

Matthias Driess, Heinrich Nöth (Eds.)

Molecular Clusters of the Main Group Elements



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Matthias Driess, Heinrich Nöth (Eds.)

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Preface

The past 10 years have witnessed spectacular discoveries in the field of molecular cluster chemistry of the main-group elements: that is the reason for this book! It is timely to provide a survey of a number of important developments in this field, particularly only because the synthesis, functionalization, and theoretical concepts of novel molecular cluster systems are currently one of the most promising challenges in modern inorganic chemistry. Today, molecular clusters are used as one of the profound constituents of a variety of applications, ranging from materials science with nanoscaled atomic aggregates (e.g., metal clusters as molecular transistors) to medical targets (e.g., boron-rich clusters for boron-neutron-capture-therapy, BNCT). Additionally, one can envision that obtaining simple routes to many different element clusters with tunable electronic properties could significantly accelerate the development of molecular electronics and nanorobots, which are aims of a promising future. Clusters of the chemical elements show a tremendous variety of chemical and physical properties even if they consist of identical sorts of atoms. This is due to the fact that atoms can be connected topologically differently by spatially directed chemical bonds, thus leading to a molecular polyhedral skeleton with a different shape. This is particularly evident by the spectacular discovery of the spherically shaped carbon clusters (fullerenes C_{60} , C_{70} , C_{78} etc.), which have inspired many chemists and physicists to investigate related “naked” clusters of main-group elements and their chemical functionalization. About 10 years ago, most of the cluster chemistry of the main-group elements was devoted to cluster systems that form very stable atomic aggregates (cluster skeletons). Of prime importance were polyboranes, the prototype for the investigation of cluster formation of the main-group elements. Many boron compounds (boron hydrides, heteroboranes such as carba-, aza-, and metallaboranes, and several subvalent boron halides) inherently possess aggregate (cluster) structures with a deltapolyhedral shape (e.g., tetrahedral, octahedral, or icosahedral skeletons). The secret of the extraordinary properties of these classes of compounds is based on their unusual bonding state, which cannot be described by classical (localized) two-center two-electron covalence bonds but through multiple center bonds. Multiple-center (cluster) bonds lend such systems super stability similar to that in aromatic compounds in organic chemistry. It has been the credit of W.N. Lipscomb (Nobel Prize winner 1976) who showed for the first time that deltapolyhedral structures of

polyboranes can be understood on the basis of modified valence rules by using a multiple-center-bonding description. However, more than 20 years passed before the first clusters of the boron-congeners (aluminum, gallium, indium, and thallium clusters) were synthesized. Not only that, unlike the chemistry of polyboron and heteropolyboron compounds, little or nothing was known about the formation, stability, or functionalizability of related homo- and heteronuclear molecular clusters of other heavier main-group elements, e.g., those involving group 14 and 15 elements. Since main-group chemistry has a strong and very successful tradition in Germany, several leading experts in the field of molecular cluster chemistry decided to establish the priority research program “Assembling and Functionalization of Polyhedral Clusters of the Main-Group Elements” in 1994 (until 2002) under the auspices of the German Research Council (Deutsche Forschungsgemeinschaft). The research program was devoted to the discovery of unknown territory in cluster chemistry of the main-group element. It was worth the effort: our knowledge of molecular clusters of the main-group elements dramatically increased during that period of time: this is evident when looking at the spectacular discovery of the first Al_{77} - and Ga_{84} -clusters, which represent the largest molecular main-group metal clusters hitherto structurally characterized. We believe that the novel landscape of cluster compounds discussed in this book will lead to new exciting applications in chemistry, physics, biology and materials science in the near future.

We particularly thank the German Research Council (“Deutschen Forschungsgemeinschaft”) for generous financial support during the period of the priority-program “Assembling and Functionalization of Polyhedral Clusters of the Main-Group Elements” (“Aufbau und Funktionalisierung von Polyedergerüsten aus Hauptgruppenelementen”), which enabled us to write this book. The priority-program would not have been possible without the commitment and initiatives of Prof. Dr. Walter Siebert (Heidelberg), Prof. Dr. Gottfried Huttner (Heidelberg) and the editors. We also thank Dr. Karlheinz Schmidt for his untiring supreme organizational care of the scientific projects during the priority-program. Last but not least, on behalf of all participants of the priority-program, We would like to express my thanks to the scientific referees of the program, Prof. Dr. Kurt Dehnicke (Marburg), Prof. Dr. Dieter Fenske (Karlsruhe), Prof. Dr. Bernt Krebs (Münster), Prof. Dr. Werner Kutzelnigg (Bochum), Prof. Dr. Michael Lappert (Sussex, U.K.), Prof. Dr. Günter Schmid (Essen) and Prof. Dr. Michael Veith (Saarbrücken), for their scientific advice and helpful discussions.

We hope that this book will be a source of inspiration for many colleagues in molecular and material sciences.

Bochum/München, December 2003

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1

Theory and Concepts in Main-Group Cluster Chemistry

R. Bruce King and Paul v. R. Schleyer

1.1 Introduction

The main group cluster chemistry discussed in this book can be considered to originate from two important, but apparently unrelated developments in inorganic chemistry in the 1930s. The first was the identification of the neutral boron hydrides by Stock [1]. The second was the observation by Zintl and co-workers [2–5] of anionic clusters formed from potentiometric titrations of post-transition metals (i.e., heavy main group elements) with sodium in liquid ammonia.

Understanding the structure and chemical bonding in these new types of inorganic molecules proceeded rather slowly after these original discoveries. In the 1950s, Lipscomb used the fundamental concept of three-center two-electron bonding [6–8] to develop a topological model that explained the structures of the known neutral boron hydrides of the general types B_nH_{n+4} and B_nH_{n+6} (Figure 1-1). Subsequently, Williams [9] recognized that the structures of these neutral boranes could be considered to be fragments of the “most spherical” deltahedra (Figure 1-2) with the most uniformly or most homogeneously connected vertices. Such polyhedra only have triangular faces. As many of their vertices as possible have degrees four or five. The “degree” is the number of edges meeting at a vertex. The degree is the same whether or not an external hydrogen or group is attached. The deltahedral borane dianions [10] $B_nH_n^{2-}$ and isoelectronic carboranes [11] $C_2B_{n-2}H_n$ ($6 \leq n \leq 12$) had just been discovered. Most of these species were considerably more stable than the neutral boron hydrides, B_nH_{n+4} and B_nH_{n+6} . This led to the concept of three-dimensional aromaticity, first suggested explicitly by Aihara [12] in 1978. The particularly favorable icosahedral units found in the very stable $B_{12}H_{12}^{2-}$ and in the three $C_2B_{10}H_{12}$ isomers were predicted computationally by Longuet-Higgins and Roberts in 1955 [13]. Similar B_{12} icosahedral units are also found in the structures of refractory solid state materials such as elemental boron [14] and boron carbide (B_4C) [15]. In 1971 Wade [16] recognized that the stability of the deltahedral boranes $B_nH_n^{2-}$ and isoelectronic species was related to the presence of $2n + 2$ skeletal electrons in such structures. Shortly afterwards these ideas were incorporated by Mingos [17, 18] into his “polyhedral skeletal

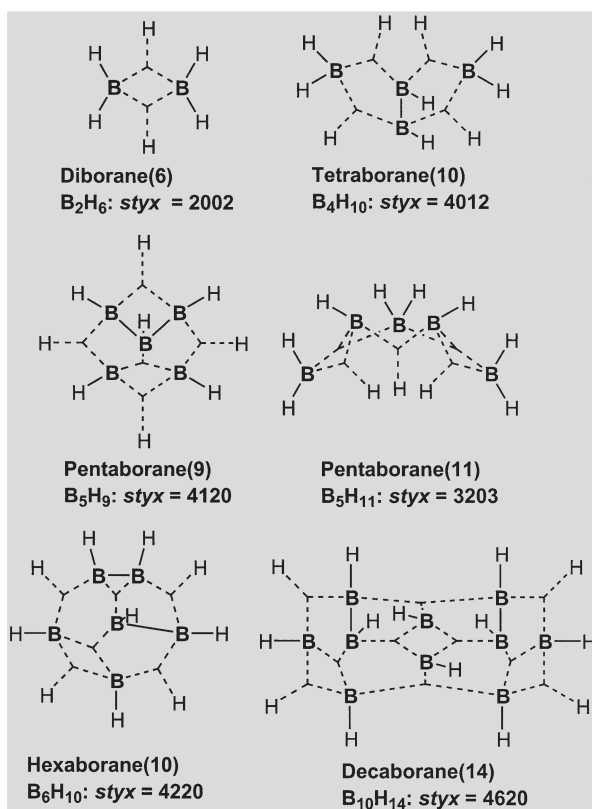


Fig. 1-1. The original neutral boron hydrides (boranes) isolated by Stock along with their *styx* numbers.

electron pair approach” for the understanding of the structural diversity of polyhedral boranes. Consequently, these theoretical electron-counting schemes are now frequently called the “Wade-Mingos rules.” Subsequent work showed that the Wade-Mingos rules are applicable not only to polyhedral boranes but also to clusters both of main group elements and of transition metals.

Understanding the nature of the anionic bare post-transition metal clusters (i.e., the heavier main group elements), first observed by Zintl and co-workers [2–5] in liquid ammonia titrations, was hindered by difficulties in isolating pure crystalline phases whose structures could be determined by X-ray diffraction methods. Corbett and co-workers finally solved this problem in 1975 [19] by complexing the alkali metal counterion with 2,2,2-crypt to obtain crystalline products. Their initial report [19] of the structure of Sb_7^{3-} was followed by the elucidation of the geometries of numerous other bare post-transition metal anions, such as E_9^{2-} and E_9^{4-} ($E = Ge, Sn$), E_5^{2-} ($E = Sn, Pb$), and E_4^{2-} ($E = Sb, Bi$) [20]. In addition, salts of bare post-transition metal cations, such as the subvalent bismuth Bi_5^{3+} , Bi_8^{2+} , and Bi_9^{5+} , were isolated from strongly Lewis acidic reaction mixtures as single

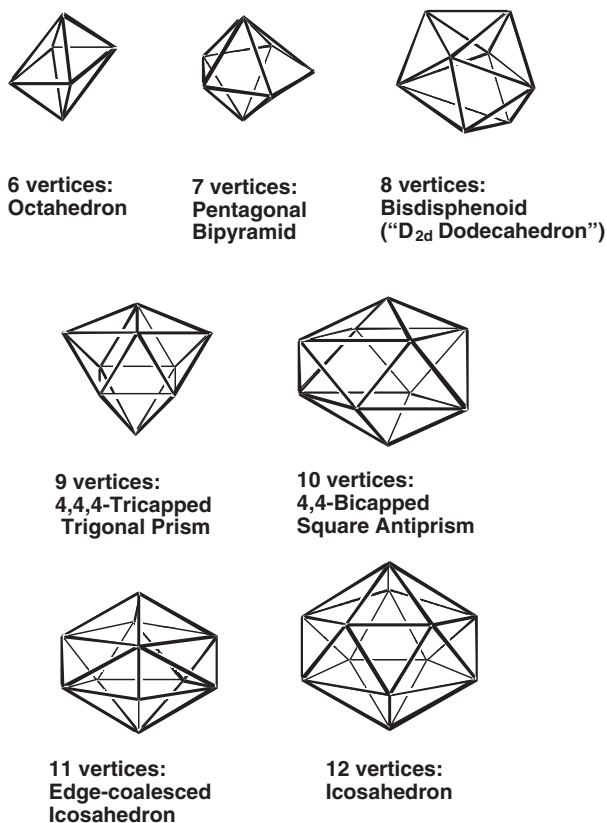


Fig. 1-2. The "most nearly spherical" deltahedra found in the boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$) and isoelectronic carboranes.

crystals, which could be characterized by X-ray analysis [21]. After sufficient structural data on bare post-transition metal clusters had accumulated, isoelectronic relationships between these clusters and the polyhedral boranes became apparent. Evidently, similar principles of structure and bonding were applicable to both types of molecules.

During the past decade the number and variety of main group element clusters has expanded drastically, particularly with the heavier group 13 metals. Thus, some organometallic group 13 metal analogues of the polyhedral boranes have been isolated and characterized including the icosahedral dianion $[Al_{12}Bu^i_{12}]^{2-}$ and the tricapped trigonal prismatic $Ga_9Bu^i_9$ (both discussed below), as well as more complicated organoaluminum and organogallium clusters that are best interpreted as fused, nested, or capped deltahedra (see Chapter 2.3.3.2) [22]. The larger organometallic clusters include Al_{69} and Al_{77} derivatives with five-fold symmetry that may be considered as icosahedral quasicrystal fragments [23]. A few examples of smaller clusters of heavier group 13 metals are also known, even including triangular

$[\text{Ga}_3\text{R}_3]^{2-}$ (R = bulky aryl group) [24], isoelectronic with the aromatic cyclopropenium cation. In addition, tin clusters exhibit a variety of interesting cage structures (see Chapter 2.5.4) [25].

1.1.1

Three-center Bonding in Boranes: Lipscomb's Equations of Balance

The unusual compositions and geometries of the neutral boron hydrides (Figure 1-1) stimulated efforts to understand their structure and bonding. In this connection, Lipscomb and co-workers [6–8] recognized that the prevalence of three-center bonds was the particular feature distinguishing three-dimensional boranes (based on the trivalent element, boron) both from the two-dimensional planar hydrocarbons (constituted by trivalent sp^2 carbons) as well as from the alkanes (which require the fourth valence of carbon to be three-dimensional). 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 and one antibonding orbital. If two electrons are available, they will just fill the bonding orbital. If the elements have nearly the same electronegativities, as in the typical hydrocarbons, the standard covalent σ -bond results.

Such two-center two-electron bonds accommodate as many electrons as atomic orbitals. Thus, if n atomic orbitals form a bonding network using two-center two-electron bonds exclusively, as in the saturated hydrocarbons, they form $n/2$ bonding (valence) orbitals which accommodate n electrons. For example, ethane C_2H_6 has one C–C and six C–H two-center two-electron bonds formed by the 14 atomic orbitals originating from the eight valence orbitals of the two carbon atoms and the six 1s orbitals of the six hydrogen atoms. These 14 atomic orbitals use the 14 valence electrons (four each from the two carbon atoms and a total of six from the hydrogen atoms) effectively, since all valence MOs are filled and all antibonding virtual orbitals are empty. The same is true of unsaturated hydrocarbons with multiple bonds.

In the cyclic 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 only two electrons can be accommodated favorably. These fill the bonding orbital to form a three-center two-electron bond. If n atomic orbitals interact to form three-center two-electron bonds exclusively, only $n/3$ bonding orbitals result and only $2n/3$ electrons can be accommodated. Hence, three-center two-electron bonding (H_3^+ is the simplest example) is utilized in “electron deficient” compounds, which have fewer bonding electrons than atomic orbitals. Diborane, B_2H_6 (Figure 1-1), is a simple example of an electron-deficient compound. The combination of the two boron and the six hydrogen atoms provides the same 14 atomic valence orbitals as the two carbons and six hydrogens of ethane. However, the two boron atoms and six hydrogen atoms provide only 12 valence electrons. Hence, diborane is electron deficient; there are not enough electrons to form seven covalent σ -bonds. This electron deficiency leads to the $\text{B}_2\text{H}_4(\mu\text{-H})_2$ diborane structure, consisting of four two-center

two-electron external B–H bonds and two three-center two-electron B–H–B bonds involving the bridging hydrogen atoms (Figure 1-1).

Using completely analogous bonding principles, Lipscomb and co-workers [6–8] delineated the topologies of the distribution of two-center two-electron B–B and three-center two-electron B–B–B bonds in the networks of boron atoms constituting the higher boron hydrides. The following assumptions constitute Lipscomb's bonding analysis:

1. Only the 1s orbital of hydrogen and the four sp^3 orbitals of boron are used.
2. Each external (i.e., terminal) B–H bond is regarded as a typical two-center two-electron single bond requiring the hydrogen 1s orbital, one hybridized boron orbital, and one electron each from the H and the B atoms. Because of the small electronegativity difference between hydrogen and boron, these bonds are assumed to be non-polar. In the polynuclear boron hydrides every boron atom may form zero or one but never more than two such external B–H bonds.
3. Each B–H–B three-center two-electron “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 allocated to satisfy, as first priority, the requirements of the external B–H single bonds and the bridge B–H–B bonds. The remaining orbitals and electrons are allocated to the skeletal molecular orbitals of the boron framework.

The relative numbers of orbitals, electrons, hydrogen, and boron atoms as well as bonds of various types were expressed systematically by Lipscomb [6–8].

Assuming that each boron atom is bonded to at least one hydrogen atom, the hydrogen balance in a neutral boron hydride B_pH_{p+q} containing s bridging hydrogen atoms, x “extra” two-center two-electron B–H bonds in terminal BH_2 groups rather than in BH groups, t three-center two-electron B–B–B bonds, and γ 2c2e B–B bonds is given by $s + x = q$. Since each boron atom supplies four orbitals but only three electrons, the total number of three-center two-electron 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:

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

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

Using this approach the structure of a given borane can be expressed by a four-digit *styx* number corresponding to the numbers of B–H–B, B–B–B, and B–B bonds, and BH_2 groups, respectively. For example the *styx* numbers for the structures for the boranes originally discovered by Stock (Figure 1-1) are 2002 for B_2H_6 , 4012 for B_4H_{10} , 4120 for B_5H_9 , 3203 for B_5H_{11} , 4220 for B_6H_{10} , and 4620 for $B_{10}H_{14}$.

“Resonance” was a central idea in the historical development of the aromaticity concept. The combination of two (or more) hypothetical “classical” Lewis contributors [26] gave a weighted-average “resonance hybrid.” This “real” structure has lower energy due to the “aromatic resonance stabilization” [27, 28]. Further examples of resonance stabilization are found in triangular molecules. Thus the cyclopropenyl cation ($C_3H_3^+$, D_{3h}) is a simple example with a $3c-2e$ π bond. There are three equivalent resonance contributors, each with a different placement of the C=C double bond. An even simpler example is H_3^+ (also D_{3h}) where the three resonance contributors have H–H single bonds. The two-electron two-center B–B bonds and the three-center two-electron B–B–B bonds in polyhedral boranes have a similar relationship to the alternating single C–C and double C=C bond Kekulé structures of benzene.

Consider the *closo*- $B_nH_n^{2-}$ ($6 \leq n \leq 12$) boranes (Figure 1-2). Such deltahedral boranes cannot have any terminal BH_2 groups or three-center two-electron B–H–B bonds but acquire two “extra” electrons from the -2 charge on the ion. Therefore $s = x = 0$ in the equations of balance (1a) and (1b); these reduce to (2a) and (2b) in which n is the number of boron atoms in the deltahedron corresponding to p in (1a) and (1b):

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

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

Solving the simultaneous equations (2a) and (2b) leads to $y = 3$ and $t = n - 2$, implying the presence of three B–B bonds and $n - 2$ B–B–B bonds in the boron skeleton. Since a deltahedron with n vertices has $2n - 4$ faces, the $n - 2$ B–B–B bonds cover exactly half of the faces. In this sense a Kekulé-type structure for the deltahedral boranes $B_nH_n^{2-}$ has exactly half of the faces covered by B–B–B bonds just as a Kekulé structure for benzene has half of its edges covered by C=C double bonds. In 1977 Lipscomb and co-workers [29] reported a variety of such Kekulé-type localized bonding structures with the lowest energies for deltahedral boranes. These structures were computed using wave functions in the differential overlap approximation.

1.1.2

Polyhedral Skeletal Electron Pair Theory: The Wade-Mingos Rules

Structural information on the boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$) shows all of these ions to have the “most spherical” deltahedral structures (Figure 1-2) as suggested by Williams in 1971 [9]. In addition Williams [9] also recognized that the loss of boron vertices from these most spherical *closo* deltahedra generates the structures of the known boranes B_nH_{n+4} and B_nH_{n+6} (Figure 1-1). Thus the *nido* boranes B_nH_{n+4} (Figure 1-3) and isoelectronic carboranes have structures which can be derived from the corresponding $B_{n+1}H_{n+1}^{2-}$ structure by the loss of the vertex with the highest degree (i.e., the most highly connected vertex). Similarly, the *arachno*

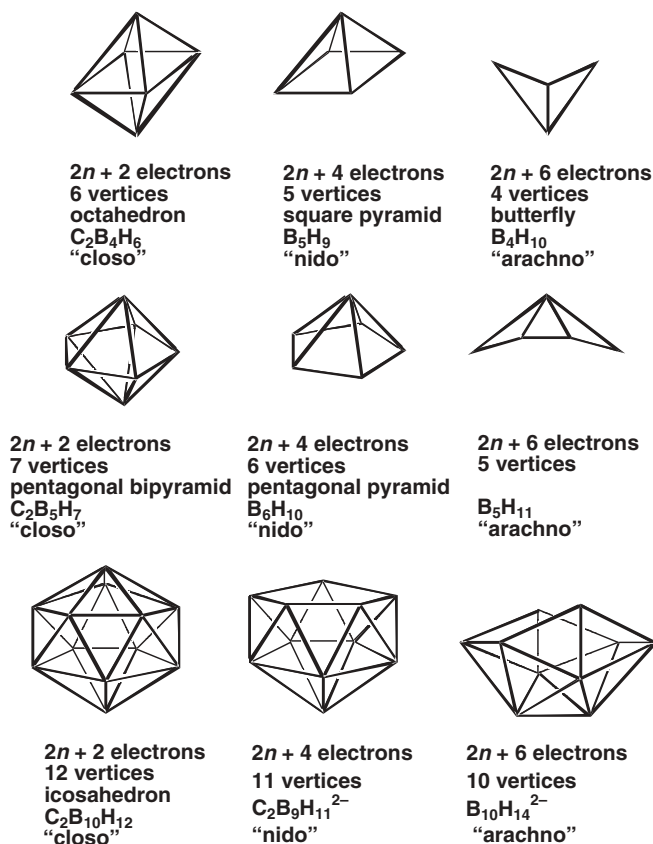


Fig. 1-3. Examples of *nido* and *arachno* boranes obtained by removal of vertices from the octahedron, pentagonal bipyramid, and icosahedron.

boranes B_nH_{n+6} (Figure 1-3) are related to those of the corresponding $B_{n+2}H_{n+2}^{2-}$ structure by the loss of a pair of adjacent vertices of relatively high degree. The role of the most spherical deltahedra (Figure 1-2) in all of these structures suggest that they are particularly stable structural units in borane chemistry, similar to the planar benzenoid rings in the chemistry of aromatic hydrocarbons and their derivatives.

The next important contribution in this area was made shortly thereafter by Wade [16], who recognized that this structural relationship could be related to the number of valence electrons associated with skeletal bonding in the boranes. Thus deprotonation of all of the bridging hydrogens from the related series of boranes $B_nH_n^{2-}$, $B_{n-1}H_{(n-1)+4}$, and $B_{n-2}H_{(n-2)+6}$ gives the ions $B_nH_n^{2-}$, $B_{n-1}H_{n-1}^{4-}$, and $B_{n-2}H_{n-2}^{6-}$. All of these ions can readily be seen to have the same number of skeletal electron pairs, namely $n + 1$, corresponding to $2n + 2$ skeletal electrons.

Consequently, Wade [16] provided an electronic rationale for the observations of Williams [9], namely that the *closo*, *nido*, and *arachno* structures are related because they share a common number of bonding molecular orbitals associated with the boron skeleton. Rudolph and Pretzer [30, 31] subsequently provided the first attempt to account for the structural and electronic relationships proposed by Williams and Wade using semi-empirical molecular orbital calculations. Finally, Mingos [17, 18] incorporated these ideas into his “polyhedral skeletal electron pair approach,” which provides a simple way of understanding the structural diversity shown by polynuclear molecules. Because of the seminal work of Wade and Mingos in understanding electron counting in polyhedral molecules, the rules assigning $2n + 2$ skeletal electrons to deltahedral boranes (Figure 1-2) and related *nido* and *arachno* derivatives (Figure 1-3) as well as other similar polyhedral molecules (e.g., certain transition metal carbonyl clusters) are frequently called the “Wade-Mingos Rules.”

Balakrishnarajan and Jemmis [32, 33] have very recently extended the Wade-Mingos rules from isolated borane deltahedra to fused borane (“*conjuncto*”) deltahedra. They arrive at the requirement of $n + m$ skeletal electron pairs corresponding to $2n + 2m$ skeletal electrons for such fused deltahedra having n total vertices and m individual deltahedra. Note that for a single deltahedron (i.e., $m = 1$) the Jemmis $2n + 2m$ rule reduces to the Wade-Mingos $2n + 2$ rule.

1.1.3

Aromaticity in Three-dimensional Clusters

1.1.3.1 From Polygonal Aromatics to Deltahedral Boranes

The *closo* boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$), along with their isoelectronic counterparts, the carboranes, $CB_{n-1}H_n^-$ and $C_2B_{n-2}H_n$, as well as the newly computed azaboranes $NB_{n-1}H_n$ [34], exemplify three-dimensional aromatics. These comprise the most nearly spherical deltahedra (Figure 1-2) in which all vertices have degrees 4 or larger and the vertex degrees are as nearly equal as possible. In such structures, BH vertices provide two skeletal electrons each. Similarly, CH vertices and their isoelectronic equivalents (e.g., BH^- and N) provide three skeletal electrons each. Each vertex atom can be considered to have four valence orbitals, but, because of the coordination higher than four, these can not be arranged tetrahedrally. One orbital forms a conventional two-center two-electron bond to a hydrogen atom or other external group (or a lone pair) leaving only three “internal” orbitals for the skeletal bonding to four or more adjacent vertices. For three-dimensional structures, these three orbitals are partitioned into two p-like, degenerate “tangential” orbitals and a unique “radial” orbital extending towards the interior. Pairwise overlap of the $2n$ twin tangential orbitals results in n bonding and n antibonding MO combinations. In the three-dimensional deltahedral systems, the tangential orbitals contribute to the bonding over the two-dimensional surface of the deltahedron, which may be regarded as topologically homeomorphic to the sphere [35]. Note that the conventional polygonal aromatics, like benzene, utilize the perpendicular set of their tangential orbitals for π bonding.

The bonding and antibonding tangential orbitals are supplemented, when allowed by symmetry, by additional bonding and antibonding orbitals formed by the overlap of the n radial orbitals. Graph-theoretical methods have been used to describe the global overlap of these n unique internal orbitals [36]. The vertices of this graph correspond to the vertex atoms of the polygon or deltahedron and the edges represent pairs of overlapping unique internal orbitals [36, 37]. The adjacency matrix [38] \mathbf{A} of such a graph can be defined as follows:

$$A_{ij} = \begin{cases} 0 & \text{if } i = j \\ 1 & \text{if } i \text{ and } j \text{ are connected by an edge} \\ 0 & \text{if } i \text{ and } j \text{ are not connected by an edge} \end{cases} \quad (3)$$

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

$$|\mathbf{A} - x\mathbf{I}| = 0 \quad (4)$$

in which \mathbf{I} is the unit matrix ($I_{ij} = 1$ 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

$$|\mathbf{H} - E\mathbf{S}| = 0 \quad (5)$$

Note the general similarities between Eqs. (4) and (5). In equation (5) the energy matrix \mathbf{H} and the overlap matrix \mathbf{S} can be resolved into the identity matrix \mathbf{I} and the adjacency matrix \mathbf{A} as follows:

$$\mathbf{H} = \alpha\mathbf{I} + \beta\mathbf{A} \quad (6a)$$

$$\mathbf{S} = \mathbf{I} + S\mathbf{A} \quad (6b)$$

The energy levels of the Hückel molecular orbitals [Eq. (5)] are thus related to the eigenvalues x_k of the adjacency matrix \mathbf{A} (equation 4) by the following equation:

$$E_k = \frac{\alpha + x_k\beta}{1 + x_kS} \quad (7)$$

In Eq. (7) 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 neighboring atoms. Because of the relationship of the set of the eigenvalues of a graph to the energy levels of the molecular orbitals of a structure represented by the graph in question as indicated by Eqs. (4) to (7), the set of eigenvalues of a graph is called the *spectrum* of the graph, even by mathematicians solely concerned with graph theory with no interest in its chemical applications.

First consider planar polygonal aromatic systems, where the twin internal orbitals (a degenerate set of tangential orbitals on each vertex atom) are related to the π MOs. These systems include benzene and its non-carbon analogues like the N_5^- [39] and P_5^- pentagons [40], the Bi_4^{2-} [41a] and Al_4^{2-} squares [40b], and the $[Ga_3R_3]^{2-}$ ($R = 2,6$ -dimesityl-phenyl) triangle [24]. In such structures, a cyclic graph, C_n , corresponding to the geometry of the polygon, describes the overlap of the unique internal (“radial”) orbitals, where n is the number of polygonal vertices. Regardless of n , the spectra of the cyclic graphs C_n [Eqs. (3) and (4)] all have odd numbers of positive eigenvalues [42] leading to the familiar Hückel $4N + 2$ ($N = \text{integer}$) π -electrons [43] (corresponding to $2N + 1$ π bonding MOs) for planar aromatic hydrocarbons. Thus, the carbon skeleton of benzene has nine bonding orbitals (six σ and three π) occupied by the 18 skeletal electrons arising from the contributions of three skeletal electrons from each CH vertex. Twelve of these 18 skeletal electrons are used for the σ CC bonding and the remaining six electrons for the π -bonding.

These same principles can be extended to systems, such as H_3^+ , with delocalized multicenter σ -bonding derived solely from the radial s-orbital combinations. The descriptive term, “in-plane aromaticity,” [44] includes such cases (see Chapter 3.2.1 for further discussion).

In three-dimensional deltahedral boranes and their relatives, the overlap among the n internal radial orbitals forms n -center core bonding and antibonding combinations. In graph theory, the complete graph, K_n , has an edge between every pair of vertices. This leads to a total of $n(n - 1)/2$ edges and best represents the corresponding overlap topology [45] as well as providing a description of an n -center 2-electron bond. In this graph–theoretical method, the underlying symmetry group is S_n of order $n!$ and corresponds to all possible permutations of the n radial orbitals rather than to the actual symmetry point group of the deltahedron.

For any value of n , the corresponding complete graph K_n has only one positive eigenvalue, namely $n - 1$, and $n - 1$ negative eigenvalues, namely -1 each, as obtained from Eq. (3), which refers to an $n \times n$ matrix, and Eq. (4). The single positive eigenvalue of the K_n complete graph corresponds to *only* one core bonding orbital. The remaining $n - 1$ orbitals arising from the negative eigenvalues of the graph–theoretical spectrum [Eq. (3)] of a deltahedron become antibonding. Combining the single bonding core orbital with the n surface bonding orbitals leads to $n + 1$ bonding orbitals for a deltahedron with n vertices. Filling each of these $n + 1$ bonding orbitals with electron pairs leads to the $2n + 2$ skeletal electrons required by the Wade-Mingos rules [16–18] for deltahedral clusters.

Furthermore, the combination of the n surface and the single core bonding orbitals in globally delocalized deltahedra corresponds to the n σ -bonding ring orbitals and the $2N + 1$ π -bonding orbitals, respectively, in polygonal aromatic systems such as benzene. Since N is always zero for globally delocalized deltahedra in this graph theoretical method, the Hückel $4N + 2$ electron rule for planar polygons is followed, just as it is for the cyclopropenylium ion $C_3H_3^+$ and related triangular species such as $[Ga_3R_3]^{2-}$ [24]. Until recently the largest deltahedral metal-free boranes following the $2n + 2$ skeletal electron rule were the icosahedral derivatives

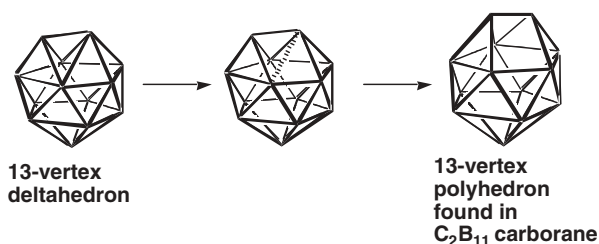


Fig. 1-4. Generation of the 13-vertex polyhedron found in 1,2- μ -[C₆H₄(CH₂)₂]-1,2-C₂B₁₁H₁₀-3Ph by breaking a single edge (hashed line) in a 13-vertex deltahedron.

B₁₂R₁₂²⁻ (R = H, halogen, alkyl, etc.) and their isoelectronic carboranes CB₁₁R₁₂⁻ and C₂B₁₀R₁₀. However, very recently [46, 47] the 13-vertex supraicosahedral carborane 1,2- μ -[C₆H₄(CH₂)₂]-1,2-C₂B₁₁H₁₀-3Ph was reported. The key to the successful synthesis of this supraicosahedral carborane was to force the two carbon vertices to remain adjacent by bridging them with the *o*-phenylene group C₆H₄·(CH₂)₂. Interestingly enough the 13-vertex polyhedron found for this carborane was not the expected deltahedron but instead a polyhedron derived from a 13-vertex deltahedron by breaking one of its 33 edges to give a single trapezoidal face (Figure 1-4).

More advanced mathematical aspects of the graph-theoretical models for aromaticity are given in other references [36, 48, 49]. Some alternative methods, beyond the scope of this chapter, for the study of aromaticity in deltahedral molecules include tensor surface harmonic theory [51–53] and the topological solutions of non-linear field theory related to the Skyrmions of nuclear physics [54].

1.1.3.2 Interstitial Polygonal Aromatic–Deltahedral Borane Relationships

The graph-theoretical $4N + 2$ Hückel rule analogy with the aromaticity of two-dimensional polygons requires that $N = 0$ in all the three-dimensional deltahedra. The Jemmis-Schleyer interstitial electron rule [55], originally introduced for *nido* “half-sandwich” species, also relates the $4N + 2$ Hückel rule to the delocalized deltahedra directly. In this treatment, N is typically 1.

In order to apply the Jemmis-Schleyer interstitial electron rule, the *closo* B_{*n*}H_{*n*}²⁻ dianions (their isoelectronic analogues are treated similarly) are dissected conceptually into two BH⁻ “caps” and one or two constituent (BH)_{*n*} rings. The BH⁻ caps contribute three interstitial electrons each but the rings (which, formally, have zero electrons in the π MOs), contribute none. Hence, six electrons, described as “interstitial,” link the bonding symmetry-adapted cap and ring orbitals together perfectly.

The bonding analysis of the 50 B₁₂H₁₂²⁻ valence electrons is illustrative. After the conceptual dissection into two BH caps and two (BH)₅ rings, two electrons each are assigned to the 12 BH bonds and to the 10 BB ring bonds. This leaves six electrons ($4N + 2$) for the interstitial bonding, which holds the rings and caps together. Icosahedral symmetrization then completes the description.

Each of the two methods, namely the graph–theory and interstitial electron methods, has its advantages and disadvantages. The Jemmis-Schleyer interstitial electron rules are directly applicable to 5, 6, and 7-vertex deltahedra (which have one ring), and to 10, 11, and 12-vertex deltahedra (which have two rings) but are less obvious for 8- and 9-vertex deltahedra. (Two $B_2H_2^-$ caps supply three interstitial electrons each to the central D_{2d} -puckered B_4H_4 ring of $B_8H_8^{2-}$, whereas the six interstitial electrons are provided by the three, widely separated central BH “caps” in D_{3h} $B_9H_9^{2-}$. In the latter, the electrons from the -2 charge on the ion can be assigned to a weak 3c2c bond involving the three BH “caps.”)

The interstitial electron rule can be applied more directly to pyramidal clusters than the graph–theoretical approximation since the latter breaks down by giving zero eigenvalues in Eq. (3) when applied to pyramids. The same ideas as those in the Jemmis-Schleyer method are needed to treat *nido* pyramids graph–theoretically.

1.1.3.3 Aromaticity Evaluations of Three-dimensional Structures: Nucleus-Independent Chemical Shift (NICS)

Chemical nomenclature and the usage of descriptive terms evolve over the years. “Aromaticity” was employed only to describe planar fully π conjugated organic and isoelectronic inorganic systems for well over a century, until it became increasingly apparent that some degree of out-of-plane distortion, for example in Vogel’s bridged [10]annulenes, could be tolerated. In such structures the p-orbitals are twisted somewhat, but π overlap is still effective. Ferrocene (and its relatives) are fundamentally different geometrically from arenes. Half-sandwich, sandwich, and multi-sandwich molecules are also clearly “aromatic” but their electronic structures involve the third dimension. Nevertheless, it can be argued that their theoretical essence is still two-dimensional, since the maximum possible molecular orbital degeneracy of such systems is only two. Likewise, Möbius systems with undulating electronic topologies provide further examples of “aromatic three dimensional molecules.” Rzepa has described inorganic examples with undulating Möbius MOs [56].

Aihara introduced the term, “three dimensional aromaticity” (featured in the title of his paper), to discuss *closo*-borane dianions in 1978 [12]. Jemmis and Schleyer applied the term to *nido* systems with six interstitial electrons [55], but their treatment emphasized the Hückel analogy, rather than the spherical character.

The fullerenes illustrate further conceptual and also practical problems, common to main group clusters generally. Clearly, fullerenes are physically three-dimensional and are aromatic (at least to some extent). But how does one know? How can one deduce the extent of aromaticity quantitatively? Is C_{60} best regarded as an assembly of interconnected planar rings, aromatic six-membered and anti-aromatic five-membered, or does it have “global” aromatic character involving the whole ensemble? C_{60}^{6-} , for example, can be regarded as just such a “super-aromatic,” where the total aromaticity is more than the sum of the contributions of the constituent rings.