apy show an intense, rather narrow second transition around 400 nm (Figure 4), which cannot be attributed to an MLCT process Re(I) → apy. The excited state connected with this transition may be viewed in connection with the unusually small g values of the corresponding anion radicals; there are several observations in the literature pointing to the possibility of charge transfer from heavy-metal centers (Mo, Tc, Re) to halide ligands.[39] An alternative assignment of this band to a (singlet) intraligand transition $\pi \rightarrow \pi^*$ would imply an unprecedented[38b] shift of more than 8000 cm^{-1} with respect to the absorption maximum of the free ligand;[40] on the other hand, the presence of two heavy metal centers with large spin–orbit coupling constants might favor intense d → d triplet absorption features as, e.g., in complexes of osmium.[41]

Although all dimers have rather low-lying π^* orbitals, the absorption maxima of the rhenium systems lie somewhat higher in energy than those of related tungsten or molybdenum tetracarbonyl complexes;[15b,c] this is a consequence of the strongly stabilized filled metal d orbitals as illustrated by very positive oxidation potentials. Considering all informations from electrochemistry, ESR, and electronic absorption spectroscopy, we arrive at comparative representations (8) for the frontier orbital situations in complexes of W(CO)$_4$,[13,15b] Re(CO)$_3$Hal, and [Ru(bpy)$_2$]$^{2+}$[9] with strongly π-accepting α-diimines.

<p style="text-align:center">8</p>
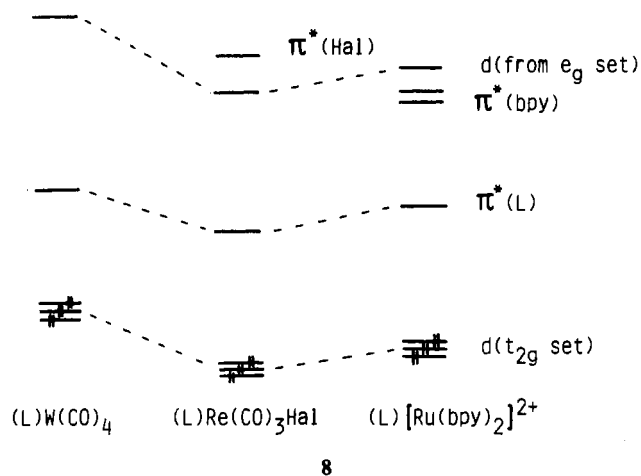
Reduction of the bpym[42] and apy dimers (Figure 4) yields absorption spectra very similar to those of corresponding ligand anion radicals[40] (Table III); the MLCT transition is reduced in intensity (half-occupied target orbital) and shifted hypsochromically because of additional d(t$_{2g}$) stabilization by the now anionic unsaturated ligand.[15,43]

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Extended Hückel MO Studies of Boranes. 1. Relative Stabilities of *closo*-B$_n$H$_n$ and -B$_n$H$_n^{2-}$

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Series of extended Hückel molecular orbital (EHMO) calculations are reported for *closo*-boranes B$_n$H$_n^{m-}$, where $n = 3$–12 and $m = 0$ or 2. Calculations have been carried out for published experimental geometries and also for hypothetical structures in which (a) all boron atoms lie on a spherical surface, and (b) all polyhedral faces are equilateral triangles with B–B = 1.70 Å, with exo-radial-hydrogen atoms at B–H = 1.19 Å. The manner in which orbital energy levels (classified by using Stone's nomenclature) and total electronic energies vary with n are noted and used to explore the pattern of disproportionation of clusters B$_n$H$_n^{2-}$, and to rationalize the existence and relative stabilities of halides B$_n$X$_n$ ($n = 4$, 7–12). The known chemical behavior of anions B$_n$H$_n^{2-}$ is well reproduced by the calculations using equilateral triangular faced model structures, suggesting that atom connectivities are more important in these systems than other structural features such as relative bond lengths or electronic features such as halogen back-donation.

This is the first of a short series of papers exploring the value of systematic EHMO calculations for understanding, explaining, or predicting aspects of the chemistry and structural preferences of closo, nido, and arachno clusters of the borane type. In the present paper we consider *closo*-borane anions B$_n$H$_n^{2-}$ and neutral closo halides B$_n$X$_n$, and show how their relative stabilities can be rationalized by calculations on model systems with equilateral triangular polyhedron faces, illustrating the importance of atom connectivities and topological influences. In subsequent papers we shall show how EHMO calculations allow the shapes of nido and arachno systems to be rationalized or predicted and draw attention to the importance of endo ligands such as the m endo-hydrogen atoms of neutral boranes B$_n$H$_{n+m}$, the locations of which

can in general be predicted from frontier orbital considerations.

The exclusively triangular-faced polyhedral structures of the borane anions B$_n$H$_n^{2-}$ ($n = 6$–12 and neutral halides B$_n$X$_n$ ($n = 4$, 7–12) (Figure 1) are familiar features of boron cluster chemistry.[1-6] The topological basis for the prevalence of deltahedral structures has been discussed by a number of authors (see, e.g., refs 7–10 and others cited therein), who have noted that such

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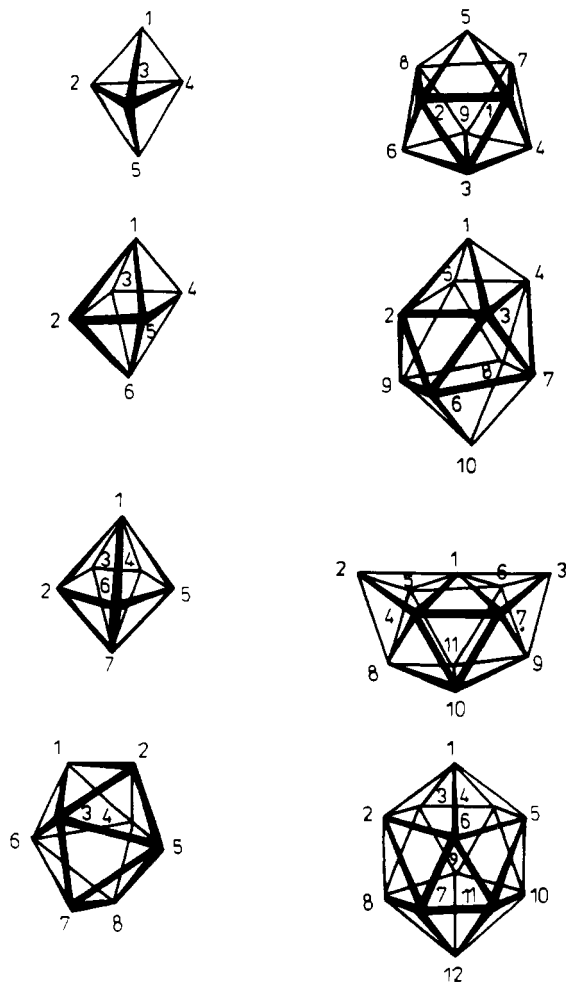(7) King, R. B.; Rouvray, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 7834.

Figure 1. Closo deltahedra with 5–12 vertices, formed from equilateral triangles.

structures maximize the number of bonding contacts and so are preferred to other possible polyhedral shapes and that the polyhedra illustrated in Figure 1 (with the exception of the tetrahedron) require $n + 1$ skeletal electron pairs for maximum skeletal bonding, so justifying the skeletal electron counting rules that are commonly used.[11-16] Although such topological arguments provide some insight into the reasons why borane anions $B_nH_n^{2-}$ are deltahedral, they do not in general yield quantitative energy comparisons for different cluster nuclearities nor do they give quantitative information on frontier orbitals that could be used to correlate chemical properties. Moreover, they do not give a general explanation for the existence of the deltahedral neutral halides B_nX_n, which have sometimes been termed "electron hyperdeficient".[1]

Some understanding of the existence of these neutral halides has come from molecular orbital treatments, which have shown the polyhedra with 4, 8, 9, or 11 vertices to be compatible with n skeletal bond pairs, whereas closo species B_nX_n with $n = 5, 6, 10$, or 12 would have open-shell configurations.[3-5,13,15,17] More importantly, molecular orbital calculations have brought a quantitative understanding of energy relationships within borane clusters (refs 18–26 and others cited therein). In particular, ab

initio calculations with extended basis sets and approximate correlation correction have optimized selected cluster geometries to afford bond lengths and angles quite close to those found experimentally (refs 27 and 28 and others cited therein). This is particularly satisfying because one of the primary motivations for the study of borane structures has been their role as a touchstone for bonding theories. Successful though these calculations are, the fact that they contain large energy contributions from electron–electron repulsions and even important contributions from correlation differences makes it difficult to use them to draw topological conclusions from energy relationships between clusters of different symmetry or to assess the effect of symmetry changes for isomeric structures.

Because these features of deltahedral borane structures seem to be well established in current theory, it seemed desirable to connect them by carrying out MO calculations on the entire range of deltahedral clusters, on a basis simple enough to permit comparison of total electronic energies and individual orbital energies from one cluster nuclearity to another and for different numbers of skeletal electron pairs. Stone has developed an elegant methodology based on spherical harmonics (tensor surface harmonic theory) to account for the bonding characteristics of deltahedral clusters,[8,29,30] but his approach treats all clusters as having spherical symmetry and uses the simple Hückel assumption that no overlap or bonding exists except for nearest neighbors. These assumptions and the problem of making a quantitative assessment of $\sigma-\pi$ interaction in Stone's TSH theory make it essentially qualitative and unsuitable for making electronic energy comparisons between clusters, even though it provides the most generally useful device to date for categorizing cluster bonding orbitals and understanding general orbital symmetries. (Extensions of TSH theory to allow its use for quantitative calculation of MO energy levels have been developed.[31,32]) A recent group theoretical approach based on the pairing principle inherent to Stone's TSH theory has been applied to deltahedral clusters and shown to provide an explanation for deviations from the $(n + 1)$ rule.[33,34] Here, in the present and subsequent papers, we show that extended Hückel MO calculations allow various features of the borane structural pattern to be rationalized, including similarities to and differences from formally analogous hydrocarbons, and provide an essentially topological basis on which to explain the relative stabilities of borane anions $B_nH_n^{2-}$ and halides B_nX_n.

Our choice of EHMO calculations, relatively primitive weapons in the theoretical chemist's armory, was made because these are the most sophisticated that do not take electron–electron repulsion into account. If we wish to extract the effects of molecular point group symmetry and atom connectivities on clusters of different nuclearities and on the energies of individual MO's as the number of skeletal electrons changes—in other words, to determine quantitative topological energy effects without the additional

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influence of large energy effects from changing electron–electron repulsion—EHMO calculations are the most sophisticated that still permit easy comparison. EHMO calculations are not topologically pure in that overlaps between all atoms are included, so that atom connectivities are less cleanly defined than in simple Hückel theory; distant-atom effects are generally small, however, and nearest-neighbor connectivities appear to dominate EHMO energy changes. Hoffmann has pioneered EHMO applications to borane clusters[35a] and has shown that important structural inferences can be drawn from the results, but no comprehensive treatment on a topologically equivalent basis has appeared, although valuable EHMO studies of smaller borane clusters and of the capping and *debor* principles have been made by several authors.[21,35b]

In order to probe as fully as possible the various structural factors at work when making comparisons over the whole range of systems $B_nH_n^{2-}$, we carried out calculations on three series of structures: (i) experimental structures, where these have been determined for anions $B_nH_n^{2-}$ ($n = 6, 8, 9, 10, 12$); (ii) hypothetical structures in which all the skeletal atoms are on a spherical surface; (iii) hypothetical structures in which all the polyhedral faces are equilateral triangles.

Carrying out calculations on experimentally determined structures has the clear advantage of fidelity to real clusters. However, apart from the problem that not all experimental structures are available (overcome by using idealized structures for the remainder, obtained from derivatives or related carboranes), the use of experimental structures suffers from another more subtle difficulty in calculations at the EHMO level. This is that EHMO calculations do not optimize correct bond lengths for boranes but predict them to be much larger than found by experiment and to be larger by varying amounts for different boranes. Thus for $B_6H_6^{2-}$ the experimental B–B distance is 1.69 Å, whereas the optimized EHT distance is 1.92 Å; the deviation is worse for $B_8H_8^{2-}$. This means that variations with nuclearity in orbital or total electronic energies of closo systems $B_nH_n^{2-}$ may reflect differences between the extent to which experimental structures depart from geometries that had been EHT optimized, rather than actual electronic differences between specific systems.

In an attempt to avoid this problem, we have carried out calculations on two series of hypothetical geometries that bracket the actual geometries. Except for $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$, in which all skeletal atoms lie on spherical surfaces and all faces are equilateral triangles, *closo*-borane structures lie between the two extremes of having all skeletal atoms on a spherical surface and all polyhedral edges equal in length. Typically, the atoms of lower coordination number lie on a sphere of radius some 15% greater than the radius of the sphere on which the more highly coordinated atoms lie, and the interatomic distances vary markedly with coordination number.[36,37]

Idealizing the cluster geometry to place all skeletal atoms on one sphere while retaining the correct molecular point group has the advantage of matching the geometry to that assumed in Stones's TSH theory. However, it requires very large variations in B–B distances for the nonregular polyhedra; for $B_7H_7^{2-}$ the equatorial bonds are 1.54 Å and the axial bonds are 1.86 Å if the radius of the skeletal sphere is set equal to the weighted average for the "experimental" structure derived from the carborane $C_2B_5H_7$. These large differences almost certainly affect the energy in ways that are highly unlikely to cancel internally for the same reasons that the experimental structure may not yield correct energy trends.

The third type of geometry considered, that assuming all polyhedral edges to be equal in length (which was the type of idealized geometry used by Hoffmann and Lipscomb[20] and by Evans[18] in earlier calculations on selected borane systems), has

the advantage of maintaining the atom connectivities and molecular point group characteristic of the cluster and keeps all energy contributions from nearest-neighbor B–B bonds constant. This affords the simplest basis for cluster energy comparisons, because any changes can only be due to symmetry and connectivity changes if no changes in bond length are permitted. However, such a geometry distorts some bond lengths substantially from the experimentally determined values, and may in addition overemphasize the role of nearest–neighbor interactions in determining cluster geometries, since it does not permit cross-cage interactions to modify neighbor B–B internuclear distances.

Method of Calculation

Calculations were carried out using the Hoffmann FORTICON program, obtained from the Quantum Chemistry Program Exchange.[38] 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. (Exploratory calculations with and without charge iteration gave similar qualitative trends.) A complete set of calculations was obtained for each nuclearity from 5 to 12 in each geometry pattern, and from 3 to 12 for the triangular assumption. In each case, all n hydrogen atoms were assumed to lie on B–H bonds radial from the center of mass of the molecule and 1.19 Å long. This produces, as has been noted before,[8] n bonding molecular orbitals below any of the skeletal bonding orbitals that are primarily exo B–H bonding and change very little with changing cluster geometry. These orbitals are not shown in our skeletal energy-level diagrams, but their energy contribution is included in the total electronic energy of the cluster.

For calculation on idealized experimental geometries, X-ray or neutron diffraction data were used, but idealized to the assumed correct molecular point group by setting symmetry-equivalent B–B bond lengths equal to the average shown for those bonds in the diffraction data. For $B_{11}H_{11}^{2-}$, a geometry was idealized to the C_{2v} point group from the geometry of $B_{11}H_{10}S(CH_3)_2^-$.[39] For $B_5H_5^{2-}$ and $B_7H_7^{2-}$, geometries were taken from estimates based on related carboranes and bond-length/atomic-connectivity trends.[40]

For calculations on spherical clusters, the radius of each sphere was set equal to the weighted average of the radii of the spheres on which the atoms lie in the experimental structure, and atomic positions were adjusted to the correct point group with B–B distances as nearly equal as possible, although as has been noted large variations are inevitable.

For calculations involving the triangular (ideal deltahedral) geometry, all B–B distances were taken as 1.700 Å. This is slightly too long for the smaller clusters and too short for the higher nuclearities, but is sufficiently close in all cases that topological features of the electronic energy should be reproduced.

It should be noted that it has been shown in previous work[42] that EHMO calculations do not select the D_{2d} dodecahedron of $B_8H_8^{2-}$ as the preferred 8-vertex polyhedron. This difficulty is not ameliorated by the present work; however, we expect to show that for closo species with the deltahedral geometries shown in Figure 1, EHMO calculations can predict correct patterns of chemical stability.

Results and Discussion

closo-**Borane Anions** $B_nH_n^{2-}$. Total electronic energies for the $B_nH_n^{2-}$ species with $n = 5$–12 are shown in Table I, calculated under each of the three geometric assumptions. In each case, the increment in electronic energy ΔE is shown, along with the difference between these increments for successive BH additions, $\Delta(\Delta E)$. The latter quantity is of interest in the following context. If we write the equation for the disproportionation of a $B_nH_n^{2-}$ cage and assume that in a condensed phase the entropy change

$$2B_nH_n^{2-} \rightleftharpoons B_{n-1}H_{n-1}^{2-} + B_{n+1}H_{n+1}^{2-}$$
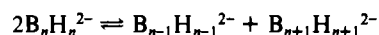
for such a reaction will be negligible and that the enthalpy change may be represented by the change in total electronic energy for the anions (that is, that there is no net change in lattice energy

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Table I. Electronic Energies and Increments for EHT Calculations on $closo\text{-}B_nH_n{}^{2-}$ Anions (eV)

species	triangular geometry			"experimental" geometry			spherical geometry		
	electronic energy	increment	Δ(ΔE)	electronic energy	increment	Δ(ΔE)	electronic energy	increment	Δ(ΔE)
$B_5H_5{}^{2-}$	-318.9354	} -60.8539	} +3.5577	-319.4615	} -60.2267	} +0.4634	-319.2696	} -60.4191	} +0.8769
$B_6H_6{}^{2-}$	-379.7893	} -57.2962	} -1.6594	-379.6887	} -59.7633	} +0.4475	-379.6887	} -59.5422	} -0.0033
$B_7H_7{}^{2-}$	-437.0855	} -58.9556	} -0.5736	-439.4520	} -59.3158	} -0.4639	-439.2309	} -59.5455	} -0.2341
$B_8H_8{}^{2-}$	-496.0411	} -59.5292	} +0.0204	-498.7678	} -59.7797	} +0.2048	-498.7764	} -59.7796	} +0.4569
$B_9H_9{}^{2-}$	-555.5703	} -59.5088	} +2.5342	-558.5475	} -59.5749	} +0.1302	-558.5560	} -59.3227	} +0.1453
$B_{10}H_{10}{}^{2-}$	-615.0791	} -56.9746	} -7.8683	-618.1224	} -59.4447	-2.4428	-617.8787	} -59.1774	} -3.2211
$B_{11}H_{11}{}^{2-}$	-672.0537	} -64.8429		-677.5671	} -61.8875		-677.0561	} -62.3985	
$B_{12}H_{12}{}^{2-}$	-736.8966			-739.4546			-739.4546		

on reaction), then the free energy change ΔG for the disproportionation becomes

$$\Delta G = (E_{n+1} - E_n) - (E_n - E_{n-1})$$
$$= \Delta(\Delta E)_n$$

That is, the quantity $\Delta(\Delta E)$ is a rough measure of the tendency of the borane anion to disproportionate, measured in electronvolts. Positive values of $\Delta(\Delta E)$ imply stability and negative values imply instability, with respect to disproportionation.

All of the assumed idealized geometries predict that $B_6H_6{}^{2-}$ and $B_{10}H_{10}{}^{2-}$ should be stable with respect to disproportionation, but the experimental geometry and the spherical geometry are perhaps questionable with respect to $B_{10}H_{10}{}^{2-}$. Equally, all geometries agree that $B_{11}H_{11}{}^{2-}$ should disproportionate readily into $B_{10}H_{10}{}^{2-}$ and $B_{12}H_{12}{}^{2-}$; this has been observed as a quantitative reaction by Klanberg and Muetterties[41] at temperatures above 250 °C. However, only the triangular (ideal deltahedral) geometry predicts $B_7H_7{}^{2-}$ to be unstable toward disproportionation, which has also been observed by the same workers.[42] They describe the preparation of $B_7H_7{}^{2-}$ by "air oxidation" of $B_8H_8{}^{2-}$, but this reaction is formally a reduction inasmuch as the electron density per boron atom is being increased; furthermore, the $Cs_2B_7H_7$ product was contaminated by large amounts of $B_6H_6{}^{2-}$ and significant amounts of $B_{10}H_{10}{}^{2-}$ and $B_{12}H_{12}{}^{2-}$ even though the starting material was reasonably pure $Na_2B_8H_8$. It is clear that not only the $B_7H_7{}^{2-}$ formed in the reaction but also the starting $B_8H_8{}^{2-}$ (and by implication any intermediate $B_9H_9{}^{2-}$) has disproportionated in the reaction. The $B_8H_8{}^{2-}$ is itself prepared by air oxidation of $B_9H_9{}^{2-}$, which would seem to be a comparable process since it is also found to yield $B_6H_6{}^{2-}$, $B_7H_7{}^{2-}$, and $B_{10}H_{10}{}^{2-}$ (along with $B_3H_8{}^{-}$, other borane anions, and small amounts of boric acid, which clearly is an oxidation product).

We may conclude from these experiments that $B_6H_6{}^{2-}$ and $B_{10}H_{10}{}^{2-}$ are stable with respect to disproportionation and that $B_7H_7{}^{2-}$, $B_8H_8{}^{2-}$, and $B_9H_9{}^{2-}$ are unstable, with $B_7H_7{}^{2-}$ showing the greatest instability. This is exactly the pattern indicated by the calculations done on the triangular (ideal deltahedral) basis, but is only roughly consistent with the calculations on the other two geometries. In the ensuing discussion, all calculations relate to triangular geometries. We surmise that the inaccuracy for the other two geometries may be due to the failure of EHMO calculations to reproduce the radial dependence of B–B bond energies, as described in the previous section.

It is well-known that $B_{12}H_{12}{}^{2-}$ ion is extremely thermally stable, toward disproportionation as well as other degradative reactions.[43] Since a 13-vertex convex deltahedron cannot be constructed from equilateral triangles, we have no $\Delta(\Delta E)$ value for $B_{12}H_{12}{}^{2-}$ and cannot quantitatively predict its stability. However, Figure 2 gives an alternative presentation of data from Table I that at least suggests considerable stability for $B_{12}H_{12}{}^{2-}$. The figure plots total electronic energy per boron atom against nuclearity and indicates stability for any n value at which the curve is concave upward and instability for any n at which the curve is concave downward. Again, n values of 6 and 10 are stable and n values of 7–9 are
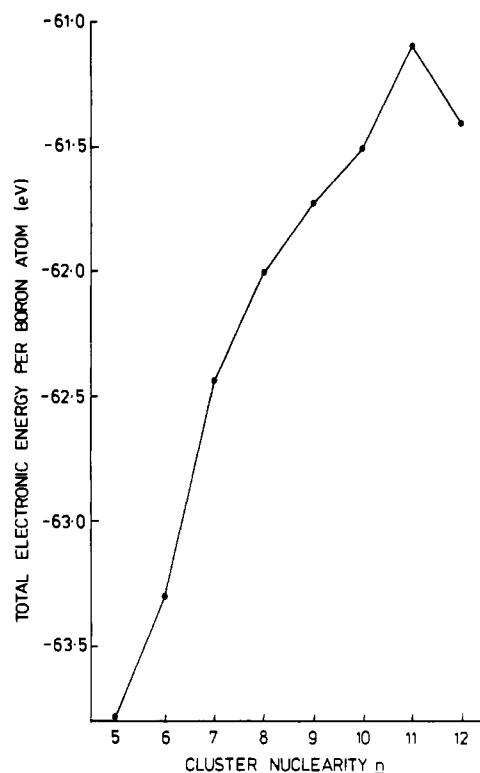
(43) Middaugh, R. L. In ref 3, p 282.

Figure 2. Total electronic energy per boron atom for $B_nH_n{}^{2-}$ clusters as a function of cluster nuclearity n (assuming equilateral-triangle cluster faces).
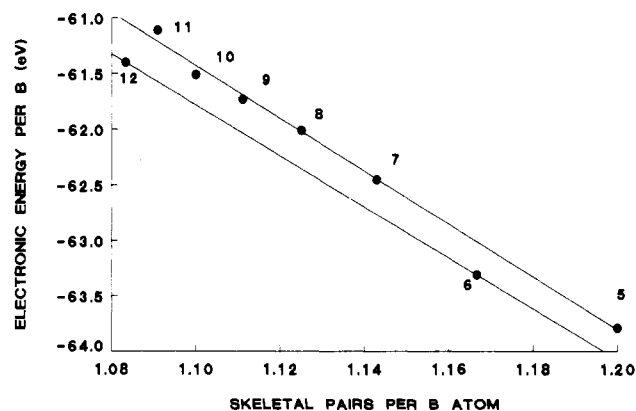

Figure 3. Total electronic energy per boron atom for $B_nH_n{}^{2-}$ clusters as a function of skeletal bonding electron density per boron atom.

unstable. $B_{11}H_{11}{}^{2-}$ is seen to be so unstable that it is difficult to imagine a degree of stability in terms of electronic energy per boron atom for a hypothetical $B_{13}H_{13}{}^{2-}$ that would make the curve concave downward at $n = 12$. It thus seems likely that the EHMO calculations correctly indicate great stability toward disproportionation for $B_{12}H_{12}{}^{2-}$ ion.
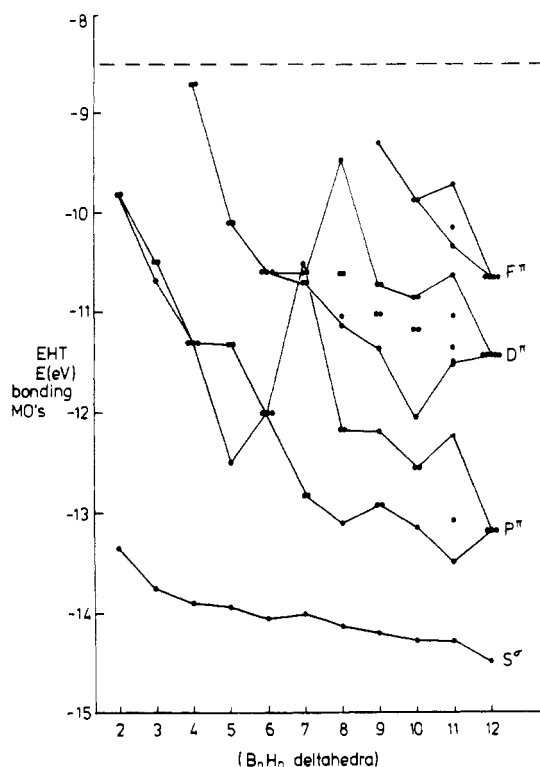
Figure 4. Individual skeletal bonding EHMO energies as a function of cluster nuclearity n. Orbital symmetries are grouped according to Stone tensor surface harmonic designations (refs 8 and 29). The dashed line indicates the nonbonding B 2p atomic orbital energy.

Table II. Electronic Energies and Increments for *closo*-B_nH_n (eV)

species	electronic energy	increment	$\Delta(\Delta E)$	HOMO degenerate
B_2H_2	−119.3336	} −59.6690		*
B_3H_3	−179.0026	} −61.3427	} −1.6737	*
B_4H_4	−240.3453	} −58.3883	} +2.9544	
B_5H_5	−298.7336	} −59.8371	} −1.4488	*
B_6H_6	−358.5707	} −57.5072	} +2.3299	*
B_7H_7	−416.0779	} −61.0241	} −3.5169	
B_8H_8	−477.1020	} −59.8661	} +1.1580	
B_9H_9	−536.9681	} −58.3702	} +1.4959	
$B_{10}H_{10}$	−595.3583	} −57.2832	} +1.0870	*
$B_{11}H_{11}$	−652.6215	} −62.9669	} −5.6837	
$B_{12}H_{12}$	−715.5884			*

The general decrease of electronic energy per boron atom with increasing n in Figure 2 is not surprising, because the number of skeletal electron pairs per boron atom, $(n + 1)/n$, also decreases with increasing n. Figure 3 plots electronic energy per boron atom against skeletal electron pairs per boron atom. From this plot it is evident that the *closo*-borane anions $B_nH_n^{2-}$ fall into two main categories, with $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$ markedly more stable than the remainder, among which $B_{11}H_{11}^{2-}$ and perhaps $B_5H_5^{2-}$ make the least effective use of their skeletal electrons, in accord with what is already known experimentally about these species.[40]

Closo Neutral Halides B_nX_n ($n = 4$–12). We have already noted the existence of deltahedral structures for several neutral halides B_nX_n. Morrison[44,45] has reported perchloro and perbromo compounds with $n = 4, 7, 8, 9, 10, 11, 12$ and a possible paramagnetic species B_6Br_6. Such species have two fewer skeletal electrons than the *closo*-borane anions and appear to represent violations of the electron-counting rules for deltahedral structures. However, EHMO calculations are ideally suited for the quantitative comparison of electronic energies between $B_nH_n^{2-}$ and a hypothetical B_nH_n taken as a model compound for the corresponding halide. This is because the absence of explicit electron–electron repulsion energy computation means that the individual enery levels in an EHMO calculation will be the same for either case; only the identity of the HOMO changes. Du-Jie[46] has shown that the pattern of EHT HOMO energies are as function of nuclearity for $B_nX_n^{2-}$ is essentially independent of whether X is H, Cl, or Br, and Preetz[47] has shown through vibrational spectra of $B_6X_6^{2-}$ that the bonding in the octahedral B_6 cage is nearly unaffected by the change from H to Cl or Br.

To this level of approximation, then, we may expect neutral B_nH_n (and by implication B_nX_n) to be stable if the HOMO for $B_nH_n^{2-}$ is nearly nonbonding, so that the electrons to be removed are not strongly held to the cluster. If we assume a strict sepa-

rability between cluster bonding orbitals and terminal hydrogen bonding orbitals (not strictly true, but a useful approximation), the nonbonding energy will be that of a boron 2p atomic orbital, −8.5 eV in these calculations. Figure 4 shows the orbital energies of clusters from $n = 2$ to $n = 12$ that have a net bonding quality (skeletal orbitals only). Stone symmetry notation[8] is used, because the usual irreducible representation notation is not very helpful when the symmetry changes at every nuclearity.

For each nuclearity in Figure 4, there are $n + 1$ skeletal bonding orbitals except for $n = 4$, for which in accordance with previous calculations there are n bonding skeletal orbitals and a degenerate pair of nearly nonbonding orbitals. It is immediately apparent that for $B_nH_n^{2-}$ the most nearly nonbonding frontier electrons are those for $n = 4, 8$, and 9, precisely the nuclearities for which the most stable deltahedral B_nX_n structures have been demonstrated. From Figure 4, it should also be possible to prepare B_7H_7 and $B_{11}H_{11}$ with deltahedral structures, but nuclearities of 5, 6, 10, and 12 would have degenerate HOMO's for B_nX_n and should have distorted nondeltahedral geometry if they exist at all. In fact, B_7Br_7, $B_{10}X_{10}$, $B_{11}Cl_{11}$, and $B_{12}Cl_{12}$ have been reported,[44,45] although the authors note that, contrary to the case for the borane anions, nuclearity 9 is more thermally stable than nuclearity 10: with some variations of solvent dependence and temperature dependence, the thermal stability of neutral B_nX_n appears to fall in the order $n = 9 > 10 > 11 > 12 > 8 > 7$. Although we would not propose a bicapped square-antiprismatic structure for $B_{10}X_{10}$ or an icosahedral structure for $B_{12}Cl_{12}$, since these would be diradicals, it is interesting to note from Figure 4 that the HOMO for B_9H_9 is lower that that for B_7H_7, B_8H_8, $B_{10}H_{10}$, $B_{11}H_{11}$, or $B_{12}H_{12}$, in keeping with this experimental observation. Bromination of $B_{11}H_{11}^{2-}$ yields $B_{10}Br_{10}^{2-}$, suggesting considerable stability for that anion.[39] $B_9X_9^{2-}$ anions have also been prepared,[48] along with $B_9X_9^{-}$ radicals (SO_2Cl_2 and I^- respectively). This is entirely consistent with the energy levels of Figure 4, in which the frontier electrons of $B_9H_9^{2-}$ are in a modestly bonding molecular orbital.

Chemical stability to disproportionation of the neutral halides may be estimated by the same approach as that for the dianions. Table II provides the data needed to calculate approximate free energies of disproportionation by this argument. However, for the neutral halides the presence of degenerate HOMO's for $B_nH_n^{2-}$ at $n = 5, 6, 10$, and 12 suggests that those nuclearities as neutral halides should be unstable with respect to distortion away from deltahedral geometry. These nuclearities are starred in Table II. We might expect a neutral B_nX_n halide to be stable if (1) its deltahedral model has a nondegenerate HOMO or completely filled degenerate HOMO set and (2) its B_nH_n model has a positive free energy for disproportionation. Such an argument indicates stability for B_4X_4, B_8X_8, and B_9X_9, which are in fact among the most stable bromides. However, the numerical values of $\Delta(\Delta E)$ in Table II will depend not only on the nondegenerate or undistorted character of the halide B_nX_n but also on those at $n − 1$ and

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$n + 1$. 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.

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

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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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