

STRAINED CONFIGURATIONS IN THREE-DIMENSIONAL ANALOGUES OF KEKULÉ-TYPE STRUCTURES FOR DELTAHEDRAL BORANES

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Dedicated to Professor Jaromír Plešek on the occasion of his 75th birthday.

Localized structures analogous to the Kekulé structures for benzenoid hydrocarbons can be constructed for the deltahedral boranes $B_nH_n^{2-}$. These localized structures contain exactly three two-center two-electron (2c-2e) B-B bonds and $n - 2$ three-center two-electron (3c-2e) B-B-B bonds. The number of equivalent such Kekulé-type structures corresponds to the index of the symmetry group of the Kekulé structure, K , in the symmetry group, D , of the deltahedron. Three-dimensional Kekulé-type structures with the following configurations exhibit excessive strain and are therefore unfavorable: (i) structures having one or more pairs of boron atoms connected simultaneously by a 2c-2e B-B bond and a 3c-2e B-B-B bond (violation of the O'Neill-Wade restrictions); (ii) structures in which the three 2c-2e B-B bonds are excessively concentrated occupying only three or four vertices (the undesirable Δ , U, and Y configurations). Computations by Lipscomb and coworkers with partial retention of diatomic differential overlap (PRDDO) suggest that wide distribution of the three 2c-2e B-B bonds throughout the deltahedron and a minimum number of empty faces are more important than maximum symmetry in leading to the most favorable Kekulé-type structure.

Keywords: Boranes; Aromaticity; Boron clusters; Symmetry; Topology.

The chemical bonding theory of two-dimensional planar hydrocarbons and isoelectronic heterocycles uses the concepts of resonance energy and aromaticity^{1,2} as originally arising from molecular orbital theory³⁻⁵, and subsequently refined by methods based on graph theory⁶⁻⁹. More recently these concepts have been extended to three-dimensional structures including particularly the polyhedral borane anions $B_nH_n^{2-}$ ($6 \leq n \leq 12$) and isoelectronic carboranes¹⁰⁻¹². The structures of these borane anions are based on the "most spherical" deltahedra (polyhedra with all faces triangles) without any degree 3 vertices¹³ (Fig. 1).

A central idea associated with aromaticity in planar benzenoid hydrocarbons is the contribution of two or more different localized structures of equivalent energy consisting of alternating carbon-carbon single and double bonds to a lower energy averaged delocalized structure known as a resonance hybrid. Such localized structures are known as Kekulé structures. In benzene itself, the two equivalent Kekulé structures contain three double and three single bonds alternating along the edges of the C_6 hexagon and are mirror images of each other (Fig. 2a).

At approximately the same time as the Kekulé structures for benzene were first proposed in the 19th century^{14,15}, some alternative structures were also suggested¹⁶ such as the Dewar¹⁷, Claus¹⁸, and Ladenburg¹⁹ structures (Fig. 2b). These alternative structures were soon found not to be useful for the description of benzene and at best represent highly strained high-energy isomers of benzene. Indeed, during the 1960s and 1970s the Dewar and

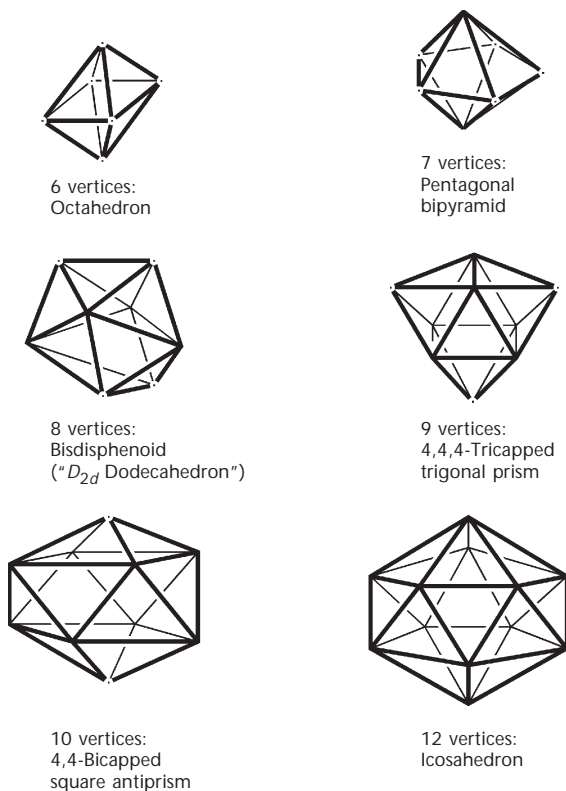


FIG. 1

The deltahedra for the boranes $B_nH_n^{2-}$ ($n = 6, 7, 8, 9, 10, \text{ and } 12$)

Ladenburg structures were realized experimentally in isolable compounds²⁰, namely the bicyclo[2.2.0]hexadienes (“Dewar benzenes”) and the prismanes²¹ (Fig. 2c).

A question of interest is how the concept of Kekulé structures can be extended to three dimensions in the deltahedral boranes. In this connection I have shown how three-dimensional analogues of localized Kekulé structures for the deltahedral borane anions $B_nH_n^{2-}$ ($6 \leq n \leq 12$) can be obtained by using three-center two-electron (3c-2e) B–B–B bonds instead of the carbon–carbon double bonds in benzenoid Kekulé structures^{22,23} (e.g., Fig. 2a). Such a Kekulé-type structure for a deltahedron with n vertices consists of $n - 2$ two-center two-electron (2c-2e) B–B bonds and exactly three 3c-2e B–B–B bonds regardless of the value of n . This leads to a total of $(n - 2) + 3 = n + 1$ skeletal orbitals corresponding to the $2n + 2$ skeletal electrons for stable deltahedral boranes required by Wade’s rules²⁴.

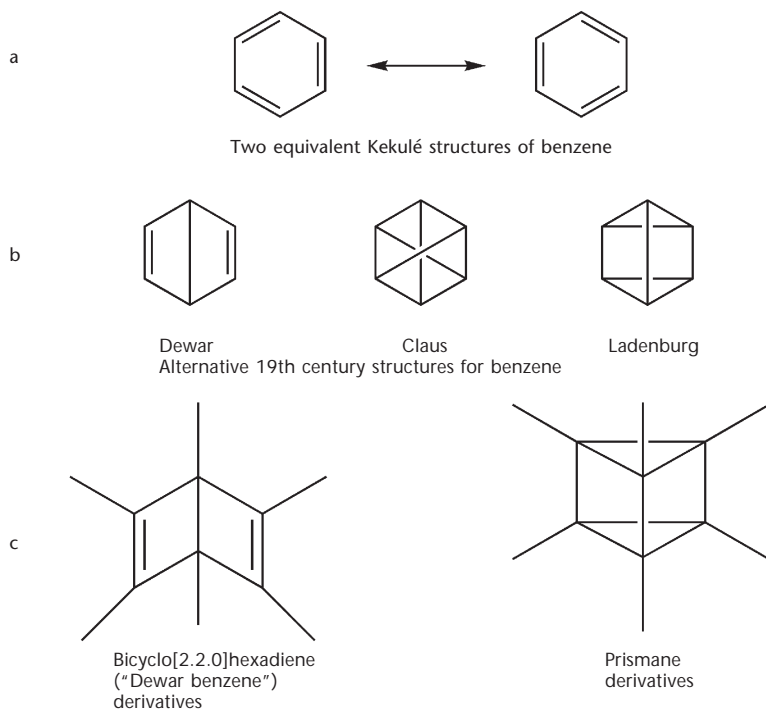


FIG. 2

The two equivalent Kekulé structures for benzene (a). Alternative structures proposed for benzene in the 19th century (b). Bicyclo[2.2.0]hexadiene (“Dewar benzene”) and prismane derivatives first synthesized in the 1960s and 1970s (c)

Using this general idea, Kekulé-type structures (Fig. 3a) can be constructed for octahedral $B_6H_6^{2-}$ having the required four 3c-2e B-B-B bonds in alternate faces of the octahedron (the shaded faces in Fig. 3a) and the required three 2c-2e B-B bonds in three of the 12 edges related by a C_3 axis (the bold edges in Fig. 3a). These Kekulé-type structures for $B_6H_6^{2-}$ can be seen from a geometrical point of view to be the equivalent of the two familiar Kekulé structures of benzene (Fig. 2a). However, from an energetic point of view these structures for $B_6H_6^{2-}$ are highly strained. Such localized structures therefore may be regarded as analogous to high-energy localized structures for benzene, such as the Claus structure (Fig. 2b) with three “*para*-connections” between the carbon atoms in the C_6 ring.

This paper examines the systematics of the three-dimensional analogues of the Kekulé-type structures for the deltahedral boranes with the objective of identifying unfavorable features of such localized structures leading to strain similar to that found in the high-energy structures for benzene (Fig. 2b). The deltahedra with 6, 7, 8, 9, 10, and 12 vertices (Fig. 1) are considered in this paper since they are of reasonably high symmetry (D_{2d} or greater) and have only degree 4 and 5 vertices. Deltahedra with 11 vertices are not considered in this paper because of the lower symmetry (C_{2v}) of the most spherical 11-vertex deltahedron found, for example, in $B_{11}H_{11}^{2-}$. This relatively low symmetry of the most spherical 11-vertex deltahedron com-

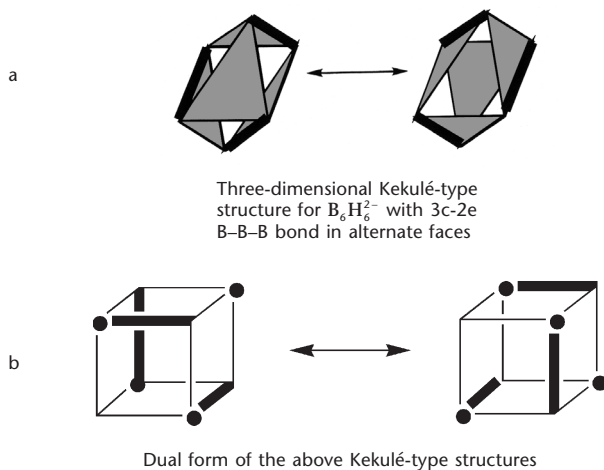


FIG. 3

Two of the Kekulé-type structures for $B_6H_6^{2-}$ having the required four 3c-2e B-B-B bonds in alternate faces of the octahedron (a). These types of Kekulé-type structures for $B_6H_6^{2-}$ in dual form (b)

plicates the study of its Kekulé-type structures because of the possibility of a large number of similar but not equivalent possible such structures. Furthermore, an 11-vertex deltahedron with only degree 4 and 5 vertices is shown to be topologically impossible²⁵ and thus the deltahedron found in $B_{11}H_{11}^{2-}$ and its carborane analogues has a degree 6 vertex in addition to degree 4 and 5 vertices.

Construction of Kekulé-Type Structures

The feature of particular interest distinguishing three-dimensional boranes from two-dimensional planar hydrocarbons is the presence of three-center bonds. In this connection Lipscomb and coworkers^{26,27} have studied the topology of the distribution of 2c-2e B-B and 3c-2e B-B-B and B-H-B bonds in the boron network of borane structures making the following assumptions:

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

2. Each external B-H bond is regarded as a typical 2c-2e bond requiring the hydrogen orbital, one hybridized boron orbital, and one electron each from the hydrogen and boron atoms. These bonds are assumed to be non-polar because of the very small electronegativity difference between hydrogen and boron.

3. Each B-H-B 3c-2e "bridge" bond corresponds to a filled three-center localized bonding orbital requiring the hydrogen orbital and one hybrid orbital from each boron atom.

4. The orbitals and electrons of any particular boron atom are first allocated to satisfy the requirements of bonding to the hydrogen atoms, *i.e.*, the 2c-2e external B-H bonds and the 3c-2e bridge B-H-B bonds. The remaining orbitals and electrons are then allocated to molecular orbitals of the boron skeleton.

The relative numbers of boron atoms, hydrogen atoms, electrons, and orbitals as well as bonds of various types can be expressed in a systematic way. For a borane B_pH_{p+q} containing s bridging hydrogen atoms, x "extra" B-H bonds in terminal BH_2 groups rather than B-H groups, t 3c-2e B-B-B bonds, y 2c-2e B-B bonds, and at least one hydrogen atom bonded to each boron atom, balancing the hydrogen atoms leads to $s + x = q$. Since each boron atom supplies four orbitals but only three electrons, the total number of 3c-2e bonds in the molecule is the same as the number of boron atoms, *i.e.*, $s + t = p$. This leads to the following equations of balance.

$$2s + 3t + 2y + x = 3p \quad (1a)$$

(orbital balance with 3 orbitals/BH vertex)

$$s + 2t + 2y + x = 2p \quad (1b)$$

(electron balance with 2 skeletal electrons/BH vertex)

Now consider the application of Eqs (1a) and (1b) to the deltahedral boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$). Such deltahedral boranes cannot have any terminal BH_2 groups or 3c-2e B-H-B bridges so that $s = x = 0$ in the equations of balance (Eqs (1a) and (1b)). This leads to the following equations in which n is the number of boron atoms in the deltahedron corresponding to p in Eqs (1a) and (1b):

$$3t + 2y = 3n \quad (2a)$$

$$2t + 2y = 2n + 2 \quad (2b)$$

Again Eq. (2a) relates to orbital balance and Eq. (2b) relates to electron balance. Solving the simultaneous equations (2a) and (2b) leads to $y = 3$ and $t = n - 2$ implying the presence of three 2c-2e B-B bonds and $(n - 2)$ 3c-2e B-B-B bonds. Since a deltahedron with n vertices has $2n - 4$ faces, the $(n - 2)$ 3c-2e B-B-B bonds 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 its faces covered by 3c-2e B-B-B bonds just as a Kekulé structure for a benzenoid hydrocarbon has half of its edges covered by C=C double bonds^{22,23}.

The number of *equivalent* Kekulé-type structures, N_K for a given deltahedral borane corresponds to the index of the symmetry group, K , of the Kekulé-type structure in the symmetry group, D , of the underlying deltahedron leading to the equation

$$N_K = |D|/|K| \quad (3)$$

in which $|D|$ and $|K|$ are the orders of the symmetry point groups D and K , respectively. Equation (3) is satisfied by the two Kekulé structures of benzene (Fig. 2a) where $D = D_{6h}$ and $K = D_{3h}$ so that $|D| = 24$, $|K| = 12$, and $N_K = |D|/|K| = 24/12 = 2$. The sum of the entire set of equivalent Kekulé-type

structures, ΣK , for a given borane deltahedron has the full symmetry of the underlying deltahedron.

Kekulé-type structures for borane deltahedra, such as those for the $B_6H_6^{2-}$ octahedron depicted in Fig. 3a, rapidly become difficult to draw and visualize for any of the deltahedra of interest. However, by converting the borane deltahedra and their Kekulé-type structures to their duals, the Kekulé-type structures become much easier to depict and visualize. In this connection a given polyhedron, P , can be converted into its dual P^* by locating the vertices of P^* above the centers of the faces of P and the centers of the faces of P^* above the vertices of P . Two vertices in the dual P^* are connected by an edge when the corresponding faces in P share an edge. The process of dualization has the following properties:

1. The numbers of vertices (v and v^*), edges (e and e^*), and faces (f and f^*) in a pair of dual polyhedra P and P^* satisfy the relationships $v^* = f$, $e = e^*$, $f = v^*$.

2. Dual polyhedra have the same symmetry elements and thus belong to the same symmetry point group.

3. Dualization of the dual of a polyhedron leads to the original polyhedron.

4. The degrees of the vertices of the polyhedron correspond to the number of edges in the corresponding face polygons of its dual. Thus the duals of the deltahedra are trivalent polyhedra, *i.e.*, polyhedra in which all vertices are of degree 3.

The following observations can be made concerning the duals of the deltahedra of interest (Fig. 4):

1. The dual of a bipyramid is a prism of the same symmetry. For example, the dual of the pentagonal bipyramid (the $B_7H_7^{2-}$ deltahedron) is the pentagonal prism.

2. The dual of a capped polyhedron is a truncated polyhedron of the same symmetry. For example, the dual of the tricapped trigonal prism (the $B_9H_9^{2-}$ deltahedron) is the tritruncated trigonal bipyramid.

3. The dual of an antiprism is a trapezohedron of the same symmetry in which all faces are equivalent trapezia, *i.e.*, quadrilaterals in which no pair of edges is parallel. For example, the dual of the ten-vertex bicapped square antiprism (the $B_{10}H_{10}^{2-}$ deltahedron) is a bitruncated tetragonal trapezohedron. The truncation of the two antipodal degree 4 vertices of a tetragonal trapezohedron to give the bitruncated tetragonal trapezohedron (Fig. 4) converts all eight equivalent trapezium faces of the original trapezohedron into equivalent non-regular pentagons.

The duals of the borane deltahedra with 6, 7, 8, 9, 10, and 12 vertices are trivalent polyhedra with quadrilateral and pentagonal faces corresponding to degree 4 and 5 vertices, respectively, of the original deltahedron.

The process of forming Kekulé-type structures for deltahedral boranes can also be dualized so that 3c-2e B-B-B bonds in deltahedral faces become special vertices and the 2c-2e B-B bonds become special edges. Figure 4 depicts a sample Kekulé-type structure for each of the deltahedral boranes in Fig. 1 in dualized form. In Fig. 4 the special vertices of the dual corresponding to the 3c-2e B-B-B bonds are marked by bold dots and the special edges corresponding to the 2c-2e B-B bonds are marked by bold lines.

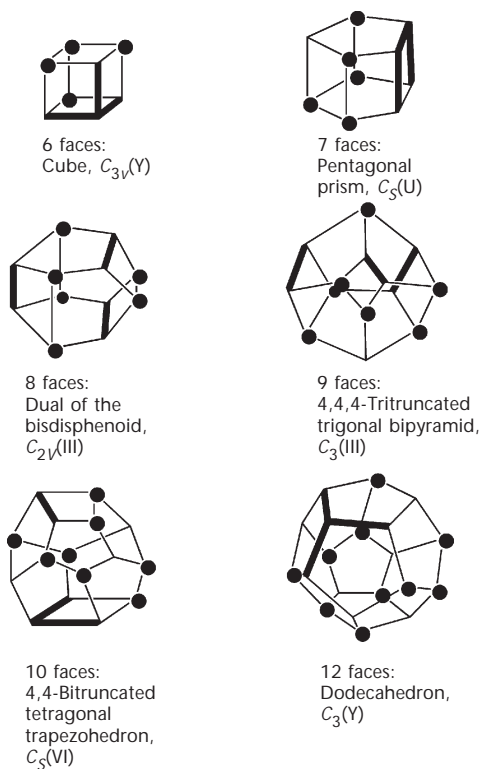


FIG. 4

The duals of the deltahedra in Fig. 1 showing a Kekulé-type structure in dual form for each polyhedron

Avoidance of Strained Configurations in the Construction of Three-Dimensional Kekulé-Type Structures

Some three-dimensional Kekulé-type structures constructed according to the rules outlined above are found to have excessive strain and thus are unfavorable localized bonding schemes for the corresponding deltahedral boranes. These strained Kekulé-type structures may be viewed as three-dimensional analogues of some of the now-obsolete 19th century alternatives to the Kekulé structures of benzene depicted in Fig. 2b. Strained three-dimensional Kekulé-type structures may be identified in two general ways: (i) the O'Neill–Wade restrictions, (ii) undesirable configurations of the three localized 2c-2e B–B bonds. In a number of cases the Kekulé-type structures of highest symmetry for a particular deltahedral borane have undesirable features leading to excessive strain so that the most favorable Kekulé structures in terms of minimum strain exhibit relatively low symmetry.

The O'Neill–Wade Restrictions

O'Neill and Wade²⁸ have discussed localized bonding schemes for deltahedral boranes using 2c-2e B–B bonds and 3c-2e B–B–B bonds with the following basic assumptions:

1. Each skeletal boron or other atom is assumed to participate in three skeletal bonds in addition to the external bond, typically to a hydrogen atom in the boranes. This assumption is also implicit in the assumptions of Lipscomb^{27,29} presented above.

2. Each edge of the skeletal B_n polyhedron must correspond to a 2c-2e B–B bond or a 3c-2e B–B–B bond. Cross-polyhedral interactions, which are significantly longer than the polyhedral edge interactions, are considered to be non-bonding. The edge length(s) of the borane deltahedron thus may be considered to correspond to boron–boron “bonding” distances either through 2c-2e B–B or 3c-2e B–B–B bonds but not both.

3. A pair of boron atoms cannot be simultaneously bonded to each other both by a 2c-2e B–B bond and one or two 3c-2e B–B–B bonds since these arrangements would require too close an alignment of the atomic orbitals involved. This assumption restricts severely the possible arrangements of 2c-2e B–B and 3c-2e B–B–B bonds that can be a valid Kekulé-type structure for a given deltahedral borane.

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

The important features of the O'Neill–Wade restrictions²⁸ can be expressed in dual form as follows:

1. The participation of three orbitals per boron atom in the skeletal bonding means in dual form that the sum of the numbers of bold dotted vertices (*i.e.*, the 3c-2e B–B–B bonds) and bold edges (*i.e.*, the 2c-2e B–B bonds) must be exactly three for every face.

2. The fact that a pair of boron atoms (*i.e.*, an edge of the original deltahedron) cannot simultaneously be a part of a 2c-2e B–B bond and a 3c-2e B–B–B bond means in dual form that no bold-dotted vertex can also be part of a bold edge.

The Kekulé-type structures for $B_6H_6^{2-}$ with the 3c-2e B–B–B bonds in alternate faces of the octahedron (Fig. 3a) can be seen to violate the O'Neill–Wade restrictions since the three pairs of boron atoms connected by a 2c-2e B–B bond (the bold edges in Fig. 3a) are also connected by 3c-2e B–B–B bonds (the shaded faces in Fig. 3a). This violation is also indicated by the dual forms of these Kekulé-type structures (Fig. 3b) where the four bold dotted vertices are also parts of bold edges. Thus the Kekulé-type structures for $B_6H_6^{2-}$ with the 3c-2e B–B–B bonds in alternate faces (Fig. 3a) can be assumed to be Kekulé structures with high strain and thus very unfavorable.

Figure 4, besides showing duals for the borane deltahedra of interest (Fig. 1), also depicts for each of the deltahedra a sample Kekulé-type structure in dualized form satisfying the O'Neill–Wade restrictions²⁸. The symmetries of an individual Kekulé-type structure for each of the deltahedral boranes of interest are listed in Table I so that Eq. (3) can be used to determine the corresponding numbers of equivalent Kekulé-type structures. The Kekulé-type structure for octahedral $B_6H_6^{2-}$ in Fig. 4, in contrast to the two equivalent structures for $B_6H_6^{2-}$ in Fig. 3a, is one of eight equivalent structures of C_{3v} symmetry satisfying the O'Neill–Wade restrictions²⁸.

Undesirable Configurations of the Three Two-Center Two-Electron Boron–Boron Bonds

The Kekulé-type structures in dual form for the deltahedral boranes, such as those depicted in Fig. 4, can be characterized by the following properties in addition to their symmetry point groups:

1. *The configurations of the three bold edges corresponding to the 2c-2e B–B bonds.* The five possible configurations, conveniently designated as Δ , Y, U,

TABLE I
The borane deltahedra, their duals, and their Kekulé-type structures

Deltahedron	Dual	Numbers of vertices (<i>v</i>), edges (<i>e</i>), and faces (<i>f</i>)			Symmetry point groups		$N_K = D / K $
		$v = f^*$	$e = e^*$	$f = v^*$	<i>D</i>	<i>K</i>	
Octahedron	Cube	6	12	8	O_h	C_{3v}	8 = 48/6
Pentagonal bipyramid	Pentagonal prism	7	15	10	D_{5h}	C_s	10 = 20/2
Bisdisphenoid	Dual of the bisdisphenoid	8	18	12	D_{2d}	C_{2v}	2 = 8/4
4,4,4-Tricapped trigonal prism	4,4,4-Tritruncated trigonal bipyramid	9	21	14	D_{3h}	C_3	4 = 12/3
4,4-Bicapped tetragonal antiprism	4,4-Bitruncated tetragonal trapezohedron	10	24	16	D_{4d}	C_s	8 = 16/2
Icosahedron	Dodecahedron	12	30	20	I_h	C_3	40 = 120/3

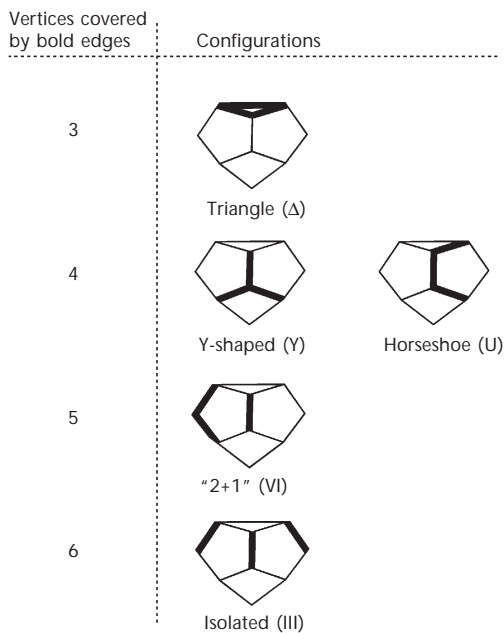


FIG. 5

The five possible configurations (Δ , Y, U, VI, and III) for the three bold edges in the dual form of the Kekulé-type structures representing the locations of the three 2c-2e B-B bonds in the original deltahedron

VI, and III, can be characterized by the total number of vertices, b , covered by the bold edges ($3 \leq b \leq 6$) and the configurations of the bold edges (Fig. 5). The Kekulé-type structures for the deltahedral boranes discussed in this paper are described by their symmetry point group designations followed by Δ , Y, U, VI, or III in parentheses to describe the locations of their 2c-2e B-B bonds.

2. *The number of vertices of the dual that are neither bold-dotted nor part of a bold edge.* Such vertices are conveniently designated as naked dual vertices and the number of such vertices will be denoted by z . Naked dual vertices correspond to faces of the original deltahedron that neither contain a 3c-2e B-B-B bond nor have an edge that is a 2c-2e B-B bond.

Now consider Euler's theorem in the following form

$$n - e + f = 2 \quad (4)$$

in which n , e , and f are the numbers of vertices, edges, and faces, respectively, of the original deltahedron. For a deltahedral borane with n boron atoms, $e = 3/2f$ and the numbers of 2c-2e B-B bonds (y) and 3c-2e B-B bonds (t) are 3 and $n - 2$, respectively, so that

$$z = n - b - 2 \quad (5)$$

using trivial algebra. For example, in the case of the $C_3(\text{III})$ Kekulé-type structure for tricapped trigonal prismatic $B_9H_9^{2-}$ depicted on the dual tritruncated trigonal bipyramid (Fig. 4), $n = 9$ and $b = 6$ for the III configuration of the three 2c-2e B-B bonds so that $z = 9 - 6 - 2 = 1$. Note that $b \leq 6$ so that for any deltahedron for $B_nH_n^{2-}$, where $n \geq 9$, there must be one or more naked vertices in the dual corresponding to empty faces in the original deltahedron.

Among the five possible configurations of the 2c-2e B-B bonds in the deltahedral borane duals (Fig. 5), three of them can be considered undesirable for the following reasons:

1. The Δ configuration requires a degree 3 vertex forming three 2c-2e B-B bonds and thus cannot occur in the deltahedra in Fig. 1, which have only degree 4 or higher vertices. The absence of degree 3 vertices appears to be a requirement for stable deltahedral boranes $B_nH_n^{2-}$ as suggested by the graph theory derived approach to three-dimensional aromaticity³⁰.

2. The U configuration corresponds to exactly three 2c-2e B-B bonds from a vertex of degree 4 or higher. This violates the O'Neill-Wade restric-

tion that either a 2c-2e B–B or 3c-2e B–B–B bond must connect every pair of boron atoms connected by an edge in the underlying deltahedron.

3. The Y configuration corresponds to the three 2c-2e B–B bonds forming the three edges of one of the triangles of a deltahedron similar to the three 2c-2e C–C bonds in cyclopropane. The Y configuration thus might be expected to exhibit some of the bond-angle strain of cyclopropane. However, the eight equivalent Kekulé-type structures for octahedral $B_6H_6^{2-}$ necessarily have the Y configuration (Fig. 4). This suggests that $B_6H_6^{2-}$, although highly symmetrical, has some bond-angle strain similar to that in cyclopropane and thus might be expected to be more chemically reactive than some of the higher deltahedral borane anions. This is in accord with experimental observations^{31,32}.

A feature common to these three undesirable configurations is that the three 2c-2e B–B bonds occupy fewer than five vertices of the underlying deltahedron. These undesirable configurations of the 2c-2e B–B bonds may thus be regarded as excessively concentrated.

Some of the highest symmetry Kekulé-type structures for the deltahedral boranes $B_nH_n^{2-}$ ($n \geq 6$) have these undesirable configurations of the 2c-2e B–B bonds, notably the $C_5(U)$ structures for $B_7H_7^{2-}$ and the $C_3(Y)$ structures for $B_{12}H_{12}^{2-}$ (Fig. 4). However, all of the Kekulé-type structures found by Lipscomb and coworkers³³ from PRDDO calculations have the desirable VI or III configurations of their 2c-2e B–B bonds except for $B_6H_6^{2-}$, where no such Kekulé-type structures are possible. This computational work³³ provides further evidence that the VI and III configurations of 2c-2e B–B bonds in Kekulé-type structures for the deltahedral boranes are significantly more favorable than the Δ , U, and Y configurations.

Figure 4 shows in dual form a representative of the highest symmetry Kekulé-type structures that were found for the six borane deltahedra in Fig. 3 and Figs 6 and 7 compare these structures with those found by Lipscomb and coworkers³³ from their PRDDO calculations. The following observations can be made:

1. *Octahedron.* Eight equivalent $C_{3v}(Y)$ Kekulé-type structures are found. Each of these structures has one face containing all three 2c-2e B–B bonds corresponding to a vertex of the dual cube where all three bold edges meet (Fig. 4). Lipscomb and coworkers³³ find the same Kekulé-type structure for $B_6H_6^{2-}$.

2. *Pentagonal bipyramid.* There are five enantiomeric pairs of equivalent $C_5(U)$ Kekulé-type structures with one naked vertex generated from an initial such structure by a C_5 rotation (Fig. 4). Lipscomb and coworkers³³ find

for $B_7H_7^{2-}$ a $C_1(VI)$ structure with no symmetry but also with no naked vertices (Fig. 6). This structure with no symmetry avoids the topological forbidden U configuration of the three 2c-2e B-B bonds.

3. *Bisdisphenoid*. There are two equivalent $C_{2v}(III)$ Kekulé-type structures without naked dual vertices ($z = 0$). These two equivalent Kekulé-type structures (Fig. 4) interchange the bold-dotted vertices and the bold-edged vertices. These are the largest possible structures for a $B_nH_n^{2-}$ deltahedral borane without naked dual vertices corresponding to empty faces. Lipscomb and coworkers³³ find two different less symmetrical (C_s and C_1) structures which likewise have the III configuration without naked dual vertices (Fig. 6). They describe their $C_1(III)$ structure as “topologically forbidden” since there is neither a 2c-2e nor a 3c-2e bond between one of the pairs of adjacent degree 5 boron vertices thereby violating one of the O’Neill–Wade restric-

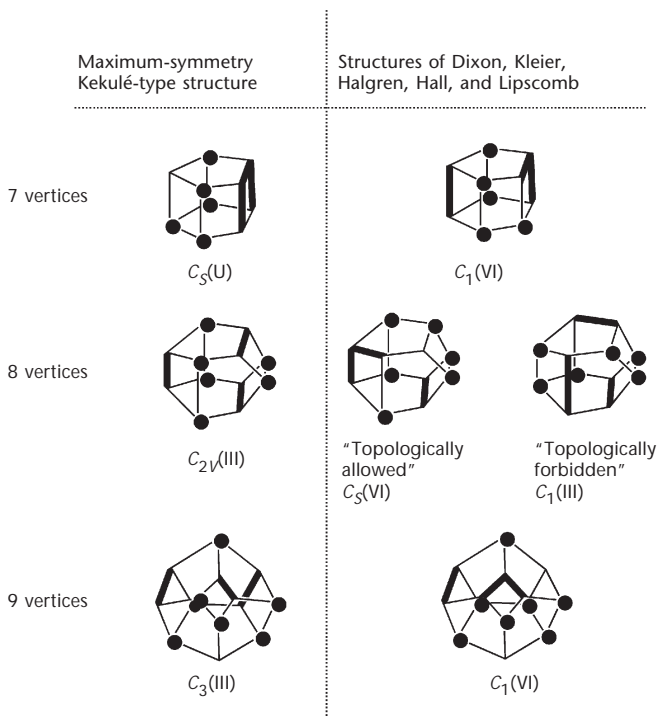


FIG. 6

Comparison of the maximum-symmetry Kekulé-type structures satisfying the O’Neill–Wade restrictions for $B_7H_7^{2-}$, $B_8H_8^{2-}$, and $B_9H_9^{2-}$ with the less symmetrical structures found by Lipscomb and coworkers³³ from PRDDO calculations

tions²⁸. This corresponds to neither a bold common edge nor a shared dot between the "front" pentagon and the "bottom" pentagon in the dual $C_1(\text{III})$ depicted in Fig. 6.

4. *4,4,4-Tricapped trigonal prism*. This deltahedron has a total of 14 (triangular) faces, which are partitioned into two faces of one type and 12 faces of a second type. The set of two equivalent faces corresponds to the two triangular faces of the underlying trigonal prism whereas each of the remaining 12 equivalent faces contains one of the three capping vertices, *i.e.*, the vertices of degree 4. The four equivalent $C_3(\text{III})$ Kekulé-type structures (Fig. 4) correspond to two enantiomeric pairs. In one enantiomeric pair one of the triangular faces of the underlying trigonal prism contains a 3c-2e B-B-B bond and the other such triangular face is an empty face corresponding to the naked dual vertex. In the second such enantiomeric pair, the roles of the triangular faces of the underlying trigonal prism are reversed. Lipscomb and coworkers³³ found a $C_1(\text{VI})$ Kekulé-type structure with no symmetry (Fig. 6).

5. *4,4-Bicapped square antiprism*. There are eight equivalent $C_5(\text{VI})$ Kekulé-type structures of $\text{B}_{10}\text{H}_{10}^{2-}$ generated from an initial such Kekulé-type structure by the operations of the D_4 point group (Fig. 4). Lipscomb and coworkers³³ described a similar $C_1(\text{VI})$ structure but with no symmetry (their "4,4,3" structure) as well as a second $C_1(\text{III})$ structure with a different configuration of the three 2c-2e B-B bonds (their "3,5,3" structure). Both of their structures (Fig. 7) appear to be local minima on their calculated energy hypersurface.

6. *Icosahedron*. Twenty equivalent enantiomeric pairs of $C_3(\text{Y})$ Kekulé-type structures are found (Fig. 4). Each of these structures has one face containing all three 2c-2e B-B bonds corresponding to a vertex of the dual dodecahedron where all three bold edges meet. Thus the $C_3(\text{Y})$ Kekulé-type structures for the regular octahedron and the regular icosahedron are analogous. The six naked dual vertices of the $C_3(\text{Y})$ Kekulé-type structure for the icosahedron have a C_3 trigonal prismatic orientation, which is distorted from an ideal D_{3h} trigonal prism to only C_3 symmetry in accord with the underlying symmetry of the Kekulé-type structure. Lipscomb and coworkers³³ found a lower symmetry $C_5(\text{III})$ structure (Fig. 7) having the minimum number of naked dual vertices ($z = 12 - 6 - 2 = 4$). The structure found by Lipscomb and coworkers³³ thus avoids the undesirable Y configuration of the three 2c-2e B-B bonds at the expense of losing the three-fold symmetry.

Gielen³⁴ has found 5 430 Kekulé-type structures for $\text{B}_{12}\text{H}_{12}^{2-}$ which can be classified into 113 general types called "canonical forms" with symmetries

C_1 (77 canonical forms), C_2 (19 canonical forms), C_3 (7 canonical forms), and D_3 (10 canonical forms). However, some of Gielen's Kekulé-type structures for $B_{12}H_{12}^{2-}$ violate the O'Neill-Wade restrictions²⁸. For example, all of the Kekulé-type structures for $B_{12}H_{12}^{2-}$ with D_3 symmetry necessarily have the Y configuration (Fig. 5) and the forbidden property of a pair of boron atoms connected both by a 2c-2e B-B bond and a 3c-2e B-B-B bond corresponding in dual form to a bold dotted vertex also being part of a bold edge.

Conclusion

Localized structures analogous to the Kekulé structures for benzenoid hydrocarbons can be constructed for the deltahedral boranes $B_nH_n^{2-}$. These localized structures contain exactly three 2c-2e B-B bonds and $(n - 2)$ 3c-2e B-B-B bonds. The number of equivalent such Kekulé-type structures corresponds to the index of the symmetry group of the Kekulé structure, K , in the symmetry group, D , of the deltahedron. The Kekulé-type structures for the deltahedral boranes are more readily visualized in the dual polyhedra where the 3c-2e B-B-B bonds become special vertices and the 2c-2e B-B bonds become special edges.

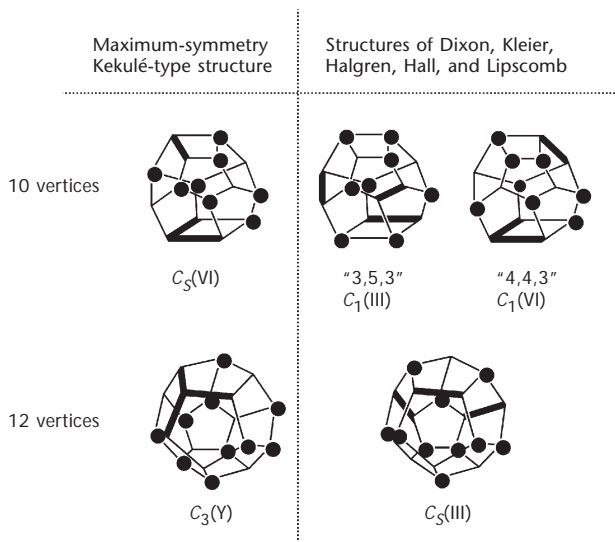


FIG. 7

Comparison of the maximum-symmetry Kekulé-type structures satisfying the O'Neill-Wade restrictions for $B_{10}H_{12}^{2-}$ and $B_{12}H_{12}^{2-}$ with the less symmetrical structures found by Lipscomb and coworkers³³ from PRDDO calculations

Some three-dimensional Kekulé-type structures are found to have excessive strain and thus describe unfavorable localized bonding schemes for the corresponding deltahedral boranes. Strained three-dimensional Kekulé-type structures exhibit the following features: (i) pairs of boron atoms connected simultaneously by a 2c-2e B–B bond and a 3c-2e B–B–B bond (violation of the O'Neill–Wade restrictions); (ii) the three 2c-2e B–B bonds are excessively concentrated occupying only three or four vertices (the undesirable Δ , U, and Y configurations). PRDDO computations by Lipscomb and co-workers suggest that wide distribution of the three 2c-2e B–B bonds throughout the deltahedron and a minimum number of empty faces are more important than maximum symmetry in leading to the most favorable Kekulé-type structure.

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