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# Three-dimensional Aromaticity in Deltahedral Borane Anions: Comparison of Topological and Computational Approaches

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## Abstract

The molecular orbital energy parameters obtained from *ab initio* SCF MO Gaussian 82 computations on the series of deltahedral borane anions $B_nH_n^{2-}$ ($n$ = 5, 6, 7, 8, 9, 10, 12) correspond more closely to $D_n$ deltahedral core bonding topology than to $K_n$ complete core bonding topology. However, core-surface mixing, as noted previously for icosahedral $B_{12}H_{12}^{2-}$, raises the energies of all of the core molecular orbitals, except the lowest energy fully symmetric core orbital, to antibonding levels. For this reason the graph-theory derived model using $K_n$ complete core bonding topology gives the correct number of bonding and antibonding orbitals and hence the correct number of skeletal electrons for the deltahedral boranes. Extension of this topological analysis to self-consistent molecular orbital computations on the perchloroborane anions $B_nCl_n^{2-}$ ($n$ = 6, 12) suggests that substitution of chlorine for hydrogen in the deltahedral boranes leads to more nearly deltahedral core bonding as well as a weakening of core bonding relative to surface bonding in accord with the expected electron withdrawing tendencies of chlorine relative to hydrogen. In addition, deltahedral borane anion computations using Gaussian orbitals rather than Slater orbitals lead to core bonding topology which is more nearly deltahedral rather than complete and weaker core bonding relative to surface bonding in accord with the more rapid decrease in the electron density of Gaussian orbitals at increasing distances relative to Slater orbitals.

## Introduction

A classical concept in organic chemistry is the aromaticity of two-dimensional planar delocalized hydrocarbons exhibiting unusual chemical stability of which benzene is the prototype [1]. More recently inorganic chemists have discovered three-dimensional *closo*-borane anions, also of unusual chemical stability of which $B_nH_n^{2-}$ ($6 \leqslant n \leqslant 12$) are the prototypes [2]. These anions have structures that are based on closed polyhedra with only triangular faces and therefore such polyhedra are often called *deltahedra*. The unusual stability of these co-called electron-deficient deltahedral boranes has led to the development of the concept of three-dimensional aromaticity [3]. A qualitative graph-theory derived model for chemical bonding in such delocalized systems [4] demonstrates the analogy between the aromaticity in the planar polygonal hydrocarbons and that in deltahedral boranes. Since these properties are based on neighborhood relationships such as the presence or absence of chemical bonds between pairs of atoms or the connectivity within the molecular structure, such properties may be considered to be related to the topology of the molecule. Tensor surface harmonic theory [5] has also been used very effectively to describe the delocalized chemical bonding in deltahedral boranes.

An important objective of recent work by one of us (R.B.K.) has been a detailed understanding of the relation between the qualitative graph-theory derived model [4] and quantitative computations on deltahedral boranes. The first effort in this direction [6] involved a comparison of the molecular orbital energy parameters predicted by the graph-theory derived model with those obtained in the original 1962 LCAO-MO extended Hückel computations of Hoffmann and Lipscomb [7] on the highly symmetrical octahedral $B_6H_6^{2-}$ and icosahedral $B_{12}H_{12}^{2-}$. Subsequent refinement of the data analysis methods [8] has allowed the comparison between topological and computational methods to be extended to some less symmetrical deltahedral boranes as well as to more sophisticated self-consistent-field but still semiempirical molecular orbital computations of Armstrong *et al.* [9].

A requirement for comparison of topological and computational methods for estimating molecular orbital energies is the availability of all orbital energy

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parameters including those of the unfilled antibonding (virtual) orbitals. Unfortunately, many of the important reported computations on deltahedral boranes [10–15] do not provide these antibonding orbital energy parameters. Therefore, we extracted this information from some recent *ab initio* SCF MO Gaussian 82 computations [16] on the deltahedral borane anions $B_nH_n^{2-}$ ($n = 5, 6, 7, 8, 9, 10, 12$). This paper reports a comparison between these computations and the predictions of the topological methods [4] and introduces a number of refinements in the previously reported approach [6, 8] for comparison of topological and computational methods. These refinements facilitate study of the less symmetrical deltahedral borane anions. In addition, they provide for the first time a means for assessing substituent effects by comparing previously reported [9] computations on the octahedral ($n = 6$) and icosahedral ($n = 12$) borane anions $B_nH_n^{2-}$ with those on their perchloro analogues $B_nCl_n^{2-}$.

## Topological Methods

The topology of a chemical bonding network can be represented by a graph in which the vertices correspond to atoms or orbitals participating in the bonding and the edges correspond to bonding relationships. Methods discussed elsewhere [4, 17–19] indicate that each eigenvalue $x_k$ of the adjacency matrix of such a graph corresponds to a Hückel molecular orbital with energy $E_k$ given by the following equation

$$E_k = \frac{\alpha + x_k\beta}{1 + x_kS} \tag{1}$$

where $\alpha$ is the standard coulomb integral, assumed to be the same for all atoms, $\beta$ is the resonance integral, taken to be the same for all bonds, and $S$ is the overlap integral between atomic orbitals on neighboring atoms. Positive and negative eigenvalues $x_k$ from eqn. (1) thus correspond to bonding and antibonding orbitals, respectively.

A difficulty in applying eqn. (1) is the need to determine three parameters $\alpha$, $\beta$ and $S$ to relate the eigenvalue $x_k$ to the corresponding orbital energies $E_k$. Any actual system provides too few relationships to determine fully all of these three parameters. Therefore, some assumptions concerning the values of $\alpha$, $\beta$ and $S$ are necessary for any comparisons to be feasible. The approach that is generally taken is to assume a zero value for $S$ thereby reducing eqn. (1) to the linear equation

$$E_k = \alpha + x_k\beta \tag{2}$$

The approach used in this paper then determines $\alpha$ from the midpoint of all of the molecular energies through taking an appropriate weighted average. For reasons dincussed later, this represents an improvement over the previously used [8] procedure for determining $\alpha$ from the midpoint of selected orbital energies. The third parameter $\beta$ is determined from specific orbital energies.

The two extreme types of skeletal chemical bonding in molecules formed by polyhedral clusters of atoms such as polyhedral borane anions or metal clusters may be called *edge-localized* and *globally delocalized* [4, 20]. An edge-localized polyhedron has two-electron two-center bonds along each edge of the polyhedron and is favored when the numbers of internal orbitals from the vertex atoms match the vertex degrees (the number of edges meeting at a vertex is its degree). A globally delocalized polyhedron has a multicenter core bond in the center of the polyhedron and is favored when the numbers of internal orbitals from the vertex atoms do not match the vertex degrees. Fully globally delocalized polyhedra are deltahedra, namely polyhedra in which all faces are triangles. The four valence orbitals of vertex boron atoms in polyhedral boranes are partitioned into one external orbital for bonding to hydrogen (e.g. in $B_nH_n^{2-}$) or another external group and three internal orbitals for the skeletal bonding. Since globally delocalized borane deltahedra are more stable than edge-localized borane deltahedra, the favored deltahedra in the $B_nH_n^{2-}$ anions are those without degree 3 vertices. This accounts for the ability to isolate stable $B_nH_n^{2-}$ anions for $6 \leqslant n \leqslant 12$ based on deltahedra with only degree 4 and 5 vertices (except for a single degree 6 vertex in $B_{11}H_{11}^{2-}$ [21]) but the inability to isolate a stable $B_5H_5^{2-}$ salt where the only possible deltahedral structure, namely the trigonal bipyramid, has two degree 3 vertices. Although $B_5H_5^{2-}$ has not been prepared, its isoelectronic, isostructural, but heteroatomic analog, $C_2B_3H_5$, is known and therefore $B_5H_5^{2-}$ has been included in this paper along with $B_nH_n^{2-}$ ($n = 6, 7, 8, 9, 10, 12$) with no indication of any unusual features for the anomalous $B_5H_5^{2-}$. The relevant deltahedra are depicted in Fig. 1 and their topological properties are listed in Table 1.

Let us now consider some important features of the chemical bonding topology in the deltahedral boranes $B_nH_n^{2-}$. In such systems [4] the three internal orbitals on each vertex atom are partitioned into two twin internal orbitals (called tangential in some treatments [22]) and a unique internal orbital (called radial in some treatments [22]). Pairwise overlap between the $2n$ twin internal orbitals is responsible for the surface bonding on the deltahedron and leads to the splitting of these $2n$ orbitals into $n$ bonding and $n$ antibonding orbitals. The magnitude of this splitting is designated as $2\beta_s$ where $\beta_s$ relates to the parameter $\beta$ in eqns. (1) and (2). This portion of the chemical bonding topology results in bonding over the two-dimensional surface of the deltahedron, which may be regarded as topologically homeomorphic to the sphere [23]. This surface bonding can be represented by a disconnected graph $G_s$ having $2n$ vertices corresponding to the $2n$ twin internal orbitals and $n$ isolated $K_2$ components; a $K_2$ component has only two vertices joined by an edge.

The surface bonding in the deltahedral boranes $B_nH_n^{2-}$ is supplemented by additional bonding and antibonding orbitals formed by global mutual overlap of the $n$ unique internal orbitals [4]. This portion of the chemical bonding topology results in an $n$-center bond directed towards the center of the polyhedron. This core bonding can be represented by a graph $G_c$ in which the vertices correspond to the vertex atoms of the deltahedron, or equivalently their unique internal orbitals, and the edges represent pairs of overlapping unique internal orbitals. The relative energies $E_c$ of the additional molecular orbitals arising from the core bonding are determined from the eigenvalues $x_c$ of the adjacency matrix $A_c$ of graph $G_c$ using $\beta$ or more specifically $\beta_c$ as the energy unit (eqns. (1) and (2)). The ratio $\beta_c/\beta_s$ measures the magnitude of the core interactions involving the unique internal orbitals relative to the surface interactions involving the twin internal orbitals.

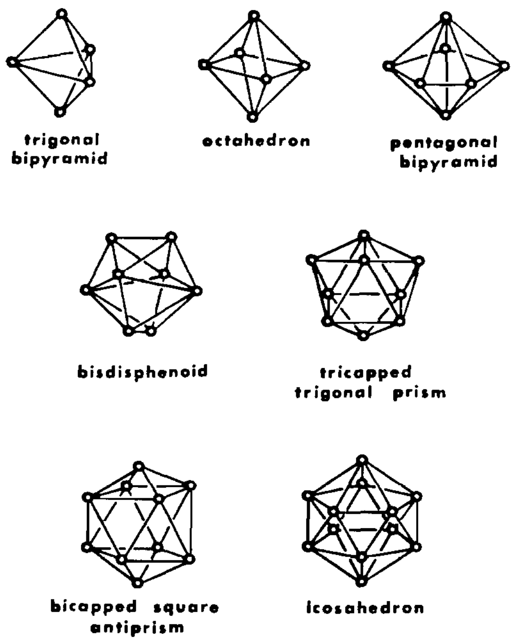

Fig. 1. The seven polyhedral structures for the *closo*-boranes $B_nH_n^{2-}$, $n = 5, 6, 7, 8, 9, 10,$ and 12.

A critical question is the nature of the core bonding graph $G_c$ for the deltahedral boranes $B_nH_n^{2-}$. The two limiting possibilities for $G_c$ are the complete graph $K_n$ and the deltahedral graph $D_n$ and the corresponding core bonding topologies can be called the complete and deltahedral topologies, respectively. In the complete graph $K_n$ each vertex has an edge going to every other vertex leading to a total of $n(n-1)/2$ edges [24]. Regardless of the value of $n$, the complete graph $K_n$ has only one positive eigenvalue, namely $n-1$, and $n-1$ negative eigenvalues, namely $-1$ each. The deltahedral graph $D_n$ is identical to the 1-skeleton [25] of the deltahedron. Thus, two vertices of $D_n$ are connected by an edge if, and only if, the corresponding vertices of the deltahedron are connected by an edge. The eigenvalues of the graphs $D_n$ for the deltahedra of interest are listed in Table 1. Note that the graphs $D_n$ for the deltahedra of interest with seven or more vertices all have at least three positive eigenvalues. However, in all cases there is a unique positive eigenvalue, which can be called the

TABLE 1. Topological properties of the deltahedra discussed in this paper

| Deltahedron | Symmetry point group | Vertices | Number of edges | Faces | Eigenvalues of the corresponding deltahedral graph[a] |
|---|---|---|---|---|---|
| Trigonal bipyramid | $D_{3h}$ | 5 | 9 | 6 | (+3.646)/0/−1/−1/−1.646 |
| Octahedron | $O_h$ | 6 | 12 | 8 | (+4)/0/0/0/−2/−2 |
| Pentagonal bipyramid | $D_{5h}$ | 7 | 15 | 10 | (+4.316)/0.618/+0.618/0/−1.618/−1.618/−2.316 |
| Bisdisphenoid '$D_{2d}$ dodecahedron' | $D_{2d}$ | 8 | 18 | 12 | (+4.541)/+1.303/+0.618/+0.618/−1.541/−1.618/ −1.618/−2.303 |
| 4,4,4-Tricapped trigonal prism | $D_{3h}$ | 9 | 21 | 14 | (+4.702)/+1.414/+1.414/+1/−1.702/−2/−2/ −2.828/−2.828 |
| 4,4-Bicapped square antiprism | $D_{4d}$ | 10 | 24 | 16 | (+4.828)/+2/+1.414/+1.414/−0.828/−1.414/ −1.414/−2/−2/−2 |
| Icosahedron | $I_h$ | 12 | 30 | 20 | (+5)/+2.236/+2.236/+2.236/−1/−1/−1/−1/−1/ −2.236/−2.236/−2.236 |

[a]The eigenvalues are listed in descending order with the principal eigenvalue in parentheses.

*principal eigenvalue*, which is much more positive than any of the other positive eigenvalues. The principal eigenvalue arises from the fully symmetric pathway of the symmetry factoring scheme used to determine the eigenvalues of the deltahedron, namely the pathway using $G_g$ components at branches from two-fold symmetry operations and $G_a$ components at branches from three-fold symmetry operations [26]. The molecular orbital corresponding to the principal eigenvalue of $G_c$ may be called the principal core orbital.

The deltahedral boranes of the stoichiometry $B_nH_n^{2-}$ have $2n+2$ skeletal electrons. The surface bonding uses $2n$ of these skeletal electrons leaving only two electrons for the core bonding corresponding to a single core bonding molecular orbital and a single positive eigenvalue for $G_c$. Thus, only if $G_c$ is taken to be the corresponding complete graph $K_n$ will the simple model given above for globally delocalized deltahedra give the correct number of skeletal electrons in all cases, namely, $2n+2$ skeletal electrons for $6 \leqslant n \leqslant 12$. Such a model with complete core bonding topology is the basis for the graph-theory derived model for the chemical bonding topology of deltahedral boranes and metal clusters discussed in previous papers [4, 19, 27, 28]. However, deltahedral core bonding topology can also account for the observed $2n+2$ skeletal electrons in the $B_nH_n^{2-}$ deltahedral boranes if there is a mechanism for raising the energies of all of the core molecular orbitals other than the principal core orbital to antibonding energy levels. The original graph-theoretical analysis [6] of the 3N Hoffmann–Lipscomb LCAO-MO extended Hückel computations [7] on icosahedral $B_{12}H_{12}^{2-}$ showed that four core orbitals would be bonding orbitals except for core-surface orbital mixing which raises the energies of three of these four core orbitals to antibonding levels leaving only the principal core orbital as a bonding core orbital. The new SCF MO computations on $B_nH_n^{2-}$ presented in this paper are also consistent with deltahedral rather than complete core bonding topology for all values of $n$ between 6 and 12 with core-surface mixing raising the energies of all core orbitals except the principal core orbital to antibonding levels.

The distinction between complete and deltahedral core bonding topology is most clearly explained for octahedral $B_6H_6^{2-}$. Among the 15 pairs of six vertices in an octahedron ($D_6$ graph) 12 pairs correspond to octahedral edges (*cis* interactions) and the remaining three pairs consist of antipodal vertices related by the inversion center and *not* connected by an edge (*trans* interactions). However, all of the 15 pairs of six vertices in a complete $K_6$ graph correspond to edges of equal weight. In an octahedral array of six points a parameter $t$ can be defined as the ratio of the *trans* interactions to the *cis* interactions. This parameter $t$ is 0 for pure octahedral ($D_6$) topology and 1 for pure complete ($K_6$) topology. Values of $t$ between 0 and 1 can be used to measure gradations of topologies between $D_6$ and $K_6$ corresponding to the weighting of edges representing *trans* interactions relative to those representing *cis* interactions in the underlying graph. Most significantly, the value of $t$ for a given computation on $B_6H_6^{2-}$ can be estimated from the energy parameters for the $A_{1g}$ and $E_g$ core molecular orbitals [6, 8]. The core bonding topology corresponding to a given computation on $B_6H_6^{2-}$ can thus be determined.

In order to determine possibilities for core-surface orbital mixing as well as core-external and surface-external orbital mixing, the representations of the relevant sets of orbitals are required. These are listed in Table 2 for the deltahedra of interest. The representation $\Gamma_\sigma$ appears in triplicate for the core, external bonding, and external antibonding orbitals and the representation $\Gamma_\pi$ appears once for the surface orbitals. Thus, the only pure orbitals are the $\pi$ surface orbitals which have irreducible representations not found in the $\Gamma_\sigma$ set; these are starred in Table 2. The purity of these surface orbitals is shown most clearly in our computations on $B_nH_n^{2-}$ derivatives by the complete absence of any hydrogen 1s components in these orbitals. The principal core orbitals, although not pure, are of such low energies that they do not mix significantly with higher energy

TABLE 2. Orbital representations for the deltahedra discussed in this paper

| Deltahedron | $\Gamma_\sigma$ (core and external orbitals) | $\Gamma_\pi$ (surface orbitals)[a] |
|---|---|---|
| Trigonal bipyramid | $2A_1' + E' + A_2''$ | $A_2' + 2E' + A_2'' + 2E''$ |
| Octahedron | $A_{1g} + T_{1u} + E_g$ | $T_{1u} + T_{2g}^* + T_{2u}^* + T_{1g}^*$ |
| Pentagonal bipyramid | $2A_1' + E_1' + E_2' + A_2''$ | $A_2'^* + 2E_1' + E_2' + A_2'' + 2E_1''^* + E_2''^*$ |
| Bisdisphenoid ('*D*$_{2d}$ dodecahedron') | $2A_1 + 2B_2 + 2E$ | $2A_1 + 2A_2^* + 2B_1^* + 2B_2 + 4E$ |
| 4,4,4-Tricapped trigonal prism | $2A_1' + 2E' + A_2'' + E''$ | $A_1' + 2A_2'^* + 3E' + A_1''^* + 2A_2'' + 3E''$ |
| 4,4-Bicapped square antiprism | $2A_1 + 2B_2 + E_1 + E_2 + E_3$ | $A_1 + A_2^* + B_1^* + B_2 + 3E_1 + 2E_2 + 3E_3$ |
| Icosahedron | $A_g + T_{1u} + T_{2u} + H_g$ | $T_{1u} + H_g + G_u^* + G_g^* + H_u^* + T_{1g}^*$ |

[a] The pure surface orbitals are starred.

orbitals belonging to the same totally symmetric $A_{1g}$-type irreducible representations. Thus, for a given computation on a $B_nH_n^{2-}$ anion the energy parameters of the pure surface orbitals and the principal core orbitals are the best numbers to use to calculate parameters of interest such as $\alpha$, $\beta_c$, and $\beta_s$.

These ideas concerning the skeletal bonding in deltahedral borane anions can be related to tensor surface harmonic theory as developed by Stone [5] and elaborated by Johnston and Mingos [29]. The orbitals of the $\Gamma_\sigma$ representation such as the $n$ core orbitals correspond to the (scalar) sphercial harmonics which for deltahedra with $n$ vertices correspond successively to the single $S^\sigma$, the three $P^\sigma$, the five $D^\sigma$, the seven $F^\sigma$ orbitals, etc., of increasing energy and nodality. The orbitals of the $\Gamma_\pi$ representation such as the surface orbitals correspond to the vector spherical harmonics which for deltahedra with $n$ vertices correspond successively to three $P^\pi$, five $D^\pi$, seven $F^\pi$ bonding/antibonding orbital pairs, etc., of increasing energy and nodality. This relates to the following aspects of the graph theory derived model for the skeletal bonding in deltahedral boranes.

(1) The principal core orbital corresponds to the $S_s^\sigma$ orbital in tensor surface harmonic theory. Since there are no $S_p^\pi$ or $\bar{S}_p^\pi$ surface orbitals, the principal ($S_s^\sigma$) core orbital cannot mix with any surface orbitals in accord with ideas discussed above.

(2) The three core orbitals of lowest energy other than the principal ($S_s^\sigma$) core orbital correspond to $P_s^\sigma$ orbitals in tensor surface harmonic theory. These orbitals correspond to the three most positive eigenvalues other than the principal eigenvalue of the corresponding deltahedra (Table 1). The $P_s^\sigma$ core orbitals mix with the $P_p^\pi$ surface orbitals so that the $P_s^\sigma$ core orbitals become antibonding with concurrent lowering of the energies of the $P_p^\pi$ surface orbitals below the energies of the other surface bonding orbitals. Thus, in computations of orbital energies of deltahedral borane anions, the lowest lying molecular orbital is the principal ($S_s^\sigma$) core orbital and the next lowest lying orbitals are three $P^\pi$ surface orbitals which will be degenerate in the case of octahedral $B_6H_6^{2-}$ and icosahedral $B_{12}H_{12}^{2-}$ but not in the cases of the less symmetrical deltahedra. This ordering of the lowest lying molecular orbitals is particularly apparent in the MNDO computations presented by Brint *et al.* [13]. However, their label of $P^\sigma$ rather than $P^\pi$ for the three orbitals immediately above the principal core orbital $S^\sigma$ obscures the relationship of their computed molecular orbitals to those predicted by the graph-theory derived method.

## Comparison of Topological and Computational Approaches

In order to relate a given computation on a deltahedral borane to topological models for its chemical bonding, all of the molecular orbital energy parameters are required including those for the unfilled antibonding (virtual) orbitals thereby precluding such an analysis for many of the published computations [10–15]. Having such information, the first step is to calculate $\alpha$, the energy 'zero point' in eqns. (1) and (2). In the original Hoffmann–Lipscomb computations [7] $\alpha$ could be taken to be zero so that its determination was no problem. In the previous paper [8] the value of $\alpha$ for the computations of Armstrong *et al.* [9] was determined from the average of the energy parameters of the pure surface orbitals. This procedure has the following two disadvantages.

(a) Only the energy parameters of the *pure* surface orbitals can be included in the averages since the energy parameters of the other surface orbitals are distorted by substantial core-surface and external-surface mixing. This introduces the possibility of sampling error.

(b) The energy parameters of both bonding and antibonding surface orbitals are required for the determination of $\alpha$. However, for $B_{10}H_{10}^{2-}$ the pure surface orbitals are all antibonding making it impossible to determine $\alpha$ by this method.

For these reasons the value of $\alpha$ corresponding to a given set of molecular orbital energy parameters was determined by taking the mean of the energy parameters for all $5n$ molecular orbitals of the $B_nH_n^{2-}$ derivative realizing that the degenerate orbitals of E, T, G, and H representations correspond to sets of 2, 3, 4, and 5 orbitals, respectively, having identical energy parameters. Hence, the parameter $\alpha$ becomes

$$\alpha = \sum_k g_k E_k \Big/ \sum_k g_k \qquad (3)$$

where $g_k$ is the degeneracy of energy level $E_k$ and the summation is over all orbitals $k$. The orbital energies listed in the tables are then $E_k' = E_k - \alpha$, such that $\sum_k g_k E_k' = 0$.

The surface energy unit, $\beta_s$, can also be estimated at this stage as the degeneracy-weighted average distance of the pure surface orbitals from the energy zero point $\alpha$. The sign of $\beta_s$ is the same as the sign of the bonding pure surface orbitals, namely positive for the Hoffman–Lipscomb energy parameters [7] and negative for the Armstrong–Perkins–Stewart energy parameters [9] as well as the new computations introduced in this paper. This method of determining $\beta_s$ from the pure surface orbitals is subject to sampling errors as noted above. In the previous paper [8] degeneracy weighting for determining $\beta_s$ (as well as $\alpha$) from the pure surface orbitals was not used. However, this only makes a difference for icosahedral $B_{12}H_{12}^{2-}$, and even in this case the difference was found to be minor.

TABLE 3. Analysis of the *ab initio* SCF MO Gaussian 82 computations on the deltahedral borane anions

| Parameter | $B_5H_5^{2-}$ | $B_6H_6^{2-}$ | $B_7H_7^{2-}$ | $B_8H_8^{2-}$ | $B_9H_9^{2-}$ | $B_{10}H_{10}^{2-}$ | $B_{12}H_{12}^{2-}$ |
|---|---|---|---|---|---|---|---|
| Principal core orbital[a] | $-1.063(A_1')$ | $-1.126(A_{1g})$ | $-1.137(A_1')$ | $-1.142(A_1)$ | $-1.157(A_1')$ | $-1.173(A_1)$ | $-1.184(A_g)$ |
| Pure surface orbitals[a] | $-0.453(E'')$ | $-0.486(T_{2g})$ | $-0.506(E_1'')$ | $-0.520(B_1)$ | $-0.444(A_2')$ | $+0.309(B_1)$ | $-0.526(G_u)$ |
| | $+0.321(A_2')$ | $+0.198(T_{2u})$ | $+0.223(E_2'')$ | $+0.087(A_2)$ | $+0.251(A_1'')$ | $+0.563(A_2)$ | $+0.156(G_g)$ |
| | $+0.527(E'')$ | $+0.548(T_{1g})$ | $+0.472(E_1'')$ | $+0.396(B_1)$ | $+0.655(A_2')$ | | $+0.445(H_u)$ |
| | | | $+0.740(A_2')$ | $+0.444(A_2)$ | | | $+0.682(T_{1g})$ |
| Lowest lying $P_\pi$ surface | $-0.828(A_2'')$ | $-0.848(T_{1u})$ | $-0.887(E_1')$ | $-0.928(B_2)$ | $-0.949(E')$ | $-0.995(B_2)$ | $-0.998(T_{1u})$ |
| Orbitals (see text)[a, b] | $-0.813(E')$ | | $-0.850(A_2'')$ | $-0.883(E)$ | $-0.885(A_2'')$ | $-0.934(E_1)$ | |
| $\alpha$ | +0.707 | +0.675 | +0.643 | +0.616 | +0.597 | +0.579 | +0.547 |
| $\beta_s$ | −0.456 | −0.429 | −0.466 | −0.415 | −0.448 | −0.436 | −0.467 |
| $\beta_c$(deltahedral) | −0.291 | −0.282 | −0.263 | −0.251 | −0.246 | −0.243 | −0.237 |
| $\beta_c/\beta_s$ | 0.638 | 0.657 | 0.564 | 0.604 | 0.549 | 0.557 | 0.507 |
| $\Delta E$ | 0.597 | 0.684 | 0.730 | 0.539 | 0.480 | 0.581 | 0.652 |

[a] The orbital energy parameters are given to $\alpha$ with negative parameters corresponding to bonding orbitals and positive parameters corresponding to antibonding orbitals. The energy unit is the hartree. The representations of the orbitals are given in parentheses. [b] These are the three surface orbitals whose energies are lowered significantly by core-surface mixing with the three $P_s^\sigma$ core orbitals.

Further analysis of the computed energy parameters either requires some special symmetry such as that found in octahedral $B_6H_6^{2-}$ or icosahedral $B_{12}H_{12}^{2-}$ or some further assumptions concerning the chemical bonding topology for the less symmetrical systems. In the cases of $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$ the core energy units $\beta_c$, and the non-adjacent atom unique internal orbital interactions (e.g. $t$ in $B_6H_6^{2-}$ and $m$ in $B_{12}H_{12}^{2-}$) can be estimated from the energy parameters of the principal core orbital and the other core orbital not mixing with surface orbitals. This method is subject to errors arising from core-external interactions. However, a comparison of the Hoffmann-Lipscomb '3*n*', '4*n*' and '5*n*' computations [7] suggests that these core-external interactions are not large.

The analysis of the molecular orbital parameters from our *ab initio* SCF MO Gaussian 82 computations on octahedral $B_6H_6^{2-}$ and icosahedral $B_{12}H_{12}^{2-}$ suggest deltahedral rather than complete core bonding topologies. Thus, for octahedral $B_6H_6^{2-}$ the parameter $t$ was found to be only 0.233, i.e. much closer to 0 than 1 indicating deltahedral ($D_6$) rather than complete ($K_6$) core bonding topology. If the core bonding topologies of the other less symmetric deltahedra are also assumed to be deltahedral rather than complete, then the core energy unit, $\beta_c$, can be found from the equation

$$\beta_c = E(A_1^\circ)/x(A_1^\circ) \qquad (4)$$

where $E(A_1^\circ)$ is the energy parameter for the principal core orbital and $x(A_1^\circ)$ is the principal eigenvalue of the corresponding deltahedral graph $D_n$ (Table 1).

Table 3 summarizes the analysis of our computations on the $B_nH_n^{2-}$ anions ($n = 5, 6, 7, 8, 9, 10, 12$) including the parameter energies for the principal core and pure surface orbitals and the values for $\alpha$, $\beta_c$, and $\beta_s$. Tables 4 and 5 summarize more detailed analyses of the octahedral and icosahedral systems, respectively, including comparisons of the results from the new computations with those from the earlier Hoffmann–Lipscomb [7] and Armstrong–Perkins–Stewart [9] computations. The refinements noted above in the procedure for determining $\alpha$ for the Armstrong–Perkins–Stewart [9] computations

TABLE 4. Analysis of computations on octahedral $B_6H_6^{2-}$ (X = H, Cl) anions[a]

| | $B_6H_6^{2-}$ | | | $B_6Cl_6^{2-}$ |
|---|---|---|---|---|
| | GD | HL5N | APS | APS |
| Core orbitals | | | | |
| $A_{1g}$ (principal) | −1.126 | +3.210 | −50.3 | −52.3 |
| $E_g$ | +0.470 | −0.888 | +13.6 | +17.7 |
| Pure surface orbitals | | | | |
| $T_{2g}$ | −0.486 | +0.493 | −5.5 | −11.1 |
| $T_{2u}$ | +0.198 | −0.416 | +9.8 | +14.8 |
| $T_{1g}$ | +0.548 | −0.671 | +11.7 | +16.0 |
| Derived parameters | | | | |
| $\alpha$ | +0.675 | 0 | +7.2 | −1.3 |
| $\beta_s$ | −0.429 | 0.527 | −8.1 | −13.2 |
| $\beta_c$ | −0.266 | 0.683 | −10.7 | −11.7 |
| $\beta_c/\beta_s$ | 0.620 | 1.296 | 1.320 | 0.886 |
| $t$ | 0.233 | 0.700 | 0.700 | 0.470 |

[a] GD = our (Gimarc–Dai) *ab initio* SCF MO Gaussian 82 computations; HL5N = Hoffmann–Lipscomb 5N computations [7]; APS = Armstrong–Perkins–Stewart computations [9]. Energy units: GD, hartrees; APS, electron volts; HL5N, dimensionless quantities given by $(\alpha - E_k)/(K - E_k)$ where $K$ is the proportionality constant between resonance integral $\beta$ and overlap $S$: $\beta_{rs} = KS_{rs}$.

TABLE 5. Analysis of computations on icosahedral $B_{12}X_{12}^{2-}$ (X = H, Cl) anions[a]

| | $B_{12}H_{12}^{2-}$ | | | $B_{12}Cl_{12}^{2-}$ |
|---|---|---|---|---|
| | GD | HL5N | APS | APS |
| Core orbitals | | | | |
| $A_g$ (principal) | −1.184 | +4.469 | −70.6 | −66.6 |
| $T_{2u}$ | +0.459 | −0.887 | +13.1 | +16.2 |
| Pure surface orbitals | | | | |
| $G_u$ | −0.526 | +0.518 | −4.7 | −3.4 |
| $G_g$ | +0.156 | −0.471 | +9.6 | +13.9 |
| $H_u$ | +0.445 | −0.678 | +11.3 | +15.4 |
| $T_{1g}$ | +0.682 | −0.782 | +11.8 | +15.8 |
| Derived parameters | | | | |
| $\alpha$ | +0.547 | 0 | +5.1 | −3.8 |
| $\beta_s$ | −0.467 | 0.580 | −7.8 | −9.2 |
| $\beta_c$ | −0.218 | 0.602 | −9.3 | −9.6 |
| $\beta_c/\beta_s$ | 0.466 | 1.039 | 1.192 | 1.043 |
| $m = 2p$ | 0.078 | 0.441 | 0.471 | 0.352 |

[a] GD = our (Gimarc–Dai) *ab initio* SCF MO Gaussian 82 computations; HL5N Hoffmann–Lipscomb 5N computations [7]; APS = Armstrong–Perkins–Stewart computations [9]. Energy units: GD, hartrees; APS, electron volts; HL5N, dimensionless quantities given by $(\alpha - E_k)/(K - E_k)$ where $K$ is the proportionality constant: $\beta_{rs} = KS_{rs}$.

make some of the numbers in Tables 4 and 5 slightly different from those reported previously [8].

### Octahedral and Icosahedral Borane Anions

Symmetry factoring methods [26] described in greater detail in an earlier paper [6] indicate that in the absence of core-surface orbital mixing and core-external orbital mixing the energy parameters of the octahedral core orbitals in $B_6H_6^{2-}$ relative to $\alpha$ are determined by the equations

$$E(A_{1g})_c = (4 + t)\beta_c \tag{5a}$$

$$E(T_{1u})_c = -t\beta_c \tag{5b}$$

$$E(E_g)_c = (-2 + t)\beta_c \tag{5c}$$

where $\beta_c$ is the core energy unit and $t$ is the ratio of *trans* to *cis* interactions. A comparison of the molecular orbital energy parameters from the $3n$, $4n$, and $5n$ computations on $B_6H_6^{2-}$ by Hoffmann and Lipscomb [7] suggests that core-external orbital mixing, unlike core-surface orbital mixing, is relatively minor. The energies of the $A_{1g}$ core orbital, readily recognized as by far the most strongly bonding core orbital, and of an antibonding $E_g$ orbital can therefore be used to calculate the parameters $\beta_c$ and $t$ given in Table 4. In cases where the two antibonding $E_g$ orbitals differ significantly in energy as in our computations (GD in Table 1) only one of the two possible choices, namely the less antibonding $E_g$ orbital, was found to give a physically reasonable positive value of $t$ between 0 and 1. The $E_g$ orbital giving such a positive value of $t$ was therefore chosen to be the core orbital leaving the more strongly antibonding $E_g$ orbital to be an antibonding external orbital.

A similar method can be used to analyze the molecular orbital energy parameters of icosahedral $B_{12}H_{12}^{2-}$ but there are added difficulties because the usable system of equations is underdetermined. The energy parameters of the four core bonding orbitals of icosahedral $B_{12}H_{12}^{2-}$ relative to $\alpha$ are thus determined by the equations

$$E(A_{1g})_c = (5 + 5m + p)\beta_c \tag{6a}$$

$$E(T_{1u})_c = [\sqrt{5}(1 - m) - p]\beta_c \tag{6b}$$

$$E(H_g)_c = (-1 - m + p)\beta_c \tag{6c}$$

$$E(T_{2u})_c = [-\sqrt{5}(1 - m) - p)]\beta_c \tag{6d}$$

where $\beta_c$ is the core energy unit, $m$ is the ratio of the *meta* (nonadjacent nonantipodal) to *ortho* (adjacent) interactions and $p$ is the ratio of the *para* (antipodal) to *ortho* interactions. However, only eqns. (6a) and (6d) can be used to calculate $\beta_c$, $m$ and $p$ since only the $A_{1g}$ and $T_{2u}$ core orbitals are free from core-surface mixing. The arbitrary auxiliary assumption [8]

$$m = 2p \tag{7}$$

is therefore introduced allowing the following equations for $\beta_c$ and $m$ to be derived from eqns. (6a) and (6d).

$$\beta_c = \frac{E(A_{1g})_c - (3.168)E(T_{2u})_c}{12.083} \tag{8a}$$

$$m = 2p = \frac{2}{11}\left(\frac{E(A_{1g})_c}{\beta_c} - 5\right) \tag{8b}$$

Using these equations gives the values for $\beta_c$ and $m$ listed in Table 5 for various computations on icosahedral $B_{12}H_{12}^{2-}$.

The values for $\beta_c$, $\beta_c/\beta_s$ and $t$ in Table 4 and $\beta_c$, $\beta_c/\beta_s$ and $m$ in Table 5 indicate the following features of the various computations on octahedral $B_6H_6^{2-}$ and icosahedral $B_{12}H_{12}^{2-}$.

(1) The $5n$ Hoffmann–Lipscomb LCAO-MO extended Hückel computations (HL5N) [7], and the Armstrong *et al.* self-consistent molecular orbital computations (APS) [9], both of which use Slater orbitals, give very similar values of $\beta_c/\beta_s$ and $t$, particularly in the case of octahedral $B_6H_6^{2-}$.

(2) Our SCF MO Gaussian 82 computations (GD) give much lower values of both $\beta_c/\beta_s$ and the non-

adjacent core orbital interaction parameters ($t$ for $B_6H_6^{2-}$ and $m$ for $B_{12}H_{12}^{2-}$) than the HL5N and APS computations using Slater orbitals. These observations suggest the following:

(a) The core bonding appears significantly weaker when Gaussian orbitals rather than Slater orbitals are used with $\beta_c/\beta_s$ for calculations using Gaussian orbitals being about half that of calculations using Slater orbitals.

(b) The non-adjacent core orbital interactions for the Gaussian calculations are so small (e.g. $t = 0.233$ for $B_6H_6^{2-}$ and $m = 0.078$ for $B_{12}H_{12}^{2-}$) that the core bonding can be approximated by deltahedral rather than complete topology. This justifies the assumption of deltahedral topology for the other deltahedral borane anions $B_nH_n^{2-}$ ($n = 5, 7, 8, 9, 10$) where the lower symmetry prevents an analysis of a type analogous to that in Table 4 for octahedral $B_6H_6^{2-}$ or in Table 5 for icosahedral $B_{12}H_{12}^{2-}$.

(c) The $T_{1u}$ orbitals, which, if pure, would be nonbonding in octahedral core topology for $B_6H_6^{2-}$ and bonding in icosahedral core topology for $B_{12}H_{12}^{2-}$, become antibonding through strong core-surface mixing as discussed in the previous papers [6, 8]. Because of this the simpler model using complete core bonding topology where $G_c = K_n$ gives the correct numbers of bonding and antibonding orbitals even though $K_n$ is a poor approximation of the actual $G_c$ derived from the computations using Gaussian orbitals.

(d) The apparent core bonding topology appears to be very sensitive to the computational approach used. Thus, for octahedral $B_6H_6^{2-}$ $t = 0.700$ for the computations using Slater orbitals (HL5G and APS) whereas $t = 0.233$ for our computations using Gaussian orbitals (GD). This may relate to the sensitivity of the non-adjacent core orbital interactions to the behavior of the relevant atomic orbitals at longer distances. Thus, elementary geometry indicates that in octahedral $B_6H_6^{2-}$ the distance between a pair of *trans* (antipodal) boron atoms is $\sqrt{2} = 1.414$ times the distance between a pair of *cis* (adjacent) boron atoms. Gaussian functions of the type $\exp(-\alpha r^2)$ fall off more rapidly at longer distances than Slater functions of the type $\exp(-\zeta r)$.

## Less Symmetrical Deltahedral Borane Anions

Table 3 summarizes the energy parameters for the important molecular orbitals (principal core orbital and pure surface orbitals) from our *ab initio* SCF MO Gaussian 82 computations on the borane anions $B_nH_n^{2-}$ including the less symmetrical $B_5H_5^{2-}$, $B_7H_7^{2-}$, $B_8H_8^{2-}$, $B_9H_9^{2-}$ and $B_{10}H_{10}^{2-}$ as well as octahedral $B_6H_6^{2-}$ and icosahedral $B_{12}H_{12}^{2-}$. The values for $\alpha$ were determined from a mean of all of the orbital energy parameters, and decrease monotonically with increasing $n$. The deltahedral core topology suggested by the more detailed analysis of the octahedral and icosahedral systems discussed above was used through eqn. (4) to determine $\beta_c$, which also decreases monotonically with increasing $n$. Table 3 presents $\beta_c$ for pure deltahedral core topologies for $B_6H_6^{2-}$ (i.e. $t$ taken to be zero) and $B_{12}H_{12}^{2-}$ (i.e. $m$ and $p$ taken to be zero) for ease of comparison with the pure deltahedral $\beta_c$ for the other deltahedral boranes in contrast to the values of $\beta_c$ in Tables 4 and 5 which were obtained from the energy parameters of the two core orbitals not mixing with the surface orbitals using eqns. (5a) and (5c) for $B_6H_6^{2-}$ and eqns. (6a) and (6d) for $B_{12}H_{12}^{2-}$ as discussed in the previous section. The pure surface orbitals were used to determine $\beta_s$ through a weighted average of their energy parameters; $\beta_s$ does *not* increase monotonically with increasing $n$ possibly owing to the sampling error discussed above. The parameter $\Delta E$ in Table 3 is the separation between the highest occupied and lowest unoccupied molecular orbitals. The fact that $\Delta E$ is lowest for $B_9H_9^{2-}$ may relate to the observation of a 226 nm ultraviolet maximum for this borane anion [21] in contrast to the observation of no ultraviolet maxima above 200 nm for the other borane anions $B_nH_n^{2-}$. The presence of the two degree 3 vertices in the trigonal bipyramid of $B_5H_5^{2-}$ would seem to preclude globally delocalized skeletal bonding as discussed above. However, there appears to be nothing exceptional in the values of $\alpha$, $\beta_s$, $\beta_c/\beta_s$ and $\Delta E$ for $B_5H_5^{2-}$ or the distribution of molecular orbital energy parameters compared with the other deltahedral borane anions $B_nH_n^{2-}$.

## Octahedral and Icosahedral Perchloroborane Anions

The experience gained by our extensive analysis of the computed orbital energy parameters has been applied to the analysis of computations on octahedral $B_6Cl_6^{2-}$ and icosahedral $B_{12}Cl_{12}^{2-}$ by Armstrong *et al.* [9] in order to assess the effect on the skeletal bonding when hydrogen atoms are substituted completely with chlorine atoms. The $B_nCl_n^{2-}$ anions are $8n$ valence orbital systems because of the three p valence orbitals containing lone pairs in addition to the s valence orbital on each chlorine atom. In the $B_nCl_n^{2-}$ anions the representation $\Gamma_\sigma$ (Table 2) appears in quadruplicate for the core, external bonding, external antibonding, and $p_\sigma$ chlorine lone pair orbitals and the representation $\Gamma_\pi$ (Table 2) appears in duplicate for the pure surface orbitals and the $p_\pi$ chlorine lone pair orbitals. The chlorine lone pair orbitals lead to $3n$ slightly bonding orbitals which separate the core, surface, and external bonding orbitals from the core, surface, and external antibonding orbitals [9]. Comparison of the molecular orbital energy parameters relative to $\alpha$ for corresponding $B_nH_n^{2-}$ and $B_nCl_n^{2-}$ derivatives suggest that the chlorine lone pair orbitals do not mix much with the important core and surface orbitals so that the methods used above to analyze the computations on $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$ can be applied meaningfully to estimate values for $\alpha$, $\beta_s$, $\beta_c/\beta_s$ and $t$ or $m$ listed in Table 4 for $B_6Cl_6^{2-}$ and Table 5 for $B_{12}Cl_{12}^{2-}$.

Comparison of the values for these parameters for $B_nCl_n^{2-}$ with those for the corresponding $B_nH_n^{2-}$ computations ($n$ = 6 and 12) reveals the following.

(1) $\beta_c/\beta_s$ is much less for $B_nCl_n^{2-}$ than for $B_nH_n^{2-}$ particularly when $n = 6$.

(2) The core interactions involving orbitals on non-adjacent atoms ($t$ in the octahedra and $m$ in the icosahedra) in $B_nCl_n^{2-}$ are about 2/3 those in the corresponding $B_nH_n^{2-}$.

These observations suggest that the core bonding is weaker in $B_nCl_n^{2-}$ relative to the corresponding $B_nH_n^{2-}$. This is in accord with the higher electronegativity of chlorine relative to hydrogen. Substitution of chlorine for hydrogen is thus likely to lead to withdrawal of electron density from the boron unique internal orbitals participating in the core bonding thereby weakening the core bonding.

## Conclusions

This paper presents *ab initio* SCF MO Gaussian 82 computations on the complete series of deltahedral borane anions $B_nH_n^{2-}$ ($n$ = 5, 6, 7, 8, 9, 10, 12) leading to molecular orbital energy parameters corresponding more closely to $D_n$ deltahedral core bonding topology than to $K_n$ complete core bonding topology. However, core-surface mixing, as noted previously [6, 8] for icosahedral $B_{12}H_{12}^{2-}$, raises the energies of all of the core molecular orbitals, except the lowest energy principal core orbital of $A_1$ symmetry, to antibonding levels. For this reason the graph-theory derived model [4] using $K_n$ complete core bonding topology gives the correct numbers of bonding and antibonding orbitals for the deltahedral boranes and hence the correct number of skeletal electrons.

This paper also presents the first study of the effect of chlorine substitution on the skeletal bonding in deltahedral boranes. Thus substitution of chlorine for hydrogen in $B_nH_n^{2-}$ to give $B_nCl_n^{2-}$ makes the core bonding topology more nearly deltahedral rather than complete and weaker relative to the surface bonding in accord with the expected electron-withdrawing tendencies of chlorine relative to hydrogen.

The *ab initio* SCF MO calculations on which this paper is based differ in two significant respects from the semiempirical methods which produced energy levels used in earlier papers of this series. First, the *ab initio* calculations handle interelectronic repulsions in a theoretically consistent way while semiempirical SCF procedures include them in an *ad hoc* way and the extended Hückel method neglects them entirely. None of the MO models treats electron repulsions in a completely proper manner. To do so would require extensions to configuration interaction or perturbation calculations to include effects of detailed electron correlation with a concomitant loss of the easy interpretability of individual orbital energies. Second, the *ab initio* SCF calculations use Gaussian orbitals based on functions of the form $\exp(-\alpha r^2)$ which in linear combination attempt to approximate the functional behavior of Slater-type functions based on the exponentials $\exp(-\zeta r)$ which can be used directly in the semiempirical calculations. The Gaussian functions differ significantly from the Slater functions both at the nuclei and at long distances from the nuclei. Gaussian AOs are calibrated for atoms and the corresponding MOs are optimized for bonding in molecules. Electron densities at longer distances, such as non-bonding or *trans*-polyhedral distances, might not be so well represented by Gaussian orbitals compared to the Slater orbitals. In this connection deltahedral borane anion computations using Gaussian orbitals lead to core bonding topology, more nearly deltahedral rather than complete, and weaker core bonding relative to surface bonding in accord with the more rapid decrease of Gaussian orbitals at increasing distances. Furthermore, dianions are not well represented by minimal basis sets. Our results show positive energies for the HOMOs of all the *closo*-carboranes considered here. Indeed, this has been pointed out by Fowler who has demonstrated that the HOMO for $B_6H_6^{2-}$ is positive even at the 6-31G* level, indicating that $B_6H_6^{2-}$ must be unstable as a free dianion but stable in a crystal field [15]. Increased basis sets can lower the energies of the occupied MOs only slightly while the numbers of vacant MOs of positive energies are greatly increased. Since the topological model requires energies of all MOs, vacant and occupied, increasing the size of the basis set will raise the center of gravity or $\alpha$ of the MO system.

## Computational Details

The *ab initio* SCF MO calculations were done with the Gaussian 82 program [30] on the IBM 3081 computer of the University of South Carolina Computer Center. The STO-3G basis set was employed throughout. Molecular geometries were optimized under point group symmetry constraints appropriate for each borane. These restrictions are appropriate because (1) to within experimental error those are the observed structures of the *closo*-boranes and (2) we wanted to use the appropriate symmetry point groups as the basis for relating calculated orbital energies within the topological model. The structures actually produced for the *closo*-borane anions by the symmetry restricted optimizations are remarkably close to those obtained from experiment as discussed elsewhere [16]. CPU times for optimizations for individual boranes ranged from 9 min for $B_5H_5^{2-}$ to 5 min for $B_6H_6^{2-}$ to 145 min for $B_{12}H_{12}^{2-}$. The time for the larger $B_6H_6^{2-}$ was shorter than that for the smaller $B_5H_5^{2-}$ because the regular octahedron has only two independent variation parameters, the B—B and B—H distances, while the trigonal bipyramid has four independent distances. Obviously, CPU times depend to some extent on the quality of the guess of the starting structure. Total CPU time for the seven structures was 435 min.

Several sets of numbers specify the results of optimized *ab initio* SCF MO calculations. The orbital energies for each borane anion $B_nH_n^{2-}$ ($n = 5, 6, 7, 8, 9, 10, 12$) will be made available in another format. Total energies, optimized B—B and B—H bond distances and Mulliken net atom populations have been published elsewhere [16].

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## References

1 G. M. Badger, *Aromatic Character and Aromaticity*, Cambridge University Press, Cambridge, 1969.
2 E. L. Muetterties and W. H. Knoth, *Polyhedral Boranes*, Marcel Dekker, New York, 1968.
3 J. Aihara, *J. Am. Chem. Soc.*, *100* (1978) 3339–3342.
4 R. B. King and D. H. Rouvray, *J. Am. Chem. Soc.*, *99* (1977) 7834–7840.
5 A. J. Stone and D. Wales, *Mol. Phys.*, *61* (1987) 747–765; A. J. Stone, *Polyhedron*, *3* (1984) 1299–1306.
6 R. B. King, *J. Comput. Chem.*, *8* (1987) 341–349.
7 R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, *36* (1962) 2179–2189; W. N. Lipscomb, in E. L. Muetterties (ed.), *Boron Hydride Chemistry*, Academic Press, New York, 1975, pp. 39–78.
8 R. B. King, *Inorg. Chem.*, *27* (1988) 1941–1947.
9 D. R. Armstrong, P. G. Perkins and J. P. P. Stewart, *J. Chem. Soc., Dalton Trans.*, (1973) 627–632.
10 D. A. Dixon, D. A. Kleier, T. A. Halgren, J. H. Hall and W. N. Lipscomb, *J. Am. Chem. Soc.*, *99* (1977) 6226–6237.
11 M. J. S. Dewar and M. L. McKee, *Inorg. Chem.*, *17* (1978) 1569–1581.
12 D. A. Kleier and W. N. Lipscomb, *Inorg. Chem.*, *18* (1979) 1312–1318.
13 P. Brint, J. P. Cronin, E. Seward and T. Whelan, *J. Chem. Soc., Dalton Trans.*, (1983) 975–980.
14 P. W. Fowler and W. W. Porterfield, *Inorg. Chem.*, *24* (1985) 3511–3518. (Extended Tensor Surface Harmonic Theory of Clusters.)
15 P. W. Fowler, *J. Chem. Soc., Faraday Trans. 2*, *82* (1986) 61–67.
16 J. J. Ott and B. M. Gimarc, *J. Comput. Chem.*, *7* (1986) 673–692.
17 K. Ruedenberg, *J. Chem. Phys.*, *22* (1954) 1878–1894.
18 H.-H. Schmidtke, *J. Chem. Phys.*, *45* (1966) 3920–3928; *Coord. Chem. Rev.*, *2* (1967) 3–8.
19 I. Gutman and N. Trinajstić, *Topics Curr. Chem.*, *42* (1973) 49–93.
20 R. B. King, *J. Math. Chem.*, *1* (1987) 249–265.
21 F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, *5* (1966) 1955–1960.
22 K. Wade, *Chem. Commun.*, (1971) 792–793; *Adv. Inorg. Chem. Radiochem.*, *18* (1976) 1–66.
23 M. J. Mansfield, *Introduction to Topology*, Van Nostrand, Princeton, 1963, p. 40.
24 R. J. Wilson, *Introduction to Graph Theory*, Oliver and Boyd, Edinburgh, 1972, p. 16.
25 B. Grünbaum, *Complex Polytopes*, Interscience, New York, 1967, p. 138.
26 R. B. King, *Theor. Chim. Acta*, *44* (1977) 223–243.
27 R. B. King, in R. B. King (ed.), *Chemical Applications of Topology and Graph Theory*, Elsevier, Amsterdam, 1983, pp. 99–123.
28 R. B. King, in J. F. Liebman and A. Greenberg (eds.), *Molecular Structure and Energetics*, Verlag Chemie, Deerfield Beach, FL, 1986, pp. 123–148.
29 R. L. Johnston and D. M. P. Mingos, *Polyhedron*, *5* (1986) 2059–2061.
30 J. S. Binkley, M. J. Frisch, D. J. DeFrees, K. Raghavachari, R. A. Whiteside, H. B. Schlegel, E. M. Fluder and J. A. Pople, *GAUSSIAN 82*, Revision H Version, Carnegie-Mellon University, Nov. 30, 1984.