allow us to do the following: (1) rationalize the observed chemical reactivity of the *closo*-$B_nH_n^{2-}$ ions and explain the apparent violation of the skeletal counting rules by the principal B_nX_n cluster halides; (2) show in at least a semiquantitative way the extent to which an added skeletal electron pair (to $n + 2$ pairs) requires the opening of the cage core to the nido geometry, and predict the observed nido isomers by explaining the empirical rule in terms of the behavior of frontier electrons; (3) demonstrate the further opening of nido to arachno deltahedral fragments on the addition of one more skeletal pair (to $n + 3$ pairs), correctly predicting remote-atom removal for $X_nH_n^{q-}$ species with $n + 3$ skeletal pairs such as $C_5H_5^-$ and explaining the adjacent-B removal empirical rule for boranes by explicitly showing the role of bridging- and endo-hydrogen atoms in those systems.

The structures of B_nH_{n+4} and B_nH_{n+6} boranes reflect a balance between the stability conferred on the frontier electrons by opening the parent closo cluster to the greatest possible extent and the stability conferred on the cluster as a whole by closing the open face to permit most favorable overlap of the endo- and bridging-hydrogen atoms that are always present. For B_nH_{n+4} stoichiometry, the observed isomer is usually determined by the electronic stability factor, while for B_nH_{n+6} systems the observed isomer is usually determined by the hydrogen-overlap factor as modified by the necessity of finding suitable sites for six extra hydrogen atoms. The next paper in this series will deal explicitly with the way in which these "topological" EHMO calculations can be used to predict the number and geometric location of the bridging- and endo-hydrogen atoms.

Acknowledgment. Financial support from the SERC is gratefully acknowledged by K.W. and M.E.J., and W.W.P. thanks the Mednick Foundation for travel support.

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Extended Hückel MO Studies of Boranes. 4. Rationalization and Prediction of Endo- and Bridging-Hydrogen Positions in Nido and Arachno Systems

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Received August 28, 1989

An idealized form of extended Hückel calculations is presented that permits prediction of the sites of bridging- and endo-terminal-hydrogen atoms and the number of each type on boranes and their anions having stoichiometry equivalent to B_nH_{n+4} or B_nH_{n+6}. Calculations are performed on the $B_nH_n^{4-/6-}$ core framework, endo hydrogens are placed on atoms having net charge greater than about -0.9, and bridging-hydrogen atoms are placed over B-B bonds having total HOMO overlap populations that are positive. Because the presence of endo-hydrogen atoms can change the identity of the core HOMO, it is necessary to run a sequence of calculations for each core yielding a predicted endo-hydrogen atom in which protons are added progressively to the B_nH_{n+6} core until all sites are exhausted. Site exhaustion is indicated by (1) complete protonation of all edges of the cluster's open face, (2) negative total HOMO overlap population for each remaining unprotonated edge of the open face, or (3) net positive charge for the sum of the HOMO overlap population and the net charge of the two atoms forming the B-B bond. Twenty-four boranes (all those for which experimental hydrogen locations have been proposed) are considered, all but two of which yield correct predictions of the number and location of endo- and bridging-hydrogen atoms; two species (B_4H_{10} and $B_9H_{14}^-$) yield predominantly correct predictions. Some generalizations are offered on the basis of the calculations to indicate patterns of endo- and bridging-hydrogen location for B_n cores of given symmetry and boron atom connectivity.

The theoretical study of borane structures has had, over a number of years, two useful effects: it has enabled chemists to understand the unusual structures of these compounds and at the same time has helped to calibrate the theoretical structures used in order to predict chemical results. At various levels of ab initio molecular orbital calculation, it is now clear that the geometries and electronic energies of boranes can be quite accurately predicted,[1] and other MO approaches such as MNDO[2] have also been very successful in dealing with specific systems. In the three previous publications in this series,[3] we have shown that a geometrically simplified and idealized version of extended Hückel molecular orbital (EHMO) calculations can give at least a semiquantitative explanation of the relative stabilities of the *closo*-boranes and B_nX_n halides, and can account for the relative stabilities of *nido*- and *arachno*-borane isomers (where the calculations lead to a general understanding of the electronic reasons for isomer choice). Because of the degree of idealization of these EHMO calculations, they provide an essentially topological comparison of the different deltahedral geometries possible for boranes in general.

Unlike *closo*-boranes, *nido*- and *arachno*-boranes have more hydrogen than boron atoms, usually B_nH_{n+4} and B_nH_{n+6} respectively for the neutral molecules. The "extra" hydrogen atoms (between two and six depending on the species) are arranged around the open face of the B_nH_n deltahedral fragment, either as endo-terminal B-H bonds lying more or less in the sphere of the cluster boron atoms or as BHB bridges lying over the edges of the open face. Part 3 of this series has shown that these endo- and bridging-hydrogen atoms dictate the isomer choice for *nido*- and *arachno*-boranes by stabilizing isomers for which these hydrogen atoms form a single island on the cluster sphere. Here we show that, for a given $B_nH_n^{q-}$ core, the numbers of endo- and bridging-hydrogen atoms can be predicted, along with their location around the open face of the cluster.

Although for a specific B_nH_n stoichiometry ab initio calculations can predict the location of endo- and bridging-hydrogen atoms quite well (as in ref 1), there has been only modest interest in developing general rules for the locations of these hydrogen atoms that would depend only on cluster core geometry or cluster-core MO's. Chemists use the empirical rules developed by Williams,[4] which rely on the coordination number of the boron atoms around

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(1) Many systems have been studied; some useful examples are as follows: (a) Guest, M. F.; Hillier, I. H. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 2004. (b) McKee, M. L.; Lipscomb, W. N. *Inorg. Chem.* **1982**, *21*, 2846. (c) Ott, J. J.; Gimarc, B. M. *J. Comput. Chem.* **1986**, *7*, 673. (d) Fowler, P. W. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 61.

(2) Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 5231; *Inorg. Chem.* **1978**, *17*, 1569.

(3) Part 1: Porterfield, W. W.; Gill, W. R.; Jones, M. E.; Wade, K. *Inorg. Chem.*, first of four papers in this issue. Part 2: Porterfield, W. W.; Jones, M. E.; Wade, K. *Inorg. Chem.*, second of four papers in this issue. Part 3: Porterfield, W. W.; Jones, M. E.; Wade, K. *Inorg. Chem.*, third of four papers in this issue.

(4) (a) Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210. (b) Williams, R. E. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67.

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the open face and, to some extent, on steric arguments. Although these generalizations are useful, they do not have a clear theoretical basis, which this paper seeks to provide. There have also been calculations at EHMO,[5] MNDO,[6] and ab initio[7] levels directed toward an understanding of the positions of bridging protons in existing boranes or of protons added to boranes in real or hypothetical proton-affinity experiments. To the extent these calculations have experimental comparison, they have been successful, but they do not offer a general insight into positions of endo- and bridging-hydrogen atoms. We shall show that our topologically idealized EHMO calculations provide a semiquantitative basis for the prediction of the numbers and locations of these and on the basis of our survey will offer modifications of Williams' rules that explain and add to them from a quantum-mechanical basis.

Method of Calculation

All calculations were performed on deltahedral fragments consisting of equilateral triangles whose edges (B–B bonds) were 1.70 Å long. Each boron atom had one exo-radial-hydrogen atom at a distance of 1.19 Å, oriented radially from the center of mass of the parent closo deltahedron. When endo-hydrogen atoms were included in the calculation, they were also at a distance of 1.19 Å from the appropriate boron atom and oriented in general so as to maintain maximum symmetry and lie near the surface of the B_n cluster sphere. When bridging hydrogen atoms were included in the calculation, they were placed 1.30 Å from each of the two boron atoms being bridged, with the BHB plane lying at a dihedral angle of 20° to the adjacent BBB face unless this yielded unacceptable crowding. This degree of bending in toward the center of the open face is fairly typical of experimental observations.[8] In addition, we have shown in part 3 of this series that this dihedral angle is necessary in order to rationalize the bridging/endo structure choices for the $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$ systems with the same B_{10} core. All deltahedral fragments were assumed to retain the B_nH_n core coordinates characteristic of the hypothetical closo parent deltahedron, without relaxation toward increased symmetry.

All the species dealt with had stoichiometry corresponding to $n + 2$ or $n + 3$ skeletal electron pairs, and the initial calculations were performed on deltahedral fragments formulated as above without endo- or bridging-hydrogen atoms: $B_nH_n^{4-}$ or $B_nH_n^{6-}$ as appropriate, with the symmetry of the core cluster chosen to be that indicated experimentally (usually by X-ray diffraction or NMR spectra; see references to Table II). Bridging- and endo-hydrogen placement was assumed to be equivalent to the progressive protonation of this core cluster, with endo hydrogens representing protonation of high net negative charges on boron atoms in the cluster and bridging hydrogens representing protonation of positive B–B total overlap populations in the HOMO for bonds around the open face of the core cluster. These charges and overlap populations were obtained by using the Hoffmann FORTICON extended Hückel program.[9] Coulomb integrals were as follows: H 1s, 13.6 eV; B 2s, 15.2 eV; B 2p, 8.5 eV. No charge iteration procedures were applied. Net atomic charges were obtained directly from the program printout; total overlap populations for the bonds in the HOMO were obtained by summing the 16 individual AO populations for the two B atoms in the HOMO overlap population matrix. Since in these idealized geometries all bond lengths are fixed, variations in the overlap population will not be influenced by that variable and will presumably be more clearly related to the symmetries of the molecule and the orbital.

Consider first the placement of endo-terminal-hydrogen atoms. We assume that a proton adopting an endo placement is being attracted by a large negative charge on that boron atom. In EHMO calculations, net charges on radial-exo-hydrogen atoms will be slightly negative and nearly constant at about −0.25 regardless of the molecule's symmetry or overall charge. The calculated charges on boron atoms, however, vary widely with the coordination number of the boron atom, its symmetry within the molecule, and the overall charge on the cluster. For example, calculation on the $B_6H_6^{4-}$ cluster with the core symmetry of B_6H_{10} yields a charge of +0.3124 for the apical atom but −0.5625 for the basal atoms. Table I shows the most negative calculated charges for boron atoms in the core clusters for which experimental geometries are known, correlated with the presence and location of endo-hydrogen atoms. It can be seen that a single endo-hydrogen atom (a BH_2 group in the overall cluster) will be present on any boron atom whose net charge is calculated to be greater than about −0.9. Similarly, two endo-hydrogen atoms (a BH_3 group) will be present on any boron atom having a calculated net charge greater than about −1.85. The fact that there seems to be a charge threshold for endo protonation may explain the earlier theoretical observation[7] that $B_6H_{11}^+$ has a bridging basal proton even though the calculated negative charge is greater in that treatment for the apical boron atom.

Table I. Highest Calculated Net Atomic Charges for $B_nH_n^{q-}$ Clusters

					positions	
species	core cluster	charge	B atom position[a]	coord No.[b]	exptl. BH_3	exptl BH_2
$B_6H_{11}^-$	$B_6H_6^{6-}$	−1.98	1	2	1	
$B_7H_{12}^-$	$B_7H_7^{6-}$	−1.87	1	2	1	
B_4H_{10}	$B_4H_4^{6-}$	−1.81	1	2		1
$B_3H_8^-$	$B_3H_3^{6-}$	−1.79	1	2		1
B_9H_{15}	$B_9H_9^{6-}$	−1.77	1	2		1
B_5H_{11}	$B_5H_5^{6-}$	−1.71	2	2		2
B_6H_{12}	$B_6H_6^{6-}$	−1.40	1	2		1
$B_9H_{14}^-$	$B_9H_9^{6-}$	−1.03	3	3		3
$B_{10}H_{14}^{2-}$	$B_{10}H_{10}^{6-}$	−1.01	1	3		1
i-B_9H_{15}	$B_9H_9^{6-}$	−0.93	1	3		1
B_8H_{14}	$B_8H_8^{6-}$	−0.88	1	3		1 (semi-bridging)
$B_4H_7^-$	$B_4H_4^{4-}$	−0.78	1, 2	3		
$B_9H_{12}^-$	$B_9H_9^{4-}$	−0.76	1	3		
$B_6H_{11}^-$	$B_6H_6^{6-}$	−0.75	3	3		
B_4H_{10}	$B_4H_4^{6-}$	−0.72	2	3		
$B_7H_{12}^-$	$B_7H_7^{6-}$	−0.71	3	3		

[a] Position refers to diagrams in Table II. [b] Coord no. refers to B atom neighbors only.

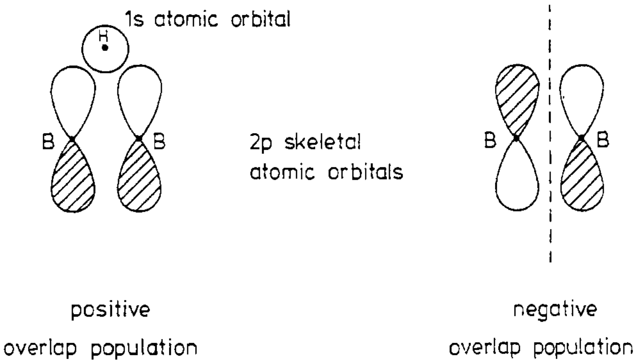

Figure 1. Relation between overlap population sign and the necessary orbital lobe symmetry for formation of a BHB bridging bond.

It is worth noting in Table I that there is a clear correlation between boron coordination number and net charge, with the atoms having the lowest coordination number showing the greatest calculated negative charge. This is consistent with the observation that endo-hydrogen atoms are always on the boron atoms surrounding the open face of the cluster, since those atoms will necessarily have lower coordination numbers.

It is clear from the data in Table I that few of the "extra" hydrogen atoms in boranes are endo terminal; most are bridging. Bridging protons will be attracted to the bonds having the greatest accessible electron density. The most accessible electrons are in the HOMO and for bridging purposes must be associated with a bond rather than with an atom. Accordingly, we expect bridging protons to be associated with deltahedral edges having high overlap populations, and because the HOMO is usually 75% or more on the open face of the deltahedral fragment,[3] we consider only those edges. It should be noted that either through symmetry or coincidence degeneracy of the HOMO can occur (accidental degeneracy being defined as a gap between the HOMO and its more stable neighbor that is on the order of *kT* at room temperature). When degeneracy is present, it is obviously necessary to consider electron availability from both orbitals.

Figure 1 indicates an important symmetry constraint on the availability of HOMO overlap electrons for bridging. Only if the sign of both boron atom lobes is the same will the formation of a three-center bridge bond be possible with a hydrogen atom having only a 1s orbital, and in the unprotonated B–B bond, this is associated with a positive overlap population. There is, of course, a symmetry problem for two boron atoms at arbitrary positions with respect to the molecular coordinate axes in that AO overlap is in general not as symmetrical with respect to the bond axis as the figure shows. We assume that this can be overcome by summing

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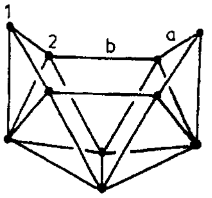
(5) (a) Evans, J. *J. Chem. Soc., Dalton Trans.* **1978**, 25. (b) Mitchell, G. F.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1017.

(6) (a) Brint, P.; Healy, E. F.; Spalding, T. R.; Whelan, T. *J. Chem. Soc., Dalton Trans.* **1981**, 2515. (b) Brint, P.; Sangchakr, B. *J. Chem. Soc., Dalton Trans.* **1988**, 105.

(7) DeKock, R. L.; Jasperse, C. P. *Inorg. Chem.* **1983**, *22*, 3843.

(8) Brill, R.; Dietrich, H.; Dierks, H. *Acta Crystallogr.* **1971**, *B27*, 2003.

(9) Howell, J.; Rossi, A.; Wallace, D.; Haraki, K.; Hoffmann, R. *QCPE No. 344*; Quantum Chemistry Program Exchange, Indiana University Chemistry Department: Bloomington, IN.



B_{10} core

	$B_{10}H_{10}^{4-}$	$B_{10}H_{10}^{6-}$
q_1 :	-0.5084	-1.0090
q_2 :	-0.1892	-0.3680
P_a :	+0.1397	-0.1930
P_b :	-0.0719	+0.1814

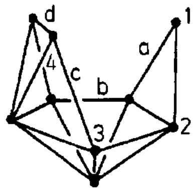
Figure 2. B_{10} core for $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$ and calculated atomic charges (q_i) and HOMO total overlap populations (P_m).

all the individual AO overlap populations for the HOMO to yield a single figure P_m, where m indicates the bond being considered on a structural diagram of the core. If P_m is positive, there is a net favorable lobal availability in the sense of Figure 1, and we propose that B–B bond to be an accessible bridging site. Pursuing the quantity a bit further, bridging will be more favorable the larger (more positive) P_m becomes. As discussion below will reveal, it seems to be generally true that bridging occurs for $P_m \geq +0.05$, but P_m rarely exceeds 0.2. This number is of course much smaller than the net charges proposed as thresholds for endo protonation, but it is precisely here that we should be reminded of the severely idealized geometry and the relatively crude character of calculations at the EHMO level. The numbers should be regarded as useful guidelines for protonation sites within a single cluster configuration, but cannot be compared with each other except in one very limited sense that will appear below.

As an example of the method of calculation, we may consider the two species $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$, whose energies for progressive protonation have already been considered in part 3 of this series of papers. The B_{10} core for these two species has the same point group and topological connectivity, and we can conveniently use the same EHMO calculation for each. Because in the EHMO approximation electron–electron repulsion is entirely subsumed in the Coulomb integral values for individual atoms, the MO energy levels and wavefunctions will be the same regardless of the net charge on the cluster. Figure 2 shows the calculated atomic charges q_i and total HOMO overlap populations P_m for these two cases, treating the core cluster as a $B_{12}H_{12}$ icosahedron with two adjacent BH units removed. From the $B_{10}H_{10}^{4-}$ values, we expect to see no endo-hydrogen atoms inasmuch as the greatest negative charge is only −0.5084, but by symmetry there are four bridging sites a (P_a = +0.1397) though bridging cannot occur at b because its HOMO overlap population is negative (P_b = −0.0719). On the other hand, from the $B_{10}H_{10}^{6-}$ values, we expect one endo-hydrogen atom at each of the two 1-positions (q_1 = +0.1814) but no bridging at any a site (P_a = −0.1930). We therefore expect the two stable protonated species to be $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$, which is correct. Furthermore, the experimentally determined sites of the four hydrogen atoms are in each case just what the guidelines have predicted.

If a calculation on a $B_nH_n^{q-}$ core cluster predicts the presence of endo-hydrogen atoms, their presence in the protonated cluster may stabilize the overall electron distribution in such a way as to change the symmetry of the HOMO and the location of suitable bridging sites. In general, therefore, it is necessary to perform a sequence of calculations: first, the core $B_nH_n^{q-}$ cluster; second, the same cluster with any endo hydrogens added as protons at the appropriate sites and P_m values reevaluated; third, the same cluster with symmetry-equivalent bridging hydrogens added as protons at the sites having the most favorable P_m and new P_m values obtained to guide the next stage of addition of bridging protons; and so on until protonation is complete.

As an example of this procedure, we may consider B_9H_{15}, whose core B_9 cluster is shown in Figure 3. The cluster has C_s symmetry, so that atom 1 and bond d are unique but the other atoms and bonds are mirrored on the other side of the open face. The results of the sequential calculation are also shown in Figure 3. In stage 1, the EHMO calculation is performed on the $B_9H_9^{6-}$ cluster, which has only exo-terminal-hydrogen atoms; it yields the prediction that atom 1 should have a single endo proton added. When this is done and the calculation run again (as stage 2), all boron atoms now have net charges too low to allow further endo protonation, but the two bonds at the a position have very favorable overlap populations and should be protonated. In stage 3, this new geometry yields a high HOMO overlap population for bond d, which should be protonated. This leads to stage 4, which in turn predicts that bonds c will be protonated, yielding the final B_9H_{15} stoichiometry with all hydrogen atoms in the experimentally determined positions. It should be noted that placement of an endo proton reduces the calculated net negative charge of the corresponding boron atom dramatically, by more than one charge unit. The placement of the endo proton out toward the center of the open face redirects electronic charge from B_1 out around the open face, as well as the obvious neutralization. Furthermore, the placement of a bridging proton over a given B–B bond sharply reduces the HOMO overlap population for that bond, because the Mulliken overlap population assignment redirects that electron density to B–H overlap more than the proton attracts additional density.



B_9 core cluster for B_9H_{15} symmetry

Stage 1: $B_9H_9^{6-}$, no endo or bridging H

q_1:	-1.7720 * 1 proton	P_a:	-0.0174
q_2:	-0.2532	P_b:	+0.0084
q_3:	-0.2881	P_c:	+0.0486
q_4:	-0.4779	P_d:	+0.1246

Stage 2: $B_9H_{10}^{5-}$, 1 endo H at atom 1

q_1:	(-0.5027)	P_a:	+0.1892 * 2 protons
q_2:	-0.2611	P_b:	-0.0571
q_3:	-0.2582	P_c:	+0.1150
q_4:	-0.4828	P_d:	-0.0381

Stage 3: $B_9H_{12}^{3-}$, 1 endo H at atom 1, 2 bridge H at bonds a

q_1:	(+0.0992)	P_a:	(+0.0177)
q_2:	+0.1306	P_b:	-0.0070
q_3:	-0.1554	P_c:	+0.0608
q_4:	-0.4152	P_d:	+0.3520 * 1 proton

Stage 4: $B_9H_{13}^{2-}$, 1 endo H at atom 1, 3 bridge H at bonds a and d

q_1:	(+0.0646)	P_a:	(+0.0480)
q_2:	+0.1490	P_b:	+0.0110
q_3:	-0.1559	P_c:	+0.1726 * 2 protons
q_4:	+0.0116	P_d:	(-0.0550)

*: most favorable protonation site
(): site already protonated

Figure 3. B_9 core for B_9H_{15} and calculated atomic charges q_i and HOMO total overlap populations P_m for stepwise protonation of $B_9H_9^{6-}$.

Results and Discussion

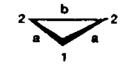
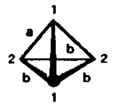
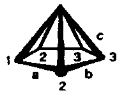
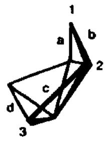
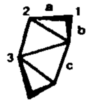
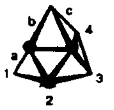
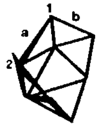
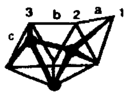
We can summarize the experience gained from Table I and the calculations on systems with bridging hydrogen atoms in the form of two rules for the placement of endo- and bridging-hydrogen atoms on *nido*- and *arachno*-boranes. At this stage, the rules rely directly on EHMO calculated parameters:

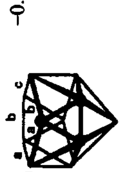
(1) If a deltahedral-fragment borane is modeled in terms of a B_n deltahedron with equal edges and an EHMO calculation is performed on the $B_nH_n^{q-}$ core of the borane cluster, the net atomic charges on the boron atoms will indicate the sites of endo-terminal-hydrogen atoms. If any boron atom has a net negative charge greater than −0.9, it will have an endo-hydrogen atom attached to it in the final cluster. If any boron atom has a net charge more negative than −1.85, it will have two endo-hydrogen atoms attached to it in the final cluster.

(2) Bridging-hydrogen atoms can be placed only over B–B bonds around the open face of a borane cluster that have a net positive total overlap population in the HOMO of the deprotonated system, and more readily over bonds having a significant total overlap population (greater than about +0.1).

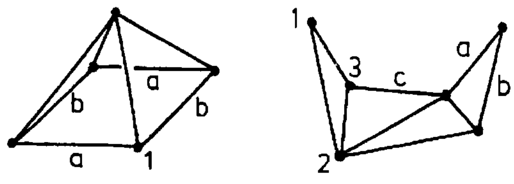
We have already noted that when degeneracy or accidental degeneracy of the HOMO occurs it is necessary to consider contributions from both orbitals to the HOMO total overlap population. These two effects are illustrated in the calculations on B_5H_9, which has symmetry-based true degeneracy, and B_9H_{12} which has accidental degeneracy. B_5H_5 is modeled as a nido octahedron, and the open face of its $B_5H_5^{4-}$ core cluster has 4-fold symmetry, leading to a doubly degenerate HOMO. If the four sides of the open face are labeled as in Figure 4, calculations give

Table II. B_nH_m Atomic Charges, Overlap Populations, and Hydrogen Sites

species	B_n core structure	q_1^a	q_2^a	q_3^a	q_4^a	P_a^b	P_b^b	P_c^b	P_d^b	predicted sites^b		obsd sites		refs
										E	B	E	B	
$B_3H_8^-$		−1.7941	−1.7941			+0.3105	−0.1677			1, 2, 2	a^2	1, 2, 2	a^2	12
$B_4H_7^-$		−0.7761	−0.7761			−0.0080	+0.3324				b^3		b^3	13
$B_4H_9^-/B_4H_{10}$		−1.8058	−0.7196			−0.0264 (+0.1700)				1, 1	(a^4)	1, 1	a^4	14, 15
$B_5H_8^-/B_5H_9$		−0.6273				+0.2167	+0.2167				a^2, b^2		a^2, b^2	16, 17
B_5H_{11}		−0.1282	−1.7072	−0.6133		+0.1582	+0.2223	+0.2084		2, 2	a, b^2, c	2, 2	a, b^2, c a^2, c?	10 16
$B_6H_9^-/B_6H_{10}/B_6H_{11}^+$		−0.5626	−0.5626	−0.5626		+0.1320	+0.1320	+0.1320			a^2, b^2, c		a^2, b^2 a^2, b^2, c	10b 11
$B_6H_{11}^-$		−1.9823	−0.2533	−0.7522		−0.1042	−0.0053	+0.2186	+0.4732	1^2	c^2, d	1^2	c^2, d	14
B_6H_{12}		−1.4016	−0.6525	−0.1848		+0.1678	−0.1151	+0.1321		1, 1	a^2, c^2	1, 1	a^2, c^2	18
$B_7H_{12}^-$[·Fe(CO)$_4$]		−1.8677	−0.2317	−0.7052	−0.4826	−0.0471	+0.1163	+0.0249		1^2	b^2, c^2	1^2	b^2, c^2	14, 19
B_8H_{12}		−0.4402	−0.2006			+0.1525	+0.0984				a^2, b^2		a^2, b^2	20
B_8H_{14}		−0.8789	−0.2158			+0.1572	+0.0705			1, 1, 1, 1	a^2	1, 1, 1, 1	a^2	21
$B_9H_{12}^-$		−0.7574	−0.2089	−0.3137		+0.1008	−0.0551	+0.1663			a^2, c		a^2, c	22
												3, 3, 4	a^2	23

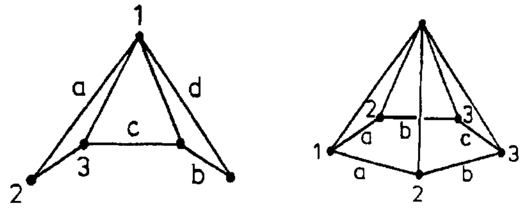
$B_9H_{14}^-$/*i*-B_9H_{15}		−0.9337	−0.2305	−1.0255	−0.2666	+0.1276	+0.1472	+0.1023		3, 3, 1	a^2, b^2, c^2		a^2, b^2, c^2	21
B_9H_{15}		−1.7720	−0.2532	−0.2881	−0.4779	+0.1892	−0.0070	+0.0608	+0.3520	1	a^2, c^2, d	1	a^2, c^2, d	24
$B_{10}H_{13}^-$/$B_{10}H_{14}$		−0.5084	−0.1892			+0.1397	−0.0719				a^4		a^3 a^4	25 26
$B_{10}H_{14}^{2-}$		−1.0090	−0.3680			−0.1930	+0.1814			1, 1	b^2	1, 1	b^2	27
$B_{11}H_{13}^{2-}$/$B_{11}H_{14}^-$		−0.3057				+0.0177	+0.2278	−0.1123			a^2, b^2		a^2, b^2	28
						+0.1339	−0.0164	+0.2638			a^2, c		a^2, c	29

[a] Calculated on $B_nH_n^{q-}$ without protonation. [b] Final prediction after allowing for sequence of protonation, degeneracy, and adjacent charges.



B_5 core for B_5H_9 B_6 core for B_6H_{12}

Figure 4. B_5 core for B_6H_9 and B_6 core for B_6H_{12}.



B_5 core for B_5H_{11} B_6 core for $B_6H_{11}^+$

Figure 5. B_5 core for B_5H_{11} and B_6 core for B_6H_{10}.

net atomic charges (which are independent of degeneracy) of −0.6273 for each of the four atoms, so that no endo-hydrogen atom should be present. One of the two degenerate HOMO's has P_a = +0.2167 and P_b = −0.1357, while the other HOMO has P_a = −0.1357 and P_b = +0.2167. The four edges are equivalent with respect to protonation because each HOMO can accommodate two protons. Figure 4 also shows the B_6 core of $B_6H_{12}^-$, which has only a C_2 rotation and cannot display true degeneracy. However, the calculation yields a HOMO with a calculated energy of −8.171 27 eV and a second HOMO with a calculated energy of −8.201 91 eV. The difference of 0.030 63 eV is only 1.2*kT* at room temperature, and presumably overlap electron density is available from both orbitals and bridge bonding. When the $B_6H_6^{6-}$ calculation is run as above, the net charge on atom 1 is −1.4016, indicating the presence of one endo hydrogen on each 1-atom. For the three symmetry-distinct edges, the total overlap populations for HOMO/2HOMO are P_a = −0.1338/+0.1399, P_b = −0.1097/+0.0293, and P_c = +0.1165/−0.0277. These values collectively indicate protonation at sites a and c, which is experimentally observed. Recalculations with the two endo-hydrogen atoms present makes little difference in this case. Accidental degeneracy still occurs, with E_{HOMO} = −8.741 78 eV and E_{2HOMO} = −8.780 36 eV, and the total overlap populations are P_a = +0.0131/+0.1678, P_b = −0.1151/+0.0236, and P_c = +0.1321/ +0.0169. These values still indicate protonation at the experimentally-verified sites a and c. Note that if only the HOMO were considered, protonation of the a site would be questionable.

We are also interested in the exhaustion of protonation sites and whether the sequential calculation stops at the correct point. In general, we observe that as protons are added to a core cluster with an initial charge of 4− or 6−, the net atomic charges will become steadily less negative or more positive and the HOMO total overlap populations will become slightly more positive. There is an obvious condition for site exhaustion, when calculation on a partially protonated core cluster yields no remaining unbridged edge with a positive HOMO total overlap population. However, there may also be circumstances in which even an unbridged B–B bond with a positive HOMO overlap population cannot be protonated for essentially electrostatic reasons. If the two atoms comprising the B–B bond have net atomic charges that are substantially more positive than the negative electronic charge associated with the HOMO overlap population, we can reasonably imagine that bridging will not occur. This pattern can be illustrated by consideration of B_5H_{11}, for which no protonated $B_5H_{12}^+$ species is known even though there is an unbridged edge on its open face, and B_6H_{10}, whose unbridged edge does protonate to $B_6H_{11}^+$. Figure 5 shows the core clusters for these species; note that for B_5H_{11} sides a and d are equivalent unless unsymmetrical protonation occurs.

Considering B_5H_{11} first, the EHMO calculation on the $B_5H_5^{6-}$ core yields net atomic charges $q_1 = -0.1281$, $q_2 = -1.7072$, and $q_3 = -0.6133$, indicating a single endo hydrogen on each 2-atom. Recalculation with these endo protons in place yields no q_i greater than −0.52 and the most favorable bridging site at c, with $P_c = +0.2084$. Adding this bridging proton and recalculating gives $P_b = +0.2223$, with all boron atoms still having a net negative charge. Adding two bridging protons at the b sites and recalculating takes us to the stoichiometry $B_5H_{10}^-$ with the following protonation-site data: $q_1 = -0.2268$, $q_2 = +0.0371$, $q_3 = +0.41922$, and $P_a = P_d = +0.1582$. Along the a bond, we have net atomic charges of −0.2268 and +0.0371 and an overlap density of 0.1582 electron. This is still electrostatically favorable in that it sums to a net negative charge. However, if we add only one more bridging proton at the a position and recalculate for what is now the neutral B_5H_{11} species, we find the following for the open bridging site along the d bond: $q_1 = -0.0017$, $q_2 = +0.1618$, and $P_d = +0.0934$. This does not sum to a net negative charge, and we therefore expect this edge to remain unbridged. Experimentally, the endo- and bridging-hydrogen sites are exactly what the above sequence of calculations has predicted, though the last hydrogen (here said to be bridging the a bond) is usually described as a "unique terminal" hydrogen[10]; it bridges bonds a and d asymmetrically, lying 1.07 Å from B_1 and 1.55 and 1.83 Å from the two B_2 atoms. We have idealized the geometry of the cluster, but the distances are fairly realistic: 1.30, 1.30, and 1.72 Å, respectively, for the last proton. It may be noted that the calculated net atomic charges would distort a proton from a symmetrical bridge position toward the observed position. Within our geometric description, we can say that there is one unbridged edge in B_5H_{11} that should be stable.

We can perform a comparable sequence of calculations on B_6H_{10}, also shown in Figure 5. The calculation on the $B_6H_6^{4-}$ core yields q_i for all atoms in the basal plane of −0.5626, indicating no endo hydrogens. The HOMO is 2-fold degenerate; if one orbital is arbitrarily chosen, the calculated overlap populations are $P_a = +0.0106$, $P_b = +0.2144$, and $P_c = -0.1155$. Adding two bridging protons at the b positions and recalculating, we observe that all basal atoms still have a net negative charge and the unbridged bonds have $P_a = +0.1227$ and $P_c = +0.2696$, so that it would appear that all five edges should protonate (to $B_6H_{11}^+$). However, if we protonate only the a sites in order to mimic the B_6H_{10} distribution of hydrogen atoms, the remaining unbridged c edge has both net atomic charges of +0.0014 and $P_c = +0.3507$ after recalculation. Since the overlap population of negative charge is substantially greater than the positive net atomic charges, we expect that protonation of the unbridged c edge could still occur. Experimentally, Shore and co-workers[11] have demonstrated that protonation can occur and that the added proton goes over the unbridged edge of B_6H_{10} to form the $B_6H_{11}^+$ product. It seems clear from these two examples that the sequence of calculations we describe does lead to the correct final stoichiometries as well as the locations of the endo- and bridging-hydrogen atoms on the clusters.

Table II summarizes the results of these sequential EHMO calculations on 24 boranes with B_nH_{n+4} or B_nH_{n+6} stoichiometry for which experimental studies have yielded proposed geometries for bridging- or endo-hydrogen atoms and for which the B_n core cluster geometry is known. The q_i values (net atomic charges) are obtained in each case from an EHMO calculation on the $B_nH_n^{4-/6-}$ core cluster with no endo- or bridging-hydrogen atoms present. On the other hand, the HOMO total overlap population values P_m are those obtained from the sequence of calculations above, with each reported P_m value being that obtained at the stage of calculation at which its protonation is predicted; negative values are those obtained at the last stage of protonation. The predicted sites of protonation take into account the necessity of sequential calculations, the effects of HOMO degeneracy, and the undesirability of protonating sites between positively charged atoms. E refers to endo-terminal-hydrogen atoms, B to bridging atoms. Examination of the table reveals that only B_4H_{10} and the $B_9H_{14}^-$/*i*-B_9H_{15} systems fail to protonate in the pattern indicated by the rules quoted at the beginning of this section. The wingtip positions of two endo hydrogens are correctly predicted for B_4H_{10}, but the HOMO resulting from recalculation with those two endo protons present does not yield a positive P_m for the four edges that are in fact bridged in the compound. The value in parentheses is P_a for the second highest occupied MO, which even under modest geometry variation is nearly $10kT$ away in the closest instance. For $B_9H_{14}^-$ the experimental structure has an endo hydrogen on the four-coordinate B_4 atom that is not predicted by our calculations; however, recalculation with three endo atoms present as indicated by experiment correctly predicts bridging hydrogens only at the a positions. Similarly, for *i*-B_9H_{15}, recalculations predict that all six edges of the open face will be protonated in bridging positions if no endo hydrogens are present, but the borderline values of q_i make it difficult to decide whether or not endo hydrogens should occur. This pair of borane species is the only example of a changed overall bridging/endo pattern on protonation of the same core cluster.

It is useful to be able to perform calculations that predict the sites of cluster hydrogen atoms, but it would be still more helpful to be able to draw generalizations from the series of calculations that would permit prediction of hydrogen sites from a knowledge of the core symmetry alone, without the need for calculation. We are not able to offer a complete scheme, but some patterns are clear from the data of Table II. The most immediate pattern is that no borane with nido stoichiometry (that is, B_nH_{n+4} or deprotonated ions with that skeletal electron count) will have endo-hydrogen atoms. In the context of our calculations, this is simply because a $B_nH_n^{4-}$ core cluster does not have a sufficiently high negative charge to give any one boron atom a sufficient negative charge accumulation. B_2H_6 is, in a sense, an exception to this statement, in that it has terminal BH_2 groups rather than BH groups, but it does not seem surprising that a dinuclear "cluster" should fail to follow rules developed on the basis of calculations on deltahedral clusters. Williams[4] has noted that "(i)n the nido species, endo-hydrogens are ... generally absent", but has not offered electronic reasons for the observation.

Once the symmetry and boron atom connectivity of the core cluster have been established, which EHMO calculations of this type permit,[3] some additional generalizations are possible. If we consider only boron neighbors in defining the coordination number of cluster boron atoms, observed coordination numbers ranging from 2 to 5. As Williams suggested, coordination number is a powerful determinant of endo- and bridge-hydrogen placement, and we can make several generalizations on that basis. First, any 2-coordinate atom in the core cluster will have at least one endo hydrogen attached. If it has two endo hydrogens, forming a BH_3 group, the adjacent B–B edges will not be bridged; in effect the BH_3 group will, as Shore[23] has suggested, be a bridging group

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for the remainder of the cluster structure. On the other hand, if the 2-coordinate boron has only one endo hydrogen attached, the adjacent B–B edges will normally be bridged, which gives what may be considered a chelating BH_4 group. Second, a 3-coordinate boron atom on the open face of the core cluster may or may not have an endo hydrogen attached, but never more than one. If a 3-coordinate boron does have an endo hydrogen, the adjacent B–B edges will not be bridged, and the boron will appear in the cluster simply as a BH_2 group. Finally, no boron atom with coordination number greater than 3 can have an endo hydrogen attached.

These generalizations on the occurrence of endo hydrogens are obviously related to the fact that EHMO calculations will tend to pile up negative charge on atoms of low coordination number. For a given skeletal geometry, skeletal MO's with increasing numbers of nodes will be most stable (hence below the HOMO and occupied) if those nodes pass near, but not through, a low-coordinate skeletal atom, because the low electron density that a node implies is no handicap if it does not occur between the two nuclei. The low-coordinate boron atom will thus be disproportionately represented in the occupied skeletal orbitals and will accumulate a high overall electron density and negative charge.

It is somewhat more difficult to offer generalizations about bridging hydrogen location. From the observed structures, it does seem clear that BHB bridges will usually involve a 3-coordinate boron atom. In particular, a bond around the open face between a 3-coordinate and a 4-coordinate boron atom will be bridged unless the presence of an endo hydrogen on the 3-coordinate boron prevents it. B–B bonds between two 4-coordinate boron atoms will be bridged only if there are no sites involving lower coordination numbers. Given the highly idealized geometric basis of our calculations, these generalizations seem to have essentially a topological origin in the nuclearity and symmetry of the core cluster, but we cannot adduce direct electronic reasons for our calculations.

In summary, the pattern of extended Hückel MO calculations presented in this series of papers is capable of predicting the occurrence of endo-terminal-hydrogen atoms in borane clusters and the number and location of both endo- and bridging-hydrogen atoms, given only the skeletal electron count and the geometric isomer of the core cluster (which can itself be predicted by these calculations). Although generalizations about these locations are possible, they do not reduce to rules as straightforward as the skeletal-electron-counting rules that have become central to cluster chemistry.

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Kinetics and Mechanism of the Reaction of Aqueous Copper(II) with Ascorbic Acid

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Received August 3, 1989

The oxidation of ascorbic acid by aqueous copper(II) has been studied under anaerobic conditions with $[Cu^{2+}]$ in the range $(1–5) \times 10^{-3}$ M, total ascorbic acid concentration of 5×10^{-5} M, and $[H^+]$ of $(0.50–10) \times 10^{-3}$ M in 1.0 M $NaClO_4/HClO_4$ at 25 °C. The kinetic effect of the chloride ion concentration in the range $(0.5–7) \times 10^{-3}$ M also has been investigated. The observed pseudo-first-order rate constant is given by $k_{obsd} = (a + b[Cl^-])[Cu^{2+}]/(K_a + [H^+])$ with $a = (4.0 \pm 0.13) \times 10^{-4}\ s^{-1}$ and $b = 0.58 \pm 0.036\ M^{-1}\ s^{-1}$. The results are discussed in terms of the probable mechanisms for the direct and chloride-catalyzed paths for the oxidation, and earlier results in the presence of acetate are reanalyzed.

Introduction

It has been known for many years that copper(II) oxidizes ascorbic acid under anaerobic conditions and catalyzes the oxidation of ascorbic acid by dioxygen. Most studies have concentrated on the copper(II)-catalyzed reaction with dioxygen and have paid limited attention to the direct copper(II)–ascorbic acid reaction although the latter may be an important initiation step and is an ever present background reaction.

The information on the rate law for the copper(II)-catalyzed reaction seems to be in some disarray. Khan and Martell[1,2] found the rate to be first order in $[O_2]$ and $[Cu^{2+}]$ with a pH dependence which indicated that both ascorbic acid (H_2A) and its conjugate base (HA^-) are kinetically active. The same dependence on $[O_2]$ had been found earlier by Barron et al.[3] and by Weissberger and co-workers.[4] Dekker and Dickinson[5] found an inverse second-order dependence on $[H^+]$. More recently, Jameson and Blackburn[6] found the rate law given by eq 1 with $k_r = 0.19$ (25 °C, 0.1 M KNO_3) and the results of Shtamm et al.[7] are in good agreement with $k_r = 0.13$ (25 °C, low ionic strength) although different chain mechanisms have been proposed to explain the results. The obvious difference between the latter two studies and that of Khan and Martell[1] seems to be that the total ascorbic acid concentration was larger than $[Cu^{2+}]$ in the latest studies.[6,7] In addition, Khan and Martell followed dehydroascorbic acid production, while Shtamm et al.[8] and Jameson and Blackburn[6] followed dioxygen loss and Shtamm and co-workers[7] also studied initial rates of Cu^+ formation. It should be noted that Jameson and Blackburn[9] have found a half-order dependence on ascorbic acid in 0.10 M KCl.

$$\text{rate} = k_r \frac{[Cu^{2+}][AH_2][O_2]^{0.5}}{[H^+]} \qquad (1)$$

Information on the direct reaction is not in a great deal better state. Shtamm et al.[7] have concluded, by extrapolation of the $[O_2]$ dependence data used to establish eq 1, that the direct reaction is insignificant relative to the Cu(II)-catalyzed O_2 reaction.

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