and to provide a quantitative confirmation of the empirical rule for isomer choice in nido clusters. Examination of the wave functions reveals that the relative energy of the possible nido isomers is closely correlated to the energy of the HOMO and that the HOMO is predominantly a ring of electron density around the open face of the nido cluster. This suggests that nido isomer choice may be dictated by the increased stability of the pair of electrons, originally associated with the missing BH unit, when it is allowed to spread out to a larger number of neighboring B nuclei. This is equivalent to the empirical rule favoring the removal of the BH unit having the largest coordination number in the closo cluster. The stability of nido and more open cluster fragments represents a balance between the stability of increased B-B bonding in more closed fragments and the stability of increased frontier electron attraction to more open-face B nuclei in a more open fragment. It may also be observed that the fundamental symmetry stability of the closo cluster influences the ease of opening it to nido or more open fragments.

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Extended Hückel MO Studies of Boranes. 3. Isomer Preferences of B_nH_{n+6} Species

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A series of extended Hückel molecular orbital (EHMO) calculations is reported for boranes with B_nH_{n+6} formulas, which are usually found to have arachno geometry. The EHMO calculations have been idealized to isolate energy effects due to changes in boron atom connectivity. The calculations are shown to correctly predict the opening of the deltahedral cage both from a closo parent and from the nido cluster framework described in the previous paper to yield an arachno fragment and quite generally to predict the correct arachno isomer if only isomers having adjacent BH units removed are considered. The origins of the adjacent-B rule for arachno isomers, well-known as an empirical observation, are seen to lie in the presence of edge-bridging- and endo-terminal-hydrogen atoms around the open face of the fragment. These hydrogen atoms stabilize a single open face in preference to two open faces, which is the core structure favored by the *arachno*-$B_nH_n^{6-}$ isomer generally. This result makes it clear why hydrocarbons (with no bridging-hydrogen atoms) that can be thought of as arachno fragments of deltahedra always favor planar structures (i.e., with two nonadjacent CH units removed), while electronically equivalent boranes favor structures more obviously derived from deltahedral clusters.

This paper continues the series of EHMO calculations described in parts 1 and 2 of this series, in which the triangulated geometry of generally deltahedral borane clusters is idealized to B-B bond lengths of 1.70 Å for all clusters regardless of nuclearity and fragments of deltahedra (as, for instance, the various nido and arachno isomers) are not allowed to relax their geometry from the closo B and H positions, even though increased symmetry might result from such relaxation. The earlier papers have shown that such calculations can reproduce the patterns of chemical reactivity of *closo*-$B_nH_n^{2-}$ ions and account for the preferred isomers of *nido*-B_nH_{n+4} species by showing that the frontier electrons are stabilized most for the observed isomers.

We now turn to the other major class of boranes, the B_nH_{n+6} species and their deprotonated anions. If we simplify the structures as for the nido species, each of these can be considered a $B_nH_n^{6-}$ anion, to be protonated as necessary to match the observed stoichiometry. The empirical rules for cluster structure[1,2] predict that such species, with $n + 3$ skeletal pairs of electrons, should have arachno structures with two vertices missing from the original parent closo deltahedron. The skeletal-electron rules themselves do not predict how the two missing vertices should be apportioned on the deltahedron, but empirical rules have been formulated[3,4] requiring the removal, first, of the most highly coordinated B atom to form the stable nido isomer and then of the most highly coordinated B atom on the nido open face to form the stable arachno isomer. The electronic reasons for the arachno rule are not obvious. Although part 2 of this series has demonstrated the electronic reasons for preferring removal of the most highly coordinated B from the closo deltahedron, electronic stability for removal of a second B should require that the most highly coordinated remaining B be taken. This will in general not be one of the atoms around the open face, but rather a remote vertex; thus, for the pentagonal-bipyramid B_7H_7, the first BH unit removed should be axial, but so should the second, leaving the planar pentagon as the favored arachno isomer. This is indeed observed for $C_5H_5^-$ with 5 + 3 skeletal electron pairs, but not for B_5H_{11}, also with 5 + 3 skeletal pairs, which is an open pyramid following the empirical rule above. Our "topological" EHMO calculations will show that cluster symmetry alone favors the removal of remote vertices (as in $C_5H_5^-$) and that the influence of the extra nonradial endo-terminal- and bridging-hydrogen atoms is the determining feature of arachno isomer selection for B_nH_{n+6} boranes and their anions.

Method of Calculation

The previous two papers have described the approach of this series of calculations. To avoid the variation of electron-electron repulsion energies between clusters, we limit the calculations to the level of extended Hückel theory. All clusters are assumed to be complete or fragments of ideal deltahedra with edges (B-B bonds) 1.70 Å long, regardless of cluster nuclearity. Each cluster is taken to be $B_nH_n^{q-}$ for purposes of initial calculation, with the n hydrogen atoms arranged as terminal B-H bonds radial from the center of mass of the closo parent and 1.19 Å long. When one or two BH units are removed from a closo cluster, the remaining atoms are not permitted to relax toward higher symmetry. This restriction helps to isolate electronic energy effects that are due to atomic connectivity alone and also tends to maintain uniform cross-cage interactions.

For the series of boranes and anions considered here, the net charge q is taken as 6- regardless of the true degree of protonation. However, as will be shown, it is necessary to explicitly include the stabilization of the arachno cluster by the endo- and bridging-hydrogen atoms. When endo-hydrogen atoms were included in the calculation, they were also placed 1.19 Å from the appropriate B nucleus, near the boron atom sphere and symmetrically disposed relative to adjacent bonds. Bridging hydrogen atoms were placed 1.30 Å from each of the two bridged boron nuclei, either in the plane of the B_3 triangle containing those two B atoms

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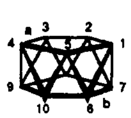
Table I. Calculated EHMO Total Electronic Energies of B_nH_{n+6} Species as $B_nH_n^{6-}$ Cores (eV)

obsd species	calcd as	*closo*-B_n E_t	best *nido*-B_{n+1} E_t	best remote *arachno*-B_{n+2} E_t	best adjacent *arachno*-B_{n+2} E_t	exptl struct[b]
$B_3H_8^-$	$B_3H_3^{6-}$	−224.9700	−225.6389 (1)[a]	−224.9700 (1, 5)[a]	−226.2644 (2, 3)[a]	*c*
B_4H_{10}	$B_4H_4^{6-}$	−276.2265	−277.1539 (1)	−291.5630 (1, 6)	−285.8497 (1, 2)	arachno (1, 2)
B_5H_{11}	$B_5H_5^{6-}$	−341.4250	−343.7372 (1)	−356.9266 (1, 7)	−349.5255 (1, 2)	arachno (1, 2)
B_6H_{12}	$B_6H_6^{6-}$	−394.6941	−405.8976 (1)	−413.4129 (3, 4)	−409.8412 (3, 5)	arachno (3, 5)
$B_6H_{11}^-$					−407.6456 (1, 3)	arachno (1, 3)
$B_7H_{12}^-$	$B_7H_7^{6-}$	−454.8627	−467.4127 (3)	−471.4071 (1, 8)	−468.8402 (1, 2)	arachno (1, 2)
B_8H_{14}	$B_8H_8^{6-}$	−517.2846	−526.4953 (1)	−530.9588 (2, 7)	−528.0392 (2, 3)	
					−526.7051 (2, 6)	arachno (2, 6)
B_9H_{15}	$B_9H_9^{6-}$	−571.1131	−582.6646 (2)	−593.3334 (1, 10)	−590.5051 (1, 4)	arachno (1, 4)
i-B_9H_{15}					−588.8955 (1, 2)	arachno (1, 2)
$B_9H_{14}^-$						
$B_{10}H_{14}^{2-}$	$B_{10}H_{10}^{6-}$	−634.2407	−649.0977 (1)	−652.5296 (1, 7)	−648.3054 (1, 2)	nido (1)

[a] Parenthetical numbers refer to atom positions in Figure 1 (atoms removed). [b] Structure references given in text. [c] See Discussion.

Table II. Relative Energies of Remote-B and Adjacent-B Isomers of $B_5H_5^{6-}$ and $B_{10}H_{10}^{6-}$ on Progressive Protonation

	species	E_{tot}, eV		species	E_{tot}, eV
	$B_5H_5^{6-}$	−349.5224		$B_5H_5^{6-}$	−356.9266
	$B_5H_7^{4-}$ (endo 2,3)	−373.0957		$B_5H_7^{4-}$ (endo 2,5)	−372.8414
	$B_5H_8^{3-}$ (bridge c)	−380.5035		$B_5H_8^{4-}$ (bridge c)	−380.0129
	$B_5H_{10}^-$ (bridge b,b)	−392.5795		$B_5H_{10}^-$ (bridge a,a)	−391.2951
	B_5H_{11} (bridge a)	−398.2321		B_5H_{11} (bridge b)	−396.9588
	$B_{10}H_{10}^{6-}$	−648.3054		$B_{10}H_{10}^{6-}$	−651.9419
	$B_{10}H_{12}^{4-}$ (endo 1,4)	−669.4966		$B_{10}H_{12}^{4-}$ (endo 1,9)	−666.6641
	$B_{10}H_{14}^{2-}$ (bridge a,a)			$B_{10}H_{14}^{2-}$ (bridge a,b)	
	vertical	−680.0360		vertical	−680.9862
	20° dihedral	−682.2069		20° dihedral	−680.9829

or tilted inward toward the center of the open face by a 20° dihedral angle. These values were taken as typical of boranes for which careful diffraction structures have been obtained (see experimental structure references).

All calculations were run by using the FORTICON program by Hoffmann et al.,[5] with the following Coulomb integral values: H 1s, −13.6 eV; B 2s, −15.2 eV; B 2p, −8.5 eV.

Results and Discussion

The results of calculations on the present idealized geometric basis are shown in Table I. At this level of calculation, bridging- and endo-hydrogen atoms are not considered, but each cluster nuclearity *n* is treated as a closo deltahedron with *n* vertices, as each symmetrically distinct nido isomer of a deltahedron with $n + 1$ vertices, and as each symmetrically distinct arachno isomer of a deltahedron with $n + 2$ vertices. Of these, the total electronic energy is shown for the closo isomer, the most stable nido isomer, the most stable arachno isomer with nonadjacent BH units removed, and the most stable arachno isomer with adjacent BH units removed. These structures are shown in Figure 1. In every case except $B_3H_3^{6-}$, the lowest energy is that for an arachno isomer with remote BH units removed. If we pursue the arguments of part 2 of this series, this shows the stability of the two "extra" pairs of skeletal electrons (beyond the number accommodated in bonding MO's for a closo cluster) as rings of electron density around the two open faces of the arachno cluster, each face having the greatest possible number of B nuclei.

We may note in passing that this is a familiar result for electronically equivalent hydrocarbons; for example, $B_5H_5^{6-}$ is entirely equivalent in EHMO terms to $C_5H_5^-$ except for precise Coulomb integral values, which differ only modestly, and of course, the planar pentagonal structure of $C_5H_5^-$ corresponds to a remote arachno isomer of C_7H_7. What is interesting in the present discussion is that the two "extra" pairs of electrons in the $B_5H_5^{6-}$, assigned to the two open pentagonal faces, correspond closely to the two pairs of electrons in the degenerate π HOMO's for the cyclopentadienide ion in their distribution.

The results in the table indicate that the geometrically idealized calculations do quite generally predict the correct arachno isomer as long as remote-B removal is excluded. That is, the calculations support the empirical rule that the observed arachno isomer will be the parent nido isomer with the highest coordinate B atom removed from the nido open face. (Specific results will be discussed below.) However, the electronic reasons for the empirical rule are not clear, because both the calculations and the observed hydrocarbon structures favor removal of remote BH units. Although it is possible to account for the isomer preferences of *nido*-boranes on the basis of cluster core symmetries and atom connectivities alone, it is clear that those symmetries and connectivities do not control the isomer preferences of *arachno*-boranes. The adjacent-B removal requirement for *arachno*-boranes must derive from the only stoichiometric and electronic property of the boranes not considered in these calculations so far: the bridging- and endo-hydrogen atoms.

With respect to the core calculations on $B_nH_n^{6-}$ shown in Table I, all observed boranes with $n + 3$ skeletal electron pairs have at least four extra hydrogen atoms, which in the context of these calculations can be treated as a progressive protonation of open-face electron density. With use of the geometric idealizations described in the previous section for the locations of these, it is possible to compare the relative energies of remote-B arachno isomers and adjacent-B isomers as protons are added one or two at a time up to the observed stoichiometry. For the observed adjacent-B isomers, protons are added in the observed locations; for remote-B isomers, protons are added in symmetrical, sterically accessible locations. Table II shows the progressive changes in total energy for remote-B and adjacent-B isomers of B_5H_{11} and $B_{10}H_{14}^{2-}$. These results clearly indicate that protonation favors the adjacent-B structure, but that the initial, fully deprotonated energy gap is sufficient that the addition of most or all of the observed extra hydrogen atoms is sometimes necessary to stabilize the observed adjacent-B structure.

In the B_5H_{11} case, the planar pentagon is a great deal more stable than the tentlike structure of the observed B_5H_{11} core, which is the basis of the stability of the cyclopentadienide ion referred to above. However, the addition of two endo protons on the 2-coordinate boron atoms in the observed structure yields a more stable system at $B_5H_7^{4-}$ than the pentagon, regardless of whether the added protons are on the same side of the pentagon or on opposite sides. As the table indicates, this margin of stability is maintained on progressive protonation up to the neutral species,

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

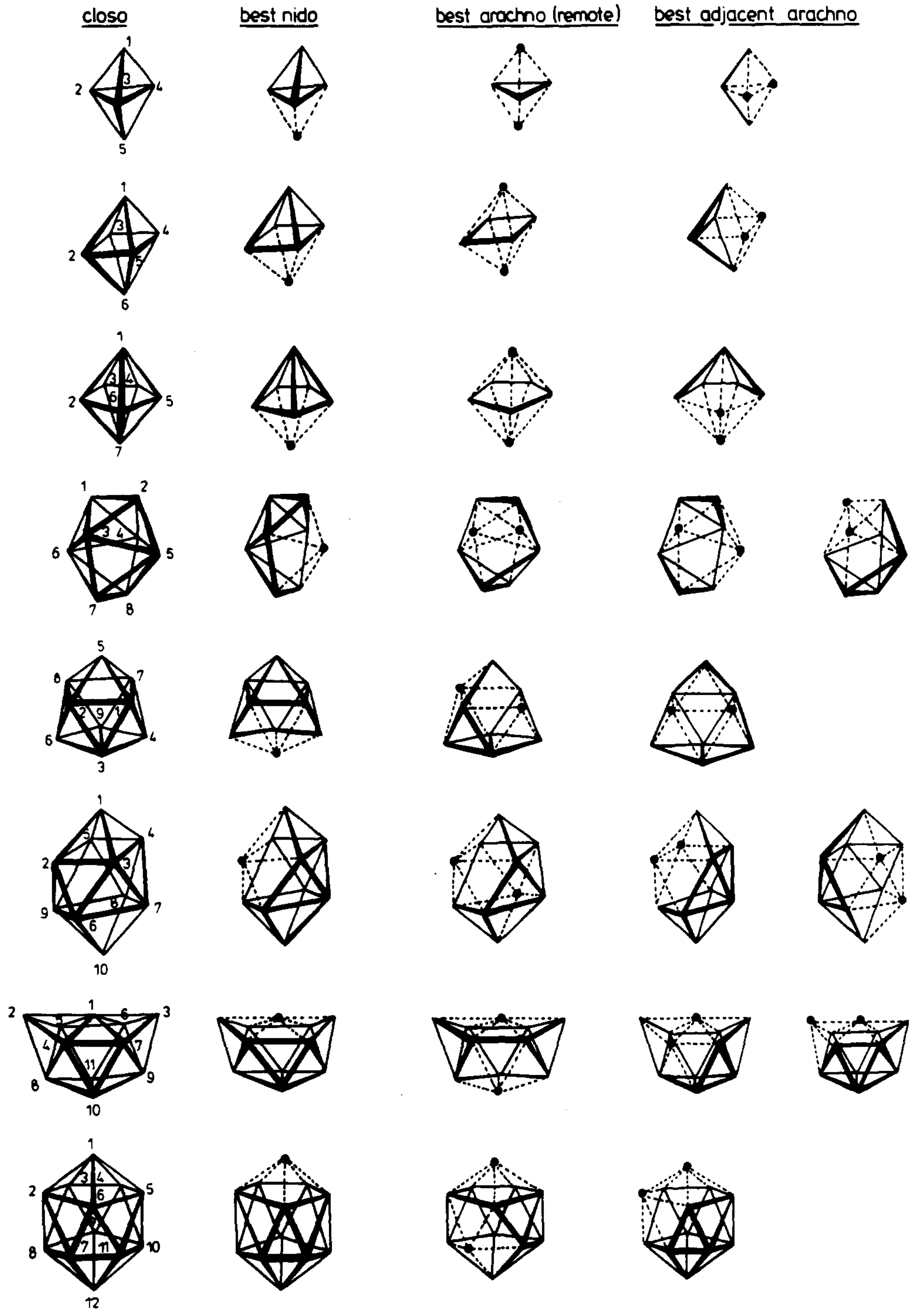

Figure 1. *closo*-Borane deltahedra and the most stable nido and arachno isomers predicted by EHMO calculations on idealized structures.

regardless of how the six added protons (two endo, four bridging) are distributed around the two open faces of the pentagon.

The $B_{10}H_{14}^{2-}$ case introduces an additional interesting feature of the observed structures. Not only is the remote-B arachno isomer more stable as the $B_{10}H_{10}^{6-}$ core, it regains its preference at the observed $B_{10}H_{14}^{2-}$ stoichiometry if the added bridging protons are placed in the plane of the B_3 face whose edge they are bridging ("vertical" placement). However, detailed structural studies of open borane clusters consistently show that bridging hydrogen atoms are tilted in toward the center of the open face with a dihedral angle of roughly 20°. When the geometry for these calculations is adjusted to reflect this tilt, the observed structure is again more stable. That is, not only the location but also the dihedral angles of the bridging-hydrogen atoms may be said to govern the isomer choices of at least some *arachno*-boranes. The seeming "attraction" of the endo and bridging hydrogens for each other is consistent with Brint's observation[6] that a set of four such hydrogen 1s orbitals in a nido cluster is equivalent to the orbitals of a BH unit present in a parent closo cluster.

The dihedral-angle effect may be seen in a related but separate comparison of calculated structures for $B_{10}H_{14}$, which has a core structure very closely related to that of $B_{10}H_{14}^{2-}$ but has four bridging hydrogen atoms instead of the two bridging and two endo atoms of the latter ion. Table III shows the sequence of calculated energies for protonation of the core of these two species. Adding endo protons is more favorable than adding bridging protons for either species for the first two added protons, and if the bridging protons are in the vertical position, the combination of two endo and two bridging protons is more favorable for both species. Only

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(6) Brint, P.; Sangchakr, B. *J. Chem. Soc., Dalton Trans.* **1988**, 105.

Table III. EHMO Total Electronic Energies (eV) for $B_{10}H_{10+n}^{(4-n)/(6-n)-}$ Isomers Differing in Placement of Bridging- and Endo-Hydrogen Atoms

	$B_{10}H_{10}^{q-}$	$B_{10}H_{12}^{(q-2)-}$	
		endo 1,4	bridge a,a
$B_{10}H_{14}$ fragment ($q = 4$)	−633.9122	−650.8318	−645.0968
$B_{10}H_{14}^{2-}$ fragment ($q = 6$)	−648.3054	−670.4613	−661.6621

	$B_{10}H_{14}^{q-}$ (vertical)		$B_{10}H_{14}^{q-}$ (20° dihedral)	
	endo 1,4; bridge a,a	bridge b,b,b,b	endo 1,4; bridge a,a	bridge b,b,b,b
$B_{10}H_{14}$	−664.7634	−663.7384	−662.4903	−664.9806
$B_{10}H_{14}^{2-}$	−684.4800	−679.3251	−682.2069	−679.8260

when the 20° dihedral angle is applied to the bridging protons do the calculations correctly predict that $B_{10}H_{14}$ should have four bridging-hydrogen atoms and $B_{10}H_{14}^{2-}$ two bridging and two endo hydrogens.

We believe that the physical reason for the calculated (and observed) adjacent-B arachno isomer preference is the contribution to bonding that arises from favorable overlap of bridging- and endo-hydrogen 1s orbitals. In the B_5H_{11} case, the group of six added hydrogen atoms has overlap integrals ranging up to 0.48 for adjacent bridging hydrogen atoms. Although our geometries are idealized, the bond lengths are sufficiently realistic that this value cannot be dismissed. The frontier orbitals do not localize electron density in these atomic orbitals to a very great extent and indeed have nodes between them, but several lower lying orbitals have relatively large coefficients (on the order of 0.20) for these six basis orbitals and bonding overlap, so that the MO energies must have been lowered as a result. The same pattern is seen for other clusters, so that we see the observed isomer preference for removal of adjacent boron atoms as, effectively, a preference for having the bridging- and endo-hydrogen atoms in a single island on the cluster sphere rather than in two groups, because these hydrogen atoms can more effectively contribute to the overall bonding in a single group. The 20° dihedral angle preference obviously contributes to the same bonding contribution. It is also possible that the absence of π-symmetry basis orbitals on the hydrogen atoms interrupts the B_n core π bonding less if the hydrogen atoms are in a single island, but we have not investigated this possibility.

We may consider the individual cases of Table I.

$B_3H_8^-$. The observed structure[7] is an isosceles triangle with one long bond (1.80 vs 1.77 Å). In this case only, the calculated EHMO energies favor the adjacent-B arachno isomer, which would be a bent three-atom open chain. Such a structure is not rigid through triangulation, and the EHMO energy is strongly influenced by the angle at the center atom, showing a minimum at 72° not far from the observed isosceles triangle. This value, unlike other calculated values in this series, is influenced by B–B bond length, exposing the faulty EHMO radial dependence described in part 1. However, in general pattern favoring closure to an acute angle suggests that the calculations are accurately reflecting the electronic behavior of the system. The failure to observe the neutral compound B_3H_9 may reflect the lower stability of the closed triangle or only a relatively unstable site for the final protonation.

B_4H_{10}. The observed structure[8] is the predicted adjacent-B arachno isomer, the butterfly. It is interesting that the structure differs from the square-planar $C_4H_4^{2-}$ exactly as B_5H_{11} differs from $C_5H_5^-$.

B_5H_{11}. The sequence of calculations leading to a predicted structure equivalent to the observed structure[9] has been shown in Table II. The sequence suggests that the observed structure may be stabilized most by the uniquely favorable sites for endo protonation at the 2-coordinate wingtip B atoms.

B_6H_{12} and $B_6H_{11}^-$. The structure[9,10] of B_6H_{12} is that of the most favorable adjacent-B arachno isomer, and the structure[10] of $B_6H_{11}^-$ is that of the next most favorable adjacent-B arachno isomer. Although there is a significant calculated energy difference between these two isomers for the $B_6H_6^{6-}$ core, the balance is presumably close as protonation progresses. The substantial difference in geometry between these two structures appears to be a clear demonstration of the cage structure influence of the endo- and bridging-hydrogen atoms.

$B_7H_{12}^-$. This structure[11] is not well determined, but appears to be that of the most stable adjacent-B arachno isomer.

B_8H_{14}. The structure[12] corresponds to the second-best adjacent-B arachno isomer, rather than the most stable. This would again appear to be a reflection of the cage structure influence of the six added protons; as part 4 of this series of papers will show, the "topological" EHMO calculations are capable of predicting sites for endo- and bridging-hydrogen atoms, and the observed isomer of B_8H_{14} has six ideal sites for protonation, while the most stable core isomer does not.

B_9H_{15} and $B_9H_{14}^-$. B_9H_{15} occurs as two isomers,[12,13] one of which corresponds to the most stable adjacent-B arachno isomer while the other (i-B_9H_{15}) corresponds to the next most stable adjacent-B isomer, as does the $B_9H_{14}^-$ ion.[14] This is a particularly strong indication that the boron atom cage connectivity in the core clusters and the resulting electronic stability determine cluster structure, because the low symmetry of the parent octadecahedron allows a total of 19 arachno isomers, of which the two observed are the two adjacent-B isomers with lowest calculated energy. In this context, it is not unreasonable that (i-B_9H_{15}) is observable even though it violates the empirical rule for stable arachno structures.

$B_{10}H_{14}^{2-}$. As for the $B_{10}H_{14}$ molecule described in the previous paper of this series, the cage structure[15] can be described as an arachno fragment of an icosahedron or as a nido fragment of an octadecahedron. Table II has described the sequence of protonation of the core in terms of icosahedral fragments because of the added symmetry of the fragments to be compared, but as Table I shows, the nido octadecahedral fragment appears more stable in these calculations. In the same way that the ratio of the length of the open face to its width was used to assign $B_{10}H_{14}$ a nido geometry, we can compare the experimental l/w for $B_{10}H_{14}^{2-}$ (1.16) to that for the idealized nido fragment (1.26) and that for the idealized arachno fragment (1.00). The observed geometry is obviously intermediate, but perhaps closer to the nido value than the arachno value, which accords with the EHMO calculations.

Summary

The current series of "topological" EHMO calculations accurately predicts the nido to arachno opening for a change from $n + 2$ to $n + 3$ skeletal pairs of electrons for borane clusters. Although this is not in itself a novel result, no previous series of molecular orbital calculations has dealt with a comprehensive set of isomer structures on a basis allowing only boron atom connectivity changes between isomers. These calculations allow us to identify geometric isomer preferences on an atom-connectivity or topological basis alone and to see immediately where cage topology is influenced by the presence of endo and bridging hydrogen atoms.

It may be useful at this point to summarize the results of the calculations in parts 1–3 of this series, which have considered in sequence the closo, nido, and arachno series of boranes. With respect to the observed borane clusters $B_nH_m^{q-}$, these calculations

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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.

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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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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.