$n + 1$. In particular, the indicated tendency of $B_{11}X_{11}$ to disproportionate is likely to be significantly affected by the probable distorted geometry of $B_{10}X_{10}$ and $B_{12}X_{12}$. The stabilities indicated in Table II appear to be qualitatively correct, but less quantitatively useful than those for the dianions in Table I.

Summary

The EHMO calculations presented in this paper, performed on *closo*-B_nH_n clusters whose geometries have been idealized to deltahedra composed of equilateral triangles, have been shown to reproduce at least semiquantitatively the patterns of chemical stability for the observed $B_nH_n^{2-}$ ions with $n = 6$–12 and qualitatively the stoichiometries and stabilities of the observed B_nX_n neutral molecules. We accordingly conclude that these patterns of chemical stability are primarily the result of symmetry and atom-connectivity patterns and that while very sophisticated ab initio calculations are necessary to reproduce the detailed geometry of boranes, they are not needed in order to understand, in molecular orbital terms, the species observed (and not observed) and their relative stabilities.

In the following papers, we show that EHMO calculations on the same basis are capable of rationalizing the geometric isomers adopted by the known *nido*- and *arachno*-boranes and *nido*- and *arachno*-borane anions, particularly in terms of the role of bridging- and endo-terminal-hydrogen atoms in dictating the choice of geometric isomers.

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

Contribution from the Departments of Chemistry, Hampden-Sydney College, Hampden-Sydney, Virginia 23943,
and Durham University Science Laboratories, South Road, Durham DH1 3LE, U.K.

Extended Hückel MO Studies of Boranes. 2. Isomer Preferences of B_nH_{n+4} Species

William W. Porterfield,*[†] Marion E. Jones,[‡] and Kenneth Wade*[‡]

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A series of extended Hückel molecular orbital (EHMO) calculations is reported for boranes with B_nH_{n+4} formulas, which are usually found to have nido 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 closo deltahedral cluster cage and to predict the correct nido isomer of those symmetrically possible. Existing empirical rules favoring removal of the highest coordinate B atom from the parent closo cluster are shown to represent a stabilization of HOMO electrons for the appropriate *nido*-$B_nH_n^{4-}$ isomer around the largest possible open face of the cluster. The margin of stability of the observed nido isomer over a closo form is related to the intrinsic stability of the closo symmetry for any given nuclearity.

In this paper, we continue the idealized "topological" EHMO calculations of the previous contribution. That paper described calculations in which the geometry of *closo*-$B_nH_n^{2-}$ clusters was represented by idealized equilateral-triangle deltahedra with a uniform B–B bond length of 1.700 Å, regardless of the nuclearity of the cluster. It is of interest to explore the ability of these idealized EHMO calculations to account for the effective empirical rules[1,2] involving skeletal electron counting that predict the formation of closo, nido, or arachno isomers for $B_nH_n^{q-}$, as q increases. These rules, however, only suggest that a borane with $n + 2$ skeletal electron pairs should form a nido cluster (for example), without indicating which of several possible nido isomers from a parent closo deltahedron should be chosen. It should be possible not only to show that such a borane should prefer to adopt a nido geometry but also to use these simplified EHMO calculations to understand the effects of molecular symmetry and atomic connectivity on the relative stability of the various possible nido isomers.

Williams[3] has proposed an effective empirical rule for the preferred nido isomer in each deltahedral case: The observed nido isomer will correspond to the loss of a vertex having the highest coordination number from the closo parent. The rule is useful and in general reliable, but there are ambiguities or failures. $B_4H_7^-$ has the correct skeletal electron count to adopt a nido geometry and does, but the atom that is lost from the parent trigonal bipyramid is a low-coordinate apical atom (yielding a B_4 tetrahedron), not a high-coordinate equatorial atom (which would yield a B_4 butterfly geometry). B_8H_{12} also has the correct skeletal electron count to adopt nido geometry, but is found to have a still more open structure that may be thought of as *arachno*-B_{10} or even as still more fragmented B_{11} minus three vertices (hypho) or B_{12} minus four vertices (klado). At the same time, the rule, which is essentially topological in nature, is powerful enough that it should be possible to use the previously developed "topological" EHMO calculations to develop an electronic explanation of the reasons for nido isomer selection, and perhaps to understand the reasons for the exceptions as well.

This paper will undertake approximate molecular orbital calculations to give numerical comparisons of isomer energies, but on the previously developed basis simple enough to retain topological relationships and make coordination number connectivity features visible within the calculated energies. The patterns that develop from the broad array of B_nH_{n+4} species will allow us to see a simple physical basis for the existing empirical rule for isomer selection.

Method of Calculation

The previous paper has outlined 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. The geometries of clusters are restricted to deltahedra or deltahedral fragments, and we expect the calculations to predict whether the geometric isomer adopted by a species having n boron atoms will be a closo deltahedron with n vertices or a nido fragment from a deltahedron with $n + 1$ vertices; the predicted geometry will be that having the lowest energy from this range, in which only atom connectivity changes.

As in the previous paper, we maintain the maximum possible degree of topological comparability by treating each nido isomer as being derived from a parent deltahedron that has the idealized molecular point group symmetry and is composed of equilateral triangles in which each side (B–B internuclear distance) is 1.70 Å. No relaxation of the boron cluster core is permitted on atom removal, even though the resulting structure may have less than the maximum symmetry possible for that pattern of atom connectivities. Another simplifying assumption intended to retain geometric comparability is that the bridging- and endo-terminal-hydrogen atoms present in all known boranes having nido geometries are not considered; all isomers are considered to have the formula $B_nH_n^{4-}$, with the n hydrogen atoms arranged as exo-terminal B–H bonds, radial from the

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[†] Hampden-Sydney College.

[‡] Durham University Science Laboratories.

(1) Wade, K. *J. Chem. Soc., Chem. Commun.* **1971**, 792.

(2) Mingos, D. M. P. *Nature (Phys. Sci.)* **1972**, *236*, 99.

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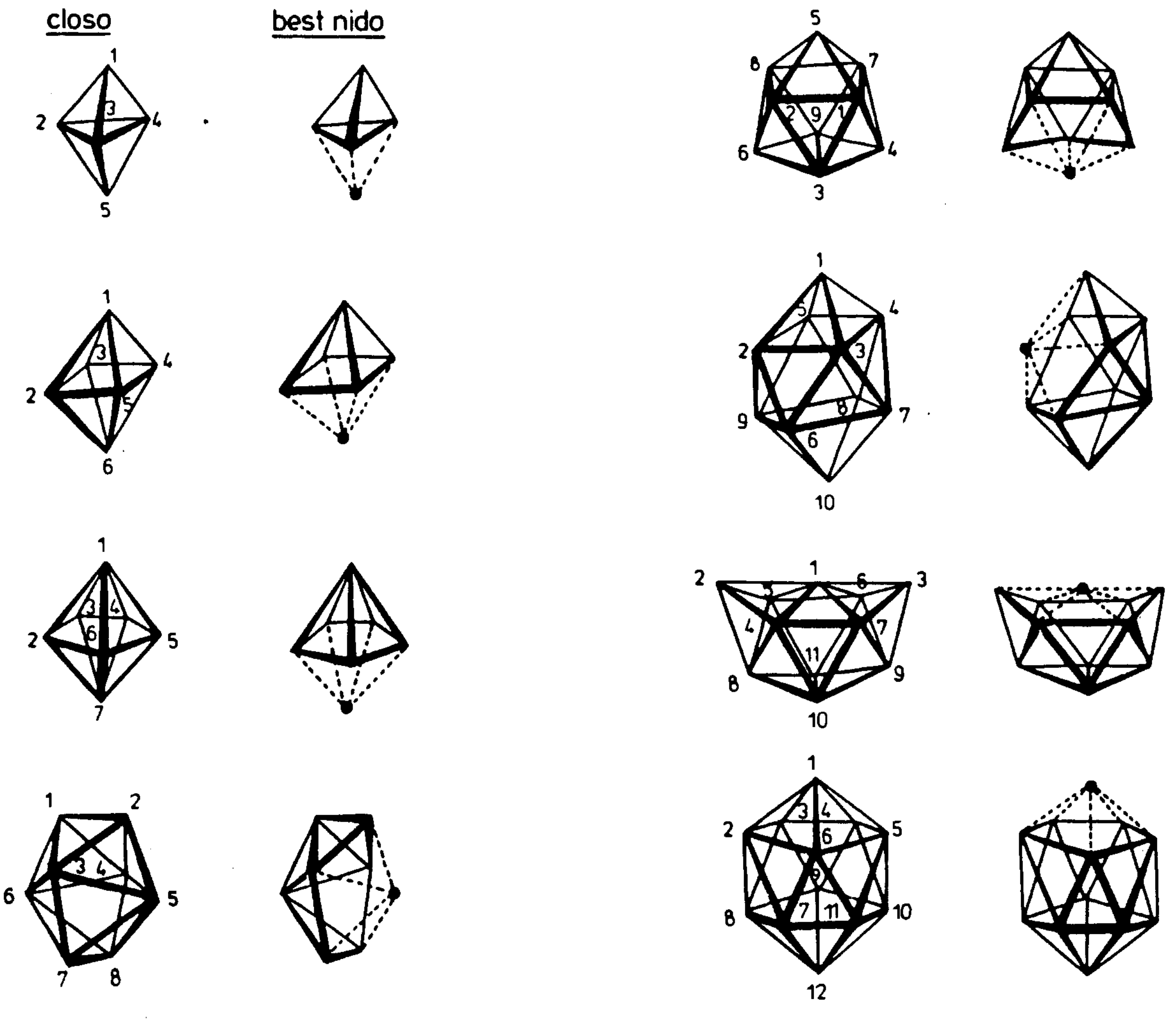

Figure 1. Closo and most stable nido deltahedra with 5–12 vertices, formed from equilateral triangles.

center of mass of the closo parent, with a B–H bond length of 1.19 Å. Williams[3] has shown that the bridging and endo hydrogens are fundamentally responsible for the stability of the observed species, so that this seems an unacceptably sweeping approximation; in addition, Brint[4] has demonstrated the essential orbital equivalence of a set of four endo or bridging H 1s orbitals around an open ring of four, five, or six boron atoms to those of the boron atom (from the closo cluster) they replace.[5] However, we shall show that boron cage connectivity alone is responsible for the observed isomer preferences.

The EHMO calculations were run by using the FORTICON program by Hoffmann et al.,[6] with the following Coulomb integral values: H 1s, −13.6 eV; B 2s, −15.2 eV; B 2p, −8.5 eV. B_nH_n deltahedra were formed as above for all $n = 4$–12, and total electronic energies were tabulated for $n + 2$ skeletal electron pairs in closo and all symmetrically distinct nido isomers.

Results and Discussion

Most B_nH_n deltahedra with n between 3 and 12 show fairly high symmetry in their molecular point groups, so that there is a considerable degree of equivalence between deltahedral vertices and not many nido isomers are possible. For example $B_9H_9^{q-}$ as an idealized tricapped trigonal prism has only two nido isomers, corresponding to the removal of a prismatic atom or a capping atom. The exception is the $B_{11}H_{11}^{q-}$ octadecahedron, which has only C_{2v} symmetry and hence five nido isomers. Table I shows the calculated EHMO total electronic energy for the known B_nH_{n+4} species (or their anions) as $B_nH_n^{4-}$ equivalents, allowing an energy comparison for the closo form and all nido isomers. Figure 1 shows the closo and the favored nido cluster cores for these systems. It can be seen from the table that each $B_nH_n^{4-}$ species does indeed increase its stability by going from a closo to a nido geometry, though $B_4H_4^{4-}$ is ambiguous because at this level of geometric approximation there is no skeletal difference between the closo and the preferred nido structures. This stabilization by opening of the cluster structure is not a new result, but it gives confidence that the severe geometric approximations introduced above have not damaged the ability of the calculations

Table I. Calculated Energies of Closo and Nido Isomers of B_nH_{n+4} Clusters

known species	EHMO core	E_{tot} for *closo*-B_n, eV	E_{tot} for *nido*-B_{n+1}, eV	experimental geometry	ref
$B_4H_7^-$	$B_4H_4^{4-}$	−275.1635	−274.7029 (1)[a]	nido (1)[a]	8
			−273.3578 (2)		
B_5H_9	$B_5H_5^{4-}$	−330.1804	−336.2850 (1)	nido (1)	9
B_6H_{10}	$B_6H_6^{4-}$	−387.2417	−397.0188 (1)	nido (1)	10
			−391.8080 (2)		
B_8H_{12}	$B_8H_8^{4-}$	−509.7169	−513.4069 (1)	more open[b]	11
			−511.6806 (4)		
$B_9H_{12}^-$	$B\,H_9^{4-}$	−569.3015	−572.0106 (1)	nido (2)	12
			−572.9060 (2)		
$B_{10}H_{14}$	$B_{10}H_{10}^{4-}$	−624.6599	−635.1283 (1)	nido (1)	14
			−629.9626 (8)		
			−629.8169 (10)		
			−628.8986 (4)		
			−628.7235 (2)		
$B_{11}H_{13}^{2-}$	$B_{11}H_{11}^{4-}$	−684.3203	−694.6942 (1)	nido (1)	15

[a] Numbers refer to atom positions in Figure 1. [b] See Discussion.

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

(5) See also the several structural approaches and calculations described in the references to part 1: Porterfield, W. W.; Jones, M. E.; Gill, W. R.; Wade, K. *Inorg. Chem.*, preceding paper in this issue.

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

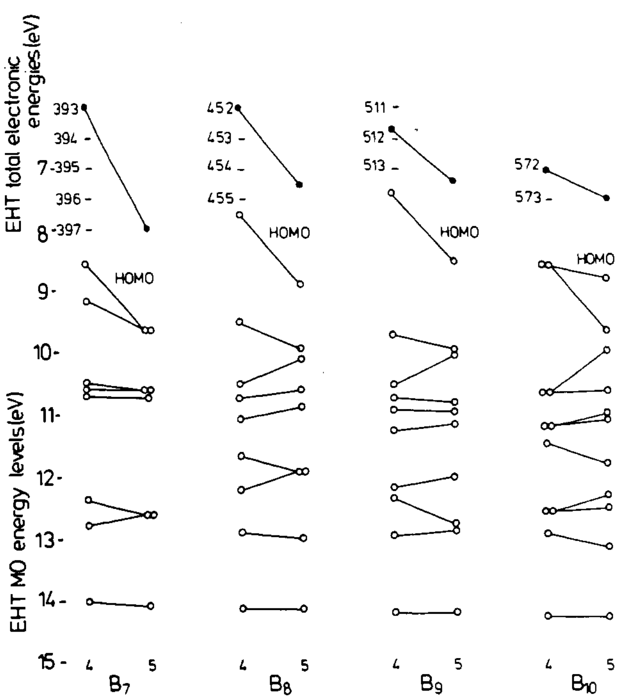

Figure 2. EHT energy level comparison for $B_nH_n^{4-}$ nido isomers, n = 7-10, for removal of 4-coordinate or 5-coordinate B atoms. Arbitrary sections of total energy axis at top show the change of total electronic energy for comparison with HOMO change.

to reproduce cluster stability patterns. Furthermore, as the table also shows, the calculations predict the correct nido isomer in every case, although B_8H_{12} requires an extended discussion. That is, since we have reduced the structural variations between isomers to atomic connectivity alone, the calculations show that the isomer preference is controlled by atomic connectivity. This is, of course, Williams' empirical rule.

The physical electronic basis for the empirical rule, however, is not immediately obvious. Whatever the electron distribution within the cluster may be, the removal of a high-coordinate BH unit in preference to a low-coordinate BH unit means disrupting more bonding contacts in the closo parent cluster; it is not clear why this should be desirable. The calculations can help in this consideration. Figures 2 and 3 show the upper portion of the energy-level diagram for the closo parent nuclearities from 7 to 11 as BH units with different coordination numbers are removed to form the various nido isomers (the B_6 and B_{12} parents have only one nido isomer). At the top of each figure is plotted the total energy of the nido isomers, with the scale adjusted to allow for orbital occupancy. It can be seen that in each case the preponderant change in total electronic energy is fairly closely parallel to the change in the HOMO energy (or energies if a degenerate orbital is involved). The energy of lower lying orbitals is, in general, little changed or changed in ways that provide near-cancellation with a neighbor orbital. Isomer preference for nido structures thus seems to be dominated by the HOMO electrons, which are obviously stabilized by removal of the highest coordinate BH unit from the closo parent.

How are the HOMO electrons distributed within the $B_nH_n^{4-}$ cluster? If we examine the basis-AO coefficients in the HOMO for each structure, we find quite generally that the HOMO electrons are concentrated around the open face of the nido cluster, to the extent of perhaps 70–80%. Figure 4 shows the AO combinations for the degenerate HOMO's of the preferred nido isomer of $B_6H_6^{4-}$ with size scaled to LCAO coefficient magnitude and also shows the combined values of the squared coefficients for each atom. Very little HOMO electron density is on the atom away from the open face, which is a typical result. It is as if the HOMO electrons formed a ring around the open face of the cluster. Stone[7] has addressed the HOMO distribution qualitatively within the structure of his tensor surface harmonic theory, suggesting that the frontier orbitals determine the structure through being stabilized most by the largest possible open ring. This is entirely consistent with our results, but Figures 2 and 3 provide a quantitative substantiation of the argument. In Stone's terminology for cluster MO's, any n-fold closo cluster has one S^{σ} MO centered in the cluster and n bonding MO's, formed from tangential p atomic orbitals, in the cluster-sphere surface. If we identify the resulting n bonding electron pairs in the sphere surface with the n atoms in the closo core, then a *nido*-$B_nH_n^{4-}$ cluster corresponds to the removal of a BH^{2+} unit from a bonding electron pair in *closo*-$B_nH_n^{2-}$. The remaining sphere–surface electron pair, at least notionally located near the now-vanished B nucleus in the closo parent, is now attracted out toward the neighbor B nuclei defining the open face, forming the ring of HOMO electron density around the open face that Stone predicts and we calculate. We may suggest, however, that the HOMO electrons are stabilized more

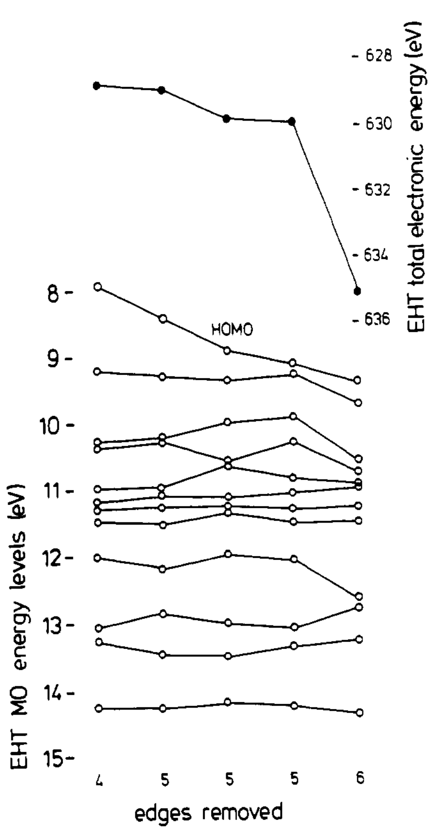

Figure 3. EHT energy level comparison for $B_{11}H_{11}^{4-}$ nido isomers, for removal of 4-, 5-, and 6-coordinate atoms. Section of the total energy axis at top shows the change of total electronic energy for comparison with the HOMO change.

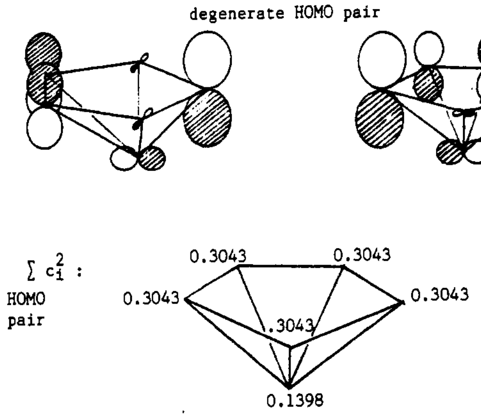

Figure 4. Basis atomic orbital contributions to degenerate HOMO's for $B_6H_6^{4-}$ (sizes scaled to coefficients c_i) and $\sum c_i^2$ for each atom in HOMO pair.

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(7) (a) Stone, A. J. *Inorg. Chem.* **1981**, *20*, 563. (b) Stone, A. J.; Alderton, M. J. *Inorg. Chem.* **1982**, *21*, 2297.

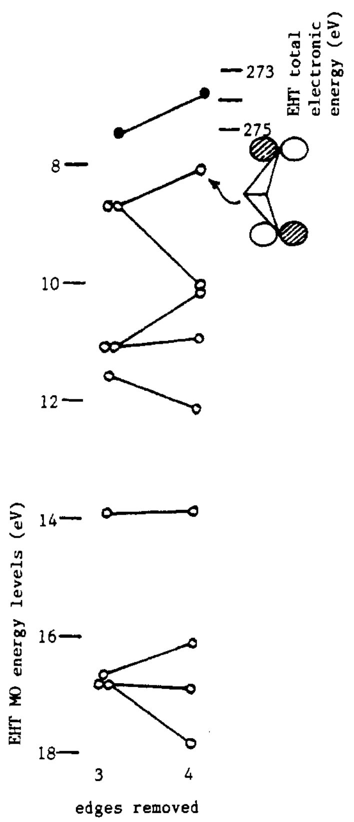

Figure 5. EHT energy level comparison for $B_5H_5^{4-}$ nido isomers, for removal of 3- and 4-coordinate atoms. Section of the total energy axis at top shows the change of total electronic energy for comparison with the HOMO change. HOMO symmetry is shown for the nido butterfly structure.

by attraction to the greatest possible number of open-face B nuclei than simply by distribution in the largest ring, although the resulting predictions are the same.

It will be useful to consider the individual cases presented in Table I at this point in order to enhance our understanding of the electronic and geometric character of these cluster compounds.

$B_4H_7^-$. The observed structure is tetrahedral with three edge-bridging hydrogen atoms around a single face.[8] This is consistent with the EHMO energies given in Table I, although it should be noted that here the closo and nido (minus apical BH) isomers are skeletally identical and differ only in the orientation of the three BH bonds around the "open" face of the nido isomer. This orientation removes the full tetrahedral degeneracy of the resulting energy levels but changes them very little. The energy of the butterfly nido isomer is fairly strongly influenced by the dihedral angle between the two B_3 triangles, because, as Figure 5 indicates, the HOMO is essentially π-antibonding across the wingtips, stabilizing the butterfly isomer as the dihedral angle opens up. However, in general the total electronic energy of the two possible nido isomers parallels the energy of the HOMO, just as for the larger clusters in Figures 2 and 3; what is significantly different here is the great stability of a tetrahedral cluster containing six skeletal pairs of electrons, so that the closo/nido tetrahedral geometry is lower in energy than the nido butterfly geometry, even though the open face contains fewer atoms. It may be noted that the trigonal bipyramid is the only deltahedron that can yield a high-symmetry nido fragment of this sort.

B_5H_9. The observed structure is a square pyramid with four edge-bridging-hydrogen atoms,[9] correctly predicted by the empirical rule as a *nido*-B_6 octahedron. The EHMO calculations correctly indicate the preference for the more open nido structure, although the symmetry of the octahedron allows only one nido isomer. The atom connectivities of some borane clusters can be equally well represented by fragments of any higher deltahedron up to the icosahedron, but this species could only be a fragment of a 6-, 9-, or 10-atom deltahedron.

B_6H_{10}. The structure is a pentagonal pyramid with four bridging hydrogen atoms on the pentagonal open face;[10] a fifth bridging hydrogen atom can be added by protonating to $B_6H_{11}^+$, which has the same skeletal geometry. This corresponds to the loss of a high-coordinate B atom from a closo pentagonal bipyramid and is correctly predicted by both the empirical rule and by the EHMO calculations.

$B_7H_7^{4-}$. No equivalent protonated species have been observed.

B_8H_{12}. The structure has an open six-membered ring corresponding to an arachno fragment of the bicapped square antiprism in Figure 1.[11] The extra electron pair beyond the number required for a closo geometry opens the cluster more than can be accomplished by removing only one atom from the closo deltahedron. If the EHMO calculations are extended to fragments of larger deltahedra and the most stable isomer is chosen from each deltahedral fragment, the relative energies (eV) are as follows:

closo-B_8	*nido*-B_9	*arachno*-B_{10}	*hypho*-B_{11}	*klado*-B_{12}
−509.7169	−513.4069	−512.7745	−515.7715	−516.1665

Of these, the three largest deltahedral fragments all correspond to the observed structure. The indicated total energy favors an icosahedral fragment, but the balance between isomers is fairly fine. It seems likely that the choice of a nido isomer is influenced by the intrinsic symmetry stability of the closo parent (as outlined in the preceding paper). If the closo parent is relatively unstable (e.g., $B_7H_7^{2-}$, $B_{11}H_{11}^{2-}$), the nido fragment should be correspondingly easier to form (B_6H_{10}, $B_{10}H_{14}$). Here the potential nido-parent $B_9H_9^{2-}$ closo cluster is by comparison more stable, and the removal of a single BH is not as strongly topologically favored.

B_9H_{12}. The structure is a bicapped square antiprism with one high-coordinate BH vertex removed.[12] This determination is consistent with the empirical rule and with the EHMO results, but not with the prediction made by using a 2:1 bonding potential.[13]

$B_{10}H_{14}$. Many workers have noted that this structure may equally well be regarded as a *nido*-B_{11} octadecahedron or as an *arachno*-B_{12} icosahedron. For our idealized equilateral-triangle clusters, these two possibilities may be distinguished by considering the ratio of the length l of the boat-configuration six-membered open face to its width w. In the idealized *nido*-B_{11} fragment, $l/w = 1.267$, while for the *arachno*-B_{12} fragment, $l/w = 1.000$. From the experimental structure determination,[14] $l/w = 1.265$, supporting the assignment of the structure as *nido*-B_{11} as both the empirical rule and the EHMO calculations predict.

$B_{11}H_{13}^{2-}$. The structure is a nido icosahedral fragment,[15] as predicted by the empirical rule and by these calculations. The large change in the total energy seen in the table corresponds to the relative instability of the closo octadecahedron.

Summary

The idealized EHMO calculations reported here, which emphasize atomic-connectivity differences between clusters and isomers because of the constant B–B bond length used in all geometries, have been shown to accurately predict the opening effect seen for borane clusters with $n + 2$ pairs of skeletal electrons

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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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Contribution from the Departments of Chemistry, Hampden-Sydney College, Hampden-Sydney, Virginia 23943, and Durham University Science Laboratories, South Road, Durham DH1 3LE, U.K.

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

William W. Porterfield,*,† Marion E. Jones,‡ and Kenneth Wade*,‡

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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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† Hampden-Sydney College.

‡ Durham University Science Laboratories.

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