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Nido-*n* (*n* = 8, 10, 12) Borane and Carborane Clusters and Second Moment Scaling

Stephen Lee

University of Michigan, Department of Chemistry, Ann Arbor, Michigan 48109-1055

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We show that second moment scaled Hückel theory can be used to predict the structures of nido-*n* boranes and carboranes. In particular we optimize the geometries of $B_8H_8^{4-}$, $B_{10}H_{10}^{4-}$, $B_{12}H_{12}^{4-}$, $C_4B_4H_8$, $C_2B_8H_{10}^{2-}$, $C_4B_6H_{10}$, and $C_4B_8H_{12}$. The theory can be used to predict the overall qualitative shape and approximate bond distances. Our predicted geometries accord well with experiments which find that $C_4B_4H_8$ and $C_4B_8H_8R_4$ (R = alkyl group) are anomalous vis-à-vis the structural systematics of Wade's rules.

It has recently been shown that a modified form of Hückel theory is able to account for the structures of the pure metallic and non-metallic elements, alloys, intermetallic phases, and cluster compounds.[1] We call this modification second moment scaling. The modification itself is quite simple. In unmodified Hückel theory one assumes the total electronic energy is $E = \sum_i E_i n_i$ where E_i is the energy of the *i*th molecular orbital and n_i is the occupation number of electrons for the *i*th molecular orbital. If one is interested in calculating the relative energy of two different molecular geometries one calculates ΔE, where $\Delta E = \sum_i E_i(1)n_i(1) - E_i(2)n_i(2)$. In this expression $E_i(1)$, $n_i(1)$, $E_i(2)$, and $n_i(2)$ refer respectively to the first and second of the two differing molecular geometries. Unfortunately ΔE is not a reliable indicator of the relative stability of the two geometries when the two geometries have different coordination numbers in their constituent atoms.[2] In second moment scaled Hückel theory one corrects for this error by assuming that $\Delta E = \sum_i \gamma E_i(1)n_i(1) - E_i(2)n_i(2)$. The factor γ is defined to be $\gamma = \{\sum_i (E_i(2))^2/\sum_i (E_i(1))^2\}^{1/2}$. The rationale behind this scaling procedure is discussed in ref 3.

Very recently we have shown that the method of second moment scaling can be used to predict the variations in bond distances found in borohydrides, several hydrocarbons, gallium and some transition metal carbonyl structures.[3e] In this earlier work we used an iterative procedure to find the exact geometries which minimize the second moment scaled Hückel electronic energy.[3e,4] For numerical reasons, these earlier studies were restricted to optimizations in relatively high point group symmetries. For example, in the case of $B_8H_8^{2-}$, $B_9H_9^{2-}$, and $B_{10}H_{10}^{2-}$, we found the minimum energy positions for the boron atoms subject to the respective constraints of D_{2d}, D_{3h}, and D_{4d} point group symmetry. We chose these three point groups as they correspond to the experimentally known point group symmetries of these three molecules.[5] In this earlier work we found that second moment scaled Hückel theory was able to account for the variation in bond lengths in a semi-quantitative fashion. The average error when comparing our theoretically optimized structure to the known experimental structure was 0.05 Å. Due to the limitation of our scaling procedure we considered only terminal hydrogen (i.e., one-coordinate, nonbridging hydrogen) atoms. Furthermore, we fixed the B–H bond to a single fixed length throughout our geometry optimizations.

In the present article we will again keep all B–H (and C–H) bond distances constant. This paper differs from the earlier work however in that we try to no longer assume a priori the point group symmetry of the molecules which we wish to optimize. We implement this change in two ways. First, we will assume only minimal point group symmetries in the current work. Second, as the starting point of our optimizations, we choose geometries which are not at all the final predicted minimum energy structures. The goal of this project is therefore to see if second moment scaled Hückel theory can calculate without the use of foreknowledge the equilibrium molecular geometry of reasonably sized cluster compounds.

Closo and Nido Structures

In this article we consider the effect of chemical reduction on the shape of lower symmetry borohydride clusters. This is a general problem which has been extensively studied from both experimental and theoretical viewpoints. These earlier studies have resulted in a standard model whose predictive power has been amply demonstrated and whose theoretical underpinnings are well understood.[6] This model is generally called Wade's rules. In Wade's rules, one assumes the overall structure of a cluster is determined by the number of valence electrons associated to the cluster itself. Clusters of the form $B_nH_n^{2-}$ adopt the closo form. Closo molecules are approximately spherical polyhedra that have only triangular faces. Wade's rules further state that the addition of a pair of electrons (which turns the $B_nH_n^{2-}$ cluster into a $B_nH_n^{4-}$ one) results in the formation of a nido cluster. The $B_nH_n^{4-}$ nido cluster has the same form as the $B_{n+1}H_{n+1}^{2-}$ closo

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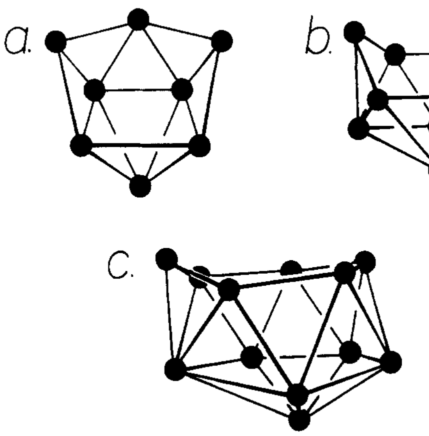

Figure 1. Some nido-*n* structures: (a) nido-8(v); (b) nido-10(vi); (c) nido-12(vi). These are the putative structures of $B_8H_8^{4-}$, $B_{10}H_{10}^{4-}$, and $B_{12}H_{12}^{4-}$ if one follows Wade's rules for borohydrides exactly. In this drawing we indicate the locations of only the boron atoms.

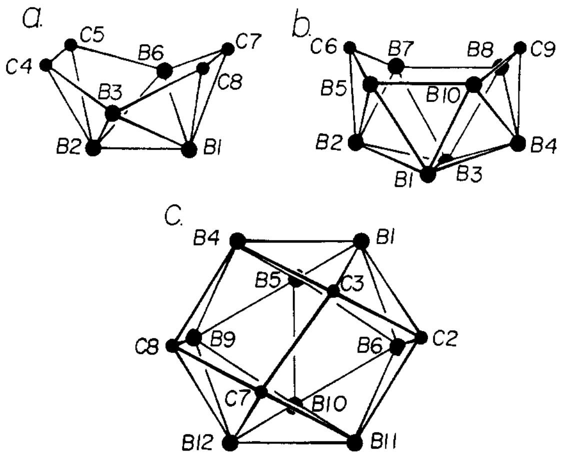

Figure 2. Some carborane structures: (a) nido-8(vi) (shown here is $C_4B_4H_8$); (b) nido-10(vi) (shown here is $C_2B_8H_{10}^{2-}$); (c) nido-12(iv + iv) (shown here is $C_4B_8H_{12}$). Only boron or carbon atoms are shown.

cluster except that the boron atom which is coordinated to the greatest number of other boron atoms in the parent closo cluster is removed. The predicted forms of $B_8H_8^{4-}$, $B_{10}H_{10}^{4-}$, and $B_{12}H_{12}^{4-}$ are shown in Figure 1. We adopt the nomenclature of R. E. Williams in our discussion of these nido structures.[7] In Williams' nomenclature the three molecules illustrated in Figure 1 are respectively nido-8(v), nido-10(vi), and nido-12(vi). In this system the nido designation refers to the overall number of valence cluster electrons, the Arabic numerals refer to the number of vertices in the cluster polyhedron, and the Roman numerals indicate the number of atoms in the open face of a given nido shape.

While Wade's rules in general are tremendously useful in rationalizing the structures of nido compounds, the rules appear to underestimate the structural complexity of both the nido-8 and the nido-12 families. In the latter case there are seven known structural types.[8] Since in our calculations we consider mainly homoatomic polyhedral clusters, we restrict our attention to the known borane and carborane structures. In these two families, the only nido-8 clusters whose structures have been determined unambiguously are B_8H_{12} and $C_4B_4H_8$.[6f,9] Neither adopt the structure predicted by Wade's rules. Instead both have the nido-8(vi) structure shown in Figure 2a. One encounters similar irregularities in the nido-12 boranes and carboranes. The only three nido-12 compounds with one and only one terminal hydrogen (or alkyl group) per boron or carbon atom, which according to Williams' critical review[7] have unambiguous structures, appear to be $R_4C_4B_8H_8$ (R = methyl, ethyl, and *n*-propyl groups). All three alkyl derivatives appear to have two competing structural forms. Careful thermodynamic measurements show that it is the nido-12(iv + iv) form illustrated in Figure 2c, which is the thermodynamic product at low temperature in all three cases.[8] However, the nido-12(vi) cluster has only a slightly higher enthalpy (around 2 kcal/mol). This latter structure has a more favorable entropy associated with it, and therefore it too is experimentally observed. However as our calculations correspond to the energetics at absolute zero, we will focus primarily on the nido-12(iv + iv) geometry.

Among all the nido-*n* geometries it is the nido-8 and nido-12 families which provide the greatest number of exceptions to Wade's rules. We therefore decided to find the optimal geometries for these systems using our second moment scaled Hückel Hamiltonian method. As this method has proven to be quite accurate in predicting the bond lengths of *homoatomic* clusters with terminal ligands, the systems which we initially investigated were $B_8H_8^{4-}$ and $B_{12}H_{12}^{4-}$. The former is a nido-8 compound while the latter is nido-12. It should be noted that neither molecule has been synthesized. However, as it is generally true that isoelectronic compounds which involve chemically similar atoms are isostructural, we initially regard $B_8H_8^{4-}$ and $B_{12}H_{12}^{4-}$ as paradigms for their respective classes. As a further test of our method we also optimized the geometries of $C_4B_4H_8$, $C_2B_8H_{10}^{2-}$, $C_4B_6H_{10}$, and $C_4B_8H_{12}$.

Calculational Procedure

We used the same algorithm in all the geometry optimizations reported in this article. First, we restricted all B–H bond distances to 1.17 Å. Second, we required that the B–H bonds extend in a purely radial manner with respect to the center (of mass) of the cluster. Third, we required that there be one and only one terminal hydrogen per boron or carbon atom. Even with these constraints, the number of remaining free parameters is quite large. We therefore made the additional assumption that the molecule had either a C_2 rotation axis or a mirror plane within it. This additional assumption reduces the number of parameters roughly by a factor of 2. It should be noted that as almost all known clusters are at least of C_2 or C_s symmetry, this constraint should not affect the overall utility of our method. Finally, in several cases (to wit $B_8H_8^{4-}$, $B_{10}H_{10}^{4-}$, $C_4B_4H_8$, and $C_2B_8H_{10}^{2-}$) it became clear that the minimum energy structure was of C_{2v} symmetry, and we then finished the structural refinement in the higher point group.

Our calculations were based on a double iterative procedure. We varied each individual parameter, holding all other geometry parameters fixed, over a range of approximately 0.1–0.2 Å. In so doing, we found the value for the parameter (within this range) which minimized the overall energy. We then determined in a similar manner the optimized values for the remaining parameters in both an iterative and cyclic manner. After repeated calculations, a convergent structure was reached. For any one particular geometry, we determined the correct second moment scaled energy by the following procedure. We first calculated the second moment, μ_2, where $\mu_2 = (1/n)\sum_i E_i^2$, n is the number of molecular orbitals, and E_i is the energy of the ith molecular orbital. We then proceeded in an iterative way to expand or shrink the central main group atoms in a uniform manner. This geometrical process left *all* bond angles unchanged. However, we did not alter the B–H bond lengths. These bonds were kept constant at 1.17 Å throughout our calculations. After several iterations we produced a geometry which had a second moment which equaled a preselected value. This preselected value was generally chosen to be the μ_2 of the parent closo–*n* structure. The procedure outlined above is somewhat cumbersome. In most cases it required finding the molecular orbital diagram between 10^3 and 10^4 times. We used the undistorted closo structure as the starting point for our calculations. We also took the various known nido structures as alternative starting points. In certain systems several local minima were found. We report here the lowest in energy amongst this set of local minima.

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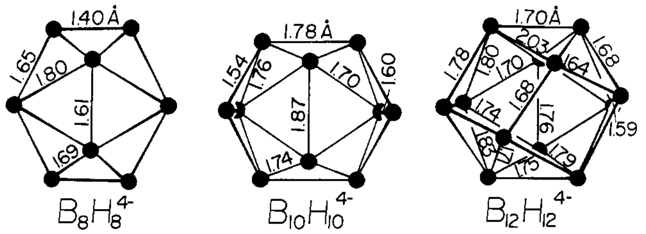

Figure 3. Optimized geometries for (a) $B_8H_8^{4-}$, (b) $B_{10}H_{10}^{4-}$, and (c) $B_{12}H_{12}^{4-}$. Distances are given in Å. The Hückel atomic parameters used in our calculations are reported in ref 10a,b. In this drawing we indicate only the positions of the boron atoms.

We used this same procedure in optimizing the carborane structures. For these calculations we placed the carbon atoms in positions which corresponded to experimentally known isomers. It should be noted that in many cases the known isomers have alkyl groups replacing the H atoms. We did not consider the effect of different alkyl substitutuents. As the main interest of the second moment scaling technique is to study boron–boron and boron–carbon bond formation, we left all C–H bond distances at the same length as the initial B–H distances. Finally in the case of the carboranes, we chose as our second moment standard the structure which corresponds to the optimized $B_nH_n^{4-}$ cluster in which the appropriate boron atoms have been replaced by carbon atoms. Besides the modifications due to second moment scaling we used a standard Hückel method in our molecular orbital calculations. The diagonal matrix elements of our Hückel Hamiltonian were taken from a set of parameters developed by R. Hoffmann and others.[10] We used the Wolfsberg–Helmholz approximation in calculating off diagonal matrix elements.[11] Unlike extended Hückel calculations, we solved the secular equation $H\psi = E\psi$ and not $H\psi = ES\psi$.

Results

In Figure 3 we show our optimized geometries for $B_8H_8^{4-}$, $B_{10}H_{10}^{4-}$, and $B_{12}H_{12}^{4-}$. It may be seen that our optimized geometries for $B_8H_8^{4-}$, $B_{10}H_{10}^{4-}$, and $B_{12}H_{12}^{4-}$ are in perfect agreement with the known nido-8, nido-10, and nido-12 borane and carborane geometries shown in Figure 2.[12] In the case of the nido-12 system, where there are two known carborane structures, our calculated geometry corresponds to the nido-12(iv+iv) structure known to be of lower enthalpy. Furthermore, neither the calculated $B_8H_8^{4-}$ geometry nor the calculated $B_{12}H_{12}^{4-}$ geometry is in accord with the geometries predicted by Wade's rules.

The differences in energy between the Wade's rule geometries and our optimized structures can be understood by directly analyzing the molecular orbitals. In the case of $B_8H_8^{4-}$ the energetic reason why the nido-8(vi) structure is 2.6 eV lower than the nido-8(v) structure is readily explained. Examination of the molecular orbital diagrams of these two geometries shows that the HOMO (*h*ighest *o*ccupied *m*olecular *o*rbital) of the nido-8(vi) structure is 2.5 eV lower in energy. Therefore the increased stability of this HOMO orbital accounts for nearly all the additional stability of the nido-8(vi) geometry. In Figure 4 we show the principal components of the HOMO orbitals for these two geometries. In the case of the nido-8(vi) geometry the HOMO consists of two π bonding combinations on the left and right sides of the lower portion of Figure 4. The two boron atoms connected by the dotted line (see Figure 4) are σ antibonding. However, in the nido-8(vi) geometry this central σ antibonding interaction is weak as the two boron atoms are not bonded to each other. In turning to the nido-8(v) geometry, we form an additional bond between the aforementioned boron atoms. As this short distance leads to an unfavorable σ interaction, the HOMO has little orbital character on these atoms. The majority of the electron density is found on the two boron atoms shown at the top of Figure 4. Therefore, it may be seen that the HOMO of the nido-8(vi) geometry has bonding π character while the corresponding nido-8(v) HOMO is essentially nonbonding. This difference accounts for the difference in energies.

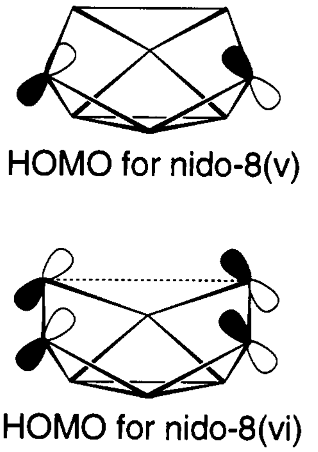

Figure 4. HOMO of the nido-8(v) and nido-8(vi) geometries. Only the principal characters of the boron orbitals are shown in this figure. Not shown are boron orbitals with comparatively small coefficients and all hydrogen orbital contributions.

Table I. Comparison of Bond Lengths (Å) of Theoretically Optimized $C_4B_8H_{12}$ and the Experimentally Determined $C_4B_8H_8(CH_3)_4$ Nido-12(iv + iv) Structures

bond	theory	expt[a]	bond	theory	expt[a]
C2–C3	1.40	1.47 (4)	B5–B9	1.79	1.70 (1)
C3–C7	1.51	1.53	B5–B10	1.83	1.80
C2–B6	1.57	1.70	B5–B6	1.86	1.79 (1)
B4–B5	1.65	1.76 (8)	B1–B5	1.88	1.80 (4)
B1–C2	1.67	1.69 (3)	B4–C8	1.90	1.71 (2)
B4–B9	1.69	1.79 (4)	B1–B6	1.98	1.80 (4)
B1–C3	1.72	1.66 (4)	C3–B4	2.49	2.15
B1–B4	1.75	1.83 (4)			

[a] For experimental values we report the average of the bonds which should be equal in pure C_2 symmetry. The values in parentheses correspond to the experimental variation of crystallographically inequivalent bonds.

In a similar manner we optimized the geometries of $C_4B_4H_8$, $C_2B_8H_{10}^{2-}$, $C_4B_6H_{10}$, and $C_4B_8H_{12}$. In each case we found that the optimized geometry corresponded to the experimentally known geometries. In the case of $C_2B_8H_{10}^{2-}$ we found two local minima. The first was a nido-10(vi) structure are the latter a nido-10(iv + iv) structure. However, the nido-10(iv + iv) structure in this case was 6 eV/molecule less stable than the more open nido-10(vi) structure. We also found two local minima for the $C_4B_8H_{12}$ stoichiometry. These geometries were the nido-12(iv + iv) and nido-12(vi) forms. Our results indicate that the nido-12(iv + iv) structure is 4 eV lower in energy. This is in sharp contrast to the small measured difference in energy. Our optimized structure may be directly compared to the known X-ray structure for $(CH_3)_4C_4B_8H_8$ (a nido-12(iv + iv) compound). We compare bond distances for this structure in Table I. It may be seen that the agreement between theory and experiment is only qualitatively

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(11) Wolfsberg, M.; Helmholz, L. *J. Chem. Phys.* **1957**, *20*, 83.

(12) Six well established nido-10(vi) clusters are as follows. (a) $B_{10}H_{14}$, $B_{10}H_{13}^-$: Sneddon, L. G.; Huffman, J. C.; Schaeffer, R. O.; Streib, W. E. *Chem. Commun.* **1972**, 474. Siedle, A. R.; Bodner, G. M.; Todd, L. J. *J. Inorg. Nucl. Chem.* **1971**, *33*, 3671. (b) 5,7-$C_2B_8H_{12}$: Garrett, P. M.; Ditta, G. S.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1971**, *93*, 1265. (c) 5,6-$C_2B_8H_{12}$: Rietz, R. R.; Schaeffer, R. *J. Am. Chem. Soc.* **1971**, *93*, 1263. (d) $C_2B_8H_{10}^{2-}$: Stibr, B.; Janousek, Z.; Base, K.; Hermanek, S.; Plesek, J.; Zakharova, I. A. *Collect. Czech. Chem. Commun.* **1984**, *49*, 1891.

Table II. Calculated Bond Distances (Å) for $C_4B_4H_8$, $C_2B_8H_{10}^{2-}$, and $C_4B_6H_{10}$

	$C_4B_4H_8$		
C4–C5	1.33	B1–C7	1.74
B3–C4	1.61	B1–B3	1.90
B1–B2	1.61		
	$C_2B_8H_{10}^{2-}$		
B5–C6	1.49	B1–B5	1.80
B2–C6	1.64	B5–B10	1.82
B1–B2	1.74	B1–B3	1.91
B2–B5	1.78		
	$C_4B_6H_{10}$		
C6–C7	1.46	B2–C7	1.78
B5–C6	1.51	B1–C10	1.79
B2–C6	1.66	B1–B5	1.83
B5–C10	1.73	B2–B5	1.87
B1–B2	1.75	B1–B3	1.92
B1–B4	1.75		

[a] For $C_4B_6H_{10}$ C7 and C10 occupy the sites of B7 and B10 in the $C_2B_8H_{10}^{2-}$ structure (see Figure 2).

correct. We list in Table II the calculated bond distances for $C_4B_4H_8$, $C_2B_8H_{10}^{2-}$, and $C_4B_6H_{10}$. The coordinates for $B_8H_8^{4-}$, $B_{10}H_{10}^{4-}$, $B_{12}H_{12}^{4-}$, $C_4B_4H_8$, $C_2B_8H_{10}^{2-}$, $C_4B_8H_{10}$, and $C_4B_8H_{12}$ are given in the supplementary material which accompanies this article.

Conclusion

In this paper we show that second moment scaled Hückel theory is able to rationalize the structure of $C_4B_4H_8$, $C_2B_8H_{10}^{2-}$, $C_4B_6H_{10}$, and $C_4B_8H_{12}$. We use this same calculational method to predict the structures of the unknown compounds $B_8H_8^{4-}$, $B_{10}H_{10}^{4-}$, and $B_{12}H_{12}^{4-}$. We find that these three compounds should be isostructural with their isoelectronic analogs. Our results further demonstrate the inherent limitations of Wade's rules. While Wade's rules are of course a very important part of our understanding of electron-deficient cluster geometries, they are not able to predict or rationalize the structures of either the nido-8 or nido-12 boranes or carboranes.

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Supplementary Material Available: Tables giving a summary of the optimized geometry data and optimized atomic coordinates (8 pages). Ordering information is given on any current masthead page.