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Author's Review

Three-Dimensional Analogues of Kekulé Structures in Borane Chemistry

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The topology of overlap of the atomic orbitals participating in the requisite delocalization for an aromatic system can be described by a graph, the eigenvalue spectrum of which can be related to molecular orbital energy parameters as determined by Hückel theory. Such aromatic systems can be classified according to the nodality of overlapping atomic orbitals. In particular the three-dimensional deltahedral boranes $B_nH_n^{2-}$ and carboranes $B_{n-2}C_2H_n$ ($6 \leq n \leq 12$) are examples of anodal orbital aromatic systems since the delocalization in their bonding arises from overlap of anodal radial boron or carbon sp hybrids. The concept of Kekulé structures for two-dimensional benzenoid hydrocarbons can be extended to delocalized three-dimensional polyhedral boranes by using three-center B–B–B bonds instead of carbon-carbon double bonds. Such structures for *closo* deltahedral boranes $B_nH_n^{2-}$ have three two-center B–B bonds and and $n - 2$ three-center B–B–B bonds with exactly half of the $2n - 4$ faces of deltahedron covered by the three-center B–B–B bonds. Related structures for *nido* boranes derived from protonation of the hypothetical $B_nH_n^{4-}$ and *arachno* boranes derived from protonation of the hypothetical $B_nH_n^{6-}$ without producing BH_2 vertices contain a total of six (two-center B–B + three-center B–H–B bonds) and $n - 4$ three-center B–B–B bonds for the *nido* boranes and a total of nine (two-center B–B + three-center B–H–B bonds) and $n - 6$ three-center B–B–B bonds for the *arachno* boranes. The feasibility of *deltahedral* species isoelectronic and isolobal with the neutral $B_nH_n^{4-}$ (*e.g.*, the »boron subhalides« B_nX_n, X = Cl, Br, I) and the tetraanion $B_nH_n^{4-}$ in addition to the very stable $B_nH_n^{2-}$ can be evaluated by the existence of satisfactory Kekulé-type structures with B–B two-center and B–B–B three-center bonds and the degeneracies of the highest occupied and lowest unoccupied molecular orbitals.

INTRODUCTION

The chemical bonding theory of two-dimensional planar hydrocarbons and isoelectronic heterocycles makes use of the concepts of resonance energy and aromaticity as originally arising from molecular orbital theory[1–3] and subsequently refined through graph-theory derived methods.[4–10] More recently similar concepts have

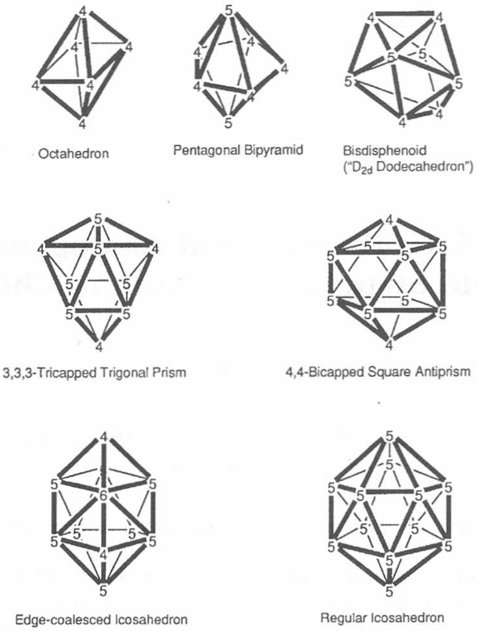

Octahedron
Pentagonal Bipyramid
Bisdisphenoid ("D_{2d} Dodecahedron")
3,3,3-Tricapped Trigonal Prism
4,4-Bicapped Square Antiprism
Edge-coalesced Icosahedron
Regular Icosahedron

Figure 1. The deltahedral found in the deltahedral boranes $B_nH_n^{2-}$. The numbers in the vertices indicate their degress. Note that all of the vertices have degrees 4 or 5 except for one degree 6 vertex of the 11-vertex edge-coalesced icosahedron.

been applied to the chemical bonding of the three-dimensional polyhedral boranes $B_nH_n^{2-}$ $(6 \leq n \leq 12)$[11,12] and isoelectronic carboranes in which the boron or carbon atoms form deltahedra with no degree 3 vertices depicted in Figure 1.

A central idea in the aromaticity in planar benzenoid hydrocarbons, which are constructed by edge-sharing fusion of hexagons of sp^2 carbon atoms, is the contribution of two or more different structures of equivalent energy consisting of alternating carbon-carbon single and double bonds known as *Kekulé structures* (Figure 2) to a lower energy averaged structure known as a *resonance hybrid*. In benzene itself the two equivalent Kekulé structures contain three double and three single bonds alternating along the six edges of the C_6 hexagon. This paper extends the concept of Kekulé structures to the three-dimensional deltahedral borane anions $B_nH_n^{2-}$ $(6 \leq n \leq 12)$. Such Kekulé structures make use of three-center B–B–B bonds instead of the carbon-carbon double bonds in benzenoid Kekulé structures. Lipscomb's semitopological method[13–16] for studying the electron and orbital balance in boron networks containing mixtures of B–B two-center and B–B–B three-center bonds is essential for extending the concept of Kekulé structures from two-dimensional benzenoid hydrocarbons to three-dimensional deltahedral boranes.

Figure 2. The two Kekulé structures of benzene.

THE THREE-CENTER BONDING IN BORANES

The feature of particular interest distinguishing three-dimensional boranes from two-dimensional planar hydrocarbons is the presence of three-center bonds. In the usual two-center two-electron covalent bond, two atoms supply two orbitals, one centered on each atom. These atomic orbitals interact to form one bonding orbital and one antibonding orbital so that if two electrons are available they will just fill the bonding orbital and constitute the standard covalent bond, such as the C–C and C–H σ-bonds typically found in hydrocarbons (Figure 3). The usual two-center bond of this type provides a place for as many electrons as atomic orbitals. Thus if *n* atomic orbitals are used to form two-center bonds they form *n*/2 bonding orbitals and accommodate *n* electrons. In the three-center two-electron bonding found in boranes, three atoms supply three orbitals, one on each atom. These atomic orbitals interact to form one bonding and two antibonding orbitals so that two electrons may just fill the bonding orbital to form a three-center bond (Figure 3). If *n* atomic orbitals interact to form only three-center bonds, they form only *n*/3 bonding orbitals which can accommodate only 2*n*/3 electrons. Thus three-center bonding is used in so-called »electron deficient compounds« in which there are fewer bonding electrons than atomic orbitals.

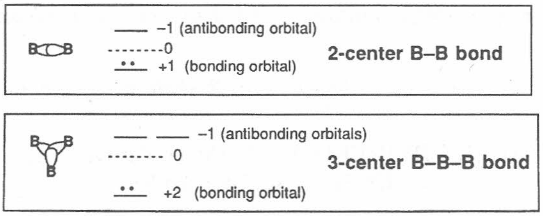


Figure 3. Comparison of 2-center B–B bonds and 3-center B–B–B bonds.

Lipscomb[14] has studied the topology of the distribution of two-center B–B and three-center B–B–B bonds in networks of boron atoms. The following assumptions are inherent in Lipscomb's methods:

(1) Only the 1s orbital of hydrogen and the four sp^3 orbitals of boron are used.

(2) Each external B–H bond is regarded as a typical two-center two-electron single bond requiring the hydrogen orbital, one hybridized boron orbital, and one electron each from the hydrogen and boron atoms. Because of the very small electronegativity difference between hydrogen and boron, these bonds are assumed to be non-polar. In polynuclear boron hydrides every boron atom may form zero or one but never more than two such external bonds.

(3) Each B–H–B three-center »bridge« bond corresponds to a filled three-center localized bonding orbital requiring the hydrogen orbital and one bybrid orbital from each boron atom.

(4) The orbitals and electrons of any particular boron atom are allocated to satisfy first the requirements of the external B–H single bonds and the bridge B–H–B bonds. The remaining orbitals and electrons are allocated to framework molecular orbitals.

The relative numbers of orbitals, electrons, hydrogen, and boron atoms as well as bonds of various types can be expressed in a systematic way. For a boron hydride B_pH_{p+q} containing s *bridging* hydrogen atoms, x *extra* B–H bonds in terminal BH_2 groups rather than BH groups, t three-center B–B–B bonds, and y two-center B–B bonds, balancing the hydrogen atoms leads to $s + x = q$ assuming that each boron atom is bonded to at least one hydrogen atom. Since each boron atom supplies four orbitals but only three electrons, the total number of three- center bonds in the molecule is the same as the number of boron atoms, namely $s + t = p$. This leads to the following equations of balance:

$$2s + 3t + 2y + x = 3p \text{ (orbital balance with 3 orbitals/BH vertex)} \quad (1a)$$

$$s + 2t + 2y + x = 2p \text{ (electron balance with 2 \textit{skeletal} electrons/BH vertex)} \quad (1b)$$

THE GRAPH-THEORY DERIVED APPROACH TO DELOCALIZATION IN POLYHEDRAL BORANES

Ideas based on graph theory can be used to describe Hückel theory, which was first applied to conventional two-dimensional aromatic systems.[17–20] The graph G is used to describe the overlap of the atomic orbitals involved in the delocalized bonding in aromatic systems in which the vertices V correspond to orbitals and the edges E correspond to orbital overlaps. The adjacency matrix[21] $\boldsymbol{A}$ of such a graph can be defined as follows:

$$\boldsymbol{A}_{ij} = \begin{cases} 0 \text{ if } i = j \\ 1 \text{ if } i \text{ and } j \text{ are connected by an edge} \\ 0 \text{ if } i \text{ and } j \text{ are not connected by an edge} \end{cases} \quad (2)$$

The eigenvalues of the adjacency matrix are obtained from the following determinantal equation:

$$|\boldsymbol{A} - x\boldsymbol{I}| = 0 \quad (3)$$

in which $\boldsymbol{I}$ is the unit matrix ($I_{ii} = 1$ and $I_{ij} = 0$ for $i \neq j$). These topologically derived eigenvalues are closely related to the energy levels as determined by Hückel theory which uses the secular equation

$$|\boldsymbol{H} - E\boldsymbol{S}| = 0 \quad (4)$$

Note the general similarities between equations (3) and (4). In equation (4) the energy matrix $\boldsymbol{H}$ and the overlap matrix $\boldsymbol{S}$ can be resolved into the identity matrix $\boldsymbol{I}$ and the adjacency matrix $\boldsymbol{A}$ as follows:

$$\begin{aligned} \boldsymbol{H} &= \alpha\boldsymbol{I} + \beta\boldsymbol{A} \\ \boldsymbol{S} &= \boldsymbol{I} + S\boldsymbol{A} \end{aligned} \quad (6)$$

The energy levels of the Hückel molecular orbitals (equation (4)) are thus related to the eigenvalues x_k of the adjacency matrix $\boldsymbol{A}$ (equation (3)) by the following equation:

$$E_k = \frac{\alpha + x_k\beta}{1 + x_k S} \tag{6}$$

In equation (6) α is the standard Coulomb integral, assumed to be the same for all atoms, β is the resonance integral taken to be the same for all bonds, and S is the overlap integral between atomic orbitals on neighbouring atoms.

The two extreme types of skeletal chemical bonding in polygonal or polyhedral molecules may be called *edge-localized* and *globally delocalized*.[22–25] An edge-localized polygon or polyhedron has two-electron two-center bonds along each edge and is favored when the number of internal orbitals from each vertex atom matches the degree of the corresponding vertex. A globally delocalized polygon or polyhedron has a multicenter bond involving all of the vertex atoms; such global delocalization is a feature of fully aromatic systems. Delocalization is favored when the numbers of internal orbitals do *not* match the vertex degrees.

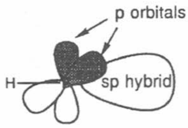
The graph theoretical model of aromaticity uses a graph G to describe the overlap of valence orbitals represented by its vertices V. Such valence orbitals can be classified by their *nodalities*, *i.e.*, the number of nodal planes. Thus an *anodal* orbital has no nodal planes like an s orbital and is the type of bybrid orbital used in σ-bonding. A *uninodal* orbital has a single nodal plane like a p orbital and a *binodal* orbital has two nodal planes like a d orbital. Binodal aromaticity involving d orbitals is found in certain polyoxometalates such as derivatives of the types $M_6O_{19}^{m-}$ and $XM_{12}O_{40}^{n-}$ (M = V, Nb, Mo, W).[26] The types of aromaticity arising from this classification are given in Table I.

TABLE I

Types of aromaticity

Compound Type	Formulas	Dimensions	Vertex Atoms	Overlapping Orbitals		
				Type	Nodes	Adjacent Atom Interactions
Deltahedral Borane Anions	$B_nH_n^{2-}$ $(6 \leq n \leq 12)$	3	B	sp	0	B–B
Planar Hydrocarbons	$C_nH_n^{6-n}$	2	M	p	1	C–C
Macrooctahedral and Macrocuboctahedral Polyoxometalates	$M_6O_{19}^{m-}$ $XM_{12}O_{40}^{m-}$ (M = V, Nb, Mo, W)	3	C	d	2	M–O–M

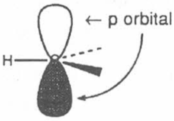
The deltahedral boranes are examples of aromatic systems constructed from anodal orbitals. The vertex B–H unit in a deltahedral borane anion $B_nH_n^{2-}$ can be depicted as follows:



I

In structure **I** the boron atom has two anodal sp hybrids. The sp hybrid depicted by a balloon participates in the delocalized bonding represented by the graph G. The deltahedral boranes are thus anodal orbital aromatic systems.

The deltahedral boranes can be contrasted with the planar polygonal hydrocarbons, which are examples of aromatic systems constructed from uninodal orbitals. The vertex C–H unit in $C_5H_5^-$, C_6H_6, or $C_7H_7^+$ can be depicted as follows.:



II

In structure **II** the uninodal p orbital of the carbon atom participates in the delocalized bonding represented by the graph G. The planar polygonal hydrocarbons are thus uninodal orbital aromatic systems.

The graph-theoretical approach to aromaticity is best illustrated by first considering benzene as a prototypical planar polygonal aromatic bydrocarbon since other approaches to the bonding in benzene are familiar to many chemists. A CH vertex of benzene can be represented schematically by structure **II**. The four carbon valence orbitals of the sp^3 manifold are divided into three sp^2 hybrids and a single p orbital. One of the sp^2 hybrids is bonded to the external hydrogen atom leaving two sp^2 hybrids and the p orbital as internal orbitals. Among the three internal orbitals the two equivalent sp^2 hybrids are twin internal orbitals or *tangential* orbitals whereas the single p orbital is a unique internal orbital or *radial* orbital. The uninodality of this unique internal orbital defines the nodality of the aromaticity.

The internal orbitals of the six carbon atoms form the benzene skeletal bonding including the delocalization responsible for its aromaticity. Pairwise overlap of the (2)(6) = 12 twin internal orbitals around the circumference of the hexagon is responsible for splitting these 12 orbitals into 6 σ-bonding and 6 σ^*-antibonding orbitals leading to the so-called σ-bonding of benzene. This σ-bonding of benzene is supplemented by the so-called π-bonding arising from overlap of the six unique internal orbitals, namely the single p orbital on each of the carbon atoms (see structure **II**).

The overlap of these unique internal orbitals can be described by the C_6 cyclic graph, which is the hexagon. The eigenvalue spectrum of the hexagon (equation (3)) is +2, +1, +1, −1, −1, −2 (Figure 4, lower right) leading to three π bonding and three π^* antibonding orbitals. The total benzene skeleton thus has 9 bonding orbitals (6σ and 3π) which are filled by the 18 skeletal electrons which arise when each of the CH vertices contributes three skeletal electrons. Twelwe of these skeletal electrons are used for the σ-bonding and the remaining six electrons for the π-bonding.

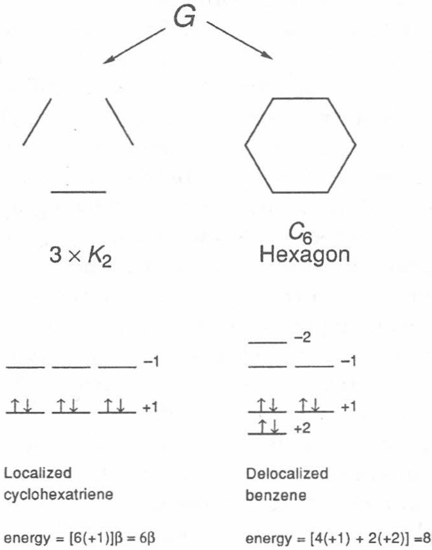


Figure 4. Aromatic stabilization of benzene through global delocalization.

Figure 4 illustrates how the delocalized bonding in benzene from the C_6 overlap of the unique internal orbitals, namely the p orbitals, leads to aromatic stabilization. In a hypothetical localized »cyclohexatriene« structure where the interactions between the p orbitals on each carbon atom are pairwise interactions, the corresponding graph G (Figure 4, upper left) consists of three disconnected line segments (*i.e.* 3 x K_2). This graph has three +1 eigenvalues and three −1 eigenvalues. Filling each of the corresponding three bonding orbitals with an electron pair leads to an energy of 6β from this π bonding. In a delocalized »benzene« structure where the delocalized interactions between the p orbitals on each carbon atom are described by the cyclic C_6 graph (Figure 4, upper right), filling the three bonding orbitals with an electron pair each leads to an energy of 8β. This corresponds to a resonance stabilization of $8\beta - 6\beta = 2\beta$ arising from the delocalized bonding of the carbon p orbitals in benzene.

Similar ideas can be used to describe the anodal aromaticity in the boranes $B_nH_n^{2-}$ and carboranes $B_{n-2}C_2H_n^{2-}$ ($6 \leq n \leq 12$) based on deltahedra (Figure 1), with vertices of degrees four or five being strongly favored. Consider the simplest deltahedral borane, namely the octahedral $B_6H_6^{2-}$, as an example of such a deltahedral borane. A BH vertex of $B_6H_6^{2-}$ can be represented schematically by structure **I** depicted above. The four boron valence orbitals of its sp^3 manifold are divided into two sp hybrids and two extra p orbitals. One of the sp hybrids is bonded to an external hydrogen atom leaving the second sp hybrid and the two extra p orbitals as internal orbitals. Among these three internal orbitals the two equivalent p orbitals are the twin internal orbitals or *tangential* orbitals whereas the single sp hybrid is a unique internal orbital or *radial* orbital. The anodality of this unique internal orbital defines the anodality of this aromaticity.

The internal orbitals of the six boron atoms form the skeletal bonding in $B_6H_6^{2-}$ including the delocalization responsible for its aromaticity. The pairwise overlap of the (2)(6) = 12 twin internal orbitals, namely the two p orbitals on each of the six boron atoms, leads to six bonding and six antibonding orbitals over the surface of the polyhedron. This surface bonding in $B_6H_6^{2-}$ is supplemented by *core* bonding arising from overlap of the six unique internal orbitals, which are the single sp hybrids on each of the six boron atoms directed towards the core of the polyhedron. The topology of this core bonding can be represented by a graph G_c. The two limiting possibilities for G_c for a deltahedral borane or carborane are the complete graph K_n and the deltahedral graph D_n, and the corresponding core bonding topologies may 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.[27] For any 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 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 graph D_n for the deltahedra of interest with seven or more vertices all have at least three positive eigenvalues but one of these eigenvalues, conveniently called the *principal eigenvalue*, is much more positive than any other of the positive eigenvalues. The bonding molecular orbital from the delocalized core bonding in a deltahedral borane or carborane corresponding to the single positive eigenvalue of K_n or the principal eigenvalue of D_n may be called the *principal* core orbital. Since deltahedral boranes $B_nH_n^{2-}$ and carboranes $B_{n-2}C_2H_n$ have $2n + 2$ skeletal electrons, of which $2n$ are used for the surface bonding, there are only two electrons available for the core bonding, corresponding to a single core bonding molecular orbital and a single positive eigenvalue for G_c. Thus deltahedral boranes are three-dimensional aromatic systems with $4k + 2 = 2$ core bonding electrons where $k = 0$, analogous to the $4k + 2$ π-electrons where $k = 0$ ($C_3H_3^+$), 1 ($C_5H_5^-$), C_6H_6, $C_7H_7^+$), or 2 ($C_8H_8^{2-}$) for the planar two-dimensional uninodal orbital aromatic systems discussed above. Furthermore, 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 $6 \le n \le 12$. 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 carboranes discussed in previous papers.[22–25] However, the deltahedral core bonding topology represented by the deltahedral graph D_n 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. This possibility was already indicated in the original graph-theoretical analysis[28] of the $3n$ Hoffmann-Lipscomb LCAO-MO extended Hückel computations[29] on icosahedral $B_{12}H_{12}^{2-}$, which showed that the four core orbitals corresponding to positive eigenvalues of the icosahedral graph D_{12} 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.

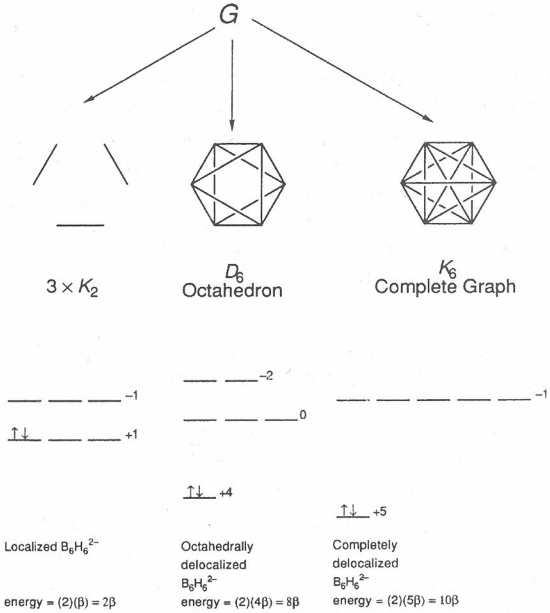


Figure 5. Aromatic stabilization of $B_6H_6^{2-}$ through delocalization represented by the octahedral (D_6) and complete (K_6) graphs.

Figure 5 illustrates how the delocalized bonding in $B_6H_6^{2-}$ arising from overlap of the unique internal orbitals, namely the radial sp hybrids on each boron atom, can lead to aromatic stabilization. In a hypothetical localized structure in which the interactions between the radial sp hybrids are pairwise interactions, the corresponding graph G_c (Figure 5, left) is three disconnected line segments (*i.e.*, 3 x K_2). The spectrum of this graph has three +1 eigenvalues and three –1 eigenvalues. Filling one of the bonding orbitals with the available two core bonding electrons leads to an energy of 2β from the core bonding. In a completely delocalized structure where the core bonding is described by the complete graph K_6 (Figure 5, right), this electron pair is in a bonding orbital with an eigenvalue of +5 corresponding to an energy of $(2)(5\beta) = 10\beta$. The aromatic stabilization of completely delocalized $B_6H_6^{2-}$ is thus $10\beta - 2\beta = 8\beta$ assuming the same β unit for both the localized and complete delocalized structures. In an octahedrally delocalized $B_6H_6^{2-}$ where the core bonding is described by the deltahedral graph D_6 corresponding to the 1-skeleton of the octahedron (Figure 5, center) the core bonding electron pair is in a bonding orbital with an eigenvalue of +4 corresponding to an energy of $(2)(4\beta) = 8\beta$. The aromatic stabilization of octahedrally delocalized $B_6H_6^{2-}$ is thus $8\beta - 2\beta = 6\beta$. Thus the aromatic stabilization of $B_6H_6^{2-}$ is considerable regardless of whether the delocalized core bohnding is considered to have the complete topology represented by the complete graph K_6 or the octahedral topology represented by the deltahedral graph D_6.

Vertices of degrees 4 or greater appear to be essential for the stability of deltahedral boranes of the type $B_nH_n^{2-}$. Thus although the borane anions $B_nH_n^{2-}$ ($6 \leq n \leq 12$) are very stable, the five-boron deltahedral borane $B_5H_5^{2-}$ based on a trigonal pyramidal structure with two (apical) degree 3 vertices has never been prepared. Such degree 3 vertices lead to two-electron two-center bonds along each of the three edges meeting at the degree 3 vertex and leave no internal orbitals from degree 3 vertices for the multicenter core bond. However, the dicarbaborane $C_2B_3H_5$ isoelectronic with the carbon atoms in the degree 3 apical vertices of the trigonal bipyramid can be isolated.[30] The carbon-boron bonds along the 6 B–C edges of the C_2B_3 trigonal bipyramid in the isolable species 1,5–$C_2B_3H_5$ can be interpreted as edge-localized bonds leading to three-coordinate boron atoms similar to the B–C bonds and boron environment in trimethylboron $(CH_3)_3B$.

THREE-DIMENSIONAL KEKULÉ STRUCTURES IN DELTAHEDRAL BORANES AND RELATED POLYHEDRAL SPECIES

The two-center B–B bonds and three-center B–B–B bonds in polyhedral boranes can be components of Kekulé-type structures similar to the C–C single and C=C double bonds in planar hydrocarbons. First consider boranes of the stoichiometry $B_nH_n^{2-}$ ($6 \leq n \leq 12$) with one terminal hydrogen on each boron atom based on the deltahedra depicted in Figure 1. Such deltahedral boranes cannot have any terminal BH_2 groups or three-center B–H–B bonds and have two »extra« electrons for the –2 charge on the ion so that $s = x = 0$ in the equations of balance (Equations (1a) and (1b), which then reduce to the following equations in which n is the number of boron atoms in the deltahedron corresponding to p in equations (1a) and (1b):

$$3t + 2y = 3n \text{ (orbital balance for } B_nH_n^{2-}) \tag{7a}$$

$$2t + 2y = 2n + 2 \text{ (electron balance for } B_nH_n^{2-}) \tag{7b}$$

Solving the simultaneous equations (7a) and (7b) leads to $y = 3$ and $t = n - 2$ implying the presence of three two-center B–B bonds and $n - 2$ three-center B–B–B bonds. Since a deltahedron with n vertices has $2n - 4$ faces, the $n - 2$ three-center B–B–B bonds will cover exactly half of the faces. In that sense a Kekulé-type structure for the deltahedral boranes $B_nH_n^{2-}$ has exactly half of the faces covered by three-center B–B–B bonds just like a Kekulé structure for a benzenoid hydrocarbon has half of the edges covered by C=C double bonds.

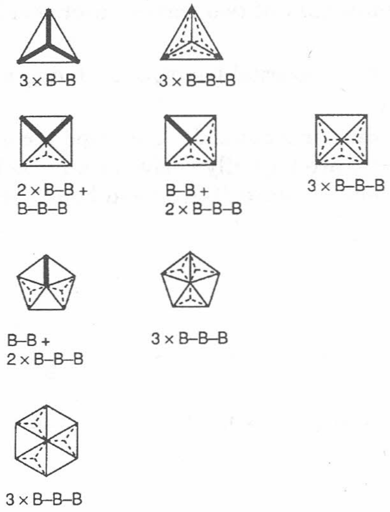


Figure 6. The bonding networks by which atoms at vertices of partiuclar degrees can bond to their skeletal neighbors. Two-center B–B bonds are indicated by bold edges whereas three-center B–B bonds are indicated by dotted lines meeting in the center of a face.

O'Neill and Wade[31] have discussed such localized bonding schemes using two-center B–B bonds and three-center B–B–B bonds with the following basic assumptions:

(1) Each skeletal atom is assumed to participate in three skeletal bonds in addition to the external bond, typically to a hydrogen atom;

(2) Each edge of the skeletal B_n polyhedron must correspond to a two-center B–B bond or a three-center B–B–B bond;

(3) A pair of boron atoms cannot be simultaneously bonded to each other both by a two-center B–B bond and one or two three-center B–B–B bonds since these arrangements would require too close an alignment of the atomic orbitals involved;

(4) Cross-polyhedral interactions, which are significantly longer than polyhedral edge interactions, are considered to be non-bonding.

(5) When individual bond networks do not match the symmetry of the polyhedron in question, resonance between plausible canonical forms needs to be invoked.

These assumptions, particularly assumption 3, pose certain restrictions on the combinations of two-center B–B and three-center B–B–B bonds meeting at polyhedral vertices of vaious degress (Figure 6):[31]

(1) Degree 3 vertices: Only three two-center B–B bonds along the polyhedral edges correasponding to edge-localized bonding or three three-center B–B–B bonds in the polyhedral faces are possible;

(2) Degree 4 vertices: At least one three-center bond must meet at each degree 4 vertex since there are not enough internal orbitals to form exclusively two-center B–B bond along each of the four edges of a degree 4 vertex;

(3) Degree 5 vertices: A minimum of two three-center bonds must meet at each degree 5 vertex;

(4) Degree 6 vertices: All three internal bonds at each degree 6 vertex must be three-center B–B–B bonds.

Now let us consider similar localized structures for *nido* boranes, which have $2n + 4$ skeletal electrons and are formally derived from the hypothetical $B_nH_n^{4-}$ tetra-anions by protonation of one or more B–B single bonds (Figure 7). The structures of the *nido* boranes may also be derived from a $B_{n+1}H_{n+1}^{2-}$ deltahedron by removal of a single vertex.[32–36] For example, the *nido* boron hydrides B_5H_9 and B_6H_{10} are formally derived from pyramidal $B_5H_5^{4-}$ and $B_6H_6^{4-}$by tetraprotonation. Generalization of equations (1a) and (1b) to $B_nH_n^{4-}$ with $s = x = 0$ leads to the equations

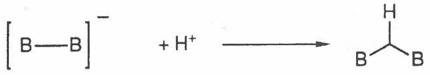


Figure 7. Protonation of a B–B two-center bond to give a B–H–B three-center bond.

$$3t + 2y = 3n \text{ (orbital balance for } B_nH_n^{4-}\text{)} \tag{8a}$$

$$2t + 2y = 2n + 4 \text{ (electron balance for } B_nH_n^{4-}\text{)} \tag{8b}$$

Solving the simultaneous equations (8a) and (8b) leads to $y = 6$ and $t = n - 4$. Note that the square pyramid in the hypothetical $B_5H_5^{4-}$ and the known B_5H_9 is the smallest possible *nido* polyhedron as well as the smallest *nido* structure with a B–B–B three-center bond. Thus $t = 1$ and $y = 6$ for the hypothetical $B_5H_5^{4-}$, which upon the tetraprotonation gives pentaborane-9, B_5H_9, with $t = 1$, $y = 2$, and $s = 4$, with the fewest boron atoms for a stable neutral borane without an insulating BH_2 vertex. Note also that for a neutral *nido* borane B_nH_{n+4} such as B_5H_9, B_6H_{10}, B_8H_{12}, and $B_{10}H_{14}$, $y = 2$ and $s = 4$ for all n assuming, of course, the absence of BH_2 vertices.

Addition of two more skeletal electrons to the *nido* structures gives the *arachno* structures formally derived from $B_nH_n^{6-}$ with structures based on a $B_{n+2}H_{n+2}^{2-}$ deltahedron by removal of a pair of vertices. Generalization of equations (1a) nd (1b) to $B_nH_n^{6-}$ with $s = x = 0$ leads to the equations

$$3t + 2y = 3n \text{ (orbital balance for } B_nH_n^{6-}\text{)} \tag{9a}$$

$$2t + 2y = 2n + 6 \text{ (electron balance for } B_nH_n^{6-}\text{)} \tag{9b}$$

Solving the simultaneous equation (9a) and (9b) leads to $y = 9$ and $t = n - 6$. Note that the *arachno* structure *without* BH_2 *vertices* must contain at least seven boron atoms to have a B–B–B three-centre bond. Hexaprotonation of hypothetical $B_nH_n^{6-}$ gives neutral *arachno* boron hydrides B_nH_{n+6}. However the common *arachno* neutral boron hydrides including B_4H_{10}, B_5H_{11}, B_6H_{12}, B_8H_{14}, and B_9H_{15} but not *i*-B_9H_{15} have BH_2 vertices[37] whose boron atoms cannot participate fully in the delocalization similar to the CH_2 groups in hydrocarbons such as cyclohexane with only two internal orbitals.

O'Neill and Wade[31] consider the feasibility of *deltahedral* structures isoelectronic and isolobal with B_nH_n which are either neutral such as the B_nX_n halides,[38] have a –2 charge such as the stable deltahedral borane anions $B_nH_n^{2-}$, or have a –4 charge related to the 8-vertex species $(C_5H_5)_4Ni_4B_4H_4$[39] using the following criteria:

(1) The feasibility of drawing a satisfactory Kekulé-type structure using two-center B–B and three-center B–B–B bonds;

(2) The degeneracies of the highest occupied and lowest unoccupied molecular orbitals (HOMO's and LUMO's, respectively).

The latter criterion relates to the closed-shell configuration for the dinegative anions $B_nH_n^{2-}$ and thus the requirements of a non-degenerate HOMO for neutral B_nH_n also to have a closed shell configuration and a non-degenerate LUMO for tetranegative $B_nH_n^{4-}$ also to have a closed shell configuration. The conclusions from this study are summarized in Table II. From these observations the deltahedral species B_nH_n ($n = 8$, 9, and 11) are seen to be potentially stable with 0, –2, and –4 charges whereas the deltahedral species B_nH_n ($n = 6$, 7, 10, and 12) are seen to be stable only with a –2 charge. This is in approximate accord with the stability of the neutral halide species B_nX_n.[38]

TABLE II

Feasibility of Deltahedral B_nH_n Species with 0, –2, and –4 Charges

Deltahedron	Formula	Degeneracies		Existence of Kekulé Structure for $B_nH_n^z$		
		HOMO	LUMO	0	–2	–4
Octahedron	B_6H_6	3	3	+	+	+
Pentagonal Bipyramid	B_7H_7	2	2	–	+	–
Bisdisphenoid	B_8H_8	1	1	+	+	+
Tricapped Trigonal Prism	B_9H_9	1	1	+	+	+
Bicapped Square Antiprism	$B_{10}H_{10}$	2	2	–	+	–
Edge-coalesced icosahedron	$B_{11}H_{11}$	1	1	+	+	+
Icosahedon	$B_{12}H_{12}$	4	4	+	+	+

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SAŽETAK

Trodimenzijsko poopćenje Kekuléovih struktura u kemiji borana

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Topologija prekrivanja atomskih orbitala koje sudjeluju u delokalizaciji u aromatskim sustavima može se opisati grafom čiji je spektar jednostavno povezan s molekulsko-orbitalnim energijama sustava. Aromatski sustavi mogu se klasificirati u skladu s čvornim svojstvima pre-

krivajućih atomskih orbitala. Tako su npr. trodimenzionalni deltahedarski borani, $B_nH_n^{2-}$, i karborani, $B_{n-2}C_2H_n$ ($6 \le n \le 12$), primjeri za bezčvorno-orbitalne aromatske sustave, jer delokalizacija u njima dolazi od prekrivanja orbitala bez čvorova, tj. radijalnih sp-hibrida bora ili ugljika. Pojam Kekuléovih struktura poznat u dvodimenzijskim benzenoidima može se proširiti na trodimenzijske, delokalizirane poliedarske borane, ako se umjesto dvostruke veze ugljik-ugljik u prvospomenutim sustavima koristi tro-središna veza B–B–B u potonjima. Mogućnost postojanja deltahedarskih vrsta izoelektronskih i izolobalnih s neutralnim, B_nX_n, i vrlo stabilnim tetraanionskim molekulama $B_nX_n^{4-}$, (X = H, Cl, Br, I), može se procijeniti na osnovi postojanja prikladne strukture Kekuléova tipa s vezama B–B i trosredišnim vezana B–B–B te na osnovi degeneracije najviše zauzete i najniže nezauzete molekulske orbitale.