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EXTENSIONS OF THE VALENCE THEORY OF BORON COMPOUNDS

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Use of three-center bonds in the more open boron hydrides, ions and derivatives, and of molecular orbitals in the more compact polyhedral-like compounds has yielded[1, 2] descriptions of known compounds, predictions of new molecular and ionic species, and interpretations of some intermediates in reactions and tautomerization. Some extensions here of these ideas are (1) an accounting of the bonding in the new type of boron hydride, $B_{10}H_{16}$, (2) a fuller statement than heretofore given of the substitutional invariance of the valence theory, (3) a second principle of polymerization, besides that shown in $B_{10}H_{16}$, and (4) structural proposals for expected molecular species heretofore incompletely described or overlooked.

Bond Accounting.—The recent discovery of a new type[3] of boron hydride, intermediate between the borides and previously known boron hydrides, introduces a kind of B atom which has no terminal H atoms attached. Let r be the number of such B atoms, let p be the number of B atoms which have at least one terminal H atom, and let x be the number of additional H atoms in excess of one terminal H on all B atoms of the molecule or ion. If the formula of the species of charge c is $B_r B_p H_{p+q+c}{}^c$, then the hydrogen, orbital, and electron balances give the equations

$$s + x = q + c$$
$$s + t = p + r + c$$
$$t + y = p + 3r/2 - c - q/2$$

where there are s bridge H atoms, t three-center BBB bonds, and y two-center BB bonds. In the form given above, the formula of $B_{10}H_{16}$ is $B_2 B_8 H_{8+8+0}{}^0$, and the resulting equations of balance are $s + x = 8$, $s + t = 10$, and $t + y = 7$. One of the solutions ($s = 8$, $t = 2$, $y = 5$, and $x = 0$) corresponds to the three-center bond description of this known molecule. If x is the number of extra H atoms in addi-

tion to the H of the BH group, this formulation also describes species having BH_3 groups, such as $B_2H_7^-$ which presumably is H_3BHBH_3 ($r = 0, p = 2, q = 6, c = -1$) with a possibly unsymmetrical three-center BHB bond. For this ion the values $s = 1, t = 0, y = 0, x = 4$ satisfy the appropriate equations $s + x = 5$, $s + t = 1$, and $t + y = 0$.

Topological Invariance.—The description of valence and structure of all presently known derivatives of boron hydrides and their ions can be reduced either to the above description or to the molecular orbital description of the hydrides and ions. This reduction, a kind of topological invariance, is of several types, including (1) the replacement of H^- by L where L is an electron pair donor ligand, such as $N(CH_3)_3$, (2) the replacement of H by D, a halogen, an alkyl group or an aryl group, (3) the replacement of a bridge H atom by XR_2 to be bonded then by two X—B bonds, where X is N or P and R is H, an alkyl group or an aryl group, (4) the replacement of a three-center bonded H^- by a three-center bonded CH_3^-, for which there are no known boron compounds, and (5) the substitution of heteroatoms in the boron framework, e.g., C for B^-, Be for B^+, N for B^{-2}, Al for B, etc.
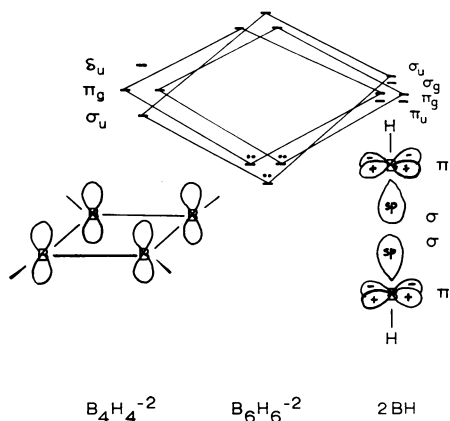

FIG. 1.—Simplified description of bonding in $B_6H_6^{-2}$. Each B of planar $B_4H_4^{-2}$ forms three bonds in the molecular plane. Energy levels of the π system are shown above. Only the σ_u and π_g molecular orbitals of $B_4H_4^{-2}$ are of appropriate symmetry to combine with linear combinations of corresponding symmetry from the two BH groups. Thus three electron pairs are required in addition to the four B—B bonds, making a total of seven pairs for boron-boron bonding in the octahedral $B_6H_6^{-2}$ ion.

Consider C as the heteroatom to be substituted for the isoelectronic B^-. The most stable species would be related to the most stable and compact polyhedral ions[4-7] ($B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$) or to the predicted $B_6H_6^{-2}$ and $B_5H_5^{-2}$ ions[4, 5, 8, 9] by replacement of one, two or more B^- by C. The species with higher symmetry are probably more stable, partly because these structures have the largest proportion of the comparatively more stable B—C bonds, but mechanism of formation may yield preferentially species with C—C bonds in some instances. These compact polyhedral arrangements may yield possible positive ions, as yet unknown, which may be further stabilized by substitution of alkyl, aryl, or halogen for the terminal H atoms. Replacement of BH not involved as part of a BH_2 group or a BHB bridge may also be possible in such ions as $B_{10}H_{13}^-$, $B_{10}H_{14}^{-2}$ or in the expected $B_4H_7^-$, $B_9H_{14}^-$, $B_{10}H_{15}^-$ or $B_{10}H_{16}^{-2}$ ions. Next in order of stability might be the substitution of C for B^- at BH_2 groups not linked by BHB bonds. Finally, the relative instability of a BHC bridge may lead to a rearrangement, or to ionization of H^+ especially if the ion has a positive charge.

Furthermore, there may exist classes of heteroatom hydrides not included among the known polyhedral ions. Therefore, descriptions of molecular orbitals in new polyhedra and simplified descriptions of bonding in known polyhedra are useful. The $B_5H_5^{-2}$ (D_{3h}), $B_6H_6^{-2}$ (O_h), and $B_7H_7^{-2}$ (D_{5h}) ions may be used to illustrate these points. Remove the apical BH groups, thus leaving planar $B_3H_3^{-2}$, $B_4H_4^{-2}$, and $B_5H_5^{-2}$ units, which are treated by the usual molecular orbital methods employed for aromatic hydrocarbons. The in-plane bonding of each unit has 3, 4, and 5 single bonds, respectively, and there are two extra electrons left over for the molecular orbitals formed from the p_z orbitals. For each of these units one σ molecular orbital and one π pair of molecular orbitals exist, and these are combined with corresponding orbitals of the two BH units above and below the molecular plane, as shown in Figure 1 for $B_6H_6^{-2}$. The $B_3H_3^{-2}$ unit, prepared for bonding, has no δ orbital, while the single δ orbital in $B_4H_4^{-2}$ and the pair of δ orbitals in $B_5H_5^{-2}$ are not of appropriate symmetry to bond to the BH units. Hence the bonding of two BH units to $B_3H_3^{-2}$, $B_4H_4^{-2}$, or $B_5H_5^{-2}$ requires, in each case, three electron pairs as shown. Therefore $B_5H_5^{-2}$, $B_6H_6^{-2}$, and $B_7H_7^{-2}$ may exist each with a -2 charge in its most stable state.

In addition, there may exist classes of heteroatom hydrides not included among the known polyhedral ions. For example, one may press the analogy of the σ, π system in[10] $B_4H_7^-$, B_5H_9, and $B_6H_{11}^+$, not only to the series CB_3H_7, B_5H_9 and BeB_5H_{11},

FIG. 2.—Collapse of the B_{10} framework of $B_{10}H_{12}L_2$ (left) when $B_{10}H_{10}^{-2}$ (right) is formed. New contacts are formed between atoms 6 and 9, between 6 and 8, and between 5 and 9 as indicated by the dotted lines in the left-hand figure. Either the 7,10 pair or the 5,8 pair of boron atoms become apices of the $B_{10}H_{10}^{-2}$ polyhedron. Dr. M. F. Hawthorne has indicated to me that he has reached a similar conclusion.
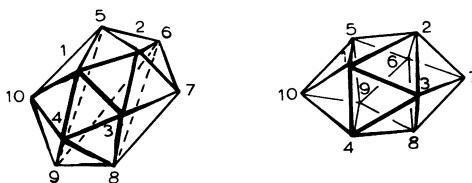
but into the aromatic series. For example, one can combine neutral BH with planar C_4H_4, which needs two more π electrons, to form HBC_4H_4 of C_{4v} symmetry. The analogues to the above series are then $HBC_5H_5^+$ and $HBC_3H_3^-$, of symmetries C_{5v} and C_{3v} respectively. The last compound is interestingly related by substitution of C for B^- to the very tentatively suggested[11] tetrahedral structure for cyclobutadiene.

Second Principle of Polymerization.—In addition to a direct B—B bond, known in $B_{10}H_{16}$ as well as in boron and the borides, the bridging of H atoms in various hydrides and ions suggests that stable units such as[6] $B_{10}H_{10}^{-2}$ or $B_{12}H_{12}^{-2}$ may be polymerized by linking of these polyhedra or their fragments through bridge H atoms. The electronic structure within each polyhedron is assumed to be retained in such polymers, and hence a formal way of describing the polymerization is to replace two B—H bonds, one from each polyhedron, by a BHB bridge. Formally this amounts to loss of H^-. For examples, two $B_{10}H_{10}^{-2}$ ions joined by one BHB bridge would give $B_{20}H_{19}^{-3}$ ion, two $B_{10}H_{10}^{-2}$ ions joined by two BHB bridges would give $B_{20}H_{18}^{-2}$ ion, an infinite number (x) of $B_{12}H_{12}^{-2}$ ions each joined to four others by BHB bridges would give a $(B_{12}H_{10})_x$ polymer which may further lose H_2 from 2BH to form direct B—B bonds. Linking of one or two BH_2 groups by bridge H atoms might result in $B_{11}H_{12}^-$ or $B_{12}H_{14}$ from $B_{10}H_{10}^{-2}$, or in $B_{13}H_{14}^-$ or $B_{14}H_{16}$
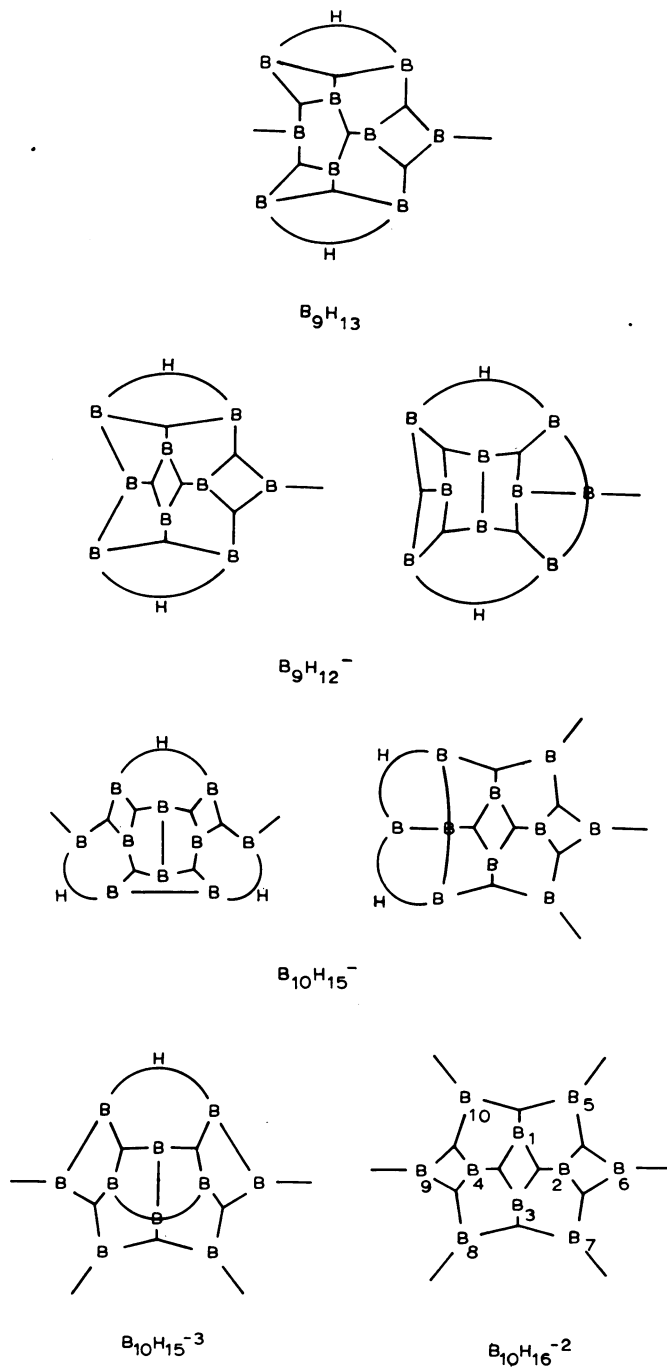
FIG. 3.—Proposed valence structures for the known $B_9H_{12}^-$ ion, and for unknown B_9H_{13}, B_{10}-H_{15}^{-3}, $B_{10}H_{16}^{-2}$, and $B_{10}H_{15}^-$.   One terminal H atom has been omitted from each B atom for simplicity.   Possibilities for H rearrangement (BH$_2$ to bridge H and BH) occur around the periphery of the negatively charged structures, and hence these structures are only representative, but they suggest the possibility of existence of ions or derivatives based upon these boron arrangements.   For example, the extra 6,9 protons on $B_{10}H_{16}^{-2}$ (0806) can easily become bridge H atoms to give a 2624 topological structure.

from $B_{12}H_{12}^{-2}$ as a result of similar application of this principle, but the BH_2 units may show instability.   In general, the linking of two polyhedra by a pair of bridges, rather than one, would be expected to yield more stable structures.   Such dimers or polymers might well occur for other negative ions, for various amine derivatives, heteroatom homologues, substitution derivatives, and in structures also containing B—B links between units.   Indeed, such a B–B bond may well be formed in solution by loss of H^+ to a Lewis base from BHB where only one such bridge occurs, e.g. in $B_{20}H_{19}^{-3}$ which might then take up protons elsewhere.

New Proposed Structures.—Overlooked in previous applications[12, 13] of the theory of three-center bonding in hydrides and ions are structures for B_9H_{13}, $B_{10}H_{15}^{-3}$, and $B_{10}H_{16}^{-2}$.   In addition, structures for $B_{10}H_{15}^-$ and $B_9H_{12}^-$, both referred to previously,[13, 14] are shown in full (Fig. 3).   A search for B_9H_{13} as distinct from the known B_9H_{15} molecule may be worth the effort.   The $B_{10}H_{15}^{-3}$ and $B_{10}H_{16}^{-2}$ structure may be related, by the L for H^- equivalence described above, to $B_{10}H_{14} \cdot 3$ Pyridine (e.g., $B_{10}H_{13}L_2^- \cdot LH^+$) and to $B_{10}H_{14} \cdot 2$ [2-Br Pyridine],[15] i.e., $B_{10}H_{14}L_2$. Indeed, the discovery of the $B_{10}H_{16}^{-2}$ formula in the valence theory was prompted by the unsolved question[16] of the H atom positions in a heavy atom derivative of a $B_{10}H_{14}L_2$ structure.

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