

When Do Close B–B Contacts Imply a Bond, and When Not: The Case of Five-Vertex Boron-Containing Deltahedra?

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Abstract: Although simple theoretical considerations suggest that the B–B distances should be shorter in five-vertex *closo* deltahedra than in the six-vertex deltahedra, boron-containing five-vertex deltahedra show a wide range of B–B distances in the equatorial belt of the trigonal bipyramid which are longer than those in their square-bipyramid analogs. High-quality *ab initio* molecular orbital calculations at the Hartree–Fock and MP2 levels have been performed on $(\text{BX})_n(\text{Y})_2$ systems ($n = 3$ and 4) varying the apical group Y and substituent X on the equatorial boron. Geometrical optimizations show how these distances broadly correlate with the electronegativity of the axial atoms. For the case of $(\text{BX})_n(\text{Y})_2$ molecules with $n = 3$ with X = H and Y = N, this B–B distance is calculated to be quite short (1.65 Å) but for Y = SiH and X = NH₂ much longer (1.96 Å). This calculated variation in B–B distance, in accord with experimental values when available, is significantly larger than when $n = 4$. The result is two sets of molecules, those which appear to obey Wade's rules and form regular deltahedra ($n = 4$ for all X, Y, and $n = 3$ for X, Y = H, N) and those where the B–B distance is either so long or the computed B–B overlap population negative so that each of the equatorial boron atoms are essentially three-coordinate. (This occurs for Y ≠ N, all X, and $n = 3$.) There is a strong effect of the electronegativity of the axial atoms. These electronic differences are readily understood by examination of the orbitals of the molecular building blocks.

Introduction

Boron-containing clusters have attracted much attention over the years.^{1–3} They have led to a diverse chemistry, especially when substituted to give a wide variety of heteroboranes. This latter group of molecules includes the organoboranes, systems containing second-row atoms such as Ga and Si, and the important class of molecules where an organometallic fragment replaces one of the vertices. The vital step in the development of rules with which to understand the unusual structures (at the time) of this series of systems was made by Wade,⁴ and today we have his set of rules which allow ready prediction of structure, not only for these systems but also for the related series of carbocations and transition metal cluster compounds. The rules were put on a very general footing by Stone.⁵ The key feature is that the number of skeletal electron pairs⁶ (SEP) determines the geometrical structure.

The main feature of this theoretical approach is that since there are invariably a smaller number of electron pairs than there are interatomic contacts (usually assigned one pair of electrons for a bond in the classical sense) then the bonding in these systems is described as “delocalized” or non-classical. The quintessential two-dimensional example of delocalized bonding is that of the π -system of benzene (three electron pairs but six

close contacts). Thus the electronic situation in the cluster molecules is often described as being the analog of aromaticity, but in three dimensions, the Wade ($N + 1$) electron pair rule⁴ ($N =$ number of vertices) replacing the Hückel ($2n + 1$) electron pair rule ($n = 0, 1, 2, \dots$). Some systems, however, may be described in terms of either completely classical or partially classical electronic pictures. There are several *nido* or *arachno* examples of this type. For example, the molecule $(\text{CH})_4(\text{BMe})_6$ is not a *nido* borane but has an adamantane-like structure.⁴

Although $(\text{BH})_5^{2-}$ or $\text{B}_5\text{H}_5^{2-}$ is not known, the isoelectronic species $(\text{BH})_3(\text{CH})_2$ (**1a**) has been characterized.⁷ The most stable isomer with this stoichiometry is the one shown and could be written in a completely classical sense as in **1b**. The analogous phosphorus compound **2a** can be written as in **2b**.⁸ Such a scheme cannot be written for the next members of the series $(\text{BH})_4(\text{CH})_2$ or $(\text{BH})_4\text{P}_2$ or even larger deltahedra. Furthermore, there is an empty orbital at boron lying in the equatorial plane in all the classical descriptions which suggests the need for electron-donor substituents in the equatorial belt when such description dominates the bonding scheme. Perhaps the obvious way to distinguish classical and non-classical bonding schemes from each other is to examine interatomic separations; the classical scheme has no formal bond between the boron atoms. However, boron–boron distances show quite a range in such clusters, and depend on cluster size, coordination number, and whether bridging hydrogen atoms are present. For the *closo* series the B–B distance increases with size (1.69 Å in $\text{B}_6\text{H}_6^{2-}$, 1.77 Å in $\text{B}_{12}\text{H}_{12}^{2-}$, for example).⁹ A simple prescription^{10,11} can be used to put these in perspective. For

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Table 1. Optimized Structural Distances (Å) and Selected Mulliken Charges (*q*) and Overlap Population (*h*) for the Closo 5-Vertex Cage (BX)₃Y₂ Optimized at the RHF and MP2 Level

	X, Y						
	H, N	H, CH	H, P	H, SiH	NH ₂ , CH	NH ₂ , P	NH ₂ , SiH
	RHF						
B-B	1.7753	1.8852	1.9727	2.5309	1.9619	2.2212	2.6778
B-Y	1.4940	1.5552	1.9109	2.0100	1.5762	1.9567	2.0481
B-X	1.1728	1.1797	1.1799	1.1827	1.4038	1.3921	1.3901
Y-Y	2.1739	2.2217	3.0689	2.7602	2.1922	2.9558	2.6867
<i>q</i> (B)	0.365	0.170	-0.109	-0.085	0.442	0.181	0.136
<i>q</i> (Y)	-0.548	-0.383	0.137	0.259	-0.491	-0.077	0.138
<i>q</i> (X)	0.000	0.019	-0.018	-0.015	-0.758	-0.733	-0.735
<i>h</i> (B-B)	0.030	0.015	-0.046	-0.086	-0.033	-0.125	-0.091
<i>h</i> (B-Y)	0.319	0.386	0.294	0.395	0.399	0.337	0.403
<i>h</i> (B-X)	0.406	0.402	0.411	0.402	0.397	0.408	0.398
<i>h</i> (Y-Y)	-0.152	-0.187	-0.128	-0.462	-0.208	-0.257	-0.552
	MP2						
B-B	1.7553	1.8438	1.8570	2.0829	1.9318	2.0867	2.5917
B-Y	1.5168	1.5530	1.9082	1.9399	1.5728	1.9402	2.0225
B-X	1.1724	1.1777	1.1802	1.1835	1.4090	1.4044	1.3965
Y-Y	2.2570	2.2616	3.1570	3.0443	2.2178	3.0418	2.7213
<i>q</i> (B)	0.360	0.159	-0.138	-0.119	0.440	0.177	0.150
<i>q</i> (Y)	-0.540	-0.377	0.177	0.249	-0.488	-0.051	0.129
<i>q</i> (X)	0.000	-0.018	0.021	-0.001	-0.761	-0.739	-0.742
<i>h</i> (B-B)	0.034	0.024	-0.028	-0.052	-0.033	-0.137	-0.100
<i>h</i> (B-Y)	0.304	0.384	0.287	0.387	0.398	0.330	0.406
<i>h</i> (B-X)	0.406	0.401	0.405	0.000	0.394	0.395	0.391
<i>h</i> (Y-Y)	-0.120	-0.165	-0.090	-0.271	-0.191	-0.176	-0.499

an *m*-vertex *closo* deltahedron, the function $[(m + 1)/m][1/x_1 + 1/x_2]$ is a good way to measure the bond order between two vertices respectively connected to x_1 and x_2 other vertices. Using the observed distances in $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$ as reference values, this expression leads to a prediction of 1.68 Å for the equatorial B-B distances (and 1.63 Å for the equatorial-axial distances) in the unknown molecule $B_5H_5^{2-}$. The observed value of the equatorial B-B distances⁷ in $(BH)_3(CH)_2$ is 1.85 Å, a significant difference (Δ) of 0.169 Å from that predicted for the all-boron molecule. In contrast, this difference is not seen for the equatorial linkages in $(BH)_4(CH)_2$ which are found¹² experimentally to be 1.724 Å, just a little shorter than those in the all-boron molecule ($\Delta = -0.05$ Å). Notice that the experimental distances are longer than expected for the five-vertex molecule, and that there is a larger difference between unsubstituted and substituted molecules by comparison with the six-vertex molecule. It is even more interesting to compare the very different B-B distances found in $(BH)_3(CH)_2$ (1.85 Å), certainly a bonding situation, and the recently characterized $P_2(R_2NB)_3$ type cages, **3**, $P_2(PrNB)_2(Me_3Si)_2NB$, and $P_2(tmb)_3$ ($tmb = 2,2,6,6$ -tetramethylpiperidino),⁸ where the B-B distances average 2.19 Å, surely a nonbonding situation. (For clarity though we show B-B "bonds" even though they are long.) What are the electronic factors behind the fascinating behavior of the five-vertex molecules? Why do they behave in a different way from the six-vertex molecules while, in terms of overall geometry, both obey the Wade SEP rules? This paper explores this problem by comparing high-level *ab initio* molecular orbital calculations on a set of $(BX)_n(Y)_2$ molecules containing *n* equatorial X-substituted boron atoms in a ring (belt) and two axial Y units. The study has been limited to *n* = 3 (five-vertex molecules) and *n* = 4 (six-vertex molecules) but the analysis allows extension to larger *n* values. An interpreta-

tion of the results which will pinpoint the vital electronic difference is based on an analysis of the cage orbitals.

Computational Details

All calculations were carried out with a 6-311G** basis set using the Gaussian 92 package of programs.¹³ Correlation energies were estimated using second-order Møller-Plesset perturbation theory (MP2).¹⁴ Geometrical optimization was performed using gradient methods at the Hartree-Fock (HF) level. For the smaller molecules geometry optimization was also performed at the MP2 level.

The molecules studied are examples from the series $(BX)_n(Y)_2$ (where *n* = 3, 4; X = H, NH₂; and Y = N, P, CH, SiH). This allows us to mimic the influence of the X = N(Pr)₂, N(SiMe₃)₂, and N(CR₂(CH₂)₃-CR₂) substituents⁸ at the equatorial sites and the nature of the axial ligand. We also performed calculations on $B_5H_5^{2-}$ and $B_6H_6^{2-}$ for completeness (a set of calculations on a larger set of these dianion cages is to be found in ref 9). While Y = N and SiH do not correspond to experimentally observed systems, calculations on these molecules will permit a better understanding of the structural differences found between second- and third-row elements at the axial sites. These are represented experimentally only by CH and P in the five- and six-vertex cages. The trans isomers (1,5 form for *n* = 3 and 1,6 form for *n* = 4) were always used. This is certainly the most stable form of $(BH)_3(CH)_2$ and the only known form of $(BNR_2)_3(P)_2$.

The calculated geometries and energies (in hartrees) at the RHF and MP2 (when available) levels for the series of molecules are given in Tables 1 and 2. The calculations reported in this paper use a level of calculation well proven in theoretical studies on compounds of this type. For example, our geometrical results for the two molecules $(BH)_n(CH)_2$ (*n* = 3, 4), shown in Tables 1 and 2, are virtually identical to those reported in the study of ref 15 which used a slightly smaller basis set. Similar agreement for the ions is found with results of ref 9. The HF and MP2 optimized structures were found to be similar with systematically slightly shorter B-B distances at the higher level. The

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Table 2. Optimized Structural Distances (Å) and Selected Mulliken Charges (*q*) and Overlap Population (*h*) for the Closo 6-Vertex Cage (BX)₄Y₂ Optimized at the RHF and MP2 Level

	X, Y						
	H, N	H, CH	H, P	H, SiH	NH ₂ , CH	NH ₂ , P	NH ₂ , SiH
	RHF						
B–B	1.6472	1.7088	1.7937	1.8879	1.7251	1.8352	1.9574
B–Y	1.5761	1.6187	1.9556	1.9798	1.6255	1.9632	1.9951
B–X	1.1680	1.1735	1.1758	1.1798	1.4496	1.4469	1.4536
Y–Y	2.1236	2.1542	2.9770	2.9242	2.1486	2.9463	2.8139
<i>q</i> (B)	0.223	0.059	-0.152	-0.122	0.411	0.178	0.219
<i>q</i> (Y)	-0.555	-0.354	0.264	0.296	-0.430	0.140	0.168
<i>q</i> (X)	0.054	0.025	0.020	0.007	-0.827	-0.815	-0.816
<i>h</i> (B–B)	0.224	0.232	0.282	0.238	0.202	0.245	0.202
<i>h</i> (B–Y)	0.230	0.292	0.216	0.295	0.293	0.235	0.304
<i>h</i> (B–X)	0.3910	0.393	0.403	0.387	0.305	0.312	0.309
<i>h</i> (Y–Y)	-0.187	-0.230	-0.167	-0.361	-0.240	-0.216	-0.433
	MP2						
B–B	1.6561	1.7091	1.7765	1.8754			
B–Y	1.6064	1.6218	1.9604	1.9722			
B–X	1.1696	1.1736	1.1777	1.1805			
Y–Y	2.1992	2.1632	3.0100	2.9195			
<i>q</i> (B)	0.228	0.061	-0.157	-0.123			
<i>q</i> (Y)	-0.560	-0.358	0.277	0.296			
<i>q</i> (X)	0.052	0.025	0.018	0.007			
<i>h</i> (B–B)	0.229	0.232	0.286	0.240			
<i>h</i> (B–Y)	0.217	0.292	0.215	0.296			
<i>h</i> (B–X)	0.392	0.393	0.401	0.385			
<i>h</i> (Y–Y)	-0.162	-0.226	-0.153	-0.359			

HF calculations thus properly reproduce the geometries of these systems. In addition, variations in the B–B distances as a function of X, Y, and *n* in (BX)_nY₂ were found to be parallel at the HF and MP2 levels of calculations. So although MP2 values are also reported in the tables, the bulk of our discussion will center around the HF results.

Results

First we compare the observed, calculated, and predicted bond lengths for the dianions. The distances in B₆H₆²⁻ are calculated to be 1.74 Å compared to the 1.77 Å found in the crystal. Those for B₅H₅²⁻ are calculated to be 1.87 Å (*B*_{eq} – *B*_{eq}) and 1.68 Å (*B*_{eq} – *B*_{ax}) compared to the predicted distances of 1.68 and 1.63 Å (see above). Thus the calculations immediately reveal an anomaly with the equatorial distances in B₅H₅²⁻ which we noted earlier in the experimental data on known derivatives.

Because of the intrinsic difference in calculating anionic and neutral compounds we make no attempt to compare these two sets of systems. For this reason, additional numerical data on the ions are not included in the tables of results. We will now focus on the neutral cages whose results are collected on Tables 1 and 2. The calculated equilibrium geometry of (B(NH₂))₃P₂ compares well with experimental studies⁸ on complexes of this type (B(NR₂))₃P₂ in general, which indicates that our level of calculations properly reproduce the electronic state of affairs in this type of molecule. The B–P distance is calculated to be very close to the experimental value (1.957 Å (calc), 1.94–1.96 Å (exp)). The B–N separation (1.392 Å) is calculated to be within the range of experimental B–N distances⁸ (1.38–1.41 Å). The nonbonding distances are also well matched by calculations (B–B 2.221 (calc) vs an average of 2.19 Å (exp); P–P 2.956 Å (calc) vs an average of 2.98 Å (exp)) showing that all angles in the cage are properly reproduced. Finally the NH₂ group prefers energetically to lie perpendicular to the equatorial plane as found experimentally for all NR₂ groups. Since our calculations well reproduce geometric details of both the five- and six-vertex cages we can be confident that our level of calculation provides a good electronic description of a range of cages with short and long B–B distances. We can thus safely discuss the influence of X, Y, and *n* on the geometry of these molecules using the results of the computations.

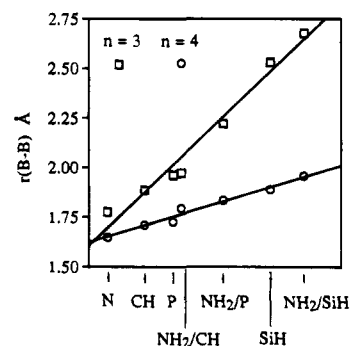


Figure 1. The calculated variation in B–B distance for some (BX)_n(Y)₂ molecules. The abscissa (unmarked) is selected to allow a pictorial view of the data but does roughly scale with electronegativity for those systems which do not contain equatorial NH₂ groups. (X, Y are only indicated for some compounds. Where only Y is given X = H.)

Figure 1 shows the calculated variation in B–B distance for some of the neutral molecules of this study. The ordinate is chosen in a way to allow a pictorial view of the data and ready comparison between first- and second-row Y systems. (In fact it scales with electronegativity, N > C > P > Si.) No importance should be attached to the lines connecting the points drawn to guide the eye. The B–B distances vary over a large range in the five-vertex molecules, the shortest being obtained for Y = N (1.775 Å) and the longest for Y = SiH (2.531 Å) for a given X (H). Changing a second-row for a third-row element at the axial site significantly increases the B–B distance (1.885 Å for Y = C–H and 2.531 Å for Y = SiH). Decreasing the electronegativity at the axial site within a given row (N to CH or P to SiH) increases the B–B distance. The introduction of the NH₂ substituent at the basal site also significantly elongates the B–B equatorial bond. The orientation of the NH₂ substituent was studied for the case of Y = P, CH. Rotating the NH₂ group from an in-plane orientation (i.e., for NH₂ lying in the equatorial plane) by 90° considerably stabilizes the molecule (78 kcal/mol for the whole compound or 26 kcal/mol per B–NH₂ unit for Y = P). It also leads to a significant lengthening of the B–B equatorial bond (2.097 to 2.221 Å) and a shortening of the B–N bond (1.451 to 1.392 Å).

In the six-vertex system, the influence of X and Y is similar to that calculated in the five-vertex molecules although the magnitude of the spread of B–B distances is smaller (1.647 Å for Y = N and 1.888 Å for Y = SiH). Remarkably, although from considerations suggested by Wade the B–B distance should be shorter for the five-vertex system, in fact they are shorter for the six-member clusters.

Five-Vertex vs Six-Vertex Deltahedra. It thus appears from both calculation and structural data available experimentally that the geometry of the trigonal equatorial belt in the five-vertex deltahedron is considerably more sensitive to chemical variation within the cage than is the square equatorial belt in the six-vertex deltahedron. In the former, the B–B distance changes from a clearly bonding situation to distances which must be viewed as nonbonding, while in the latter short B–B distances indicating a bonding situation within the square equatorial belt are maintained for all cases. The trigonal bipyramid has been noted by Lipscomb and co-workers¹⁶ as being the most anomalous member of the closo boranes and certainly these calculations over a reasonable electronegativity range of axial groups bear out this statement. These structural changes found by calculation cannot be accommodated within the realm of the SEP rules and a broader discussion of the bonding problem is necessary to unearth the origin of this much richer structural picture.

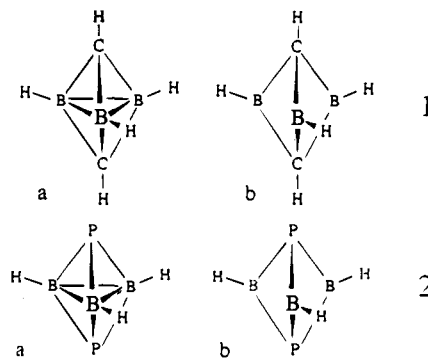
Strain Effects in the Five-Vertex Deltahedron. From the computations, the general trends upon changes in the nature of the axial site are similar in both three- and four-membered rings except that the variations are enormously amplified in the case of the former, especially for the cases of (X, Y) = (NH₂, P), (H, SiH). A first explanation which comes to mind is associated with the strain within the base itself and at the axial site.

An important observation for these (BH)_n(Y)₂ molecules with *n* = 3 is that they contain in-plane B–B–B angles of 60°. These would be energetically penalizing in carbon-containing molecules where most of the theoretical and experimental interest has lain. In cyclopropane the strain energy per CCC angle has been estimated¹⁷ at 11–12 kcal mol⁻¹ and in tetrahdrane¹⁸ at 135–140 kcal mol⁻¹ in total or around 12 kcal mol⁻¹ per C–C–C angle. Although these figures are useful, the strain energy of 60° B–B–B angles may well be quite different (smaller) from those of their organic analogs. We noted earlier the much longer-than-expected equatorial distances in (BH)₃–(CH)₂ (1.85 Å) but these are similar in fact to those found¹⁹ for the boron “cyclopropane” analog B₃H₈⁻ (an *arachno* trigonal bipyramid). The unique B–B distance here is 1.80 Å and the two containing bridging H atoms 1.77 Å. Thus a part of the increase in B–B distances found for (BH)₃(Y)₂ molecules is surely due to strain of this type.

There is strain at the apices too. If X = P then for a typical P–B distance of 1.96 Å the B–P–B angles at the apex are 55°. This increases to 60° if the B–B distance is chosen to be 2.00 Å. Some of these energetic contributions are readily estimated. The strain energy per 60° P–P–P angle has been estimated²⁰ at 2 kcal mol⁻¹, which implies a strain energy in **2** of around 14 kcal mol⁻¹. (We have to be careful in such comparisons since²⁰ no P₈ isomer is found by calculation to be

more stable than two P₄ units.) This can be relieved in the systems studied, either by shortening the P–B distance (unlikely) or lengthening the B–B bonds. The actual B–P–B angle in **2** is 70° and this is indeed achieved by stretching the B–B bonds. In the case of *n* = 4 or higher there is a similar problem; there are now *n* 55° angles at phosphorus. Whether they are just as strained as in the classical case for *n* = 3 is not clear. Although it is difficult to get sensible estimates of the strain in these molecules which do not lie in the organic mainstream, an upper limit for *n* = 3 might be around 50 kcal mol⁻¹. In any case it will be the most highly strained system of all of the closo carboranes. We have already noted that relief of strain, especially at the apices, is one route toward longer B–B distances. That it can only be a part of the picture is shown on Figure 1 and Table 1 by the dramatic increase in calculated B–B distance when NH₂ groups are attached to the equatorial B atoms. Electronic effects are thus vital too.

Electronic Effects in the Five- and Six-Vertex Deltahedra. The computed Mulliken Bond Overlap Population (MOP) is one criterion to estimate the presence of a bond between two atoms. There are, of course, other ways to discuss bonding, but since our interest is solely comparative, any given scheme should just be satisfactory. One does of course have to be especially careful in the interpretation of the MOP in calculations such as ours which use such large basis sets. It is safer to consider just the trends in the overlap populations and this we will do. The first striking result which appears from the values of the B–B overlap population is that they are systematically smaller in the five-vertex than in the six-vertex cage even when the B–B distances are short. As a matter of fact, for X, Y = H, N, the B–B MOP is less than 0.05 for *n* = 3 while it is about 0.23 for *n* = 4 at both levels of calculation. Extrapolating this result the B–B MOP is negative in the case of *n* = 3 for B–B distances longer than 1.9 Å while this is never the case for *n* = 4, even at long B–B distances. This result runs counter to the usual correlation between coordination number and bond lengths. Invariably the lower the coordination, the shorter the bond length. Chemical changes within the cage drastically affect the values of the MOP too. It is positive for (BH)₃(CH)₂ but negative for (BH)₃(P)₂ (a variation of 0.061) while the B–B distance has increased by only 0.1 Å. A change twice as large in B–B distance in the six-vertex deltahedron (Y = N, SiH) leads to only a small reduction (0.02) of the B–B MOP. It is clear that the bonding situations within the two cages are quite different. Lipscomb et al.¹⁶ have noted that the situation is unusual here in that it is possible to draw the *n* = 3 systems using purely two-center, two-electron linkages as we indicated in **1a**, **1b** and **2a**, **2b**. Literal interpretation of the overlap



(16) (a) Graham, G. D.; Marynick, D. S.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 2939. (b) Camp, R. N.; Marynick, D. S.; Graham, G. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 6781. (c) Dixon, D. A.; Klier, D. A.; Halgreen, T. A.; Hall, J. H.; Lipscomb, *J. Am. Chem. Soc.* **1977**, *99*, 6226.

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(18) Schulman, J. M.; Venanzi, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 4739. Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 329.

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(20) Häser, M.; Schneider, U.; Ahlrichs, R. *J. Am. Chem. Soc.* **1992**, *114*, 9551.

population results from our calculations similarly indicates that (BH)₃(P)₂ is built from 2-center, 2-electron bonds and has thus

(21) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

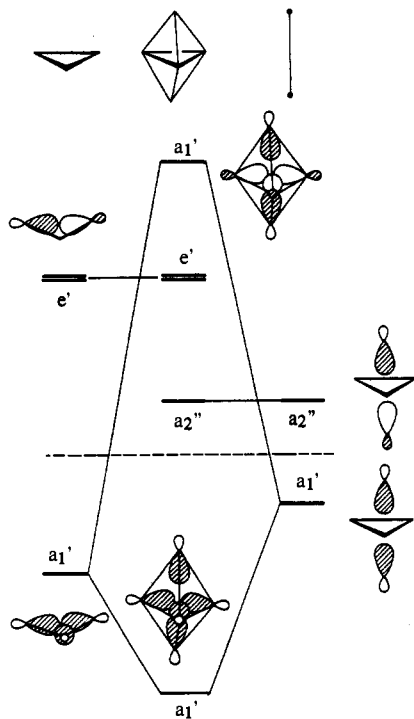


Figure 2. Orbital interaction diagram for the in-phase and out-of-phase radial orbitals of the axial sites with the orbitals of the equatorial sites for the trigonal bipyramid ($n = 3$). The horizontal dashed line indicates the energy of a nonbonding p orbital of a cage atom. (There are interactions ignored in this diagram, see text.)

no electronic relationship with the deltahedra described by a delocalized picture which follow the SEP rules, but $(\text{BH})_4(\text{CH})_2$ is more delocalized and can thus be described with the SEP rules. Other than for $(\text{BH})_3(\text{N})_2$ all other computed B-B overlap populations are negative for $n = 3$. By way of contrast without exception the systematically positive computed B-B overlap populations for $n = 4$ indicate that the 6-vertex cage is a delocalized Wade cage in all cases.

Assembly of Orbital Diagrams. We have noted, in contrast to the five-vertex molecule, it is not possible to describe the six-vertex cage by $2c-2e$ bonds and that there must be a fundamental difference in the description of the electronic structure of the two deltahedra. In fact this striking difference between $n = 3, 4$ is accessible using some straightforward electronic arguments. We begin by reminding the reader of the general form of the orbitals of the $\text{B}_{n+2}\text{H}_{n+2}^{2-}$ species for $n = 3, 4$. Assembly of these diagrams from the n -membered $(\text{BH})_n$ ring with the addition of two axial groups immediately leads to insights into this problem. (The basic orbital picture is given in ref 21.)

It will be insightful to assemble the orbital picture of the complete deltahedron from those of the group of equatorial atoms ($n = 3, 4$) plus those of the apices. Consider first (Figure 2) the interaction of the in-phase radial orbital (a_1') of the axial sites for the trigonal bipyramid ($n = 3$). This orbital interacts with the a_1' orbital of the equatorial sites which is B-B bonding within the equatorial belt. The result is a new orbital which is still B-B bonding but also B-apex bonding. In contrast (Figure 3) the out-of-phase combination of the tangential orbitals, e'' , of the axial sites will interact with the e'' orbital of the equatorial sites. Importantly this orbital is strongly B-B antibonding within the equatorial belt. The in-phase combination of the same tangential orbital (e') can interact with the e' set of the base but the interaction is small because of a poor overlap. The crucial part of this description is that e'' orbitals of the equatorial belt which are B-B antibonding mix strongly into the ground state which leads to significant weakening of

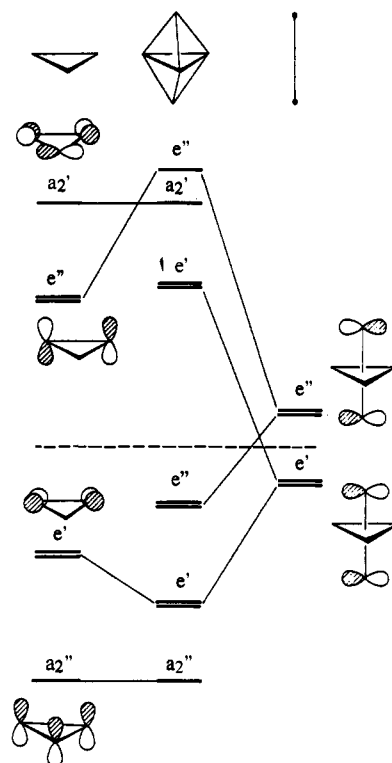


Figure 3. Orbital interaction diagram for the tangential orbitals of the axial sites with the orbitals of the equatorial sites for the trigonal bipyramid ($n = 3$). The horizontal dashed line indicates the energy of a nonbonding p orbital of a cage atom. (There are interactions ignored in this diagram, see text.)

the linkages between the equatorial belt atoms while creating strong bonds between the equatorial belt and the axial sites. Notice that in Figures 2 and 3 ($n = 3$) and 4 and 5 ($n = 4$), mixing between radial and tangential orbitals (such as a_2'' orbitals for $n = 3$) has been ignored even though they are symmetry matched. This is supported by a large energy gap and the fact that it does not change the fundamental bonding picture.

Applying the same reasoning to the six-vertex deltahedron is illuminating. The a_{1g} orbital of the square base interacts (Figure 4) with the radial set of the axial sites in a very similar way to the corresponding a_1' and a_1'' orbitals of the triangle. The a_{2u} orbital located on the axial sites, however, remains nonbonding. The important difference between five- and six-vertex deltahedra comes from the orbitals of the square base which interact (Figure 5) with the tangential e_g set of the axial sites. These orbitals are much less antibonding than in the triangular set. They are in fact rigorously nonbonding within the Hückel framework. This means that electrons which are transferred to this e_g set do not contribute to the weakening of the square equatorial belt but yet still contribute to the bonding between the equatorial belt and the axial sites. Since the other orbitals of the equatorial belt are either bonding (a_{1g}, a_{2u}) or also nonbonding (e_u) within the equatorial belt, there is no tendency to weaken bonds between equatorial atoms when building bonds to the axial sites.

We can also extrapolate the present analysis to cages with larger equatorial belts. As the equatorial belt size increases the orbitals which have only one nodal plane perpendicular to the equatorial plane and play the role of e'' ($n = 5$) or e_g ($n = 6$) should remain nonbonding or should even become a little bonding. Interaction with the orbitals from the axial sites could then even lead to strengthening of the equatorial belt B-B bonds. Seven-vertex molecules have perfectly "normal" B-B distances.

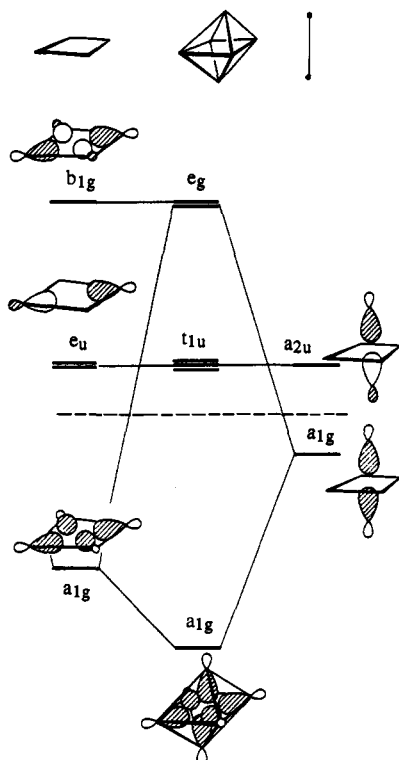
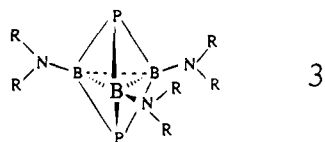


Figure 4. Orbital interaction diagram for the in-phase and out-of-phase radial orbitals of the axial sites with the orbitals of the equatorial sites for the square bipyramid or octahedron ($n = 4$). The horizontal dashed line indicates the energy of a nonbonding p orbital of a cage atom. (There are interactions ignored in this diagram, see text).

The influence and conformational preference of the single-face π donor (NH_2) substituent of the basal sites can be understood in a similar way. Suppose first that the NH_2 groups are perpendicular to the equatorial base (the preferred conformation, 3). In the five-vertex system, the p lone pairs of the NH_2



units fall into an e' and a'_2 set. They therefore match in symmetry the corresponding orbitals of the equatorial belt. Notice the strong antibonding character of the a'_2 orbital of the equatorial belt. Interaction between these orbitals thus leads to electron transfer from the lone pairs into these B-B antibonding orbitals and will effectively weaken the B-B bond. In the six-vertex cage the situation is qualitatively similar and the e_u and a_{2g} orbitals are respectively B-B nonbonding and strongly B-B antibonding. Therefore the presence of NH_2 groups should lengthen the B-B bond in exactly the same fashion as described above for the vertex tangential orbitals in both $n = 3, 4$ situations. This is indeed found from the calculations both in terms of computed distances and the MOPs.

The conformational preference of the NH_2 groups is straightforward. When these units lie perpendicular to the base, the B-centered a'_2 combination is fully available for interacting with the N a'_2 orbital. The B-centered lower e' combination can also interact with the e' combination of N lone pairs since it is only weakly involved with the axial sites. These interactions between N lone pairs and the B-centered e' and a'_2 orbitals lead to π bonds between N and B. Rotating the NH_2 moiety by 90° , a distortion which forces them to lie within the base would require the N lone pairs to interact with the a''_2 and e'' B-centered

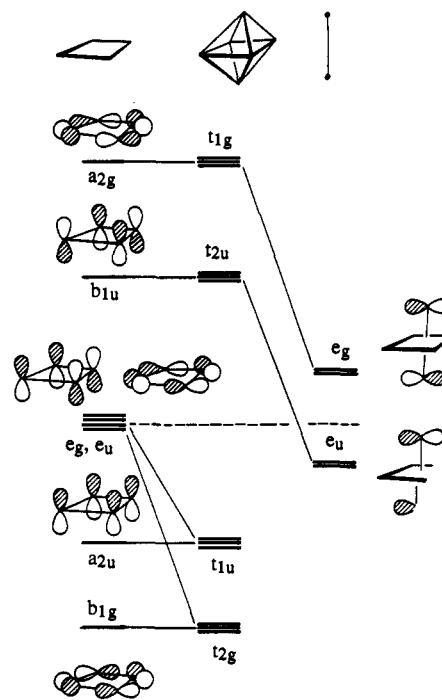


Figure 5. Orbital interaction diagram for the tangential orbitals of the axial sites with the orbitals of the equatorial sites for the square bipyramid or octahedron ($n = 4$). The horizontal dashed line indicates the energy of a nonbonding p orbital of a cage atom. (There are interactions ignored in this diagram, see text.)

orbitals which are already strongly involved with the axial sites and therefore not readily available for additional interaction. The result is no efficient stabilization of the N lone pairs and no π B-N bonds when the NH_2 units lie within the basal plane. These ideas are confirmed in a quantitative way by the calculated values of the MOPs. Of course steric factors strongly discourage the latter conformation too.

From the above discussion, one can readily understand why the equatorial B-B bonds are intrinsically weaker in the five-vertex than in the six-vertex cage. From the broad set of calculations which we have presented for both $n = 3, 4$, the crucial role of the axial atoms is clear to see. The more electropositive the axial atom the greater the weakening of the equatorial B-B bonds since there is more electron transfer into the B-B equatorial belt orbitals. The single face π donor attached to the equatorial sites plays the same electronic role in both cages with the p lone pair lying preferably within the basal site. Electron donation from this lone pair into the cage again weakens the basal B-B bonds. The crucial difference between the two systems ($n = 3, 4$) is that this interaction has a large effect on the shape of the five-vertex cage since there is essentially no bond within the equatorial belt but a smaller effect in the six-vertex cage because of the presence of a strong B-B bond within the equatorial belt.

Figure 1 has been constructed in a qualitative way to best illustrate the data. Within each row of the Periodic Table the ordinate follows the electronegativity of the axial atoms. Clearly if the interaction in the five-vertex system between the tangential orbitals of the axial and their partners of the equatorial atoms can be reduced then the B-B linkages of this system will be short and the system described as non-classical. This is certainly indicated for the case of $Y = \text{N}$, which appears from the calculations to have a Wade's rule structure. Another route may be to decrease the effective interaction between these orbitals by employing an axial ligand which contains a strongly bound π system, or by changing the nature of the apical unit by variation of R in $Y = \text{SiR}$ or CR.

Thus the calculated variation in B-B distance shows that these molecules fall into two sets. The divisions are relatively arbitrary of course: (i) those which appear to obey Wade's rules and form regular deltahedra ($n = 4$ for all X, Y, and $n = 3$ for X, Y = H, N) and (ii) those where the B-B distance is either so long, or the computed B-B overlap population negative so that each of the equatorial boron atoms are essentially three-coordinate. (This occurs for $Y \neq N$, all X, and $n = 3$.) It is certainly very interesting indeed that the essential electronic factor which switches the five-vertex system from non-classical to classical, but not for the six-vertex system, is simply the nodal properties of the orbitals of the trigonal plane and square. (Parenthetically we note that there may well be similar effects

in cluster compounds built from transition metal-containing fragments isolobal to the BH, P, etc., units used here.) Finally we remark that an analysis of the electron density distribution in these molecules, from the $B_3C_2H_5$ cage to those with longer distances for both $n = 3, 4$, using X-ray diffraction data should be a useful probe of the electron density in the equatorial belt.

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