5H_8Br (MP, 32-34°) AND B_5H_8I (MP, 53°)

The position of substitution is clearly indicated by both H and B^{11} resonance spectra to be the more negative apex boron atom of B_5H_9. It is, therefore, remarkable that the apparent rates of deuteration of the apex and basal terminal hydrogen atoms of B_4H_9 by B_2D_6 are the same (*35*) to within ±10%. Koski, Kaufman, and Lauterbur (*35*) remark that they have not eliminated mechanisms in which only terminal apex (or base) H atoms exchange, followed by rapid intramolecular redistribution of H and D atoms among all terminal positions. While they considered this mechanism unlikely and hence favored direct exchange, it may be important to reconsider this mechanism in view of the strong preference of halogens for the apex position.

Mention of the terminal-hydrogen substituted B_2H_5Br seems desirable to complete this section, and perhaps to remind us that no bridge halogens have been found. But the existence of Cl bridges in $BeCl_2$, of CH_3 bridges in $Al_2(CH_3)_6$, and of N bridges in $B_2H_5NH_2$ and $B_2H_5N(CH_3)_2$ suggest that these or similar possibilities may exist for substituted boron hydrides or boron hydride ions.

V. The Equations of Balance

The relative numbers of orbitals, electrons, hydrogen, and boron atoms, and bonds of various types can easily be expressed in a systematic way. The procedure developed by Eberhardt *et al.* can be simplified as follows. For a boron hydride, B_pH_{p+q}, containing s H bridges, x extra B-H groups, t three-center B-B-B bonds and y two-center B-B bonds, the equations of balance may be written in a simplified form as follows. The hydrogen atom balance is simply $s + x = q$. Since each boron supplies four orbitals but only three electrons, the total number of three-center bonds in the molecule is the same as the number of boron atoms, $s + t = p$. Finally, if we consider BH as the bonding unit, each of which then supplies one electron pair, these p pairs are used up as three-center B-B-B bonds, two-center B-B bonds, and in supplying half of each pair to each extra hydrogen; thus $p = t + y + q/2$.

The results, summarized in Table I, will be essential in the topological theory which will now be outlined.

VI. A Topological Theory of Boron Hydrides

Without the introduction of some formal arguments which abstract the common structural features of the known hydrides, the three-center

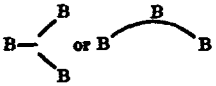
TABLE I

TABLES OF *s*, *t*, *y* AND *x* FOR BORON HYDRIDE STRUCTURES, B_pH_{q+p}*

B_2H_2	B_2H_4	B_2H_6		B_3H_3	B_3H_5	B_3H_7	B_3H_9			
0200	2010 1101	2002		0300	2110 1201	3011 2102	3003			
B_4H_4	B_4H_6	B_4H_8	B_4H_{10}	B_4H_{12}						
0400	2210 1301	4020 3111 2202	4012 3103	4004						
B_5H_5	B_5H_7	B_5H_9	B_5H_{11}	B_5H_{13}	B_5H_{15}					
0500	2310 1401	4120 3211 2302	5021 4112 3203	5013 4104	5005					
B_6H_6	B_6H_8	B_6H_{10}	B_6H_{12}	B_6H_{14}	B_6H_{16}	B_6H_{18}				
0600	2410 1601	4220 3311 2402	6030 5121 4212 3303	6022 5113 4204	6014 5105	6006				
B_7H_7	B_7H_9	B_7H_{11}	B_7H_{13}	B_7H_{15}	B_7H_{17}	B_7H_{19}	B_7H_{21}			
0700	2510 1601	4320 3411 2502	6130 5221 4312 3403	7031 6122 5213 4304	7023 6114 5205	7015 6106	7007			
B_8H_8	B_8H_{10}	B_8H_{12}	B_8H_{14}	B_8H_{16}	B_8H_{18}	B_8H_{20}	B_8H_{22}	B_8H_{24}		
0800	2610 1701	4420 3510 2602	6230 5321 4412 3503	8040 7131 6222 5313 4404	8032 7123 6214 5305	8024 7115 6206	8016 7107	8008		
B_9H_9	B_9H_{11}	B_9H_{13}	B_9H_{15}	B_9H_{17}	B_9H_{19}	B_9H_{21}	B_9H_{23}	B_9H_{25}	B_9H_{27}	
0900	2710 1801	4520 3611 2702	6330 5421 4512 3603	8140 7231 6322 5413 4504	9041 8132 7223 6314 5405	9033 8124 7215 6306	9025 8116 7207	9017 8108	9009	
$B_{10}H_{10}$	$B_{10}H_{12}$	$B_{10}H_{14}$	$B_{10}H_{16}$	$B_{10}H_{18}$	$B_{10}H_{20}$	$B_{10}H_{22}$	$B_{10}H_{24}$	$B_{10}H_{26}$	$B_{10}H_{28}$	$B_{10}H_{30}$
0.10.0.0	2810 1901	4620 3711 2802	6430 5521 4612 3703	8240 7331 6422 5513 4604	10.0.5.0 9141 8232 7323 6414 5505	10.0.4.2 9133 8224 7315 6406	10.0.3.4 9125 8216 7307	10.0.2.6 9117 8208	10.0.1.8 9109	10.0.0.10

*
s **= number of hydrogen bridges,** $B\overset{\frown}{\quad}B$

t **= number of boron-boron three-center bonds,**



y **= number of boron-boron single bonds, B-B**
x **= number of extra H atoms on B-H; i.e., BH_2 groups**
$s + x = q,\ s + t = p,\ p = t + y + q/2.$

bond approximations described above lead to a large variety and number of possible hydrides. The topological ideas to be described here are those of Dickerson and Lipscomb (*15*) and are capable of very considerable extension to other systems. The major principles are concerned with the ways in which various types of bonds are able to connect the framework B-H units that are adjacent to one another:

(a) Assume that each boron must be connected to each adjacent boron atom by at least one two-center or three-center bond of some kind.

(b) Define the connectivity of a boron atom as the number of adjacent boron atoms in the molecule. Define the excess connectivity (*EC*) as connectivity minus three.

(c) Define the excess negative connectability of a bond arrangement at the site of a given boron atom as the number of orbitals which it requires from that boron atom minus the number of other boron atoms which are connected to the given one by that bond arrangement. A bond arrangement may be several bonds considered as a unit.

Definition (b), applied to the more compact icosahedral and octahedral fragments to which our predictions are limited for convenience, is illustrated in Fig. 18. Definition (b), applied to various bonds and bond arrangements, leads to the excess negative connectabilities (*ENC*) shown in Fig. 19. Note that a B-B single bond or a B-H-B three-center bridge bond, when isolated from other bonding arrangements, connects two borons and uses one orbital from each so that addition of these bonds

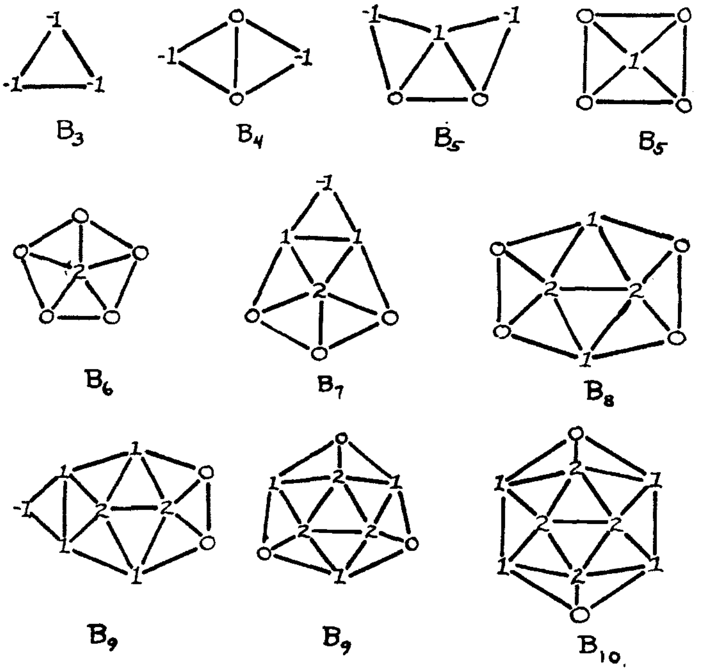


FIG. 18. Excess connectivities of possible boron-hydride frameworks.

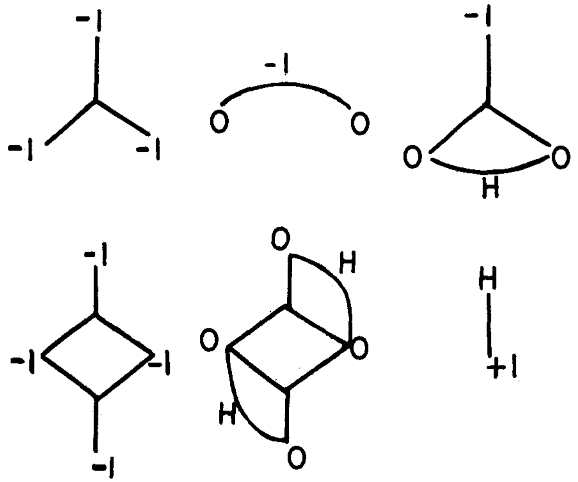


FIG. 19. Excess negative connectabilities of various bonds. Note that the extra B-H, which forms a BH_2 group, removes a boron orbital without connecting that boron to any other boron.

produces no change in the *EC* of a framework. Also note that if every boron were of connectivity 3, i.e., $EC = 0$, the three orbitals left after forming the B-H bond would suffice to form a framework of simple covalent bonds, provided enough electron pairs are available. Hence, any $EC > 0$ must be removed by addition of three-center B-B-B bonds, and any $EC < 0$ must be removed by adding extra H's to form BH_2 groups. It is also permissible, as shown by the so far unique example of a boron atom in B_5H_{11}, to add an extra H to a boron of $EC > -1$, thereby raising the *EC* of that boron atom by 1. Hence the procedure to be followed is:

(a) Make a topological sketch of the assumed boron framework, indicating the *EC* at each boron site.

(b) Add extra B-H bonds to every boron of $EC = -1$, and possibly to certain borons of $EC = 0$ or 1, but not to a boron of $EC = 2$.

(c) Add three-center B-B-B bonds or arrangements of them, such as shown in Fig. 19, in such a way that the *EC* at every boron site is reduced to zero.

(d) Complete the molecule with B-B and B-H-B bonds, subject to the equations of balance (Table I).

It must be emphasized that this type of topological theory is not limited to three-center bonds. Its extension to other types of semilocalized multi-centered molecular orbitals might well prove useful in an extensive study of valence in certain intermetallic compounds in which the nearest neighbors can easily be recognized, especially if the number of nearest neighbors is not too large. This type of theory is, moreover, not limited to finite molecules, single polyhedral fragments, or icosahedral fragments.

In order to eliminate from consideration certain structural features not present among the known boron hydrides, some further principles may be stated in order of decreasing reliability:

(a) All known boron hydrides have at least a plane of symmetry. Low symmetry appears to provide reactive points which are averaged over when symmetry is introduced. A new hydride probably would have at least a plane or some other twofold element of symmetry.

(b) No two adjacent boron atoms can be connected by both a central and an open three-center bond, because such an arrangement gives a very unfavorable angle between valence orbitals.

(c) Borons of $EC = 2$ do not contribute to a B-H-B bridge or to an extra B-H, for reasons relating to unfavorable valence angles between orbitals. This assumption restricts B-H-B bridges to the edge of the framework, and BH_2 groups to the outer boron atoms.

(a) Each boron of $EC = -1$ will probably be bonded by one hydrogen bridge to at least one of its two adjacent borons. Again this principle is based upon the requirement that angles between valence orbitals shall not be too small.

(e) An edge boron of $EC = 1$ will probably not be connected to two other borons by hydrogen bridges. This is probably the weakest of our assumptions.

As an example, consider the B_3 hydrides based on a B_3 triangle. Only the 3003 B_3H_9 structure mentioned earlier (*18*) is satisfactory (see Section IIID). The reader may find it instructive to try to draw the B_3H_7 and B_3H_5 possibilities (B_3H_3 is impossible), and show that all have unsatisfactory angles about boron for reasonable hybrid orbitals. The least unsatisfactory of these is the 2102 B_3H_7 with C_s symmetry in which the single bond shown in Fig. 17a has been converted to a central three-center bond.

As a second example, consider the possible B_9 hydrides (*15*) based on the framework shown in Fig. 18. Two adjacent borons of $EC = 2$ require at least four three-center B-B-B bonds and hence $t \geqslant 4$. There is at least one B-H group because of the one boron of $EC = -1$, and hence $x \geqslant 1$. At least one bond from this boron of $EC = -1$ to the other borons is a hydrogen bridge, and with the plane of symmetry we require $s \geqslant 2$. These restrictions eliminate most of the possibilities in Table I, leaving 3611, 2702, 5421, 4512, 3603, 5413, 4504, and 5405 as possibilities, and restricting the number of hydrogen atoms to between 13 and 19. A more detailed study of these possibilities yields only the valence structures shown in Fig. 20. Note that the first three have the same nuclear arrangement and correspond merely to different ways of drawing valence bonds. The last structure is distinct, however, and has three BH_2 groups. When the structure of Fig. 20(d) was introduced into the least-squares

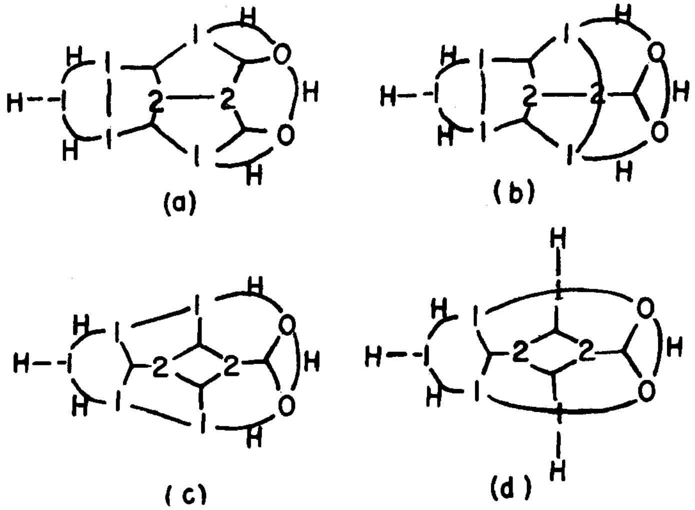


FIG. 20. Possible B_9 hydride valence structures.

refinement of the X-ray data (*16*), the two hydrogen atoms in the additional BH_2 groups refined to the bridge positions shown in Fig. 20(a), (b), or (c).

The importance of this topological extension of the valence theory is that it yields so few predictions (*15*), which may be summarized as follows:

B_4 (icosahedral fragment) gives the established B_4H_{10} structure uniquely.

B_5 (icosahedral fragment) yields uniquely the established geometrical arrangement for B_5H_{11}.

B_5 (octahedral fragment) yields the established B_5H_9 structure if a fourfold axis is required.

B_6 yields two possible B_6H_{10} structures, one with no BH_2 groups, and one with one BH_2 group. The former is the structure determined in an X-ray diffraction study (*23*). B_6 also leads to a B_6H_{12} structure, with two BH_2 groups on borons of $EC = 0$, probably a reactive situation.

B_7 yields no satisfactory structures based on an icosahedral fragment.

B_8 yields two B_8H_{12} structures and one geometrical arrangement for B_8H_{14}.

B_{10} yields only the established $B_{10}H_{14}$ structure.

It is possible that some new hydride, perhaps less stable than the known ones, will violate some of these assumptions. This is particularly likely for reaction intermediates. Hence an examination has been made (*23*) of some of the more likely possibilities which may occur if the symmetry restriction is removed. It is further quite likely that the present form of the valence and topological theory will be of aid in the elucidation of reaction mechanisms.

VII. Possible Boron Hydride Ions

It is easy to extend the foregoing topological arguments to boron hydride ions (*42*). Consider ions of the charges $c = -2, -1, 1,$ and 2 in the form $B_pH^c_{p+q+c}$. The modified equations of balance are $s + x = q + c$, $s + t = p + c$, and $t + y = p - c - q/2$. The structures derived by the procedures described in Section VI can easily be drawn in topological form from the four numbers s, t, y, and x, which precede the formula. These possible ions are classified as the following types:

(a) Ions similar in geometrical structure to known hydrides: The 4450 $B_{10}H_{14}^{-2}$ ion of C_{2v} symmetry is the only ion of this type, and is probably the most interesting of all of the ions. Except for a probable contraction of the two 2.0-Å B . . . B contacts towards a more normal value, the geometry of this ion is probably very similar to that of the well-known 4620 $B_{10}H_{14}$ structure, or is possibly a tautomeric form.

(b) Ions similar in electronic structure to known hydrides: The prediction (*43*) of the B_5H_9-like ions, $B_4H_7^-$ and $B_6H_{11}^+$, was based upon analogies of these compounds to C_6H_6, $C_5H_5^-$ and $C_7H_7^+$. Equivalent orbital transformations reduce these to 3030 $B_4H_7^-$ and 5210 $B_6H_{11}^+$ ions in the present description.

(c) Ions derived from known hydrides by removal of H^+ from a B-H-B bridge bond: These structures satisfy our rules if the electron pair is used to form a B-B bond. It is obvious how a list of these ions can be made from the known and hypothetical neutral hydrides, and hence such a list will not be given here. However, the 2013 $B_3H_8^-$ ion (*25*) is probably either a member of this class or of class (d).

(d) Ions derived from known hydrides by removal of H^+ from a B-H (terminal) bond: Terminal hydrogens tend to be less negative (*21*) than bridge hydrogens and might ionize off more readily, although the resulting ion usually does not have as satisfactory a valence structure as the ion produced in class (c). The various terminal hydrogen atoms in the known hydrides are attached to borons of different formal charge (*18*) and those attached to the more positive boron atoms will presumably ionize off more readily. The four borons of type II in $B_{10}H_{14}$ are more positively charged than the others, and hence possible ionization of one or more of the attached hydrogens may be suggested; presumably the pair of borons of type I are as positive or next most positive and should also be considered as ionizable. There is some evidence that $B_{10}H_{14}$ has an ionizable hydrogen (*20*) and the series of salts $NaB_{10}H_{13}$, $Na_2B_{10}H_{12}$, etc., may be suggested. When this suggestion is combined with the class (a) type, $Na_2B_{10}H_{14}$, we expect another series beginning with $Na_3B_{10}H_{13}$, etc.

(e) Ions derived from addition of H^+ to a single B-B bond on the edge: The $B_6H_{11}^+$ ion derived by addition of a proton to the strained single B-B bond in the known (*23*) 4220 B_6H_{10} structure is expected to be stable. Although no other of the known hydrides based upon icosahedral fragments have this structural feature, several of the possible hydrides and ions do, and might become stabilized by the addition of one or two protons.

(f) Other ions based upon icosahedra or icosahedral fragments: Ions like the 3122 $B_5H_{10}^-$ ion and the 3100 $B_3H_6^+$ ion may also exist, as may the 2113 $B_4H_9^-$ and 2440 $B_8H_{10}^{-2}$, which have one or more single B-B bonds along the edge; see class (e). Probably the most promising ion (*47*) of this type is $B_{12}H_{12}^{-2}$, which is an 0.10.3.0 resonance hybrid in our localized-bond description.

(g) Ions based upon tetrahedra, octahedra, or their fragments: Our bonding scheme applies to any geometrical framework in which one can say that only close contacts represent valence interactions, and hence includes 0230 $B_4H_4^{-2}$, (0400 B_4H_4), 2040 $B_4H_6^{-2}$, 3030 $B_4H_7^-$ also listed in class (b), (4020 B_4H_8), 5010 $B_4H_9^+$, and 6000 $B_4H_{10}^{+2}$, all based on a tetrahedral boron arrangement; 2240 $B_6H_8^{-2}$, 3230 $B_6H_9^-$, 0430 $B_6H_6^{-2}$ (see Eberhardt *et al.*, *18*), 1420 $B_6H_7^-$, (2410 B_6H_8), and 3400 $B_6H_9^+$, all based on an octahedral boron arrangement; and a similar series based on the B_5H_9 arrangement. Within each of these groups, these ions are interrelated by the process describing class (e) as the charge increases, or class (c) as the charge decreases. Ions involving features not present in the known hydrides have been omitted.

While the above classifications and lists probably do not exhaust all possibilities, it may be hoped that the omissions do not overlook any obviously promising stable ions. For example, we have not considered ions based on linked polyhedra or linked fragments of polyhedra. We have not tried to list completely the results of applying the processes of classes (c), (d), and (e) to all ions listed above. Also, we have not taken complete account of a very suggestive isomerization mechanism indicated in the topological theory (*15*) and shown in Fig. 21 for the $B_{10}H_{13}^-$ ion derived by process (c) above. For B_6H_{10} the left side is favored; for $B_{10}H_{13}^-$ apparently the right side, which places negative charge on the BH_2 group, is favored. A similar tautomerism can be drawn between the 4450 (C_{2v}) and 2632 (C_{2v}) and 0814 (C_2) $B_{10}H_{14}^{-2}$ structures. Finally, these principles are applicable to types of polyhedra other than those discussed here.

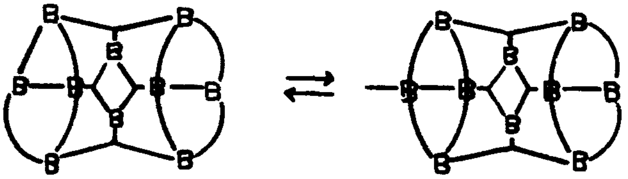


FIG. 21. Tautomeric forms for $B_{10}H_{13}^-$. Most of the ambiguities remaining in the topological theory are related by a similar tautomerism (*15*).

The available experimental evidence for ionic boron hydride fragments suggests that much careful experimental work is desirable. Stock (*68*) mentions $Na_2B_2H_6$ and $Na_2B_4H_{10}$, from which the original hydrides B_2H_6 and B_4H_{10} are at least partly recoverable. He also describes (*69, 70*) $Na_2B_5H_9$, and $Na_2B_4H_8$ as a decomposition product of $Na_2B_4H_{10}$. Recent work (*25, 31*) has shown that the diborane reaction gives $NaBH_4$ and NaB_3H_8. The remarkable $B_2H_7^-$ ion (*10*), prepared by reaction of BH_4^- with B_2H_6, may possibly be formed only in solution or only when BH_4^- can react with the double hydrogen bridge which occurs in B_2H_6 but not in the higher hydrides. This ion probably consists of a single BHB bond between two BH_3 groups.

In summary, the more stable ions are probably $B_{12}H_{12}^{-2}$, $B_{10}H_{14}^{-2}$, $B_{10}H_{13}^-$, $B_6H_{11}^+$, $B_3H_8^-$, $B_4H_7^-$, $B_6H_6^{-2}$, $B_5H_{10}^-$, $B_3H_6^+$. The fact that both positive and negative ions might exist leads to the suggestion (*43*) of purely ionic hydrides, possibly prepared by reactions of salts of these ions with one another.

VIII. The Boron Halides

Aside from the well-known trihalides, BX_3, the structures of only B_2F_4 (*71*), B_2Cl_4 (*3*), and B_4Cl_4 (*1, 2*) are established. At least three more halides (*73, 72*) $(BCl_{0.9})_x$, soluble in organic solvents; $(BCl_{0.6})_x$, insoluble in solvents; and a probably two-dimensional polymer, $(BCl)_x$, have been described. Although it is probably unwise to formulate a general theory from these few examples, at least some of the aspects of boron halide structures may be stated.

The importance of "back coordination" of the extra electrons on Cl in stabilizing BCl_3 relative to its dimer has long been recognized. Presumably the primary B-Cl bonds are planar "σ-type" sp^2 hybrids. The remaining "π" orbital of boron perpendicular to the molecular plane can accept an average of an electron pair from orbitals of similar symmetry from the Cl atoms. This type of electron transfer is not possible in BH_3 because no orbitals of H have the symmetry of the "π" orbital of B, and hence BH_3 dimerizes. The fact that B_2F_4 and B_2Cl_4 are planar, at least in the solid state, also suggests that "π" orbital interactions are of importance either within the molecule or between different molecules in the solid. Again this explanation accounts for the non-existence of B_2H_4. A similar explanation in molecular orbital language appropriate to the tetrahedral B_4Cl_4 molecule has been given by Longuet-Higgins (*46*) in order to account for the stability of B_4Cl_4 and the nonexistence of the comparable B_4H_4.

In deriving the principles of boron chloride structures, we shall make the following assumptions:

(a) Terminal BCl_2 groups can occur, with three-coordinated boron.

(b) No Cl bridges occur; if this assumption is to be modified, we must expect that the Cl bridge involves single bonds to each boron, similar to the situation (*57*) in $BeCl_2$.

(c) BCl_2 are terminal groups, and hence any B-Cl bond can be replaced by a B-BCl_2 group. Thus we may limit consideration to polyhedra or fragments with terminal B-Cl bonds which can later be replaced by terminal B-BCl_2 groups.

(d) If the formula of a boron chloride is represented as B_pCl_{p+q}, then the equations of balance (*18*) are for the electron balance

$$p + q + 2t + 2y = 3p$$

and for the orbital balance

$$p + q + 3t + 2y = 4p.$$

Note that the assumption of no bridge Cl atoms and no BCl_2 groups at this stage requires that $s = x = 0$. The above two equations give $t = p$, from which we find $y = -q/2$ from either of the above equations. Values for s, t, y, and x are thus 0, p, $-q/2$ and 0. But $y \geqslant 0$, and hence $q \leqslant 0$; moreover, y is integral, so that q is an even negative number or zero.

Suppose we illustrate these principles with a discussion of a molecule of approximate composition B_8Cl_8 or $B_{10}Cl_8$. The possible formulas are, according to the above rules: B_4Cl_4, B_5Cl_5, B_6Cl_6, B_7Cl_7, B_8Cl_8, B_6Cl_4, B_7Cl_5, B_8Cl_6, B_9Cl_7, and $B_{10}Cl_8$. All such molecules are to have terminal Cl groups replaced, if necessary, by BCl_2 groups in order to bring the total number of Cl atoms to eight. A B_8Cl_8 possibility based upon a B_4 tetrahedron is tetrahedral B_4Cl_4 with each Cl replaced by BCl_2. A B_8Cl_6 model with two tetrahedral B_4Cl_3 groups joined by a single B-B bond, after which we replace two Cl atoms with BCl_2 groups, leads to a $B_{10}Cl_8$ molecule of the form $Cl_2B—B_4Cl_2—B_4Cl_2—BCl_2$. These two models do not, by any means, exhaust all of the possibilities but they do illustrate the ideas.

If the polymers are based on B_4 tetrahedra, a suitable linear polymer might be $—B_4Cl_2—B_4Cl_2—B_4Cl_2—$, and a suitable sheet-like polymer might be B_4Cl linked by three bonds to three neighboring B_4Cl groups, etc.

The molecule $(BCl_{0.9})_x$ (where $x \sim 10$) is currently under investigation by X-ray diffraction methods (*29*).

IX. Reactions among Boron Hydrides

Although BH_3 has not been observed experimentally, the kinetics of the initial stages of several reactions of diborane (*13*, *9*) render the steady-state equation (*5*),

$$B_2H_6 \rightleftarrows 2BH_3, \qquad (1)$$

followed by the reaction

$$BH_3 + B_2H_6 \rightarrow \text{(higher products)} \qquad (2)$$

as the generally accepted initial reactions. The discussion will be simplified if we consider first this and the later work relating to these initial reactions, after which we shall return to a consideration of the further reactions in the synthesis of the higher hydrides.

The initial stages of B_2H_6 polymerization (*13*, *9*), of exchange (*48*) between B_2H_6 and D_2, of exchange (*48*) between B_2H_6 and B_2D_6, of exchange (*65*) between B_2H_6 and $B_2{}^{10}H_6$, and of reaction (*74*) of B_2H_6 with C_2H_4, all support this mechanism. Experimentally, all of these reactions are 3/2 order with respect to diborane concentration, as may be derived from the mechanism by writing Eq. (1) as a steady state, $K = (BH_3)^2/(B_2H_6)$, so that

$$\frac{d(\text{higher products})}{dt} = k(BH_3)(B_2H_6) = k\sqrt{K}(B_2H_6)^{3/2}$$

is the rate-determining step of the initial stage.

In summary, the B_2H_6—B_2D_6 exchange reactions are:

$$B_2H_6 \rightleftarrows 2BH_3$$

$$B_2D_6 \rightleftarrows 2BD_3$$

$$BH_3 + B_2D_6 \rightarrow BH_3BD_3 + BH_3$$

$$BD_3 + B_2H_6 \rightarrow BH_3BD_3 + BH_3$$

$$(BD_3 + BH_3 \rightleftarrows BH_3BD_3)$$

the third and fourth being rate determining. The B_2H_6—D_2 exchange is summarized by the reactions:

$$B_2H_6 \rightleftarrows 2BH_3$$

$$BH_3 + D_2 \rightleftarrows BH_2D + HD \text{ (surface)}$$

$$BH_2D + B_2H_6 \rightleftarrows B_2H_5D + BH_3,$$

where the last equation is rate determining.

The B_2H_6—C_2H_4 reaction is of importance partly because it gives support to the idea that the initial higher product is B_3H_9 or $B_3H_7 + H_2$. The initial stages of the mechanism suggested (*74*) are:

$$B_2H_6 \rightleftarrows 2BH_3$$

$$B_2H_6 + BH_3 \rightarrow B_3H_9$$

$$B_3H_9 + C_2H_4 \rightarrow B_2H_5Et + BH_3.$$

The last two reactions are then repeated starting with B_2H_5Et in place of B_2H_6 to obtain $B_2H_4Et_2$, which reacts with BH_3 to give $B_3H_7Et_2$. At this stage an autocatalytic reaction appears,

$$B_3H_7Et_2 + B_2H_6 \rightarrow 2B_2H_5Et + BH_3,$$

so that B_2H_6 and C_2H_4 compete for these later products. The autocatalytic effect increases considerably as the final product BEt_3 appears, and if $2(B_2H_6) > (C_2H_4)$, the reaction becomes explosive.

The present literature (*13*, *9*, *60*) on the polymerization to higher hydrides around 100°C may be summarized in the sequence of reactions

$$B_2H_6 \rightleftarrows 2BH_3 \qquad (1)$$

$$BH_3 + B_2H_6 \rightleftarrows B_3H_9 \qquad (2)$$

$$B_3H_9 \rightleftarrows B_3H_7 + H_2 \qquad (3)$$

$$B_3H_7 + B_2H_6 \rightleftarrows B_5H_{11} + H_2 \qquad (4)$$

or, combining (3) and (4)

$$B_3H_9 + B_2H_6 \rightarrow B_5H_{11} + H_2 \qquad (3')$$

$$B_5H_{11} + H_2 \rightleftarrows B_4H_{10} + BH_3 \qquad (5)$$

$$B_4H_{10} + B_5H_{11} \rightarrow B_5H_9 + 2B_2H_6 \qquad (6)$$

Reaction (1) is apparently very rapid. Combination of (1) and (2) gives the reaction its 3/2 power dependence on diborane concentration. Reaction (3) or (3′) presumably is rate controlling. Combination of (4) and (5) is the recognizable reaction, $B_3H_7 + B_2H_6 \rightarrow B_5H_{11} + H_2$, which is questioned by R. Schaeffer and others as a single step and is currently being investigated. Reaction (5) is nearly an equilibrium, discovered by Burg and Schlesinger (*11*); it has been invoked (*60*) to account for the sharp braking of the rate of H_2 formation as the B_5H_{11} concentration rises. Reaction (6), which may not be a single step, is the slowest reaction in the above list. Reactions (5) and (6) account nicely for the later cleavage of B_5H_{11} to B_2H_6 which is formed along with B_5H_9, apparently with the same activation energy and at an apparent rate about 2.5 times the rate of formation of B_5H_9 (*60*). Reaction (3′), which may be two steps with B_5H_{13} as an intermediate, avoids formation of the electron deficient intermediate, B_3H_7. The slow reaction, $B_4H_{10} + H_2 \rightarrow 2B_2H_6$ should also be included as a minor reaction (*11*). Nevertheless, hydrogen inhibition appears to merit further study in these reactions.

The importance of further isotope-exchange studies of the boron hydrides and simple reactions among them can hardly be overemphasized. Such systematic studies as those by W. S. Koski and his co-workers will continue to clarify possible mechanisms of these reactions. It is conceivable (*23*) that all of the hydrides containing BH_2 groups, B_2H_6, B_4H_{10}, B_5H_{11}, and B_9H_{15}, undergo reversible dissociation into BH_3 and intermediates such as BH_3, B_3H_7, B_4H_8, and B_8H_{12} which will add BH_3, H_2 or react with one another or other hydride molecules. It seems unlikely, on the other hand, that the more stable relatively highly condensed B_nH_{n+4} hydrides undergo associations with BH_3 to form a B_nH_{n+6} hydride (*34*). The relation of these rather general speculations to the pyrolysis is that at higher temperatures, near 100°C, the reactions of B_4H_{10} may be those of B_3H_7, and the reactions of B_5H_{11} may be those of B_4H_8 which could add H_2 to give an unstable form of B_4H_{10} or $B_3H_7 + H_2$, as suggested by the reverse of reaction (5). Thus the mechanism of the pyrolysis can hardly be said to be understood clearly, but the stage of understanding of the structures of various possible reaction intermediates from the valence theory is sufficiently advanced that one can hope for some help from the structural concepts in the elucidation of the mechanisms and intermediates.

So far the important results of the isotopic-exchange experiments may be summarized as follows (*33*): (a) Exchanges occur in which BH_3 remains an entity, as in the B_2H_6 self-exchange; the rate of deuterium exchange is three times the rate of boron exchange. (b) Exchanges occur where BH_3 exchanges with terminal hydrogen and not with bridge hydrogen, as in B_5H_9 and $B_{10}H_{14}$. (c) Intramolecular exchange appears to occur in B_5H_{11} and in B_4H_{10}, as was first noted in the $Al(BH_4)_3$ and later in $B_3H_8^-$ and B_3H_7 addition compounds. Very little is known of the further reactions which lead to $B_{10}H_{14}$ and polymers but a mass spectroscopic study (*22*) of the reaction at 78°C for 24 hr of isotopically enriched $B_2{}^{10}H_6$ and $B_5{}^{11}H_9$ indicates that half of the boron atoms in the resulting $B_{10}H_{14}$ come from B_5H_9. Also, exchange between B_2H_6 and B_5H_9 occurred, possibly involving a pair of B atoms at each step.

Finally, the efficient interconversions of certain boron hydrides into others by chemical reagents well below room temperatures and under conditions adaptable to large-scale production is a very significant discovery (*8*). The starting material, B_5H_{11}, which is relatively easily obtainable from pyrolysis reactions, can be converted in 98% yield to B_4H_{10} by water at about 0°C according to the reaction

$$B_5H_{11} + 3H_2O \rightarrow B_4H_{10} + 2H_2 + B(OH)_3.$$

Also $[(CH_3)_2N]_2BH$ below 0°C converted 0.7 mole of B_5H_{11} into 0.6 mole of B_5H_9, some B_2H_6 and B_4H_{10}, 0.04 mole of B_6H_{10} and small amounts of other products. This same reagent produces a high yield of B_5H_9 from B_4H_{10}. Production of B_6H_{10} even in small yields by these methods is especially interesting because it is difficult to obtain by the pyrolysis method. The low temperatures in these processes give some promise that new hydrides, less stable than the presently known ones, might possibly be prepared.

Notes Added in Proof

1. A NEW BORON CHLORIDE B_8Cl_8

The structure of the boron chloride referred to at the end of Section VIII has now been solved, as shown in Fig. 22. The molecular symmetry is D_{2d}, and the polyhedron is a new one among small molecules containing boron. As has been shown (*18*) in other examples, the three-center bond description is not appropriate in highly condensed molecules unless resonance is invoked, and hence a molecular orbital description is preferred. A convenient description starts with *sp* hybrids along each B-Cl bond. The resulting eight *sp* hybrids pointing toward the center of the molecule may then be formed into linear combinations which give two bonding orbitals. Then the local π orbitals on each B may be also made into linear combinations requiring six bonding pairs. These eight pairs, together with the eight other pairs in B-Cl bonds, and the lone pairs on Cl then give a filled

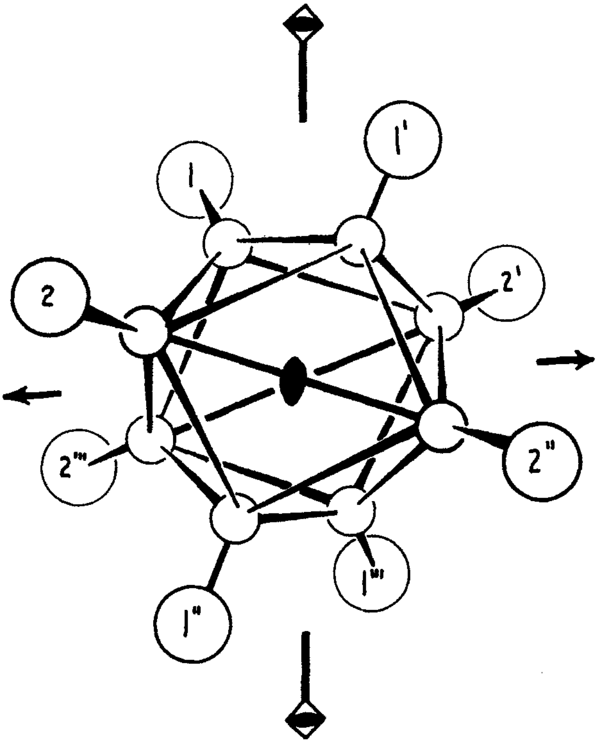


FIG. 22. The B_8Cl_8 structure, showing the positions of axes of symmetry. Small circles represent boron and large circles represent chlorine.

orbital description of the molecule. As in B_4Cl_4, the lone pairs on Cl may interact with low-lying unfilled molecular orbitals of the boron framework (*46*).

A systematic investigation of molecular orbitals in related B_8 polyhedra is now under way in order to see whether this structure is unique for all reasonable B_8 possibilities.

2. Topology of $B_aH_bO_c$ Compounds

The recent report by W. H. Bauer and S. E. Wiberley [*Abstr. 133rd Meeting Am. Chem. Soc., San Francisco,* p. 13L, (1958)] and by J. A. Hammond (private communication) of a possibly electron deficient compound $B_4H_{12}O$ has suggested the investigation of valence rules for this and similar compounds. Assume that $B_{p-n}H_{p-n+q}O_n$ satisfies the same bonding rules as the boron hydrides. Then the equations of orbital balance, electron balance, and hydrogen balance (*18*) are

$$\begin{aligned}
&4p = p - n + 2s + x + 3t + 2y + z\\
&3(p - n) + 6n = p - n + s + x + 2t + 2y + 2z\\
&s + x = q
\end{aligned}$$

where z is the number of unshared pairs. From these equations a complete topological representation of possible formulas may be derived. If desired, the assumptions that there are no BH_3 or OH groups can easily be removed, and more general formulas may be obtained.

As a simple pertinent example, suppose that we examine formulas of the type $B_4H_{4+q}O$. Since there are more orbitals than electrons, it is very likely that $z = 0$. Hence these equations become

$$\begin{aligned}
&16 = q + s + 3t + 2y\\
&14 = q + 2t + 2y\\
&s = x = q
\end{aligned}$$

and the $s\ t\ y\ x$ numbers are, for all possible q,

$q =$	14	12	10	8	6	4	2	0
	2.0.0.12	1.1.0.11	0.2.0.10	0218	0226	0234	0242	0250
		2.0.1.10	1119	1127	1135	1143	1151	
			2028	2036	2044	2052	2060	

Note that q is restricted to the range 0–14, inclusive. If $x > 4$, there is an OH group, which seems unlikely, and hence q probably lies between 0 and 6, inclusive. A reasonable type of formula would then require the oxygen at the center, and hence we surmise that $t = 0$. With these fairly drastic assumptions, we then arrive at a 2044 $B_4H_{10}O$, a 2052 B_4H_8O, and a 2060 B_4H_6O as likely possibilities. Of these, the first seems most preferable and the second, the least. Thus, we venture a guess that the compound is $B_4H_{10}O$ with four single B-O bonds and two bridge hydrogens each between a pair of BH_2 groups.

It is worth noting that in the formula B_4H_gO there are two more orbitals than electrons for all values of g, and hence two three-center bonds are required.

An example of a compound with more electrons than orbitals is the hypothetical $B_2H_2O_3$ (J. A. Hammond, private communication) for which $n = 3$, $p = 5$ and $q = 0$. The equations give $s = x = 0$ and $z - t = 4$, but it is unlikely that there are both unshared pairs and three-center bonds, and so the most likely bond numbers are $s = 0$, $t = 0$, $y = 7$, $x = 0$, and $z = 4$. Two BH groups each joined to three oxygen atoms are plausible, but there must also be one O-O bond; but formulas in which boron is three—coordinated are also possible.

3. AMMONIATES OF BORON HYDRIDES

In a series of seven papers, R. W. Parry, D. R. Schultz, S. G. Shore, P. R. Girardot, G. Kodama, R. C. Taylor, and A. R. Emery [*J. Am. Chem. Soc.* **80,** 4 (1958)] have shown, among other things, that $B_2H_6 \cdot 2NH_3$ is $H_2B(NH_3)_2{}^+BH_4{}^-$. These studies follow an earlier set of studies by S. G. Shore, R. W. Parry, E. L. Lippert, W. N. Lipscomb, and E. W. Hughes [*J. Am. Chem. Soc.* **77,** 6084 (1955); **78,** 502, 503 (1956)] in which the structure of the monomer was proved to be H_3NBH_3, now shown to have a dipole moment of 4.9 Debyes [J. R. Weaver, S. G. Shore, and R. W. Parry, *J. Chem. Phys.* **29,** 1 (1958)].

These studies lend themselves to some generalization. R. W. Parry (private communication) has suggested that $B_4H_{10} \cdot 2NH_3$ might conceivably be $H_2B(NH_3)_2{}^+B_3H_8{}^-$. On the other hand, $B_5H_9 \cdot 4NH_3$ does not seem to be based upon known positive or negative ions, and hence an investigation of its structure, as well as investigations of the other ammoniates, would be well worth undertaking.

A further generalization of these and other reactions of boron hydrides has led Parry and Edwards (private communication) to classify reactions of boron hydrides on the basis of their known structures. The types of reactions are (a) symmetrical cleavage (to BH_3) of a double bridge bond, (b) unsymmetrical cleavage (to $BH_2{}^+$) of a double bridge bond, (c) loss of H_2, and (d) loss of H^+. Some of these reactions have been suggested before on the basis of isotopic exchange studies, and intramolecular rearrangement is not included among these reactions. However, these types of reactions appear to systematize the interpretations of nearly all of the reactions of the boron hydrides.

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