Inorg. Chem. **1984**, *23*, 1521–1525

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Structures of Atom Clusters. Nido, Arachno, Hypho, and Planar Aromatic Molecules

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Received March 22, 1983

A mathematical modeling procedure has been developed to predict the structures of boron hydride and related compounds. The closo compounds are considered as clusters of boron atoms in which each atom is bonded to all other atoms. The nido, arachno, and hypho compounds are then obtained by successive addition of electron pairs to the cluster. Calculation of the complete range of possible structures leads to a classification that is significantly different from previous classifications and is in better agreement with experimental crystal structures. An important feature of the new classification is that different isomers are possible for the arachno and hypho compounds. Structures for the arachno compounds range from icosahedral fragments, similar to the nido compounds, to planar aromatic molecules.

Introduction

One of the most important rationalizations for the understanding of the chemistry of the boron hydrides and related molecules is the classification into a number of homologous series with each succeeding series having an additional pair of electrons.[1] The first series is the *closo*-$B_nH_n^{2-}$ compounds (where $n = 6$–12), which consist of compact polyhedral arrangements of boron atoms, with successive series being based on *nido*-$[B_nH_n(\text{electron pair})]^{4-}$, *arachno*-$[B_nH_n(\text{electron pair})_2]^{6-}$, and *hypho*-$[B_nH_n(\text{electron pair})_3]^{8-}$. The structural relation between the first three series proposed by Williams[2] and developed by Rudolph[3] is based on the replacement of one and two boron atoms of the highest coordination number from a closo anion by one and two pairs of electrons to form the nido and arachno compounds, respectively, with no change in structure of the remaining skeletal atoms. The ease of protonation of these additional electron pairs leads to the observed molecules, *nido*-B_nH_{n+4} and *arachno*-B_nH_{n+6}. This classification is now widely accepted[4] for the boron hydrides and the mixed carbon–boron hydrides and to some extent has replaced the earlier description of these structures as fragments of icosahedra.

However, this classification based on *closo*-borohydride anions has a number of deficiencies. One is that *nido*-B_8H_{12}[5] is observed to have the structure predicted for *arachno*-$B_8H_8^{6-}$ rather than that predicted for *nido*-$B_8H_8^{4-}$; the structures predicted for the neighboring *nido*-$B_7H_7^{4-}$ and *nido*-$B_9H_9^{4-}$ have not yet been experimentally confirmed. It may also be noted that the same structures are predicted for *nido*-$B_{10}H_{10}^{4-}$ and *arachno*-$B_{10}H_{10}^{6-}$. Another problem is that the classification cannot be used to deduce the structures of the carbon hydrides. An obvious example is benzene, which has the electron count of an arachno compound, isoelectronic with B_6H_{12}. However, the structure derived from dodecahedral *closo*-$B_8H_8^{2-}$ by replacement of two boron atoms in adjacent dodecahedral *B* sites by electron pairs is nonplanar, consisting of four triangular units sharing edges.

The object of this work was to extend our mathematical modeling of the structures of the closo compounds[6,7] to nido, arachno, and hypho compounds in order to remove the above inconsistencies and to more accurately predict the structures of these molecules.

Method

It is assumed that the skeletal arrangement can be modeled as a collection of boron atoms and additional electron pairs. Nonskeletal atoms or groups are considered to be unimportant in determining the structure. Each boron atom and each additional electron pair are considered to interact simultaneously with *all* other boron atoms and additional electron pairs, the interaction between any pair depending only on the distance between them. Previous work[6] based on fitting the calculated shape of the *closo*-boron hydrides against the experimental structures has shown that the bonding energy $u_{\text{B-B}}$ between any two boron atoms separated by a distance $d_{\text{B-B}}$, in arbitrary units, is adequately modeled by the 2:1 expression (1). This expression has been used to predict the structures and the modes of rearrangement of all the closo compounds.[7]

$$u_{\text{B-B}} = \frac{1}{d_{\text{B-B}}^{2}} - \frac{1}{d_{\text{B-B}}} \qquad (1)$$

To mathematically model the structures of the nido and arachno compounds, it is necessary to devise similar expressions for the boron–electron-pair interactions and, less importantly, the electron-pair–electron-pair interactions. The boron–electron-pair interaction was obtained by fitting the experimental shape of *nido*-$B_{10}H_{14}$[8] to a double-reciprocal potential function of the type

$$u_{\text{B-ep}} = \frac{a}{d_{\text{B-ep}}^{x}} - \frac{b}{d_{\text{B-ep}}^{y}}$$

Fitting was achieved with use of the simplex technique,[9] which yielded a variety of functions of almost equally good fit. However, all functions were similar in having a minimum near 2.0 arbitrary units as observed for the boron–boron potential (1), but with about twice the bonding energy. When the values of x and y were rounded off to the nearest integer, the best fit was obtained with the expression

$$u_{\text{B-ep}} = \frac{2.2}{d_{\text{B-ep}}^{4}} - \frac{1.2}{d_{\text{B-ep}}} \qquad (2)$$

Increases in the values of x and y lead to potential wells with sharper minima, the interaction being more critically dependent upon distance. Such a function is given by (3), which represents the extreme that allows any reasonable fit with the structure of $B_{10}H_{14}$.

$$u_{\text{B-ep}} = \frac{16}{d_{\text{B-ep}}^{8}} - \frac{1}{d_{\text{B-ep}}} \qquad (3)$$

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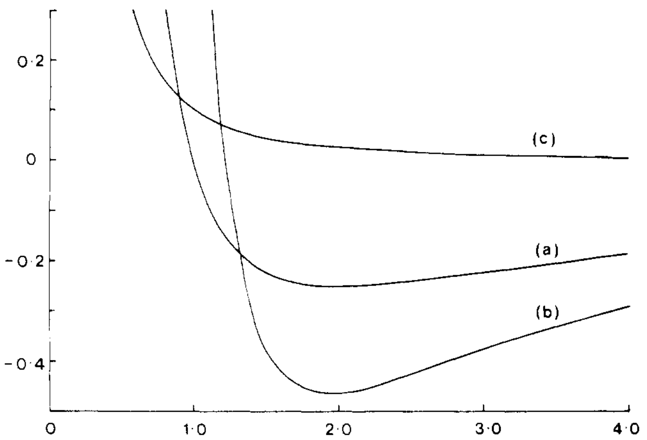

Figure 1. Potential energy as a function of distance: (a) boron–boron interaction; (b) boron–electron-pair interaction; (c) electron-pair–electron-pair interaction.

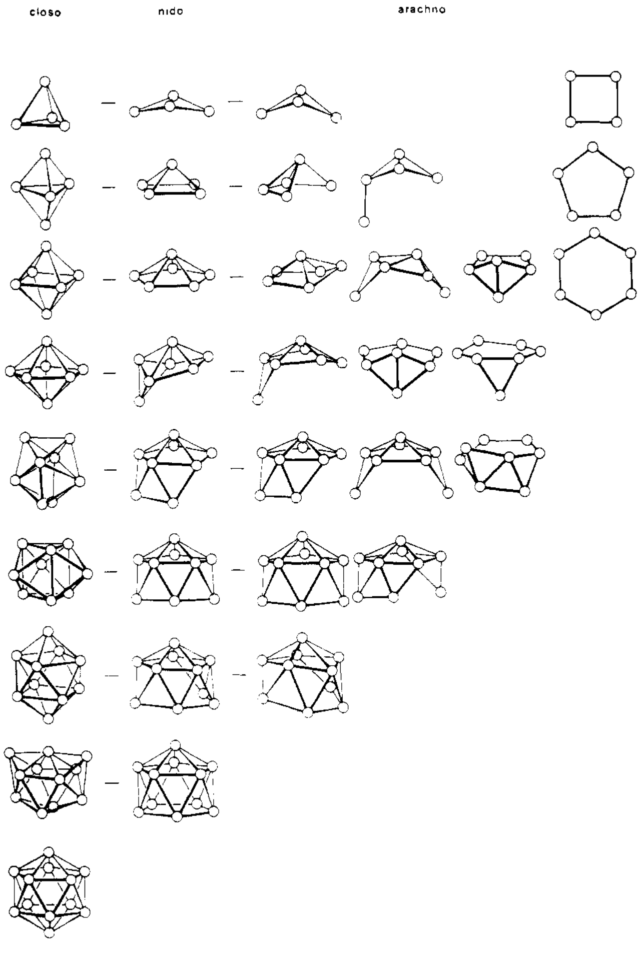

Figure 2. Structures of *closo*-, *nido*-, and *arachno*-boranes, $B_nH_n^{2-}$, $B_nH_n^{4-}$, and $B_nH_n^{6-}$, respectively.

The function chosen to describe the purely repulsive interaction between two or more additional electron pairs is not critical in determining the positions of the atoms, although it does to some extent determine the distance between these additional electron pairs. The function (4) used in this work was chosen so that the structure of B_9H_{15}[10] was reproduced. These energy functions are shown in Figure 1.

$$u_{\text{ep-ep}} = \frac{0.1}{d_{\text{ep-ep}}^2} \tag{4}$$

Table I. Boron-Boron Distances (Arbitrary Units) for *nido*-$B_nH_n^{4-}$

$B_nH_n^{4-}$	symmetry	atoms	B-B
$B_4H_4^{4-}$	C_{2v}	1-2	1.885
		1-3	2.142
$B_5H_5^{4-}$	C_{4v}	1-2	1.803
		2-3	2.096
$B_6H_6^{4-}$	C_{5v}	1-2	1.856
		2-3	1.823
$B_7H_7^{4-}$	C_s	1-2	1.732
		1-4	2.021
		1-5	1.614
		2-3	2.028
		2-6	1.853
		4-5	1.752
		4-7	2.075
		5-7	1.703
$B_8H_8^{4-}$	C_{2v}	1-2	1.683
		1-3	1.775
		1-4	1.797
		3-4	1.743
		4-5	1.884
$B_9H_9^{4-}$	C_{3v}	1-2	1.682
		1-4	1.762
		1-5	1.754
		4-5	1.814
$B_{10}H_{10}^{4-}$	C_{2v}	1-2	1.750
		1-3	1.670
		1-4	1.729
		2-3	1.827
		2-6	1.803
		2-7	1.874
		3-7	1.755
$B_{11}H_{11}^{4-}$	C_{5v}	1-2	1.819
		2-3	1.834
		2-8	1.913
		7-8	1.838

The structure of any number of atoms and electron pairs can be calculated by using the functions (1), (2) (or (3)), and (4). The structures were fully optimized by the Fletcher–Powell method,[9] allowing variation of all $3n - 6$ variables in an n-center system. A large variety of starting approximations were used, some quite grotesque. In some instances the latter resulted in an atom being "lost" to the system, but in most cases the system settled down into a well-defined structure.

Results

The structures of the closo, nido, and arachno compounds located as potential energy minima by the potential functions (1), (2), and (4) are accurately summarized in Figure 2. The additional pairs of electrons in the nido and arachno compounds are not shown but are located in the large "holes" in the structures. Selected results for hypho compounds, in which there are three additional pairs of electrons, are referred to later. Only those boron–boron vectors that are less than 2.2 arbitrary units are denoted by lines. There was only one structure that could be found for each closo and nido compound, but different structural isomers were found for many of the arachno and hypho compounds.

A detailed comparison between calculated and experimental structures for the closo compounds has been given previously.[6,7]

Nido Compounds. The shortest boron–boron distances (1.6–2.1 arbitrary units) are listed in Table I, with atom numbering in Figure 3. The next shortest boron–boron distances are more than 2.8 arbitrary units and correspond to the 1,3-positions of a B_4 square or a B_5 pentagon. The shortest boron–boron distances calculated for $B_5H_5^{4-}$ are those to the apical atom, 1.803 arbitrary units, compared with 2.096 for the other four B–B distances. This order is in agreement with the experimental structures of B_5H_9,[11] in which the distances

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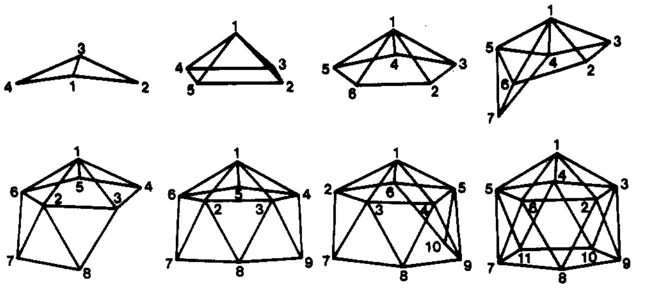

Figure 3. Atom labeling of *nido*-$B_nH_n^{4-}$.

are 1.69 and 1.80 Å, respectively, and of $B_5H_7(CH_3)_2$,[12] 1.67 and 1.81 Å, respectively. The reverse distortion is predicted for $B_6H_6^{4-}$, the five distances to the apical atom being slightly longer than the other five, 1.856 and 1.823 arbitrary units, respectively. This is in agreement with the experimental structure of B_6H_{10},[13] in which the average distances are 1.77 and 1.73 Å, respectively, although there are large distortions from fivefold symmetry due to the presence of only four bridging hydrogen atoms. With the exception of $B_{10}H_{14}$, which was used to obtain eq 2 in the first instance, the structures of the larger nido compounds are not known or are not known with sufficient precision to enable a detailed comparison between calculated and experimental boron–boron distances to be made. However, the observed structures for $C_2B_4H_8$,[14] $C_2B_4H_6(CH_3)_2$,[14] $B_6H_9^-$,[15] and $B_{10}H_{13}^-$[16] are consistent with these calculations. Examples of four-, seven-, and eleven-skeletal-atom systems are not known. The potential surface for C_4H_4, with use of MINDO/3, predicts that an irregular tetrahedral structure,[17] similar to that calculated here for the isoelectronic $B_4H_4^{4-}$ (Figure 2), is more stable than a regular tetrahedral structure.

All nido compounds consist of B_3 triangles sharing edges. The structures predicted for $B_4H_4^{4-}$, $B_5H_5^{4-}$, $B_6H_6^{4-}$, $B_7H_7^{4-}$, $B_{10}H_{10}^{4-}$, and $B_{11}H_{11}^{4-}$ are the same as in Rudolph's classification. (A slightly different structure is predicted for $B_7H_7^{4-}$ if the potential function (3) is used instead of (2), in which one atom is bonded to two of the atoms forming the pentagonal base of the pentagonal pyramid, rather than three as in Figure 2.) However, the structures predicted for $B_8H_8^{4-}$ and $B_9H_9^{4-}$ are not the same as those in Rudolph's classification, as shown in Figure 4. Rudolph's predicted structure for *nido*-$B_8H_8^{4-}$ is based on the tricapped-trigonal-prismatic structure of *closo*-$B_9H_9^{2-}$ with loss of one of the prismatic atoms. The additional electron pair is situated outside a five-membered ring of boron atoms, the molecule retaining one mirror plane. The structure found in this work has the additional electron pair situated outside a six-membered ring of boron atoms, the resulting structure having C_{2v} symmetry. The crystal structure of *nido*-B_8H_{12}[5] is in agreement with the structure predicted in this work.

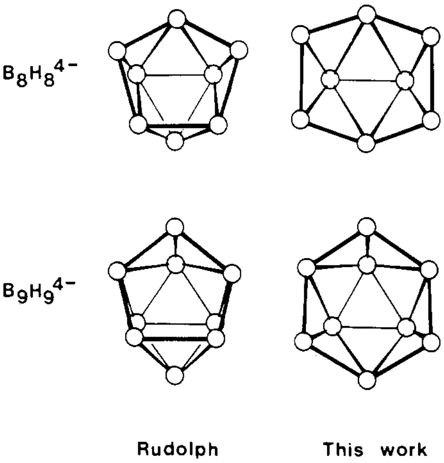

Figure 4. Comparison of the structures of *nido*-$B_8H_8^{4-}$ and *nido*-$B_9H_9^{4-}$ predicted by Rudolph[3] and in this work, viewed from the direction of the additional electron pair.

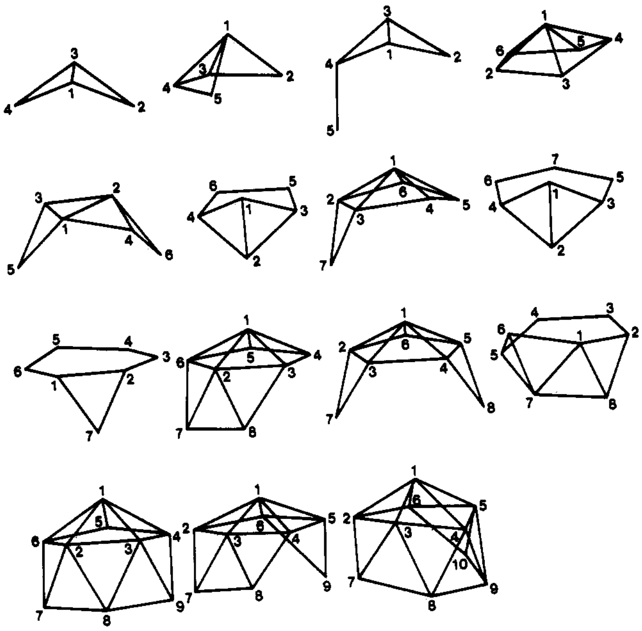

Figure 5. Atom labeling of *arachno*-$B_nH_n^{6-}$.

The structure predicted in this work for *nido*-$B_9H_9^{4-}$ is that formed by the removal of one triangular face from an icosahedron so that the additional electron pair is situated outside a puckered six-membered ring of boron atoms. This structure again has a higher symmetry, C_{3v}, than that suggested by Rudolph by removal of one of the antiprismatic atoms from the bicapped-square-antiprismatic structure of *closo*-$B_{10}H_{10}^{2-}$, in which the electron pair sits outside a five-membered ring, the only symmetry being a mirror plane. No experimental structures are known to decide between these two alternative predictions.

Arachno Compounds. The shorter boron–boron distances (1.6–2.1 arbitrary units) are listed in Table II, with atom numbering in Figure 5. In all cases one of the isomers of $B_nH_n^{6-}$ has the same connectivity as the compound predicted in Rudolph's classification, but the versions calculated in this work generally have higher symmetries. The first arachno isomers shown in Figure 2 are constructed by the edge sharing of triangular B_3 units and with one exception are closely related to the nido compounds with the same number of boron atoms; that is, the single pair of electrons in a nido compound is replaced by a cis arrangement of two pairs of electrons. The other limiting type of arachno compound is the planar aromatic molecules with a trans arrangement of the two additional electron pairs. Additional isomers were located for some compounds that contain both planar rings and triangular units as structural features, are fragments of an icosahedron different from those observed for the nido compounds, or are fragments of a bicapped hexagonal antiprism.

Two isomers were found for *arachno*-$B_4H_4^{6-}$. The first consists of two triangular units sharing an edge, and the second

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Table II. Boron–Boron Distances (Arbitrary Units) and Energies (Arbitrary Units) for *arachno*-$B_nH_n^{6-}$

$B_nH_n^{6-}$	symmetry	atoms	B–B	energy
$B_4H_4^{6-}$	C_{2v}	1–2	1.910	−5.0529
		1–3	1.739	
	D_{4h}	1–2	1.835	−5.1597
$B_5H_5^{6-}$	C_s	1–2	2.090	−6.8618
		1–3	1.814	
		2–3	1.696	
		3–4	1.711	
	C_s	1–2	1.888	−6.5704
		1–3	1.747	
		1–4	1.771	
		4–5	1.730	
	D_{5h}	1–2	1.696	−6.9857
$B_6H_6^{6-}$	C_s	1–2	1.705	−8.8991
		1–3	1.857	
		1–4	1.636	
		2–3	1.760	
		2–6	1.947	
		3–4	1.911	
	C_2	1–2	1.913	−8.9151
		1–3	1.732	
		1–4	1.704	
		1–5	1.804	
		3–5	1.817	
	C_2	1–2	1.595	−8.9556
		1–3	1.803	
		3–5	1.698	
		5–6	1.791	
	D_{6h}	1–2	1.580	−8.9739
$B_7H_7^{6-}$	C_s	1–2	1.695	−11.1761
		1–4	1.657	
		1–5	1.824	
		2–3	1.802	
		2–6	1.819	
		2–7	1.762	
		4–5	1.832	
	C_2	1–2	1.686	−11.1866
		1–3	1.698	
		3–5	1.574	
		5–7	1.652	
	C_s	1–2	1.666	−11.1586
		1–6	1.557	
		1–7	1.658	
		3–4	1.605	
		4–5	1.638	
$B_8H_8^{6-}$	C_{2v}	1–2	1.587	−13.6497
		1–3	1.713	
		1–4	1.694	
		3–4	1.859	
		4–5	1.784	
	C_s	1–2	1.643	−13.6411
		1–3	1.680	
		1–6	1.754	
		2–3	1.812	
		2–6	1.698	
		2–7	1.673	
		3–4	1.921	
		3–7	1.946	
	C_2	1–2	1.731	−13.6184
		1–6	1.722	
		1–7	1.781	
		1–8	1.620	
		2–3	1.642	
		2–8	1.662	
		3–4	1.740	
$B_9H_9^{6-}$	C_{3v}	1–2	1.793	−16.3864
		1–4	1.895	
		1–5	1.813	
		4–5	1.836	
	C_s	1–2	1.726	−16.3318
		1–3	1.555	
		1–5	1.621	
		2–3	1.712	
		2–6	1.747	
		2–7	1.848	
		3–7	1.692	
		5–6	1.890	
		5–9	1.747	
		7–8	1.781	
$B_{10}H_{10}^{6-}$	C_{2v}	1–2	1.806	−19.3193
		1–3	1.696	
		1–4	1.964	
		2–3	1.955	
		2–6	1.816	
		2–7	1.823	
		3–7	1.687	

is a square plane. Distorted-octahedral arrangements of four atoms and two additional electron pairs are completed by a cis arrangement of electron pairs in the first isomer and by a trans arrangement of electron pairs in the second isomer. The first structure is experimentally observed for B_4H_{10},[18] while the second structure is observed for compounds of the heaver p-block elements such as Se_4^{2+}.[19]

Three possible isomers are predicted for *arachno*-$B_5H_5^{6-}$. The first contains a cis arrangement of electron pairs with edge sharing of three triangles and is the observed structure for B_5H_{11}.[8] The second is a more opened-out structure with one boron atom being closely bonded to only one of the other four boron atoms. In the first structure the mirror plane contains one boron atom and the two electron pairs, whereas in the second structure the mirror plane contains three boron atoms. The third structure is a planar pentagon with a trans arrangement of electron pairs and is the observed structure for the cyclopentadienyl ion, $C_5H_5^-$.

Four possible isomers are predicted for *arachno*-$B_6H_6^{6-}$. Two contain cis arrangements of additional electron pairs and are composed of edge-sharing triangles. The first of these is a distorted pentagonal pyramid related to *nido*-$B_6H_6^{4-}$, and the second is a more opened-out structure that contains the 2:2:2 pattern of boron atoms found from the ^{11}B NMR spectrum of B_6H_{12}.[20] The other two isomers contain a trans arrangement of additional electron pairs. The first of these also contains the 2:2:2 pattern of skeletal atoms and is the structure of benzvalene, C_6H_6.[21] The last isomer has the benzene structure.

Three isomers are predicted for $B_7H_7^{6-}$. The first is composed of triangles sharing edges with a cis arrangement of additional electron pairs and is similar to *nido*-$B_7H_7^{4-}$. The second isomer predicted has the same type of structure as benzvalene. The stereochemistry of the third isomer is dependent upon the form of the boron–electron-pair potential. The potential function (2) produces a structure consisting of a hexagon and a triangle sharing an edge, whereas the potential function (3) produces a planar seven-membered ring, as in the tropylium ion, $C_7H_7^+$.

Three isomers were located for *arachno*-$B_8H_8^{6-}$ with use of the potential functions (1), (2), and (4) (Figure 2). The most stable isomer contains a cis arrangement of additional electron pairs and is an icosahedral fragment with a structure similar to that of *nido*-$B_8H_8^{4-}$. The ^{11}B NMR spectrum of B_8H_{14}[22]

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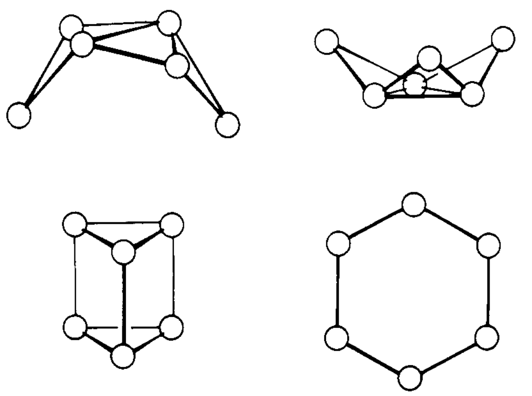

Figure 6. Isomers of *hypho*-$B_6H_6^{8-}$.

is consistent with this structure. The other isomers are an alternative fragment of an icosahedron with a cis arrangement of electron pairs and a trans structure containing a six-membered ring, which may be imagined as a fragment of a bicapped hexagonal antiprism. The replacement of potential 2 by potential 3 allows higher energy structures to occur as local minima. One of these is similar to benzvalene and the second isomer of $B_7H_7^{6-}$, and others may be considered as alternative fragments of an icosahedron or a bicapped hexagonal antiprism.

The two isomers of $B_9H_9^{6-}$ are the two possible icosahedral fragments with three adjacent boron atoms missing. NMR data are consistent with these structures for *i*-B_9H_{15} and *n*-B_9H_{15},[22] and X-ray data show $B_9H_{13}(CH_3CN)_2$[23] has the first structure and *n*-B_9H_{15}[10] the second.

The final arachno compound considered is $B_{10}H_{10}^{6-}$, for which the only structure predicted is an icosahedron with two adjacent boron atoms missing. This structure is known for $B_{10}H_{14}^{2-}$[24] and $B_{10}H_{12}(\text{ligand})_2$.[25]

The total bonding energy for each structure is given in Table II, although it is not clear if the small calculated differences are chemically significant, particularly as no account is taken of the number or position of hydrogen atoms in these calculations. For example, the most stable structure for *arachno*-$B_6H_6^{6-}$ is benzene (energy = −8.9739) followed by benzvalene (−8.9556), the B_6H_{12} structure (−8.9151), and the distorted pentagonal pyramid (−8.8991). It may also be noted that a similar difference in calculated energy is found between the two observed isomers of *arachno*-$B_9H_9^{6-}$ (−16.3864 and −16.3318).

Hypho Compounds. Addition of electron pairs along the sequence closo, nido, arachno, hypho, and so on to additional series results in increasingly opened-out structures with lower connectivity resulting from loss of triangular faces and/or multiple bonds. Alicyclic compounds and aliphatic compounds are eventually formed, with an increase in the number of possible isomers.

To consider only a single example, four isomers of *hypho*-$B_6H_6^{8-}$ are shown in Figure 6. The first isomer contains triangular B_3 units with a cis arrangement of three electron pairs and is closely related to one of the arachno isomers of $B_6H_6^{6-}$. This structure is known for $B_6H_{10}(P(CH_3)_3)_2$.[26] If the three cis electron pairs are arranged as an equilateral triangle, a second isomer composed of B_3 triangles is created. A third isomer is a trigonal prism with the three additional electron pairs located outside the three rectangular faces and is the observed structure for Te_6^{4+}.[27] The fourth isomer correspond to cyclohexadiene, C_6H_8, with two electron pairs on one side of the ring and one electron pair on the other.

Discussion

The usefulness of the concept of treating boron hydrides and related compounds as members of the homologous series *closo*-$[B_nH_n]^{2-}$, *nido*-$[B_nH_n(\text{electron pair})]^{4-}$, *arachno*-$[B_nH_n(\text{electron pair})_2]^{6-}$, and *hypho*-$[B_nH_n(\text{electron pair})_3]^{8-}$ is confirmed. However, the structural predictions based on merely replacing B–H groups in the closo compounds by electron pairs without any skeletal rearrangement are not always correct. On the other hand, if the bond between a skeletal atom and an electron pair is stronger than that between two skeletal atoms, the resulting structures are in excellent agreement with experimental data.

An important general feature of the results obtained in this work is that the nido compounds, with the exception of $B_5H_5^{4-}$, and those arachno compounds which are constructed from B_3 triangles are more accurately depicted as fragments of icosahedra than as fragments of the closo compounds. It is noteworthy that the square-pyramidal $B_5H_5^{4-}$ is the only nido structure predicted that cannot be represented as an icosahedral fragment and that B_5H_9 is the only structurally characterized nido compound that is not an icosahedral fragment.

The first of the arachno isomers shown in Figure 2 is structurally similar to the nido compound with the same number of boron atoms, so that the two electron pairs of the arachno compound occupy the same general space as the single electron pair in the nido compound. The single exception to this rule is *arachno*-$B_5H_5^{6-}$, which is an icosahedral fragment not closely related to the square-pyramidal *nido*-$B_5H_5^{4-}$. The structural similarity between the nido compounds and some of the arachno isomers has resulted in some confusion, for example as to whether B_8H_{12} should be considered as an arachno compound on the basis of Rudolph's structural classification or as a nido compound on the basis of its electron count.[28] No such ambiguity occurs with the results obtained from this work.

The structural classification that is described here should only be used for boron hydrides and very closely related compounds. Structures of clusters containing a mixture of grossly dissimilar atoms, for example boron and a transition metal, cannot be reliably predicted from the present method.

Acknowledgment. This work is supported by the Australian Research Grants Scheme.

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