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Article

Defective Vertices in *arachno* Borane Networks

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Triangulated boron networks can be described in terms of the deviation of their local vertex environments from the degree 5 vertices found in ideal icosahedra. Vertices of degrees other than 5 or equivalent are considered to be defective vertices. This method, which was previously applied to deltahedral borane anions $B_nH_n^{2-}$ and *nido*-B_nH_{n+4} boranes, has now been applied to *arachno* boranes of the types B_nH_{n+6} and $B_nH_{n+5}^-$ ($4 \leq n \leq 10$). The known structures of the neutral *arachno* boranes B_4H_{10}, B_8H_{14}, and *n*-B_9H_{15} consist of triangulated boron networks with no defective vertices in accord with their higher stabilities relative to other neutral *arachno* boranes. In other structures of known *arachno* boranes, there are relatively small numbers of defective vertices, and these are isolated as far as possible from each other.

1. Introduction

In a previous paper,[1] I have shown how boron polyhedra can be described in terms of the deviation of their local vertex environments from the degree 5 vertices found in ideal icosahedra (where the degree of a vertex is the number of edges meeting at the vertex in question). Thus, vertices of degrees other than 5 are considered to be defective vertices. This method was applied to the *closo* deltahedral boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$) as well as the more open *nido*- boranes B_nH_{n+4} ($5 \leq n \leq 11$) and fused polyhedral boranes B_nH_{n+4} ($12 \leq n \leq 18$).

A variety of electron-richer boranes are known such as the *arachno* boranes B_nH_{n+6} with $2n + 6$ skeletal electrons. In fact, two *arachno* boranes, namely B_4H_{10} and B_5H_{11}, were among the six original boranes discovered in the pioneering work of Alfred Stock.[2] The structures of these *arachno* boranes consist of more open triangulated boron networks derived from closed deltahedra by removal of two adjacent vertices.[3] Because of their more open structures as well as their lower chemical stabilities, various models of three-dimensional aromaticity[4−6] are not considered to be as pertinent to understanding the structure, chemical bonding, and chemical reactivity for *arachno* boranes as for *closo* and *nido* boranes. Thus, more localized bonding models similar to Kekulé-type localized structures for deltahedral boranes[7−9] appear to be more relevant to the *arachno* boranes than the globally delocalized models of three-dimensional aromaticity.

The “defective vertex model” for borane structures considers only the vertex degrees without regard to the detailed nature of the chemical bonding. This paper explores a similar model for understanding the structures and chemical reactivities of the *arachno* boranes.

2. Background

The *arachno* boranes of interest are networks of boron triangles, which can be regarded as fragments of borane deltahedra. For the *arachno* boranes of stoichiometry B_nH_{n+6}, each boron atom is bonded to at least one hydrogen atom. The “extra” six hydrogen atoms appear as bridging hydrogen atoms (B−H−B bridges) or as BH_2 groups. Thus, for most of the *arachno* boranes, some of the boron vertices bear two terminal hydrogens rather than only a single terminal hydrogen like the boron vertices in the *closo* and *nido* boranes. For this reason, it is sometimes less confusing in the *arachno* boranes to consider the connectivities rather than the degrees of the boron vertices. In this context, the connectivity of a vertex includes its connections to adjacent vertices through edges of the polyhedron or network as well as bonds to either bridging or terminal hydrogen atoms. Thus, all of the boron vertices in icosahedral $B_{12}H_{12}^{2-}$ have

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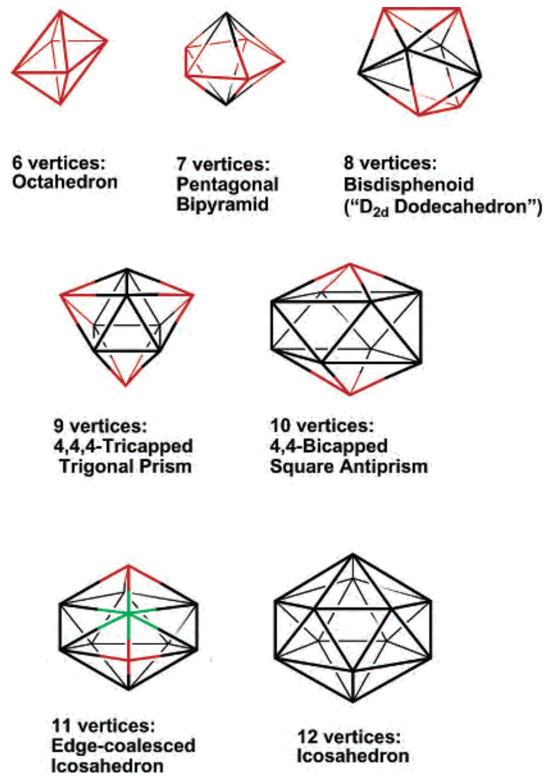

6 vertices: Octahedron

7 vertices: Pentagonal Bipyramid

8 vertices: Bisdisphenoid ("D_{2d} Dodecahedron")

9 vertices: 4,4,4-Tricapped Trigonal Prism

10 vertices: 4,4-Bicapped Square Antiprism

11 vertices: Edge-coalesced Icosahedron

12 vertices: Icosahedron

Figure 1. The borane deltahedra showing deficient vertices in red and excessive vertices in green. This coloring scheme is used in the other figures.

connectivity 6. In this case, the connectivity of a boron vertex is one more than its degree since the bond to the external hydrogen is added to the five edges meeting at the vertex in question. In terms of connectivities, the "ideal" vertices have connectivities of six as found in the icosahedral $B_{12}H_{12}^{2-}$ whereas defective vertices have connectivities different from six. Defective vertices with connectivities less than six may be considered to be *deficient vertices* whereas defective vertices with connectivities greater than six may be considered to be *excessive vertices*. Deficient vertices of connectivity 5 and excessive vertices of connectivity 7 and their adjacent edges are depicted in red and green, respectively, in the figures in this paper. Ideal vertices (i.e., those of connectivity 6) are depicted in black. Figure 1 illustrates this color coding for the deltahedra of the boranes $B_nH_n^{2-}$.

The triangulated networks of the *arachno* boranes can be characterized by the lengths of their boundaries, designated by Williams[10] by $\langle b \rangle$ where b is the length of the boundary (number of B−B edges), expressed in Roman numerals. If the *arachno* borane structures are regarded as polyhedra having exactly one nontriangular face, the boundary of the network is the polygon of the nontriangular face. The vertices of an *arachno* borane network can be divided into boundary vertices and interior vertices.

Consider Euler's theorem, $v - e + f = 2$, where v, e, and f are the numbers of vertices, edges, and faces, respectively. For an *arachno* borane network considered as a polyhedron, one face is a polygon with the b edges of the boundary, and all of the other faces are triangles. If Δ is the number of triangles, then $\Delta = f - 1$. Furthermore, all vertices of the *arachno* network can be classified into two types, namely boundary vertices lying on the boundary and interior vertices not lying on the boundary. If i is the number of interior vertices, then $v = b + i$. Euler's theorem can be restated in terms of b, i, and Δ as follows:

$$b + i - e + \Delta = 1 \tag{1}$$

Since every edge is shared by two faces, $2e = 3\Delta + b$ leading to the following relationship between the size of the boundary, the number of interior vertices, and the number of triangles in an *arachno* borane structure:

$$b + 2i - \Delta = v + i - \Delta = 2 \tag{2}$$

Equation 2 may be regarded as an analogue of Euler's theorem for *arachno* borane structures relating the number of triangles to the number of interior vertices.

The *arachno* boranes, like other boranes, can also be characterized by the *styx* set of parameters of Lipscomb[11−13] where s, t, y, and x are the numbers of B−H−B bridges, three-center B−B−B bonds in the face of a triangle in the network, two-center B−B bonds, and BH_2 vertices, respectively. For the *arachno* boranes of stoichiometry B_nH_{n+6}, $s + x = 6$ since the six "extra" hydrogen atoms must be either B−H−B bridges or BH_2 groups. Also, Lipscomb[11−13] has derived the following "equations of balance" between the *styx* parameters for a borane of formula B_pH_q:

$$2s + 3t + 2y + x = 3p \text{ (boron orbital balance)} \tag{3a}$$

$$s + 2t + 2y + x = 2p \text{ (boron electron balance)} \tag{3b}$$

Furthermore, the total number of three-center bonds (B−H−B and B−B−B) for a neutral borane can be seen to be equal to the number of boron atoms, i.e., $s + t = p$. For an *arachno* borane, B_nH_{n+6}, $t + y = p - 3$. These *styx* parameters can be used to generate localized bonding models[7−9] for the *arachno* boranes of interest.

3. *arachno* Borane Structures

Figures 2−6 illustrate the structures of the *arachno* boranes as follows: (1) The vertices correspond to B−H groups so that "−H" attached to a vertex in a figure indicates the locations of the BH_2 groups (i.e., the "extra" *endo* hydrogen atoms). Thus, in these figures the vertices of degree 5 (counting an external bond to the "extra" hydrogen of a terminal BH_2 group) are "ideal" vertices similar to all 12 equivalent boron vertices in the icosahedral borane $B_{12}H_{12}^{2-}$ (Figure 1). Such "ideal" vertices are indicated in black. (2) Deficient vertices of degree 4 are indicated in red whereas excessive vertices of degree 6 are indicated in green similar to the vertices in the deltahedra in Figure 1. (3) A viable localized bonding scheme is indicated by bold edges for two-center two-electron B−B bonds and yellow triangles for three-center two-electron B−B−B bonds. These bonds are allocated so that each boron atom uses all four valence orbitals

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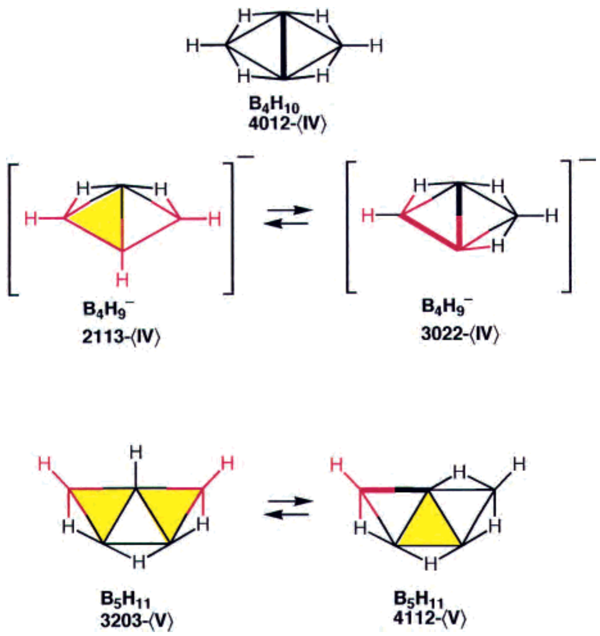

Figure 2. (a) The *arachno* boranes with four boron atoms, B_4H_{10} and $B_4H_9^-$. (b) The two structures for B_5H_{11}.

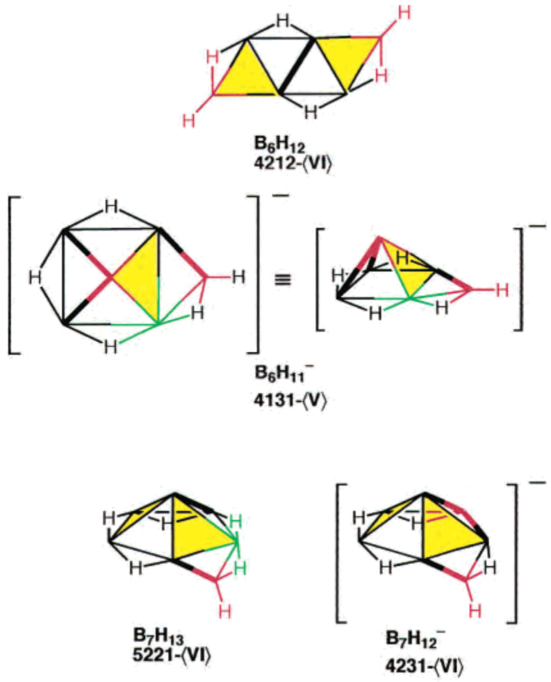

Figure 3. (a) The *arachno* boranes with six boron atoms, B_6H_{12} and $B_6H_{11}^-$. (b) The *arachno* boranes with seven boron atoms, B_7H_{13} and $B_7H_{12}^-$.

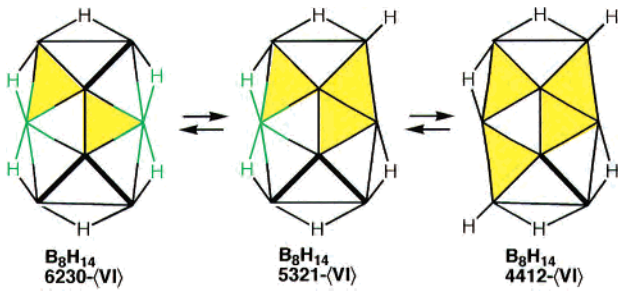

Figure 4. Three structures for B_8H_{14}.

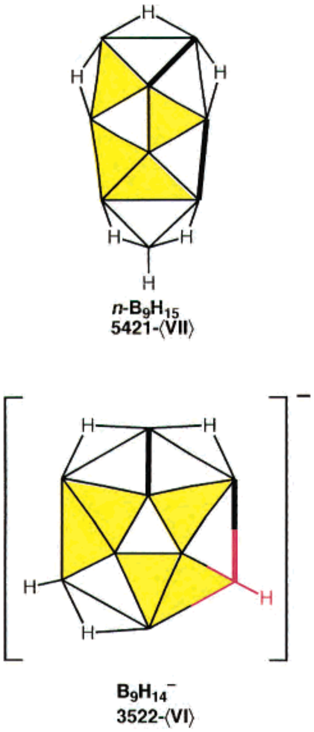

Figure 5. (a) The structure of n-B_9H_{15}. (b) The structure of $B_9H_{14}^-$.

of its sp^3 manifold. (4) The Lipscomb *styx* number and the length of the boundary ⟨*b*⟩ are indicated below the structure.

3.1 *arachno* Boranes with Four Boron Atoms (Figure 2a). The simplest neutral *arachno* borane B_4H_{10} with *styx* number 4012-⟨IV⟩ has no defective vertices. It is one of the original boranes discovered by Stock[2] and is the borane produced in the largest quantity from Stock's original reaction of magnesium boride with acid. Deprotonation of B_4H_{10} gives an *arachno* borane anion $B_4H_9^-$. The 2113-⟨IV⟩ structure of $B_4H_9^-$ has three defective vertices whereas the alternative less symmetrical 3022-⟨IV⟩ structure has only two defective vertices. No structural studies appear to be available on $B_4H_9^-$ salts. However, NMR studies[14] indicate a fluxional species. The more symmetrical 2113-⟨IV⟩ structure was proposed for $B_4H_9^-$, but the 3022-⟨IV⟩ structure favored by fewer defective vertices cannot be excluded from the available data.

3.2 *arachno* Boranes with Five Boron Atoms (Figure 2b). Two structures for the *arachno* borane B_5H_{11} are the 3203-⟨V⟩ structure with two isolated defective vertices and the 4112-⟨V⟩ structure with only one defective vertex. Both X-ray and electron diffraction data confirm the 4112-⟨V⟩ structure with the smaller number of defective vertices.[10,15]

3.3 *arachno* Boranes with Six Boron Atoms (Figure 3a). The 4212-⟨VI⟩ structure for B_6H_{12} of C_2 symmetry with a defective vertex at each end of the molecule was deduced by ^{11}B NMR[16] and subsequently confirmed by electron diffraction.[17] Shore and co-workers[14] have prepared the ion $B_6H_{11}^-$ by addition of BH_3 to $B_5H_8^-$. On the basis of NMR

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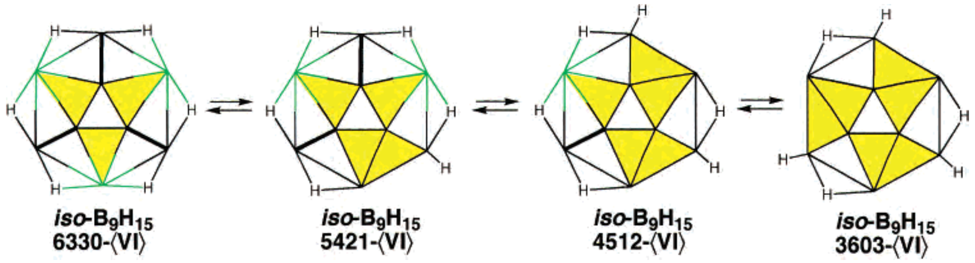

Figure 6. Four structures for *iso*-B_9H_{15}.

spectra, they postulated a 4131-⟨V⟩ structure. This is the smallest *arachno* borane with an interior vertex.

3.4 *arachno* Boranes with Seven Boron Atoms (Figure 3b). Corcoran and Sneddon[18] obtained a B_7H_{13} borane by the $PdBr_2$-catalyzed coupling of B_2H_6 and B_5H_9. They proposed a structure derived from diborane by replacing one of the bridges with a μ-B_5H_8 unit derived from pentaborane. However, a 5221-⟨VI⟩ structure for B_7H_{13} based on an adduct of BH_3 to the B−B two-center two-electron bond in B_6H_{10} has only a single deficient vertex and a single excessive vertex and thus should be a favorable structure.

The deprotonated *arachno* heptaborane $B_7H_{12}^-$ has been obtained by Shore and co-workers.[14] They suggest a 4231-⟨VI⟩ structure based on limited NMR data. However, definitive structural data on $B_7H_{12}^-$ are not yet available. This structure has two isolated defective vertices.

3.5 *arachno* Boranes with Eight Boron Atoms (Figure 4). A sequence of three *arachno*-⟨VI⟩ structures are possible for B_8H_{14} where B−H−B bridges on excessive vertices are successively converted to terminal BH_2 groups with a decrease of the total vertex degree by one each time. This process relieves the excess connectivity of the excessive vertices. The 4412-⟨VI⟩ structure has no defective vertices and is consistent with the NMR data of Moody and Schaeffer.[19]

3.6 *arachno* Boranes with Nine Boron Atoms (Figures 5 and 6). There are two isomers of the neutral *arachno* nonaborane, B_9H_{15}. The more stable isomer, known as "*n*-B_9H_{15}", has a 5421-⟨VII⟩ structure with an unusual heptagonal border (i.e., $b = 7$) and no defective vertices (Figure 5a).[20,21]The second isomer of B_9H_{15}, namely "*iso*-B_9H_{15}", has a hexagonal border (i.e., $b = 6$). A sequence of four *arachno*-⟨VI⟩ structures is possible for *iso*-B_9H_{15} in which B−H−B bridges are successively converted to terminal BH_2 groups with a decrease of the total vertex degree by one each time this happens (Figure 6) similar to the process already discussed for B_8H_{14}. The final isomer 3603-⟨VI⟩ has no defective vertices. The *arachno* borane anion $B_9H_{14}^-$ has a closely related 3522-⟨VI⟩ structure with only a single defective vertex (Figure 5b).[22] Protonation of $B_9H_{14}^-$ generates *iso*-B_9H_{15} rather than *n*-B_9H_{15} in accord with the greater similarity of the structure of *iso*-B_9H_{15} than *n*-B_9H_{15} to that of B_9H_{14}.

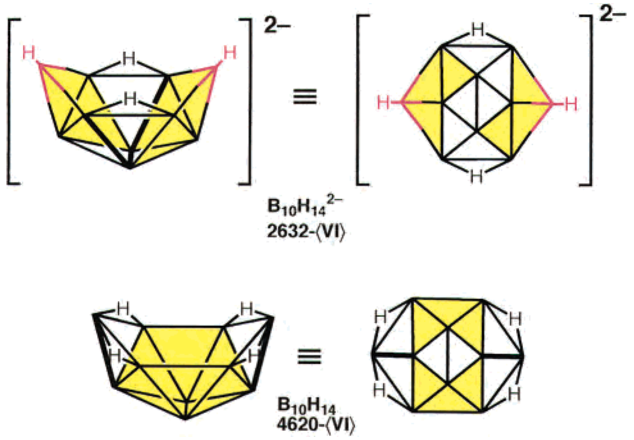

Figure 7. Comparison of the structures of *arachno*-$B_{10}H_{14}^{2-}$ and *nido*-$B_{10}H_{14}$.

3.7 *arachno* Boranes with 10 Boron Atoms (Figure 7). The B_{10} network in *arachno*-$B_{10}H_{14}^{2-}$ is very similar to the B_{10} network in the very stable *nido*-$B_{10}H_{14}$, since removing a pair of adjacent vertices in an icosahedron gives the same B_{10} network as removing the unique degree 6 vertex from the 11-vertex deltahedron in $B_{11}H_{11}^{2-}$ depicted in Figure 1. However, whereas *nido*-$B_{10}H_{14}$ has four B−H−B bridges and no defective vertices, *arachno*-$B_{10}H_{14}^{2-}$ has only two B−H−B bridges, two BH_2 groups, and a defective vertex at each BH_2 group.

4. Summary

The analysis in this paper shows that the concept of defective vertices discussed previously for *closo* and *nido* boranes also appears to be valid for *arachno* boranes despite their more open structures. Thus, the distribution of "excess" hydrogen atoms in B_nH_{n+6} and $B_nH_{n+5}^-$ species as B−H−B bridges and terminal BH_2 groups generally occurs to minimize the number of vertices with connectivities other than six as illustrated by the specific examples discussed in this paper. When defective vertices must be present because of other structural limitations, they are generally isolated as far apart as possible.

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