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EFFECTS OF ORBITAL VACANCIES IN BORON COMPOUNDS

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Abstract - Addition of H_2 to BH_3 yields BH_5, which is shown to be of C_s symmetry. Rearrangement mechanisms and hydrogen loss have been examined.

Intermediates such as B_3H_7 and B_4H_8 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 BH_3 may be expected to add. A study of diborane formation indicates favoritism for simultaneous H···B and B···H reaction of compounds of the two distinct BH_3 reactants. Reactions of BH_3 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 ($^1\Sigma_+$). 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 3σ 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.

BH_3

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 BH_3CO. Theoretical studies are consistent with the planar D_{3h} structure. We now turn to a very weak adduct between BH_3 and H_2.

BH_5

When BH_4D is produced by reaction (4) of BH_4^- with D_3O^+ 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 BH_4D decomposes (A candidate for this second possibility is that D remains at the apex of tetragonal

pyramidal BH_4D). We shall strongly favor the first possibility (a). First we examine geometries for BH_5 (Fig. 1), then internal rearrangements, and

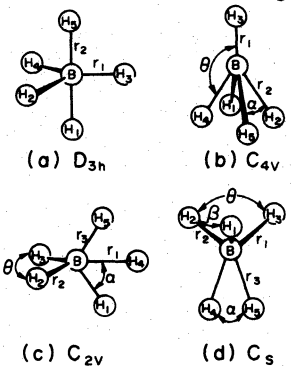


Fig. 1. Four plausible structures for BH_5: (a) D_{3h}, where H_1BH_5 is collinear, r_1 = 2.252 au and r_2 = 2.280 au; (b) C_{4v} with H_3B along the four-fold axis, r_1 = 2.172 au, r_2 = 2.287 au, θ = 117.3°, α = 77.9°; (c) C_{2v} where the two-fold axis is along H_4B, r_1 = 2.492, r_2 = 2.191 au, r_3 = 2.370 au, θ = 123.0°, α = 56.0°; (d) C_s (I and III) where H_1B lies in the symmetry plane: $r_1=r_2=r_3$ = 2.280 au, θ = 106.8°, α = 46.6°, β = 116.4° for C_s(I), and r_1 = 2.192 au, r_2 = 2.205 au, r_3 = 2.807 au, θ = 115.4°, α = 32.1°, β = 117.4° for C_s(III).

then ask which hydrogens are lost as H_2 from the theoretical point of view. At the 431G (SCF) level, energies in au are -27.386 for D_{3h}, -27.403 for C_{4v}, -27.423 for C_{2v}, -27.427 for C_s(I), -27.454 for C_s(III), and -27.476 for BH_3+H_2. While the C_s(III) structure is the most "stable," it is not in a minimum at the SCF level, where BH_5 is unstable with respect to BH_3+H_2. Our estimate (5) of corrections for electron correlation predicts only marginal stability for BH_5 (relative to BH_3 and H_2), and more detailed molecular orbital studies by others (6,7) have predicted that BH_5 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 H_2. All of these theoretical studies favor the C_s geometry (Fig. 1(d)), like that predicted earlier (8) for CH_5^+.

Of course, if the incoming D^+ converts BH_4^- to the C_s structure of BH_5 one may expect loss of HD. The experimental evidence is furthermore consistent with a small amount of scrambling in BH_4D, and mechanisms for this process are implicit in the structures of Fig. 1. A study of the pathway (5) indicates that the C_{2v}, C_s and C_{4v} structures are good transition states for interconversion of the C_s structures (Figs. 2 and 3). Barriers pre-

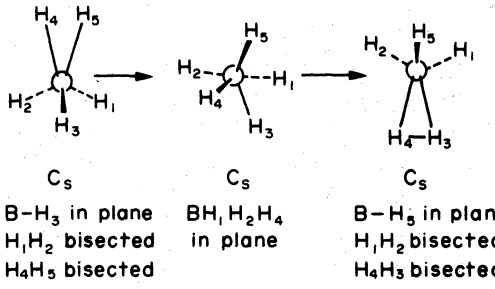


Fig. 2. One plausible pathway for internal rearrangement of BH_5 passes through the C_s intermediate in which H_5 and H_3 are related to the axial positions of a hypothetical trigonal bipyramid of even higher energy.

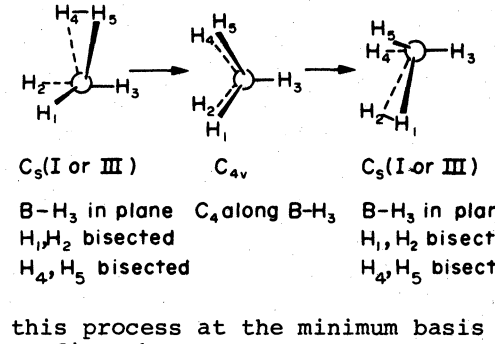


Fig. 3. In the C_{4v} intermediate the equivalent axial positions of the less stable trigonal bipyramidal BH_5 are either H_2 and H_5 or H_1 and H_4.

dicted for this process at the minimum basis set level are 20 kcal/mole if the intermediate has C_{2v} or C_s symmetry and 30 kcal/mole if the intermediate has C_{4v} symmetry. Experimental studies of the gas phase exchange of D_2 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 HBF_2 with D_2 has an activation energy

of 18 kcal/mole (10), and probably does proceed through a multicentered molecular orbital between HBF_2 and D_2.

In predicting which pair of hydrogen atoms is lost from these structures, it is sufficient to refer all to trigonal bipyramidal BH_5 of D_{3h} symmetry. Overlap populations are 0.04 e for axial-equatorial, -0.05 e for axial-axial and -0.07e 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 C_{4v}, C_{2v} or C_s symmetries. For example, in the tetragonal pyramidal C_{4v} 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 BH_4^- 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 H_2 from two adjacent basal positions. Hence, the observed loss of HD leads one to favor two equivalent positions as shown in Fig. 4.

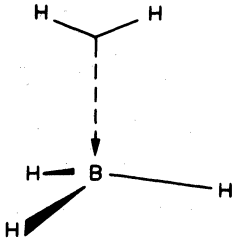


Fig. 4. Simplified valence description of bonding in BH_5, showing donation of the H-H bond into the vacant orbital of a slightly pyramidal BH_3 group.

Very different experimental results are obtained (11) when excess solid $NaBH_4$ is treated with anhydrous D_2SO_4 or DF (or isotopic inverses) in a bomb at -78°. Essentially statistical results are found, typically almost 60% H_2, 40% HD (plus 2% D_2). Perhaps the reaction occurs at a crystal surface, or the BH_4D 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 B_pH_{p+q}, and if there are v vacant valence orbitals, then

$$s + x = q$$
$$s + t = p - v$$
$$t + y = p - q/2$$

s for BHB bonds
t for BBB bonds
y for BB bonds
x for BH_2 number

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 B_4H_8 by Dupont and Schaeffer (12). For example, formulas for B_4H_8 are 4020, 2202 and 3111 for v=0, 3021, 2122 and 1203 for v=1, and 2022, 1113 and 0204 for v=2. For B_3H_7 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.

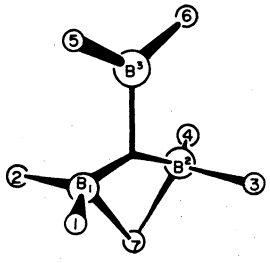
B_2H_4

The 2010 topology has two BH groups joined by two bridge hydrogens and by a single (pure π) 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_2 groups joined by a single B-B bond, and therefore each boron has a vacant orbital (π relative to the H_2B-plane). We find (13) that the staggered conformer (D_{2d}) is more stable by 13 kcal/mole than the eclipsed (D_{2h}) conformer. A previous result, at the 6-31G level, also favors D_{2d} over D_{2h}, by 11 kcal/mole (14). The staggered conformer has a hyperconjugative interaction between the vacant orbital on each boron with the π component of the localized molecular orbital on the adjacent BH_2 group. No such stabilizing interaction can occur in the planar (D_{2h}) form.

B_3H_7

At the minimum basis set SCF level the 1103 (staggered) structure (Fig. 5) is 12 kcal/mole more stable than the 2102 structure for B_3H_7.



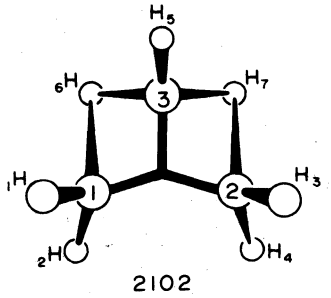
1103 ST

Fig. 5. In the 1103 (staggered) structure for B_3H_7 there is a central three-center BBB bond. The less stable 1103 (eclipsed) form has the planar $B_3H_5H_6$ group rotated by 90° about the $B_3 \cdots H_7$ axis which is the molecular two-fold axis.

The 1103 (eclipsed) structure is only 4 kcal/mole more stable than the 2102 structure. Actually, these structures are very closely related: if H_7 is moved away from B_2 the 2102 structure is almost that of 1103 (staggered) if we take identifications as B_2(2102) ——> B_3(1103 ST), and B_1 or B_3 of 2102 as B_1 or B_2 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 B_3H_7. 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 $2BH_3$ to B_2H_6 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



2102

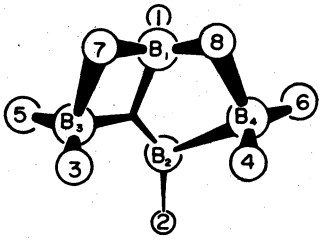
Fig. 6. In the 2102 structure for B_3H_7 there is a central three-center BBB bond. Geometrical optimization places H_6 and H_7 closer to B_3 than to B_1 and B_2, respectively, and makes the structure intermediate between 2102 and 0104 (BH_3 joined to two BH_2 groups by a central three-center BBB bond).

counting the central three-center BBB bond, is less stable than the 1103 ST structure (Fig. 5), which has at B_3 a vacant orbital which is only partly filled by the hyperconjugative interaction with the two BH_2 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.

B_4H_8

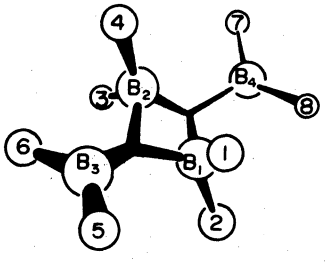
Only structures having a two-fold element of symmetry (plane, center or two-fold axis) have been considered here. The C_s 2112 structure (Fig. 7), which has one vacant orbital is slightly preferred energetically, as compared to the closely related D_{2h} 0204 ST structure (Fig. 8) which has two vacant orbitals and no bridge hydrogens. We did not study the intermediate 1203 structure (of C_1 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 C_2 2202 structure actually refined, upon



2112

Fig. 7. In the (slightly) preferred C_s 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.



0204 ST

Fig. 8. The 0204ST structure for B_4H_8 is not preferred over the 2112 structure, but is more stable than the 0204 EC structure (both BH_2 groups rotated by 90°) by 21 kcal/mole in our calculations (minimum basis set - CI level).

geometry optimization to a D_{2h} 0204 structure as the bridge hydrogens became more and more asymmetric. In the slightly favored C_s 2112 structure, hyperconjugative factors mostly from π orbitals (local) of atomic triads, $H_5B_3H_3$ and $H_4B_4H_6$, probably help in stabilizing the vacant orbital on B_2 (Fig. 7). 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

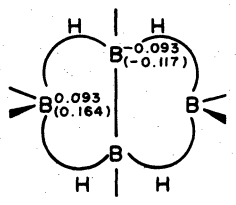
General Comments

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.

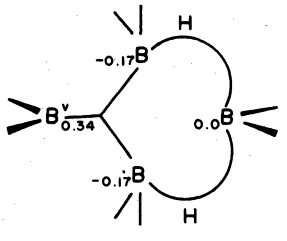
B_4H_{10}

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.



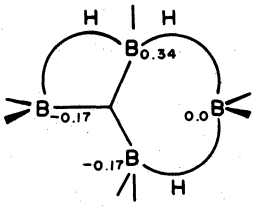
B_4H_{10} 4012

Fig. 9. Charges on BH and BH_2 groups, and in parentheses Mulliken charges on boron in B_4H_{10}.



2104

Fig. 10. The dominant (v=1) vacancy structure for B_4H_{10}. Bridge hydrogens are displaced towards the BH groups in this resonance hybrid of two equivalent valence structures.

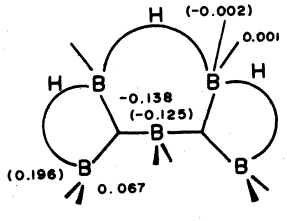


B_4H_{10} 3103

Fig. 11. A non-vacancy valence structure which also is consistent with displacement of bridge hydrogens toward the BH groups in B_4H_{10}.

B5H11

The bridge hydrogen asymmetries, B-B interactions and charge distributions in B_5H_{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_5H_{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.



B_5H_{11} 3203

Fig. 12. Charges on BH and BH_2 groups, and in parentheses Mulliken charges on boron in B_5H_{11}.

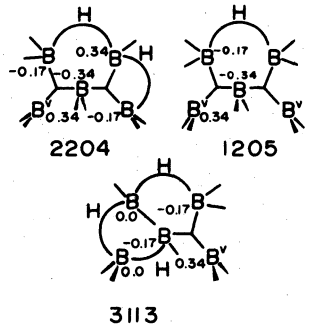


Fig. 13. Dominant (v=1) vacancy structures for B_5H_{11}. Two bridge hydrogens are displaced towards BH away from BH_2 groups, and the unique hydrogen on the apex BH interacts with either of the two BH_2 groups in the resonance hybrid of 3113 topology.

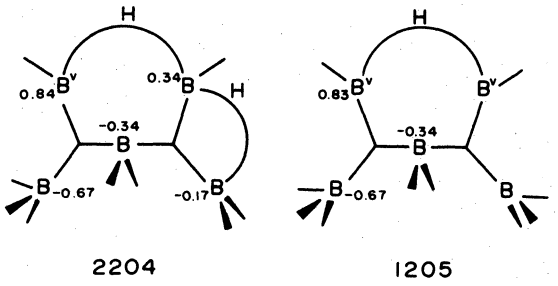


Fig. 14. Vacancy structures for B_5H_{11} which are neglected because of large atomic charges. Also, vacancy structures are neglected if adjacent borons remain unbonded (not shown).

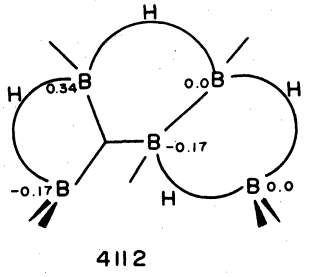


Fig. 15. Non-vacancy structure for B_5H_{11} which accounts for the unique hydrogen interaction with BH_2 groups, but which does not account for other geometrical distortions (unsymmetrical bridges and BB distances).

$B_3H_8^-$

The styx equations for a non-vacancy compound $B_pH_{p+q}^c$ 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).

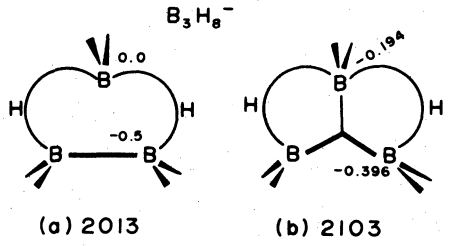


Fig. 16. Non-vacancy structures for $B_3H_8^-$ showing the three-center bond structure on the left, and the fractional bond structure on the right. The additional fractional interaction (thin line) tends to make the bridge hydrogens unsymmetrical.

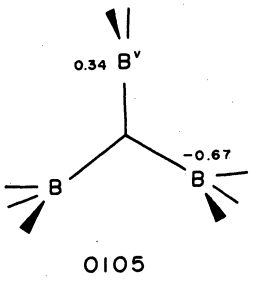


Fig. 17. Vacancy structure for $B_3H_8^-$ in which the bridge hydrogens are displaced. Compare with Fig. 16.

III. LOCALIZED MOLECULAR ORBITALS

General Comments

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

$$\Sigma\int\int\phi_i(1)\phi_i(1)\ \frac{1}{r_{12}}\ \phi_i(2)\phi_i(2)dv_1dv_2 \qquad (1)$$

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

$$\Sigma\int\int\phi_i(1)\phi_i(1)\ r_{12}^2\ \phi_i(2)\phi_i(2)dv_1dv_2 \qquad (2)$$

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 B_5H_{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).

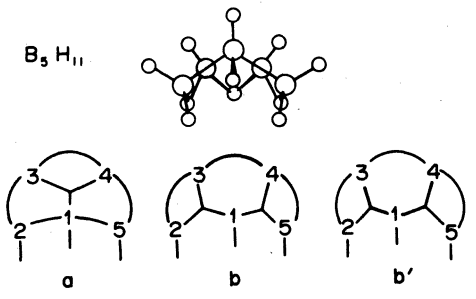


Fig. 18. Structure of B_5H_{11}. (a) Open three-center bond structure not favored by localization of molecular orbitals. (b) Favored valence structure as conventional central three-center bonds. (c) Decreased interactions of central three-center bonds toward outer BH_2 groups, from localized orbitals. One terminal hydrogen has been omitted from each boron atom in the valence structures.

However, an example of a localized (ER procedure) open three-center bond occurs in 1,2-$C_2B_4H_6$. 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

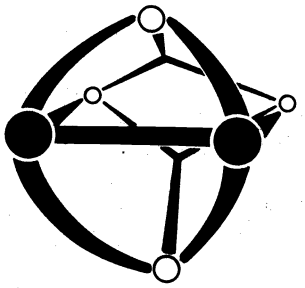


Fig. 19. Open three-center bonds through carbon atoms (black) in $1,2\text{-}C_2B_4H_6$. The six hydrogen atoms have been omitted for simplicity.

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_8H_{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.

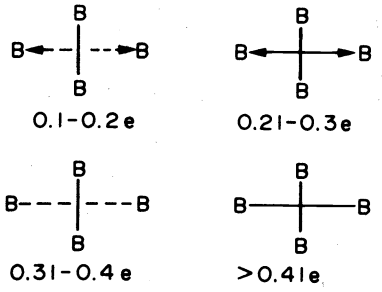


Fig. 20. Symmetrical single bond donation toward adjacent atoms, showing notation for amounts of donation of the original electron pair of the single bond. In many cases, the donation is unsymmetrical.

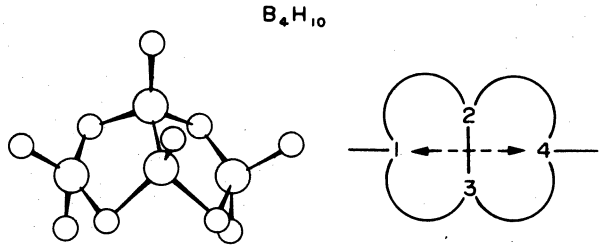


Fig. 21. Donation of 0.19 e to each BH_2 group from the "single" bond in B_4H_{10}.

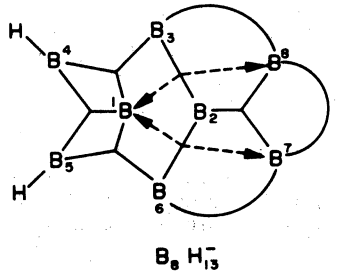
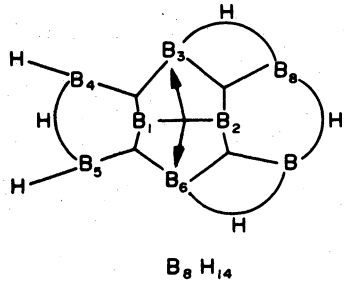


Fig. 22. Single bond donation in $B_8H_{13}^-$.



B_8H_{14}

Fig. 23. Single bond donation in $B_8H_{14}^-$. Usually this donation causes some electron withdrawal along the other bonds to the atom receiving a donation.

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 B_1 (Fig. 24), the exclusion principle is not violated, because of the fractional occupancy of the valence atomic orbitals at B_1. 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-$C_2B_4H_8$ two fractional bonds (21) to B_2 are a preferred alternative (Fig. 26) to a resonance hybrid of a single bond (e.g. B_1B_3) and a central three-center bond (e.g. $B_1B_2B_6$).

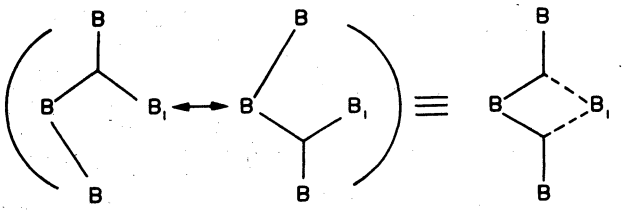


Fig. 24. In the localized molecular orbital description two fractional electron pair bonds (right) replace a resonance hybrid (in parenthesis) of a single bond and a central three-center bond.

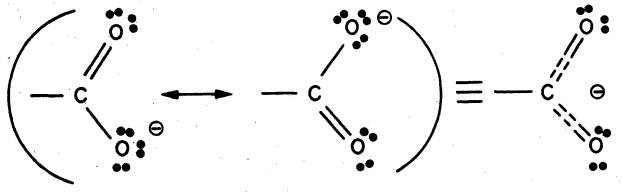
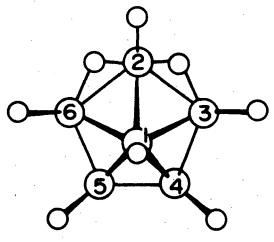


Fig. 25. Localized molecular orbitals in a carboxylate anion, showing four equivalent fractional bonds to carbon from the two oxygens. The equivalent resonance hybrid is in parentheses.

4,5-$C_2B_4H_8$



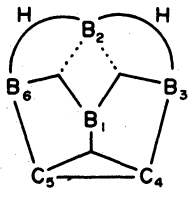


Fig. 26. Localized orbitals in 4,5-$C_2B_4H_8$, showing two equivalent fractional bonds to B_2.

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 $B_{10}H_{14}^{-2}$ 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-$C_2B_4H_6$ (Fig. 28b), and at two boron atoms in 1,7-$C_2B_{10}H_{12}$ (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-$C_2B_4H_6$, 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.

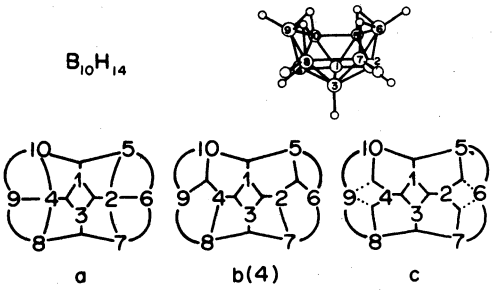
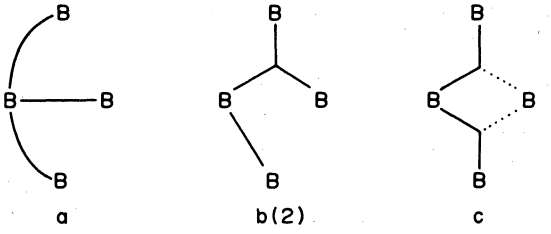


Fig. 27. Localized orbitals in $B_{10}H_{14}$ showing fractional bonds (c), which are preferred over the four equivalent resonance structures (b), and are much preferred over the nearly equivalent description having open three-center bonds (a). The diagram below shows the essential idea.



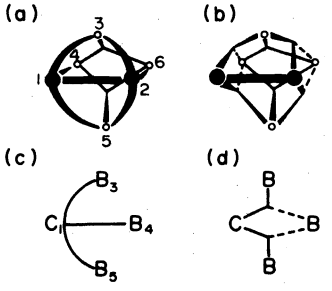


Fig. 28. An ambiguity in localization in 1,2-$C_2B_4H_6$, in which the Edmiston-Ruedenberg procedure yields (a), while the Boys procedure yields (b). The parts of the molecule which differ are idealized in (c) and (d), respectively.

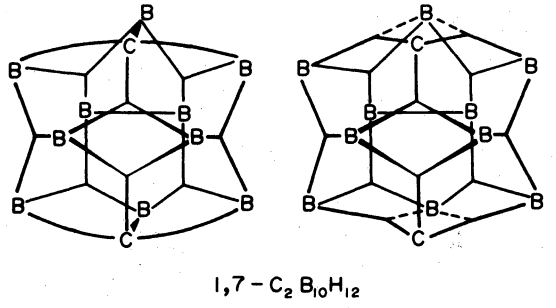


Fig. 29. Localization by Boys' procedure (right) gives fractional bonds (dotted lines) in 1,7-$C_2B_{10}H_{12}$. The Edmiston-Ruedenberg procedure would probably give the preferred valence structure (left) having open three-center bonds through carbon.

The B_5H_9 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 π systems of the 4n+2 cyclic aromatic molecules $C_nH_n^c$ of appropriate charge (22).

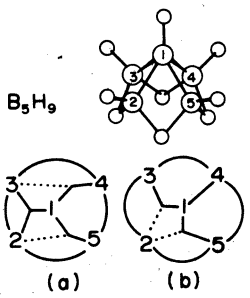


Fig. 30. Orientational ambiguity in the localized valence structures for the three pairs of electrons in the four-fold B_5H_9 framework orbitals. A continuum of valence structures, all equally preferred, lies between the extremes (a) and (b).

More complex molecules

In $C_2B_{10}H_{13}^-$ (Fig. 31) we have a simple pattern of localization predicted (23) to have little fractional bonding.

The 1,2-$C_2B_{10}H_{12}$ 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-$C_2B_{10}H_{12}$ except for orientation and identity of atoms.

The next most complex example, iso-$B_{18}H_{22}$ (Fig. 33), shows both fractional

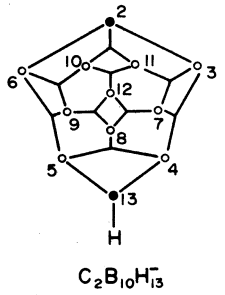


Fig. 31. Localized orbitals in the near-polyhedral $C_2B_{10}B_{13}^-$ ion. This especially simple localization in a complex species shows little significant fractional bonding.

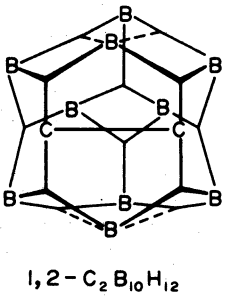


Fig. 32. Localized orbitals (Boys procedure) in 1,2-$C_2B_{10}H_{12}$, showing two fractional bonds to each of two boron atoms. Except for identities of atoms (and a back to front orientation) this valence structure is like that for the Boys localization in 1,7-$C_2B_{10}H_{12}$ (Fig. 29, right).

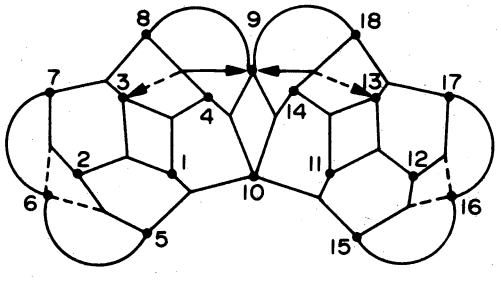


Fig. 33. The iso-$B_{18}H_{22}$ molecule, in which B_{10} has no terminal hydrogen shows fractional pairs of bonds to B_6 and to B_{16}, and shows single bond donation from B_4B_8 and from $B_{14}H_{18}$ as indicated by arrows.

bonding, and single bond donation. This single bond donation is greater toward the relatively deficient boron atom B_9 which has two bridge hydrogens.

A remarkable example of single bond donation is shown in the localized orbitals of $B_{20}H_{16}$ (Fig. 34), where each half of the molecule has clearly the reduced B_{10} framework of $B_{10}H_{14}^{-2}$ (Fig. 35).

A somewhat more complex example is that of $B_{16}H_{20}$ (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 B_{11} and B_{12} 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 B_6 (upper right) fragment leaves single bonds $B_{10}H_{16}$ and B_9H_{13}, and leaves central three-center bonds $B_{11}B_{12}B_{13}$ and $B_{11}B_{12}B_{16}$. Similar adjustments make the bonding in the remainder of the molecule rather like that (20) in $B_{10}H_{13}^{-}$, and somewhat like that in $B_{10}H_{14}$.

Finally, in $B_{10}H_{10}^{-2}$, two unique, non-symmetric localized molecular orbital structures are found (24), corresponding to different bonding patterns. In $B_{20}H_{18}^{-2}$ and in photo-$B_{20}H_{18}^{-2}$, both of which have fragments like that in $B_{10}H_{10}^{-2}$, one of these unique structures is found in $B_{20}H_{18}^{-2}$ and the other in photo-$B_{20}H_{18}^{-2}$. The choice of which unique structure occurs is governed by the placement of bridging boron atoms in $B_{20}H_{18}^{-2}$, and by the positions of the bridge hydrogens in photo-$B_{20}H_{18}^{-2}$.

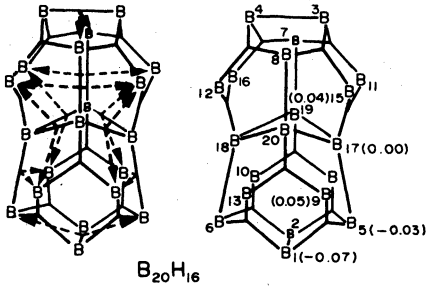


Fig. 34. In $B_{20}H_{16}$, where B_{17}, B_{18}, B_{19} and B_{20} have no terminal hydrogens, the non-donation model has a vacant orbital on each of atoms B_{11}, B_{12}, B_{15}, B_{16}, B_9, B_{10}, B_{13} and B_{14} (left). Substantial single bond donation remedies this deficiency, and is also present from single bonds B_1B_2 and B_3B_4 (right).

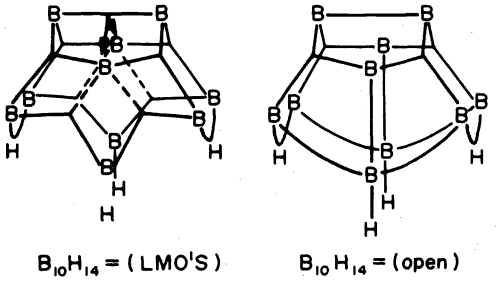


Fig. 35. Non-donation structure (right) for $B_{10}H_{14}^{-2}$ having open three-center bonds, for comparison with the non-donation structure of $B_{20}H_{16}$ (right, Fig. 34). The valence structure obtained from localized molecular orbitals is shown on the right for comparison with $B_{20}H_{16}$ (left, Fig. 34).

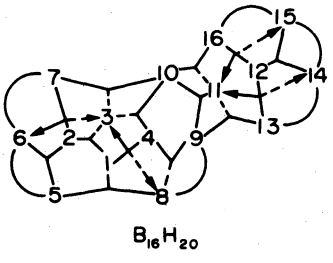
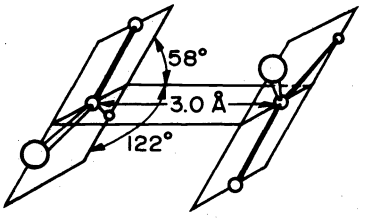


Fig. 36. $B_{16}H_{20}$ has a complex pattern of localized molecular orbitals, dominated by single bond donation, as denoted by arrows, accompanied by withdrawal of electrons from atoms B_3, B_8, and B_{11}. Note that the solid arrows donating to B_{11} represent the only connection between B_{11} and B_{12}. 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

BH_3 addition. In a theoretical study (25) of dimerization of two BH_3 molecules to make B_2H_6, the symmetrical addition (Fig. 37) was strongly favored over the unsymmetrical formation of one $H_2BH\cdots BH_3$ bridge.



Symmetry C_{2h}

Fig. 37. Geometry of approach of two BH_3 units to make B_2H_6. At this stage the distortion of BH_3 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.

This unfavorable unsymmetrical addition appears to be rather like the weak addition of H_2 to BH_3 in order to form BH_5 as discussed above. Symmetrical addition is favored, in our interpretation, because, as donation of electrons occurs along one $B\cdots H$ approach, a reverse donation occurs along the symmetrically related $H\cdots B$ approach between different BH_3 groups.

Addition of BH_3 to transient species, such as B_3H_7 or B_4H_8 is probably analogous, yielding B_4H_{10} and B_5H_{11}. Moreover, a similar addition of BH_3 to more stable boron hydrides can be envisioned with the use of the dominant vacant orbital valence structures. If we assume that BH_3 adds to a pair of boron atoms, one of which has a vacancy, such that vacancy structures yield a dipole whose groups 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[a] for predicted addition reactions from vacant orbital theory

Molecule or Ion	Vacancy sites for addition of H^-, based on boron group charges[b]		Boron pair sites for BH_3 addition[c]
	⩾0.83e	0.67e	
B_4H_{10}	B_3	---[d]	B_1 and B_4
B_5H_9	B_1,B_2	B_1,B_2	B_1 and B_2
B_5H_{11}	B_4	B_4*,[e]	B_4 and B_5
B_6H_{10}	B_3	B_2*,B_3*,[f]	B_2 and B_3
B_6H_{12}	B_2	B_2,B_3,B_6	B_1 and B_2; B_1 and B_6[f]
B_8H_{12}	B_1,B_3	B_1,B_2,B_3*	B_2 and B_3; B_3 and B_4
$B_8H_{13}^-$	B_6	B_1,B_6,B_7*	B_6 and B_7
n-B_9H_{15}	B_9	B_3*,B_6,B_9	B_1 and B_3
B_9H_{14}	B_1	B_1,B_3,B_6	----[d]
$B_{10}H_{14}$	B_6	B_6,B_7	----
$B_{10}H_{14}^=$	----	B_{10}*	B_9 and B_{10}
$B_{10}H_{13}^-$	B_6,B_9	B_5,B_6*, B_7,B_8, B_9	B_7 and B_8

[a] Unique sites only are given. The unconventional numbering is that of Epstein and Lipscomb, Reference 19.

[b] Hydride ion attack may occur at the boron for which (before H^- 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.

[c] BH_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 $\pm 0.67e^-$.

[d] A dashed line indicates that no sites are favored for addition.

[e] Those sites marked by an asterisk(*) are part of boron pair sites for BH_3 addition. They may be less favored for H^- addition because of their proximity to a -0.67e charge on a neighboring boron.

[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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