EFFECTS OF ORBITAL VACANCIES IN BORON COMPOUNDS

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Abstract - Addition of H₂ to BH₃ yields BH₅, which is shown to be of C₂ᵥ symmetry. Rearrangement mechanisms and hydrogen loss have been examined.

Intermediates such as B₃H₇ and B₄H₈ have been predicted to have vacant orbital structures in which the stability gained by filling that orbital is balanced by strain in converting a terminal hydrogen to a bridge hydrogen. Other factors, such as hyperconjugative interactions and boron framework distortions are of importance. These factors have been examined also in bridge hydrogen asymmetries and distortions from regular geometry, in the light of vacant orbital contributions to valence structures of known boranes and carboranes.

Localization procedures have refined the concepts of where an open three-center bond is useful, where single bond donation becomes important, where fractional bonds occur, and where a more complex description can usefully replace a large number of valence structures.

Vacant orbital contributions have also been used to guess where ligand (e.g. H) attack may occur, and at which pair of adjacent boron atoms BH₃ may be expected to add. A study of diborane formation indicates favoritism for simultaneous Hₕ₁B and Bₙ₋₁Hₕ₂ reaction of compounds of the two distinct BH₃ reactants. Reactions of BH₃ with higher hydrides, and of higher hydrides with each other may be expected to follow this principle.

I. VACANT ORBITALS IN TRANSIENT SPECIES

BH
A prototype of the BH units in polyhedral molecules, the diatomic BH molecule has all of its electrons paired (¹Σ⁺). Nevertheless, it is paramagnetic. The magnetic susceptibility, χ = 18.7 ppm (1), is the temperature-independent type, and arises largely from excitations from the filled 3α level. This unusual property is a forewarning that magnetic shielding in the boron hydrides and carboranes have large, sometimes dominating, contributions from the paramagnetic term. The chemistry of this unstable species has not been studied, but would probably be very interesting.

BH₃
Known as a reaction intermediate in diborane pyrolysis and other reactions, this molecule has a vacant orbital which cannot be filled by a molecular distortion. Adducts to Lewis bases have stabilities correlating with bond distance (2). It has been isolated in a matrix (3) at low temperatures, from pyrolysis of BH₃CO. Theoretical studies are consistent with the planar D₃h structure. We now turn to a very weak adduct between BH₃ and H₂.

BH₅
When BH₅D is produced by reaction (4) of BH₄⁻ with D₂O⁺ below pH 12, about 95% of the hydrogen loss occurs as HD. This interesting observation implies either (a) that the D⁺ becomes equivalent to only one resident H atom, or (b) that the D remains unique and is lost when BH₄D decomposes (A candidate for this second possibility is that D remains at the apex of tetragonal
pyramidal BH₄D). We shall strongly favor the first possibility (a). First we examine geometries for BH₅ (Fig. 1), then internal rearrangements, and

![Fig. 1. Four plausible structures for BH₅:](image)

(a) D₃h, where H₃BH₅ is collinear, r₁ = 2.252 au and r₂ = 2.280 au; (b) C₄v with H₃B along the four-fold axis, r₁ = 2.172 au, r₂ = 2.287 au, θ = 117.3°, α = 77.9°;
(c) C₂v where the two-fold axis is along H₄B, r₁ = 2.492, r₂ = 2.191 au, r₃ = 2.376 au, θ = 123.6°, α = 56.0°;
(d) C₅ (I and III) where H₅B lies in the symmetry plane: r₁=r₂=r₃ = 2.280 au, θ = 106.8°, α = 46.6°, β = 116.4° for C₅ (I), and r₁ = 2.192 au, r₂ = 2.205 au, r₃ = 2.807 au, θ = 115.4°, α = 32.1°, β = 117.4° for C₅ (III).

then ask which hydrogens are lost as H₂ from the theoretical point of view. At the 431G (SCF) level, energies in au are -27.386 for D₃h, -27.403 for C₄v, -27.423 for C₂v, -27.427 for C₅ (I), -27.454 for C₅ (III), and -27.476 for BH₅+H₂. While the C₅ (III) structure is the most "stable," it is not in a minimum at the SCF level, where BH₅ is unstable with respect to BH₃+H₂. Our estimate (5) of corrections for electron correlation predicts only marginal stability for BH₅ (relative to BH₃ and H₂), and more detailed molecular orbital studies by others (6,7) have predicted that BH₅ is stable by 2 kcal (6) and by 1.7 kcal (7). These estimates seem low by perhaps a factor of 2 or 3 in view of the probable lifetime (4,5) of about 10⁻¹⁰ sec for loss of H₂. All of these theoretical studies favor the C₅ geometry (Fig. 1(d)), like that predicted earlier (8) for CH₅.

Of course, if the incoming D⁺ converts BH₄⁻ to the C₅ structure of BH₅ one may expect loss of HD. The experimental evidence is furthermore consistent with a small amount of scrambling in BH₄D, and mechanisms for this process are implicit in the structures of Fig. 1. A study of the pathway (5) indicates that the C₂v, C₅ and C₄v structures are good transition states for interconversion of the C₅ structures (Figs. 2 and 3). Barriers predicted for this process at the minimum basis set level are 20 kcal/mole if the intermediate has C₄v or C₅ symmetry and 30 kcal/mole if the intermediate has C₂v symmetry. Experimental studies of the gas phase exchange of D₂ with diborane to yield HD may involve heterogeneous steps (9), but these studies yield an activation energy of about 20 kcal/mole. The H-D exchange in the gas phase reaction of HBF₂ with D₂ has an activation energy

Fig. 2. One plausible pathway for internal rearrangement of BH₅ passes through the C₅ intermediate in which H₅ and H₃ are related to the axial positions of a hypothetical trigonal bipyramid of even higher energy.

Fig. 3. In the C₄v intermediate the equivalent axial positions of the less stable trigonal bipyramidal BH₅ are either H₂ and H₅ or H₁ and H₄.
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of 18 kcal/mole (10), and probably does proceed through a multicentered molecular orbital between HBF₂ and D₂.

In predicting which pair of hydrogen atoms is lost from these structures, it is sufficient to refer all to trigonal bipyramidal BH₅ of D₃h symmetry. Overlap populations are 0.04 e for axial-equatorial, -0.05 e for axial-axial and -0.07 e for equatorial-equatorial pairs of H atoms. The formation of a chemical bond between two H atoms proceeds smoothly, without a barrier arising from crossing of molecular orbitals, only between the axial-equatorial pairs. This feature is retained upon distortion to C₄ᵥ, C₂ᵥ or C₅ symmetries. For example, in the tetragonal pyramidal C₄ᵥ structure of Fig. 3 the overlap populations are -0.03 e for basal-axial and 0.08 e for adjacent basal-basal pairs of H atoms. One result is that if D enters BH₄ along the four-fold axis of this structure and if this D remains uniquely in this position, it is unlikely that HD would be lost in preference to loss of H₂ from two adjacent basal positions. Hence, the observed loss of HD leads one to favor two equivalent positions as shown in Fig. 4.

Very different experimental results are obtained (11) when excess solid NaBH₄ is treated with anhydrous D₂SO₄ or DF (or isotopic inverses) in a bomb at -78°. Essentially statistical results are found, typically almost 60% H₂, 40% HD (plus 2% D₂). Perhaps the reaction occurs at a crystal surface, or the BH₄D may be formed in a state of excess internal energy so that rearrangement is facilitated in these experiments.

Styx formulas for vacant-orbital species
If a neutral boron hydride has formula BₚHₚ₊q, and if there are v vacant valence orbitals, then

\[ s + x = q \]
\[ s + t = p - v \]
\[ t + y = p - q/2 \]

Thus the number of three-center bonds s+t is reduced by the number of vacant orbitals, but the number of hydrogens (s+x+p) and the number of framework bonds (t+y) remain constant. This idea was introduced in a discussion of B₄H₈ by Dupont and Schaeffer (12). For example, formulas for B₄H₈ are 4020, 2202 and 3111 for v=0, 3021, 2122 and 1203 for v=1, and 2222, 1113 and 0204 for v=2. For B₃H₇ they are 3011 and 2102 for v=0, 2012 and 1103 for v=1, and 1013 and 0104 for v=2. These rules are easily extended to charged species, and to heteroatom species.

B₂H₄
The 2010 topology has two BH groups joined by two bridge hydrogens and by a single (pure σ) bond. This topologically disallowed structure does have four bonds to each boron, but it is less stable at the minimum basis set (Slater orbitals) by over 100 kcal/mole than either of two conformers of the 0012 topology.

These 0012 structures have two BH groups joined by a single B-B bond, and therefore each boron has a vacant orbital (σ relative to the H₂B-plane). We find (13) that the staggered conformer (D₂d) is more stable by 13 kcal/mole than the eclipsed (D₂h) conformer. A previous result, at the 6-31G level, also favors D₂d over D₂h, by 11 kcal/mole (14). The staggered conformer has a hyperconjugative interaction between the vacant orbital on each boron with the σ component of the localized molecular orbital on the adjacent BH₂ group. No such stabilizing interaction can occur in the planar (D₂h) form.
At the minimum basis set SCF level the 1103 (staggered) structure (Fig. 5) is 12 kcal/mole more stable than the 2102 structure for B₃H₇.

The 1103 (eclipsed) structure is only 4 kcal/mole more stable than the 2102 structure. Actually, these structures are very closely related: if H₇ is moved away from B₂ the 2102 structure is almost that of 1103 (staggered) if we take identifications as B₂(2102) → B₂(1103 ST), and B₁ or B₃ of 2102 as B₁ or B₂ of 1103 ST. No barrier is found between these structures, so that rearrangements of H atoms could proceed readily.

Extension of the basis sets to the 4-31G level and addition of configuration interaction to the minimum Slater set widens the energy gap between the 1103 (staggered) and the less stable 1103 (eclipsed) conformers of B₃H₇. These extensions make the 1103 (staggered) conformer only slightly more stable than the 2102 conformer, probably owing to the presence of one more bridge hydrogen in the 2102 structure. Electron-electron repulsions within a bridge bond are less than those in a single bond by about 3 kcal/mole in these conformers, and by about 6 kcal/mole in the 2BH₃ to B₃H₆ transformation at the minimum basis level including configuration interaction.

On the other hand the (bent) BHB bond has a strain of about 10 kcal/mole. Hence, the 2102 structure (Fig. 6), which has filled localized orbitals counting the central three-center BBB bond, is less stable than the 1103 ST structure (Fig. 5), which has at B₃ a vacant orbital which is only partly filled by the hyperconjugative interaction with the two BH₂ units. Thus, in small boron hydrides there is a compromise between structures having a vacant orbital (which orients to hyperconjugate if possible) and structures which fill this vacant orbital by converting a terminal BH bond to a (strained) bridge BHB bond.

B₄H₈

Only structures having a two-fold element of symmetry (plane, center or two-fold axis) have been considered here. The C₅ 2112 structure (Fig. 7), which has one vacant orbital is slightly preferred energetically, as compared to the closely related Dₕ 0204 ST structure (Fig. 8) which has two vacant orbitals and no bridge hydrogens. We did not study the intermediate 1203 structure (of C₁ symmetry) which has one vacant orbital, but it surely lies very close in energy to these two structures.

Here again there is a tendency in a strained structure to leave a vacant orbital. The filled-orbital C₂ 2202 structure actually refined, upon
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In the (slightly) preferred $C_9 2112$ structure for $B_4H_8$ there is a resonance hybrid between a valence structure having a single $B_2B_4$ bond and a central three-center $B_1B_2B_3$ bond, and a valence structure with a single $B_2B_3$ bond and central three-center $B_1B_2B_4$ bond.

In addition, aspects of orbital strain, relating to poor overlap contribute to the relative instability of the filled orbital structure. What we have here is an interplay of opposing tendencies to maximize valency and to minimize geometrical strain in these transient molecules.

II. VACANT ORBITAL CONTRIBUTIONS IN STABLE SPECIES

General Comments

When allowance is made for contributions of vacancy valence structures, we can recognize patterns of bridge hydrogen asymmetries, boron framework distortions, and probable modes of nucleophilic and electrophilic attack. Starting with the standard three-center valence structure, we look for the most satisfactory non-vacancy and vacancy valence structures in which bridges are converted to terminal hydrogens (or vice versa) and in which framework single bonds are converted into central three-center bonds (or vice versa). A new geometry is adopted which reflects a consistent set of displacements, and which is then described as a resonance hybrid of various valence structures.

Criteria for evaluation of the contribution of a given vacancy (or non-vacancy) valence structure in the hybrid are (1) the smallest number of vacant orbitals, (2) the smallest magnitudes of charges, (3) the smallest separation of charges, (4) the closest adherence to topological rules (except for vacancies), and (5) the highest symmetries (perhaps the weakest criterion). As an example of (4), we eliminate all valence structures in which adjacent boron atoms remain unconnected. We turn now to three simple examples.

$B_4H_{10}$

The displacements of bridge hydrogens toward the BH groups, away from the BH$_2$ groups, and the relatively positive BH$_2$ units (Fig. 9) are features of $B_4H_{10}$ which are correctly predicted by the vacancy hybrid (Fig. 10). The non-vacancy hybrid structure (Fig. 11) also predicts the correct asymmetry of bridge hydrogens, but does not represent the correct direction of charge separations in $B_4H_{10}$. Also a localized molecular orbital study (15) has indicated that the "single" bond of $B_4H_{10}$ (Fig. 9) shows donation of 0.19 e to each of the borons of the BH$_2$ groups: this feature is an indication of the extent of contributions of valence structures of Figs. 10 and 11 to the resonance hybrid.
Fig. 9. Charges on BH and BH$_2$ groups, and in parentheses Mulliken charges on boron in B$_4$H$_{10}$.

Fig. 10. The dominant (v=1) vacancy structure for B$_4$H$_{10}$. Bridge hydrogens are displaced towards the BH groups in this resonance hybrid of two equivalent valence structures.

Fig. 11. A non-vacancy valence structure which also is consistent with displacement of bridge hydrogens toward the BH groups in B$_4$H$_{10}$.

B$_5$H$_{11}$

The bridge hydrogen asymmetries, B-B interactions and charge distributions in B$_5$H$_{11}$ (Fig. 12) are well given qualitatively by the 2204 pair, the single 1205 and the pair of 3113 vacancy structures of Fig. 13. Examples of vacancy structures, neglected here, which have unsatisfactory charge distributions are shown in Fig. 14. Even the bridging character of the unique hydrogen on the apex boron arises naturally, even though it localizes approximately as a terminal hydrogen (15). This feature is also given by the non-vacancy structure of Fig. 15, but this valence structure does not predict the charge distribution in B$_5$H$_{11}$. Turning now to the bonding pattern, the 3113 hybrid (Fig. 13) indicates correctly that the bonding between apical B and the BH groups is stronger than the bonding between apical B and the BH$_2$ groups consistent with a striking asymmetry (15) of the two central three-center framework bonds of Fig. 12.

Fig. 12. Charges on BH and BH$_2$ groups, and in parentheses Mulliken charges on boron in B$_5$H$_{11}$.
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Fig. 13. Dominant (v=1) vacancy structures for $\text{B}_5\text{H}_{11}$. Two bridge hydrogens are displaced towards BH away from BH$_2$ groups, and the unique hydrogen on the apex BH interacts with either of the two BH$_2$ groups in the resonance hybrid of 3113 topology.

Fig. 14. Vacancy structures for $\text{B}_5\text{H}_{11}$ which are neglected because of large atomic charges. Also, vacancy structures are neglected if adjacent borons remain unbonded (not shown).

Fig. 15. Non-vacancy structure for $\text{B}_5\text{H}_{11}$ which accounts for the unique hydrogen interaction with BH$_2$ groups, but which does not account for other geometrical distortions (unsymmetrical bridges and BB distances).

$\text{B}_3\text{H}_8^-$

The styx equations for a non-vacancy compound $\text{B}_n\text{H}_{p+q}$ having BH, BH$_2$ or/and BH$_3$ groups hydrogen, and having charge c are $s+x = q+c$, $s+t = p+c-v$, and $t+y+q/2 = p-c$. The normal non-vacancy structure is the 2103 structure of Fig. 16(a). However, a localized molecular orbital study reveals a substantial interaction (0.57 e) of the single bond along the thin line of Fig. 16(b), leaving 0.74 e toward each B or the original "single" bond. This additional framework bonding displaces the bridge hydrogens away from the apex B as shown in Fig. 16b. This effect is described as a resonance hybrid in which the vacancy structure of Fig. 17 makes an appropriate contribution to the original valence structure of Fig. 16(a).

Fig. 16. Non-vacancy structures for $\text{B}_3\text{H}_8^-$ showing the three-center bond structure on the left, and the fractional bond structure on the right. The additional fractional interaction (thin line) tends to make the bridge hydrogens unsymmetrical.
III. LOCALIZED MOLECULAR ORBITALS

General Comments
Molecular orbitals of different symmetries can be linearly combined in such a way that either

$$\sum_{i} \phi_i(1) \phi_i(1) \frac{1}{r_{12}} \phi_i(2) \phi_i(2) dv_1 dv_2$$

(1)

is maximized (Edmiston and Ruedenberg (16)), or

$$\sum_{i} \phi_i(1) \phi_i(1) r_{12}^2 \phi_i(2) \phi_i(2) dv_1 dv_2$$

(2)

is minimized (Boys (17)). These procedures have been compared (18) in a number of boranes and carboranes. Without changing the total electron density, these procedures maximize the repulsive interactions of electrons within the same molecular orbital, and therefore approximate the chemists' localized electron pair bond in a totally objective way. In recent studies of all boranes and carboranes of known structures, we have obtained direct support for three-center bond descriptions, more detailed principles of bonding, and in complex examples descriptions which replace a large number of resonance hybrids. We now turn to a few examples.

Open and central three-center bonds
Alternative descriptions of the valence structure of \( \text{B}_5\text{H}_{11} \) are shown in Fig. 18. The ER localization yields the valence structure of Fig. 18b (more precisely that of Fig. 18b'), not the open three-center bond shown in Fig. 18a. In all localizations so far obtained by either the ER or Boys procedure, no open three center bond with boron as the central atom has been found. Hence, we no longer employ this description (19).

However, an example of a localized (ER procedure) open three-center bond occurs in \( 1,2-\text{C}_2\text{B}_4\text{H}_6 \). Here, the central atom is carbon (Fig. 19). A comparison of the localization by Boys' procedure is given below. Inasmuch as the charge distribution in the open three-center bond places one electron on the central atom, and one-half on each outer atom, we believe...
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that the extra nuclear charge of carbon, over that of boron, favors the open three-center bond over the central three-center bond in some carboranes.

Single bond donation to adjacent atoms. When a single bond occurs within a boron framework like that shown in Fig. 20, the localization procedures usually show additional donations to adjacent atoms. In $B_4H_{10}$ almost 0.2 e is donated to each of $B_1$ and $B_4$ (Fig. 21), which are partly relatively electron deficient because of the charge distribution in the BHB bridge bonds. These hydrogen bridges then become unsymmetrical, as described above, in such a way that the hydrogens are displaced toward $B_2$ and $B_3$. Two other simple examples are shown (20) in $B_8H_{13}^-$ (Fig. 22) and in $B_9H_{14}$ (Fig. 23). Electron withdrawal along other bonds occurs away from the atom which is the recipient of the single bond donation. This donor property of single bonds is quite general in triangulated polyhedral molecules and their fragments among boranes and carboranes.
Fractional three-center bonds. Electron withdrawal noted above, coupled with single bond donation, often gives rise to another general feature of localized orbitals: fractional three-center bonds (Fig. 24). While fractional bonds (the dotted lines) appear to enlarge the number of bonds at B₁ (Fig. 24), the exclusion principle is not violated, because of the fractional occupancy of the valence atomic orbitals at B₁. We note a similar behavior in the carboxylate group (Fig. 25) in order to convince the reader that these fractional bonds are not limited to boron chemistry.

In 4,5-C₂B₄H₈ two fractional bonds (21) to B₂ are a preferred alternative (Fig. 26) to a resonance hybrid of a single bond (e.g. B₁B₃) and a central three-center bond (e.g. B₁B₂B₆).

**Fig. 23.** Single bond donation in B₈H₁₄⁻. Usually this donation causes some electron withdrawal along the other bonds to the atom receiving a donation.

**Fig. 24.** In the localized molecular orbital description two fractional electron pair bonds (right) replace a resonance hybrid (in parenthesis) of a single bond and a central three-center bond.

**Fig. 25.** Localized molecular orbitals in a carboxylate anion, showing four equivalent fractional bonds to carbon from the two oxygens. The equivalent resonance hybrid is in parentheses.

**Fig. 26.** Localized orbitals in 4,5-C₂B₄H₈, showing two equivalent fractional bonds to B₂.
In B$_{10}$H$_{14}$ the same feature of two fractional bonds occurs at B$_6$, and again at B$_9$ in the preferred description (Fig. 27c). A similar feature occurs in the B$_{10}^-$ ion, at B$_2$ and B$_4$.

Pairs of fractional bonds are also found by Boys' localization procedure at two boron atoms in 1,2-C$_2$B$_4$H$_6$ (Fig. 28b), and at two boron atoms in 1,7-C$_2$B$_{10}$H$_{12}$ (Fig. 29, right). However, the Edmiston-Ruedenberg localization procedure, which we prefer, yields the alternative of open three-center bonds through each carbon atom in 1,2-C$_2$B$_4$H$_6$, and probably would yield the valence structure of Fig. 29 (left) if and when a similar calculation, involving all two-electron integrals, is economically feasible.

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**Fig. 27.** Localized orbitals in B$_{10}$H$_{14}$ showing fractional bonds (c), which are preferred over the four equivalent resonance structures (b), and are much preferred over the nearly equivalent description having open three-center bonds (a). The diagram below shows the essential idea.

**Fig. 28.** An ambiguity in localization in 1,2-C$_2$B$_4$H$_6$, in which the Edmiston-Ruedenberg procedure yields (a), while the Boys procedure yields (b). The parts of the molecule which differ are idealized in (c) and (d), respectively.

**Fig. 29.** Localization by Boys' procedure (right) gives fractional bonds (dotted lines) in 1,7-C$_2$B$_{10}$H$_{12}$. The Edmiston-Ruedenberg procedure would probably give the preferred valence structure (left) having open three-center bonds through carbon.
The B₅H₉ molecule shows an ambiguity in localization which is frequent, and almost typical, in a molecule having an axis of higher than two-fold symmetry. There is actually a continuum of localized structures, rotationally equivalent by an arbitrary displacement around the high symmetry axis: all of these valence structures are equally preferred (Fig. 30). This continuum of structures is present in the r systems of the 4n+2 cyclic aromatic molecules CₙHₙ of appropriate charge (22).

More complex molecules
In C₂B₁₀H₁₃⁻ (Fig. 31) we have a simple pattern of localization predicted (23) to have little fractional bonding.

The 1,2-C₂B₁₀H₁₂ structure (Fig. 32) obtained by Boys' procedure has two fractional bonds at a boron in two places in the molecule, and has a valence structure which is like that of 1,7-C₂B₁₀H₁₂ except for orientation and identity of atoms.

The next most complex example, iso-B₁₈H₂₂ (Fig. 33), shows both fractional
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bonding, and single bond donation. This single bond donation is greater
toward the relatively deficient boron atom B9 which has two bridge hydrogens.

A remarkable example of single bond donation is shown in the localized
orbitals of B20H16 (Fig. 34), where each half of the molecule has clearly
the reduced B10 framework of B10H14−2 (Fig. 35).

A somewhat more complex example is that of B16H20 (Fig. 36) where the
valence structure is dominated by the three-center bonding pattern, modified
by single bond donation and by associated electron withdrawal along
the dotted legs of the appropriate three-center bonds. However, a new
feature is that atoms B11 and B12 are connected only by single bond
donation. Even so, the structure is closely related to a more standard
three-center bond description: for example, removal of all dashed lines
and dashed arrows in the B6 (upper right) fragment leaves single bonds
B10H16 and B9H13, and leaves central three-center bonds B11B12B13 and
B11B12B16. Similar adjustments make the bonding in the remainder of the
molecule rather like that (20) in B10H13−, and somewhat like that in
B10H14−2.

Finally, in B10H10−2, two unique, non-symmetric localized molecular orbital
structures are found (24), corresponding to different bonding
patterns. In B20H18−2 and in photo-B20H18−2, both of which have fragments
like that in B10H10−2, one of these unique structures is found in
B20H18−2 and the other in photo-B20H18−2. The choice of which unique
structure occurs is governed by the placement of bridging boron atoms
in B20H18−2, and by the positions of the bridge hydrogens in photo-B20H18−2.

Fig. 34. In B20H16, where B17, B18, B19 and B20 have no terminal hydrogens, the non-
donation model has a vacant orbital on each of atoms B11, B12, B15, B16, B10, B13
and B14 (left). Substantial single bond donation remedies
this deficiency, and is also present from single bonds B1B2
and B3B4 (right).

Fig. 35. Non-donation structure (right) for
B10H14−2 having open three-
center bonds, for comparison with the non-
donation structure of
B20H16 (right, Fig. 34). The valence structure
obtained from localized
molecular orbitals is shown
on the right for comparison
with B20H16 (left, Fig. 34).

Fig. 36. B16H20 has a complex
pattern of localized molecular
orbitals, dominated by single bond
donation, as denoted by arrows,
accompanied by withdrawal of electrons from atoms B3, B6, and B11.
Note that the solid arrows donating
to B11 represent the only connec-
tion between B11 and B12. Complex
as this pattern is, it replaced
the hybrid of 216 central three-
center valence structures by a
single preferred valence structure.
III. COMMENTS ON REACTIONS

BH₃ addition. In a theoretical study (25) of dimerization of two BH₃ molecules to make B₂H₆, the symmetrical addition (Fig. 37) was strongly favored over the unsymmetrical formation of one H₂BH•••BH₃ bridge.

![Fig. 37. Geometry of approach of two BH₃ units to make B₂H₆. At this stage the distortion of BH₃ is not very great. As the hydrogen closest to the other boron begins to donate electrons, there is simultaneous donation from the symmetrically related closest hydrogen to the other boron atom.](image)

This unfavorable unsymmetrical addition appears to be rather like the weak addition of H₂ to BH₃ in order to form BH₅ as discussed above. Symmetrical addition is favored, in our interpretation, because, as donation of electrons occurs along one B•••H approach, a reverse donation occurs along the symmetrically related H•••B approach between different BH₃ groups.

Addition of BH₃ to transient species, such as B₃H₇ or B₄H₈ is probably analogous, yielding B₄H₁₀ and B₅H₁₁. Moreover, a similar addition of BH₃ to more stable boron hydrides can be envisioned with the use of the dominant vacant orbital valence structures. If we assume that BH₃ adds to a pair of boron atoms, one of which has a vacancy, such that vacancy structures yield a dipole whose group charges are large, then predicted sites of addition are shown in Table 1. Steric factors, more complex reaction pathways and other factors have not yet been taken into account. Similarly, when vacancy structures place a large positive group charge on one boron it is a candidate for ligand, e.g. hydride ion, attack (Table 1). This simple use of vacancy structures will be examined in more detail in a forthcoming publication (26).
Table 1. Sites\textsuperscript{a} for predicted addition reactions from vacant orbital theory

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Vacancy sites for addition of H\textsuperscript{−}, based on boron group charges\textsuperscript{b}</th>
<th>Boron pair sites, for BH\textsubscript{3} addition\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B_4H_{10})</td>
<td>(B_3) --- \textsuperscript{d}</td>
<td>(B_1) and (B_4)</td>
</tr>
<tr>
<td>(B_5H_9)</td>
<td>(B_1,B_2) (B_1,B_2)</td>
<td>(B_1) and (B_2)</td>
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<tr>
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<tr>
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<td>(B_3) (B_2*,B_3*,\textsuperscript{f})</td>
<td>(B_2) and (B_3)</td>
</tr>
<tr>
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<td>(B_2) (B_2,B_3,B_6)</td>
<td>(B_1) and (B_2); (B_1) and (B_6)</td>
</tr>
<tr>
<td>(B_8H_{12})</td>
<td>(B_1,B_3) (B_1,B_2,B_3*)</td>
<td>(B_2) and (B_3); (B_3) and (B_4)</td>
</tr>
<tr>
<td>(B_8H_{13})</td>
<td>(B_6) (B_1,B_6,B_7*)</td>
<td>(B_6) and (B_7)</td>
</tr>
<tr>
<td>n-(B_9H_{15})</td>
<td>(B_9) (B_3*,B_6,B_9)</td>
<td>(B_1) and (B_3)</td>
</tr>
<tr>
<td>(B_9H_{14})</td>
<td>(B_1) (B_1,B_2,B_3*)</td>
<td>--- \textsuperscript{d}</td>
</tr>
<tr>
<td>(B_{10}H_{14})</td>
<td>(B_6) (B_6,B_7)</td>
<td>---</td>
</tr>
<tr>
<td>(B_{10}H_{14}^-)</td>
<td>--- (B_{10}B_{10})</td>
<td>(B_9) and (B_{10})</td>
</tr>
<tr>
<td>(B_{10}H_{13}^-)</td>
<td>(B_6,B_9) (B_5,B_6*)</td>
<td>(B_7) and (B_8)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Unique sites only are given. The unconventional numbering is that of Epstein and Lipscomb, Reference 19.

\textsuperscript{b} Hydride ion attack may occur at the boron for which (before H\textsuperscript{−} is added) a vacancy structure predicts a vacant orbital and a positive charge of at least +0.83e, regardless of the charge on the boron in the companion non-vacancy structure. Because addition may also be likely at sites with less extreme charges, we also report vacancy sites which exhibit charges of 0.67e.

\textsuperscript{c} BH\textsubscript{3} addition is predicted to occur between a pair of borons which, in a vacancy structure, includes one vacancy center, and whose charges represent a dipole of at least +0.67e\textsuperscript{−}.

\textsuperscript{d} A dashed line indicates that no sites are favored for addition.

\textsuperscript{e} Those sites marked by an asterisk(*) are part of boron pair sites for BH\textsubscript{3} addition. They may be less favored for H\textsuperscript{−} addition because of their proximity to a -0.67e charge on a neighboring boron.

\textsuperscript{f} Where more than one site exists, the borons are listed in numerical order, not in order of probability of addition.
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