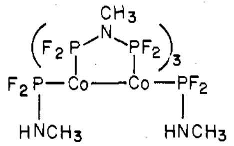
appears to be by way of metal oxidation rather than by a hydrolytic process.

The ligand $CH_3N(PF_2)_2$, a three-atom skeleton, also functions as a bidentate ligand in a bridging or chelating fashion[4-8] and is only a little weaker in π acidity than is $F_2PC_6H_{10}PF_2$;[1] vide supra. At least one noteworthy difference in the chemistry of the two ligands has appeared. While $F_2PC_6H_{10}PF_2$ forms chelates with the group 6B metals only with special precaution,[2a] $CH_3N(PF_2)_2$ has been shown to do so readily.[4] On the other hand displacement of CO from $Fe(CO)_5$[5] by $CH_3N(PF_2)_2$ gives bridged dimetal species while $F_2PC_6H_{10}PF_2$ readily gives chelates. This probably reflects the difference in bite between the three- and four-atom skeletons. It appears, however, to be a subtle factor in that in either Cr(0) or Fe(0) complexes a 90° PMP bond angle is expected.

A second feature of $CH_3N(PF_2)_2$ chemistry, which has not yet been identified for $F_2PC_6H_{10}PF_2$, is apparent hydrolysis of a P–N bond on a monodentate ligand to give a coordinated F_2PNCH_3H molecule (structure V).[7] The equivalent reaction of $F_2PC_6H_{10}PF_2$ would require hydrolysis of a P–C bond, a process much less facile as a rule than that of a P–N bond. The implication is that in comparable circumstances $F_2PC_6H_{10}PF_2$ might be expected to give higher polymers (e.g. VI). This may account in part for the insolubility of product obtained in our preliminary investigation of the reaction with $Co_2(CO)_8$.[36]



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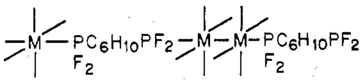

VI

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Registry No. $(PF_2C_6H_{10}PF_2)_3Mo$, 67858-57-5; *fac*-$(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$, 67858-58-6; $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$, 67858-59-7; *cis*-$Fe(CO)_3(PF_2C_6H_{10}PF_2)$, 67858-60-0; $Fe(CO)(PF_2C_6H_{10}PF_2)_2$, 67858-61-1; $Mo(C_6H_5CH_3)_2$, 12131-22-5; $Mn(CO)_5Br$, 14516-54-2; $Fe(CO)_5$, 13463-40-6.

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Molecular Orbital Studies on Large Closo Boron Hydrides

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Wave functions calculated in the partial retention of diatomic differential overlap (PRDDO) approximation are presented for hypothetical closo boron hydrides $B_nH_n^c$ with n ranging from 13 to 24. Some structures are free of distortions due to incomplete occupancy only if $c = 0$, rather than the usual -2. Selected doubly negative and three neutral structures are discussed in terms of charge stability, static reactivity indices, degrees of bonding, overlap populations, and localized molecular orbitals obtained by the Boys criterion. Observations and speculations are made on stability, relations to metallocarborane chemistry, and synthesis.

I. Introduction

Closo boron hydrides[1] and metallocarboranes[2] are among the simplest metal cluster systems. Among the wide variety of known boron hydrides, the closed-polyhedral class is well-known for its high stability.[1] Recent experimental advances in metallocarborane chemistry,[2] especially the observation of polyhedra with up to 14 vertices for a wide variety of metals, have opened the new field of supraicosahedral boron chemistry. Recently, a broad outline was presented[3] for future theoretical studies on closo boron hydrides $B_nH_n^c$ for n ranging

Table I. Bond Lengths and Orbital Exponents

(A) Bond Lengths[a]

bonds	coordination[b]	bond distances, Å
B–B	7–7	1.91
	7–6	1.84
	7–5	1.77
	6–6	1.77
	6–5	1.70
	5–5	1.63
$B-H_t$		1.19

(B) Slater Orbital Exponents

B(1s) = 4.7 B(2s) = B(2p) = 1.3 H(1s) = 1.2

[a] Same as in ref 3. [b] Includes coordination to hydrogen.

from 13 to 24, and in a preliminary communication,[4] we reported some surprising findings of an extensive molecular orbital study of these systems. Among these were the following: (i) the discovery that some structures can have the full polyhedral symmetry only if they are neutral ($c = 0$) and thus contain merely $2n$ framework electrons; (ii) the finding that there is no significant difference between the average stabilities of even- and odd-numbered polyhedra; (iii) the likelihood that 22 vertices represent an upper limit for truly stable structures.

In this paper, detailed results are presented for the theoretical studies carried out on a large set of hypothetical closo $B_nH_n^c$ structures. The computational methods that were used are summarized in section II. In section III, the results are presented and discussed. The average energy per BH unit ($\bar{E} = |E|/n$) is used as the criterion in determining the most stable $B_nH_n^{2-}$ structures. Then, these doubly negative and all neutral structures are discussed in terms of charge stability, static reactivity indices (valencies,[5] atom and group charges, and inner-shell eigenvalues), degrees of bonding,[5] overlap populations, and localized molecular orbitals (LMO's) obtained by the Boys criterion.[6] Observations and speculations are made concerning stability, relations to metallocarborane chemistry, and synthesis. The major conclusions are summarized in section IV.

II. Computational Details

Geometries were constructed as follows: (i) A set of standard bond distances,[3] dependent only on the coordination numbers of the bonded atoms, and listed in Table I(A), was chosen. Due to the great expense involved in the quantum mechanical calculations (see below), these bond lengths were used for all of the structures, and no geometry optimizations were carried out. (ii) An initial guess was made for the boron framework coordinates. (iii) The sum of the squares of the differences between the calculated and desired bond lengths was then minimized by a multidimensional variation procedure.[7] The procedure is applicable only if distances are known from each atom to at least three other atoms of the framework. This is the case for all of the structures examined here. Convergence is rapid, always occurring in less iterations than the number of coordinates in the framework ($3n$ for $B_nH_n^c$). The abundance of minima necessitates a reasonably good initial guess for the larger structures to reach the correct minimum. (iv) To determine the hydrogen coordinates, the following method was used: the extrema of the sum of the squares of the distances from the hydrogen to the neighbors of the atom to which it is attached are found, subject to the constraint of fixed B–H bond length, after all framework atom coordinates have been determined. The technique of Lagrange multipliers easily gives these two normally different extrema. Then, the extremum further away from the center of mass of the framework is chosen as the location of the hydrogen. This procedure therefore systematically considers the local symmetry of the environment around each boron as well as conserving the global symmetry.

These procedures were first tested on the "preferred" $B_nH_n^{2-}$ structures[5c] for $n = 5$–10 and 12, and the energies obtained in the partial retention of diatomic differential overlap (PRDDO)[8] approximation were always at least as low as and, sometimes, especially in cases of low molecular symmetry, considerably lower than the best results previously obtained.[5c]

As high "sphericity" has generally been considered[3] necessary for high stability, a quantity S, which gives a quantitative estimate for the sphericity of a polyhedron, was defined to see if there is a correlation between stability and S. This quantity, which is independent of the overall scale of the polyhedron, can be calculated as follows: A set of points consisting of all of the vertices of the polyhedron and the midpoints of all of its edges are defined. Then, $\langle R\rangle$ and $\langle R^2\rangle$, which are defined as the average distance and squared distance, respectively, from the center of mass of the polyhedron to this set of points are calculated. Then, $S = 1.0 - ((\langle R^2\rangle - \langle R\rangle^2)^{1/2}/\langle R\rangle)$. The S values for the limiting case of a sphere (1.0) and the five Platonic solids, the dodecahedron (0.966), the icosahedron (0.924), the cube (0.899), the octahedron (0.828), and the tetrahedron (0.723), verify that S is indeed a quantitative measure of sphericity.

The techniques mentioned above were used to compute a set of coordinates for each structure given in ref 3, as well as several others not considered there. The structures considered have at least a twofold symmetry element, consistent with the observation[9a] that all stable boron hydrides except $B_{16}H_{20}$[9b] have at least that degree of symmetry. Then, the PRDDO approximation, with the minimum basis set exponents given in Table I(B), was used on all of these structures, except XIIc of ref 3 which appeared highly implausible. The 15 structures chosen on the basis of these calculations for more detailed examination are depicted in Figure 1. For these selected structures, LMO's were obtained using the Boys[6] criterion. Twelve to fifty iterative cycles were carried out, giving reasonable convergence. The second-derivative test of Switkes, Lipscomb, and Newton[10] was used to verify that in each case the LMO's had converged to a true maximum on the LMO hypersurface and not merely to a saddle point. The results obtained provide a general idea of what to expect when LMO's are calculated for these large, and often highly symmetric, closo structures. While the existence of symmetry-nonequivalent sets of LMO's for many of these structures cannot be ruled out, due to the large expenditure of computing time for these calculations, no further localizations could be attempted, except for $B_{14}H_{14}^{2-}$ (D_{6d}).

III. Results and Discussion

First, a series of computations on alternative structures for $n = 5$–10 verified that within the limits of the theory (minimum basis sets, no geometry optimizations) the structures previously considered to be the best (trigonal bipyramid, octahedron, pentagonal bipyramid, eight-vertex dodecahedron, tricapped trigonal prism, and bicapped square antiprism) are indeed so. The alternative structures considered included (i) the square pyramid for $n = 5$, (ii) the trigonal prism for $n = 6$, (iii) the monocapped trigonal prism for $n = 7$, (iv) the bicapped trigonal prism (second best), the square antiprism, and the cube for $n = 8$, (v) the monocapped square antiprism (second best) and the monocapped cube for $n = 9$, and (vi) the tetradecahedron (second best), the pentagonal antiprism, and the two "isomers" of the "bicapped cube" for $n = 10$.

In general, closo boron hydrides are expected to be doubly negative, and topological arguments have been advanced[11] to explain this trend. However, these may break down in cases of special symmetry degeneracy, such as the hypothetical tetrahedral B_4H_4 where the resulting canonical orbitals only

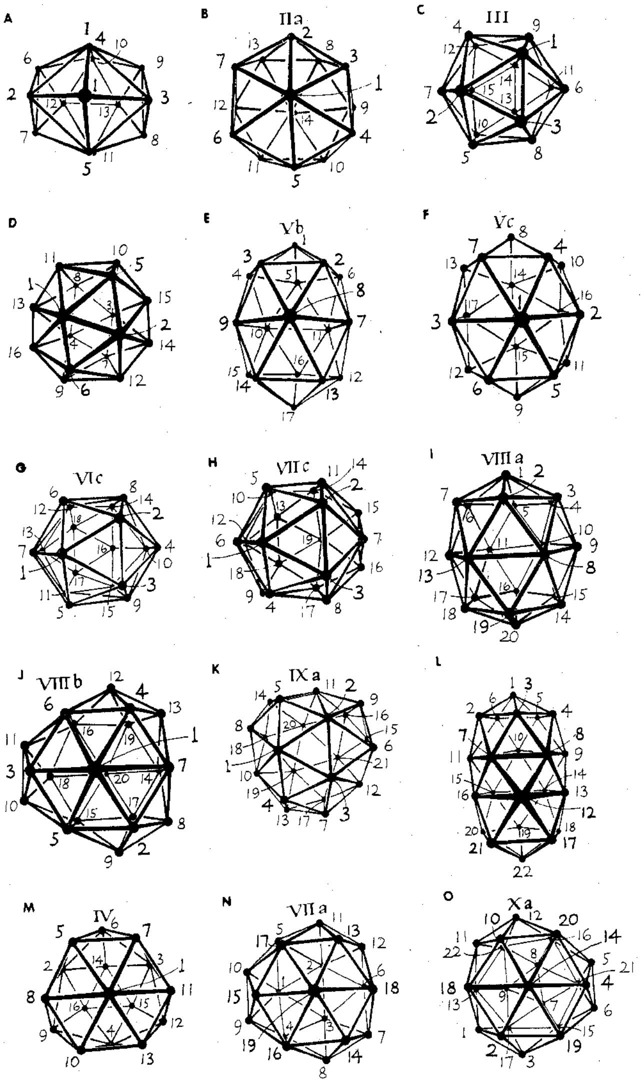

Figure 1. The 15 $B_nH_n^c$ structures selected for detailed discussion on the basis of results of PRDDO computations [the notation is (n,c; point group)]: (A) (13,−2; C_{2v}); (B) (14,−2; D_{6d}); (C) (15,−2; D_{3h}); (D) (16,−2; D_2); (E) (17,−2; D_{5h}); (F) (17,−2; C_{2v}); (G) (18,−2; D_{3d}); (H) (19,−2; C_s); (I) (20,−2; D_{6h}); (J) (20,−2; D_{3h}); (K) (21,−2; D_3); (L) (22,−2; D_{5d}); (M) (16,0; T_d); (N) (19,0; C_{3v}); (O) (22,0; T_d). Structures D and L were not considered in ref 3.

have the full symmetry of the structure if the molecule is neutral. Three such cases were discovered for the large closo structures, namely, $B_{16}H_{16}$ (T_d), $B_{19}H_{19}$ (C_{3v}), and $B_{22}H_{22}$ (T_d), which are free from distortions due to incomplete occupancy of symmetry orbitals only if treated as neutral structures with $2n$ framework electrons. However, any structure which belongs to a point group (such as C_{2v}) which has no degenerate (E or T) representations is automatically free of such distortions and the results derived for any value of c will have the full molecular symmetry. In some such cases (when the gap between the highest occupied and lowest unoccupied molecular orbital energies, $\Delta E = |E_{\text{HOMO}} - E_{\text{LUMO}}|$, is small; see below), the possibility that the structure is really neutral can only be investigated by carrying out further computations and comparisons. Due to the great computational expense involved, this possibility was not further pursued.

The criterion used for choosing the most stable $B_nH_n^{2-}$ structures was average energy per BH unit ($\bar{E} = |E|/n$), which enables comparisons to be made immediately between all of the structures. The charge-stability criterion was ΔE (defined above). This was used in preference to E_{HOMO} which has been related to the susceptibility of the closo dianions to oxidative processes,[12] because the sign of E_{HOMO} shows an unrealistic dependence on n for $5 \leq n \leq 12$, being positive at the minimum basis set level for all $B_nH_n^{2-}$ with $5 \leq n \leq 11$.[5c] On the other hand, ΔE is somewhat more independent of the expanding size of the polyhedron as n increases and may represent charge stabilities more accurately.

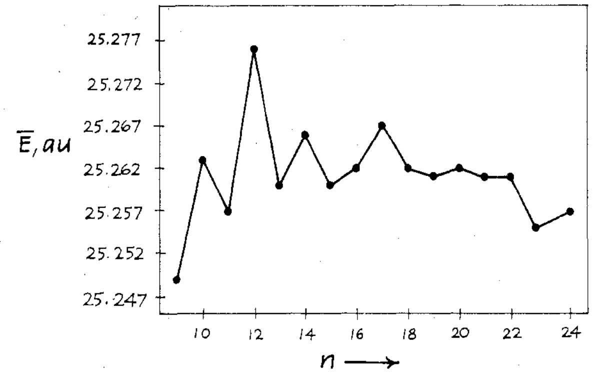

Figure 2. $\bar{E}$ (|energy| per BH unit), as a function of n for the preferred $B_nH_n^{2-}$ structures: (9;0,6,3; D_{3h}); (10;0,8,2; D_{4d}); (11;1,8,2; C_{2v}); (12;0,12,0; I_h); (13;2,10,1; C_{2v}; I); (14;2,12,0; D_{6d}; IIa); (15;3,12,0; D_{3h}; III); (16;4,12,0; D_2); (17;5,12,0; D_{5h}; Vb); (18;6,12,0; D_{3d}; VIc); (19;7,12,0; C_s; VIIc); (20;8,12,0; D_{3h}; VIIIb); (21;9,12,0; D_3; IXa); (22;10,12,0; D_{5d}); (23;11,12,0; D_3; XIa) and (23;11,12,0; C_{2v}; XIb); (24;12,12,0; T; XIIa). The notation is (n;n_7,n_6,n_5; point group; label in ref 3 where applicable), where n_7, n_6, and n_5 are the numbers of seven-, six-, and five-coordinate borons, including a terminal B–H bond for each.

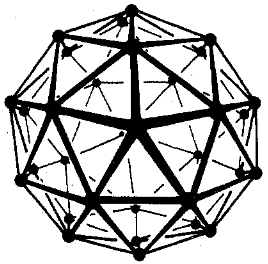

Figure 3. The 32-vertex structure of I_h symmetry.

Table II gives the values of $\bar{E}$ and ΔE for all the structures for which PRDDO computations were carried out. It can be seen that for all three values of n (16, 19, 22) for which a neutral structure was found, a highly stable doubly negative structure was also discovered. Another trend emerging from this table is that the orderings of $\bar{E}$ and ΔE tend to be similar. The only major exception to this is the case of $n = 18$, where the trends in $\bar{E}$ and ΔE are in opposite directions. The values of ΔE for many structures fall between 0.35 and 0.48 au, clearly showing high charge stability.

The 15 structures to be discussed in more detail are illustrated in Figure 1.

Figure 2 shows a plot of $\bar{E}$ vs. n for the most stable doubly negative structures for $9 \leq n \leq 24$. Two observations can immediately be made from this plot: (i) Whereas for n = 9–12, $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are remarkably more stable than $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$,[3,13] there is no significant difference in the overall stabilities of the even and odd n large closo doubly negative structures. In particular, the two highest peaks in $\bar{E}$ are at n = 17 and 14, respectively.[4] (ii) It seems probable that no closo boron hydride structure with great stability will be found for $n > 22$.[4] A subtle balance of many factors is involved in the stability trends as n increases,[3,14] not ruling out such an outcome. However, because the PRDDO program can only compute structures with up to 150 minimum basis set orbitals, it was not possible to check this hypothesis in more detail. There are $n > 24$ structures of high symmetry which cannot be ruled out without such extra calculations. One such

Table II. PRDDO $\bar{E}$ ($|E|/n$) and ΔE ($|E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}}|$) for $B_nH_n{}^c$

structure[a]	$\bar{E}$, au	ΔE, au
(A) Doubly Negative Structures ($c = -2$)		
13(C_{2v}, I)[b]	25.260	0.407
14(D_{6d}, IIa)[b]	25.266	0.477
14(O_h, IIb)	25.218	0.200
15(D_{3h}, III)[b]	25.260	0.341
16(D_2)[b]	25.262	0.381
16(D_{2d})	25.247	0.354
16(D_{2h})	25.241	0.210
17(C_{2v}, Va)	25.257	0.328
17(D_{5h}, Vb)[b]	25.267	0.444
17(C_{2v}, Vc)[b]	25.261	0.388
18(D_3, VIa)	25.256	0.402
18(D_{3h}, VIb)	25.253	0.440
18(D_{3d}, VIc)[b]	25.262	0.292
18(O_h, VId)	25.242	0.408
19(C_s, VIIb)	25.254	0.330
19(C_s, VIIc)[b]	25.261	0.343
20(D_{6h}, VIIIa)[b]	25.259	0.392
20(D_{3h}, VIIIb)[b]	25.262	0.367
20(D_{2d}, VIIIc)	25.256	0.241
21(D_3, IXa)[b]	25.261	0.407
21(C_{2v}, IXb)	25.255	0.283
21(D_{3h}, IXc)	25.251	0.383
22(D_{5d}, Xb)	25.251	0.340
22(C_{2v}, Xc)	25.256	0.368
22(D_{5d})[b]	25.261	0.397
23(D_3, XIa)	25.255	0.331
23(C_{2v}, XIb)	25.255	0.292
23(C_{2v}, XIc)	25.250	0.275
24(T, XIIa)	25.257	0.384
24(D_2, XIIb)	25.254	0.219
24(D_{3h}, XIId)	25.247	0.328
24(D_{3d}, XIIe)	25.249	0.368
24(D_{3d}, XIIf)	25.252	0.236
(B) Neutral Structures ($c = 0$)		
16(T_d, IV)[b]	25.244	0.300
19(C_{3v}, VIIa)[b]	25.243	0.293
22(T_d, Xa)[b]	25.249	0.291

[a] Notation: n(symmetry, label in ref 3 where applicable). [b] Selected for further detailed discussion on the basis of the results illustrated in this table.

structure for $n = 32$, shown in Figure 3, is an omnicapped dodecahedron of I_h symmetry, containing 20 seven-coordinate and 12 six-coordinate borons.

The values of the sphericity (S), defined and shown in the previous section to indicate quantitatively how "spherical" a polyhedron is, were found to have no correlation with stability as given by $\bar{E}$. This demonstrates that while a reasonably "spherical" shape is desirable and extremely unsymmetrical structures may not be favored, very high sphericity is not as necessary as was previously[3] thought. The criterion of overall spherical shape can only be used to eliminate some extremely unreasonable structures.

Each closo structure has a number of nido and arachno derivatives.[15] Some of these compounds which are formally related to the closo structures may be stable. There are also a large number of possible carboranes. In the most stable of these carboranes the carbons are expected[16] to occupy low-coordinate positions as far apart from each other as possible. Another factor which must be considered in deciding which sites are the most likely for occupation by carbon atoms is the atomic charge (see below); the greater electronegativity of carbon causes structures in which the carbon atoms occupy more negative sites to be more stable. Except for the preferred $B_{13}H_{13}{}^{2-}$ and $B_{22}H_{22}{}^{2-}$ structures, the most negative boron is always seven-coordinate (see Table IV). Thus, the most negative six-coordinate sites for these two structures are especially strong candidates for replacement by carbon. In other cases, the low coordination number criterion is expected to dominate over the most negative site criterion.

A set of large closo $Be_2B_nH_{n+2}{}^{2-}$ structures can be written by the formal isoelectronic replacement of B by Be^- in neutral B_nH_n. In contrast to the C atoms in carboranes, the Be atoms are likely to occupy high-coordinate vertices and to be as close to each other as possible. In this context, the synthesis of two icosahedral closo structures,[17a,b] 3-BeL-1,2-$B_9C_2H_{11}$ (L = $N(CH_3)_3$ or $O(C_2H_5)_2$), and a set of pentagonal pyramidal nido compounds,[17c,d] $B_5H_{10}BeX$ (X = BH_4, B_5H_{10}, Cl, Br, CH_3, or C_5H_5), which contain direct B–Be bonds, should be noted. Another structure[17b] has been tentatively identified as a [3-Be-1,2-$B_9C_2H_{11}$]$_n$ polymer composed of closo icosahedral monomers with repeating units linked to each other by Be–H–B bridges. The trend followed by the observed average bond lengths (R) in beryllaboranes[17d] and carboranes[17e] is $R(\mathrm{B{-}Be}) > R(\mathrm{B{-}B}) > R(\mathrm{B{-}C}) > R(\mathrm{C{-}C})$ and can be theoretically justified by the sizes of the covalent radii (r) for these elements, which follow the ordering $r(\mathrm{Be}) > r(\mathrm{B}) > r(\mathrm{C})$. Thus, a closo carborane derived by the $B^- \rightarrow C$ isoelectronic replacement is expected to occupy a smaller volume than its "parent" compound and a closo beryllaborane obtained by the $B \rightarrow Be^-$ replacement is likely to occupy a larger volume than its "parent" compound.

Table III. Energy Analysis for Selected $B_nH_n{}^c$ Structures

n(sym, label)[a]	energy[b]	NRE[c]	KE[d]	NAE[e]	ERE[f]	virial[g]
(A) Doubly Negative Structures ($c = -2$)						
13(C_{2v}, a)	−328.384	606.146	327.970	−1990.657	728.156	1.001
14(D_{6d}, b)	−353.719	688.175	353.058	−2213.514	818.562	1.002
15(D_{3h}, c)	−378.907	772.744	378.149	−2441.380	911.579	1.002
16(D_2, d)	−404.191	859.850	403.190	−2674.270	1007.038	1.002
17(D_{5h}, e)	−429.541	947.673	428.027	−2908.116	1102.875	1.004
17(C_{2v}, f)	−429.442	951.120	428.240	−2915.489	1106.687	1.003
18(D_{3d}, g)	−454.710	1042.481	453.171	−3156.558	1206.195	1.003
19(C_s, h)	−479.954	1143.125	478.270	−3416.582	1315.233	1.004
20(D_{6h}, i)	−505.189	1245.881	503.389	−3681.069	1426.609	1.004
20(D_{3h}, j)	−505.246	1243.747	503.233	−3676.235	1424.008	1.004
21(D_3, k)	−530.471	1348.433	528.356	−3944.204	1536.944	1.004
22(D_{5d}, l)	−555.752	1441.322	553.469	−4188.018	1637.475	1.004
(B) Neutral Structures ($c = 0$)						
16(T_d, m)	−403.896	861.727	402.025	−2641.958	974.309	1.005
19(C_{3v}, n)	−479.624	1145.793	477.229	−3382.431	1279.786	1.005
22(T_d, o)	−555.481	1456.925	551.955	−4176.337	1611.976	1.006

[a] The labels correspond to the ordering in Figure 1. [b] All energies are in atomic units; 1 au = 627.5 kcal/mol. Total molecular energy. [c] Nuclear repulsion energy. [d] Kinetic energy. [e] Nuclear attraction energy. [f] Electron repulsion energy. [g] Value of the virial ratio ($-E/T$).

Table IV. Valencies and Charges for Selected $B_nH_n{}^c$ Structures[a]

atom[b]	valency	charge[c]	GC[d]	ISE[e]
(A) Doubly Negative Structures ($c = -2$)				
13(C_{2v}, a)				
1(5,1)	3.612	−0.120	−0.086	−7.320
2(6,2)	3.768	−0.231	−0.194	−7.293
4(7,2)	3.746	−0.153	−0.126	−7.316
6(6,4)	3.764	−0.188	−0.163	−7.301
10(6,2)	3.744	−0.170	−0.147	−7.308
12(6,2)	3.761	−0.188	−0.165	−7.301
14(D_{6d}, b)				
1(7,2)	3.772	−0.193	−0.175	−7.312
2(6,12)	3.743	−0.161	−0.138	−7.320
15(D_{3h}, c)				
1(6,6)	3.758	−0.175	−0.151	−7.324
4(6,6)	3.713	−0.133	−0.101	−7.341
7(7,3)	3.763	−0.177	−0.163	−7.323
16(D_2, d)				
1(7,4)	3.763	−0.176	−0.150	−7.339
5(6,4)	3.719	−0.130	−0.109	−7.345
9(6,4)	3.742	−0.159	−0.128	−7.339
13(6,4)	3.731	−0.147	−0.113	−7.347
17(D_{5h}, e)				
1(6,2)	3.742	−0.147	−0.121	−7.352
2(6,10)	3.730	−0.137	−0.114	−7.356
7(7,5)	3.754	−0.160	−0.123	−7.362
17(C_{2v}, f)				
1(7,1)	3.759	−0.176	−0.136	−7.356
2(7,2)	3.758	−0.162	−0.138	−7.350
4(6,4)	3.729	−0.134	−0.113	−7.353
8(6,2)	3.751	−0.163	−0.134	−7.346
10(6,4)	3.721	−0.137	−0.102	−7.355
14(7,2)	3.772	−0.186	−0.164	−7.339
16(6,2)	3.691	−0.098	−0.067	−7.368
18(D_{3d}, g)				
1(6,6)	3.729	−0.144	−0.117	−7.363
4(6,6)	3.716	−0.131	−0.106	−7.366
7(7,6)	3.758	−0.160	−0.111	−7.364
19(C_s, h)				
1(6,1)	3.723	−0.130	−0.101	−7.373
2(6,2)	3.719	−0.121	−0.098	−7.373
4(6,2)	3.711	−0.103	−0.080	−7.381
6(7,1)	3.762	−0.163	−0.117	−7.373
7(7,1)	3.768	−0.176	−0.140	−7.367
8(7,2)	3.765	−0.174	−0.138	−7.366
10(7,2)	3.763	−0.168	−0.138	−7.369
(A) (*Continued*)				
19(C_s, h)				
12(6,1)	3.712	−0.115	−0.094	−7.376
13(6,2)	3.712	−0.124	−0.093	−7.373
15(6,2)	3.709	−0.110	−0.085	−7.373
17(6,2)	3.698	−0.114	−0.084	−7.374
19(7,1)	3.753	−0.149	−0.135	−7.356
20(D_{6h}, i)				
1(7,2)	3.750	−0.143	−0.129	−7.363
2(6,12)	3.698	−0.099	−0.072	−7.384
8(7,6)	3.772	−0.181	−0.147	−7.367
20(D_{3h}, j)				
1(7,2)	3.756	−0.154	−0.116	−7.383
2(6,6)	3.714	−0.109	−0.084	−7.384
5(7,6)	3.753	−0.162	−0.127	−7.377
8(6,6)	3.712	−0.109	−0.084	−7.384
21(D_3, k)				
1(7,6)	3.753	−0.155	−0.117	−7.387
4(6,6)	3.699	−0.084	−0.061	−7.397
7(6,6)	3.726	−0.124	−0.097	−7.383
10(7,3)	3.751	−0.158	−0.117	−7.384
22(D_{5d}, l)				
1(6,2)	3.737	−0.141	−0.107	−7.386
2(6,10)	3.732	−0.140	−0.114	−7.385
7(7,10)	3.728	−0.116	−0.065	−7.414
(B) Neutral Structures ($c = 0$)				
16(T_d, m)				
1(7,4)	3.772	−0.241	−0.180	−7.678
5(6,12)	3.624	−0.027	+0.060	−7.740
19(C_{3v}, n)				
1(7,3)	3.741	−0.163	−0.088	−7.691
4(6,3)	3.604	+0.002	+0.095	−7.744
7(6,6)	3.665	−0.079	+0.013	−7.724
13(6,3)	3.587	+0.023	+0.096	−7.750
16(7,3)	3.760	−0.194	−0.105	−7.698
19(7,1)	3.734	−0.163	−0.073	−7.721
22(T_d, o)				
1(6,12)	3.621	−0.011	+0.061	−7.741
13(7,4)	3.724	−0.138	−0.059	−7.716
17(7,6)	3.761	−0.186	−0.083	−7.703

[a] The labels for the structures correspond to the ordering in Figure 1. [b] Notation: $k(l,m)$, where k is the kth boron atom, l is its total coordination number, and m is the total number of symmetry-equivalent boron atoms of that type. [c] Atomic charge in electrons. [d] Group charge in electrons. The difference between the atomic and group charge is the hydrogen atom charge. [e] Inner-shell eigenvalue in atomic units.

A series of large, neutral closo metallocarboranes can also be constructed conceptually from the neutral boron hydrides by the replacement of BH units at vertices of high connectivity by other structural moieties each of which contributes two electrons to the framework bonding. Among these, $(Co(\pi\text{-}C_5H_5))_4B_{12}H_{12}$ and $(Fe(CO)_3)_4B_{12}H_{12}$ are strong candidates for synthesis. These two examples have T_d symmetry like the hypothetical parent neutral closo boron hydride structure.[4]

The energy partitioning and virial ratios are given in Table III for the 15 selected structures. The virial ratios are always between 1.001 and 1.006, indicating that the virial theorem is satisfied surprisingly well.

An inherent limitation in the choice of the most stable structures by any purely static quantum mechanical computation scheme, and one which is especially important for these large and complicated polyhedra, is that while the calculations may give an idea of the relative energetic stabilities, they provide no information as to which structures are easier to synthesize. It is conceivable that a structure with smaller $\bar{E}$ will be synthesized more readily in the laboratory. Seen in this light, the following remarks are in order: (i) The fact that there are precedents for the $n = 13$ and 14 structures in metallocarboranes,[2,3] and for the $n = 14$, 15, and 16 (T_d) structures in metal alloys,[3,18] shows that they are among the stronger candidates for synthesis. (ii) Studies of thermal polyhedral rearrangements in 14-vertex metallotetracarboranes[2f,g] have revealed the presence of "quasi-nido" isomers with open faces, which can be used to generate 15-vertex metallotetracarboranes by insertion of a metal–ligand group such as $Co(\pi\text{-}C_5H_5)$ into the open pentagonal face. It might be possible to continue this process even further. (iii) It might be possible to obtain $B_{17}H_{17}{}^{2-}$ from $B_{14}H_{20}$,[3,19] which has cis-fused units with open faces, by base-promoted condensation similar to a well-known synthesis of $B_{12}H_{12}{}^{2-}$.[20] (iv) Tetracarbaboranes having the polyhedral vertex arrangements of $B_{18}H_{18}{}^{2-}$ (D_3) (the second most stable structure for $n = 18$) and $B_{22}H_{22}{}^{2-}$ (prolate D_{5d}, preferred for $n = 22$) might be obtained by joining the two halves of a bis(dicarbazapyl)- and

Table V. Degrees of Bonding and Overlap Populations for Selected $B_nH_n{}^c$ Structures[a]

CT[b]	bond[c]	DOB[d]	OP[e]
	(A) Doubly Negative Structures ($c = -2$)		
	13(C_{2v}, a)		
7–6	5–2	0.429	0.319
	5–11	0.481	0.432
	5–7	0.478	0.463
7–5	5–1	0.426	0.319
6–6	8–3	0.535	0.447
	7–6	0.544	0.414
	11–8	0.564	0.478
	12–6	0.558	0.480
	12–10	0.520	0.430
	13–12	0.552	0.490
6–5	2–1	0.775	0.625
7–H_t	5–H_t	0.952	0.871
6–H_t	2–H_t	0.955	0.862
	6–H_t	0.974	0.871
	10–H_t	0.974	0.874
	12–H_t	0.979	0.872
5–H_t	1–H_t	0.969	0.856
	14(D_{6d}, b)		
7–6	1–2	0.457	0.400
6–6	3–2	0.570	0.505
	8–2	0.532	0.419
7–H_t	1–H_t	0.977	0.891
6–H_t	2–H_t	0.972	0.872
	15(D_{3h}, c)		
7–6	9–1	0.473	0.446
	9–4	0.447	0.373
6–6	2–1	0.566	0.463
	4–1	0.531	0.443
	10–5	0.640	0.526
7–H_t	7–H_t	0.975	0.894
6–H_t	1–H_t	0.975	0.875
	4–H_t	0.963	0.875
	16(D_2, d)		
7–7	2–1	0.435	0.417
7–6	1–5	0.444	0.383
	1–6	0.472	0.418
	1–11	0.459	0.394
	1–13	0.460	0.372
	1–16	0.455	0.360
6–6	9–7	0.595	0.522
	14–7	0.591	0.491
	12–7	0.495	0.374
	12–9	0.558	0.476
	16–9	0.545	0.475
	16–13	0.577	0.482
7–H_t	1–H_t	0.962	0.891
6–H_t	5–H_t	0.974	0.880
	9–H_t	0.970	0.871
	13–H_t	0.962	0.872
	17(D_{5h}, e)		
7–6	7–2	0.461	0.377
	7–8	0.439	0.378
6–6	2–1	0.534	0.453
	3–2	0.578	0.487
7–H_t	7–H_t	0.950	0.891
6–H_t	1–H_t	0.975	0.871
	2–H_t	0.977	0.880
	17(C_{2v}, f)		
7–7	2–1	0.438	0.395
	15–14	0.439	0.452
7–6	2–4	0.464	0.411
	2–10	0.462	0.388
	2–16	0.439	0.340
	1–4	0.460	0.376
	14–8	0.496	0.453
	14–16	0.452	0.376
6–6	10–4	0.547	0.458
	7–4	0.603	0.524
	8–4	0.537	0.431
	16–10	0.607	0.512
	10–8	0.546	0.465
	17(C_{2v}, f)		
6–6	14–10	0.445	0.345
7–H_t	1–H_t	0.950	0.888
	2–H_t	0.959	0.888
	14–H_t	0.965	0.889
6–H_t	4–H_t	0.976	0.881
	8–H_t	0.971	0.872
	10–H_t	0.962	0.870
	16–H_t	0.961	0.876
	18(D_{3d}, g)		
7–7	12–7	0.399	0.339
7–6	7–1	0.489	0.422
	7–5	0.510	0.426
	12–6	0.419	0.334
6–6	2–1	0.500	0.422
	5–1	0.563	0.467
7–H_t	7–H_t	0.936	0.875
6–H_t	1–H_t	0.975	0.875
	4–H_t	0.973	0.887
	19(C_s, h)		
7–7	10–6	0.412	0.349
	11–7	0.456	0.420
	11–10	0.432	0.395
7–6	6–1	0.477	0.403
	7–2	0.448	0.359
	11–2	0.469	0.392
	6–4	0.503	0.424
	8–4	0.478	0.378
	9–4	0.442	0.356
	6–12	0.417	0.331
	7–16	0.458	0.361
	11–15	0.450	0.347
	11–14	0.434	0.344
	10–12	0.509	0.445
	10–13	0.465	0.372
	10–14	0.464	0.376
	19–13	0.451	0.400
	19–17	0.447	0.373
	19–16	0.463	0.410
6–6	2–1	0.512	0.422
	4–1	0.556	0.478
	3–2	0.582	0.508
	5–2	0.576	0.482
	13–12	0.567	0.453
	18–13	0.501	0.427
	14–13	0.594	0.499
	17–16	0.618	0.523
	16–15	0.570	0.486
7–H_t	6–H_t	0.935	0.875
	7–H_t	0.950	0.888
	10–H_t	0.946	0.881
	11–H_t	0.949	0.886
	19–H_t	0.971	0.890
6–H_t	1–H_t	0.972	0.874
	2–H_t	0.976	0.881
	4–H_t	0.973	0.885
	12–H_t	0.974	0.886
	13–H_t	0.967	0.874
	16–H_t	0.969	0.881
	17–H_t	0.965	0.879
	20(D_{6h}, i)		
7–7	9–8	0.468	0.455
7–6	1–2	0.453	0.393
	8–2	0.448	0.345
6–6	3–2	0.595	0.513
7–H_t	1–H_t	0.971	0.891
	8–H_t	0.950	0.885
6–H_t	2–H_t	0.968	0.880
	20(D_{3h}, j)		
7–7	5–1	0.432	0.364
	15–5	0.423	0.347
7–6	5–2	0.468	0.382

Table V. (*Continued*)

CT[b]	bond[c]	DOB[d]	OP[e]
(A) Doubly Negative Structures ($c = -2$) (*Continued*)			
	20(D_{3h}, j)		
7-6	1-2	0.471	0.388
	5-9	0.457	0.380
6-6	8-2	0.579	0.488
	9-8	0.513	0.430
7-H_t	1-H_t	0.952	0.890
	5-H_t	0.948	0.886
6-H_t	2-H_t	0.972	0.885
	8-H_t	0.975	0.881
	21(D_3, k)		
7-7	2-1	0.431	0.362
	10-1	0.425	0.346
7-6	1-4	0.473	0.387
	1-8	0.468	0.391
	10-4	0.465	0.380
	12-7	0.462	0.385
6-6	13-4	0.563	0.479
	21(D_3, k)		
6-6	7-4	0.568	0.488
	13-7	0.534	0.433
7-H_t	1-H_t	0.946	0.891
	12-H_t	0.940	0.883
6-H_t	4-H_t	0.973	0.886
	7-H_t	0.973	0.880
	22(D_{5d}, l)		
7-7	8-7	0.460	0.401
	12-7	0.390	0.290
7-6	7-2	0.477	0.393
6-6	2-1	0.531	0.457
	3-2	0.559	0.461
7-H_t	7-H_t	0.941	0.898
6-H_t	1-H_t	0.971	0.868
	2-H_t	0.975	0.879
(B) Neutral Structures ($c = 0$)			
	16(T_d, m)		
7-6	1-5	0.457	0.392
6-6	7-5	0.518	0.420
	11-7	0.526	0.425
7-H_t	1-H_t	0.968	0.888
	5-H_t	0.955	0.868
	19(C_{3v}, n)		
7-7	2-1	0.434	0.398
	19-16	0.450	0.373
7-6	1-4	0.460	0.386
	1-9	0.450	0.347
	16-4	0.428	0.319
	18-7	0.474	0.397
	16-14	0.456	0.411
	19-14	0.443	0.365
6-6	8-7	0.546	0.475
	8-4	0.541	0.456
	14-7	0.512	0.406
	19(C_{3v}, n)		
7-H_t	1-H_t	0.936	0.884
	16-H_t	0.913	0.859
	19-H_t	0.939	0.887
6-H_t	4-H_t	0.942	0.863
	7-H_t	0.948	0.861
	14-H_t	0.966	0.879
	22(T_d, o)		
7-7	18-14	0.442	0.355
7-6	18-1	0.461	0.381
	13-1	0.447	0.371
6-6	2-1	0.532	0.440
7-H_t	14-H_t	0.943	0.886
	18-H_t	0.887	0.850
6-H_t	1-H_t	0.964	0.881

[a] The labels for the structures correspond to the ordering in Figure 1. [b] Coordination type. For the borons, coordination to a terminal hydrogen is included. Terminal hydrogens are simply indicated by H_t. [c] When the coordination numbers of two bonded atoms differ, the one with the higher coordination number is written first. [d] Degree of bonding. [e] Overlap population.

symmetrical bis(dicarbollyl)metal sandwich compound, respectively, via oxidative removal of the metal. A precedent[2f] exists for this type of reaction.

Static reactivity indices have often been used to predict and/or rationalize trends in reactivity. These results must be treated with caution, primarily because they are only reliable if the transition state is quite similar to the ground state and hence do not take the possibility of complex mechanisms into account and secondly because they do not provide much information about steric effects. Whereas there are no experimental data for $n \geq 13$, the extent of agreement with experimental trends[21] for boron hydrides and carboranes with $n \leq 12$, especially when the above-mentioned inherent limitations of the method are considered, makes it worthwhile to examine the case of $n \geq 13$ in detail.

Among the most commonly used static reactivity indices are valencies,[5a] atomic and group charges, and inner-shell eigenvalues, the values of which are listed in Table IV for the 15 structures of interest. The valency of an atom in a molecule is defined as the sum of the degrees of bonding[5a] of that atom to all the others and thus provides a general indication of how extensively that atom is involved in the molecular bonding. The atomic and group charges and inner-shell eigenvalues, on the other hand, are of greater importance for these polyhedral "superaromatic" structures, as they point out more specifically the susceptibility toward electrophilic and nucleophilic substitution reactions, which constitute a large fraction of their expected (and for $n = 5$–12, known[22]) chemistries. In general, electrophilic attack is more likely at negative atoms (most positive inner-shell eigenvalue) or groups, and nucleophilic attack is more likely at positive atoms (most negative inner-shell eigenvalue) or groups.

The following trends are found in Table IV for the doubly negative structures: (i) With increasing coordination number, valency and inner-shell eigenvalue increase, while atomic and group charges decrease. However, many exceptions can be found. (ii) For a given structure, the orderings of the sites according to these criteria parallel each other quite well. (iii) The inner shell eigenvalue criterion has the largest number of exceptions to these general trends. (iv) B is always negatively charged, while H is always positively charged. (v) As is to be expected, the magnitude of negative charge carried by a boron or B–H_t group on the average decreases with increasing n, as the "extra" charge becomes distributed over more centers.

For the neutral structures Table IV indicated the following: (i) With increasing coordination number, valency and inner-shell eigenvalue increase, while atomic and group charges decrease. The trends here are much more obvious, the only exception occurring in the ordering of inner-shell eigenvalues for $B_{19}H_{19}$ (C_{3v}). (ii) Thus, for a given structure, the orderings of the sites by the four criteria very clearly parallel each other. (iii) H is always positively charged. (iv) The seven-coordinate borons are, on the average, as negative as those in the doubly negative structures. (v) However, the six-coordinate borons are much less negative for the neutral structures. In fact, some

Table VI. Boys Localized Orbitals for Selected $B_nH_n^c$ Structures[a]

LMO	populations			% s[b]			
A-B-C	A	B	C	A	B	C	% *d*
(A) Doubly Negative Structures ($c = -2$)							
13(C_{2v}, a)							
1-H_t	1.06	0.95		37.7			7.49
2-H_t	1.07	0.94		36.8			9.38
4-H_t	1.10	0.95		27.2			14.02
6-H_t	1.07	0.96		35.6			9.69
10-H_t	1.07	0.96		37.0			9.77
12-H_t	1.07	0.96		34.7			9.49
1-3	0.86	0.84		22.5	18.6		20.45
2-6-7	0.79	0.64	0.46	26.7	24.4	23.4	23.04
6-10-4	0.69	0.68	0.61	27.7	24.1	30.2	23.46
12-10-13	0.73	0.69	0.53	25.8	27.1	29.0	24.92
5-11-7	0.71	0.66	0.58	28.2	23.7	29.0	24.06
2-1-4	0.76	0.63	0.58	19.1	25.4	27.9	24.52
11-8-13	0.79	0.69	0.43	22.7	24.9	23.9	23.06
8-3-5	0.68	0.68	0.62	28.7	22.9	33.3	25.28
12-6-7	0.75	0.67	0.58	25.2	24.4	26.0	23.31
9-3-4	0.72	0.70	0.54	27.2	23.9	33.6	25.78
10-9-13	0.78	0.75	0.27	21.5	24.5	20.5	24.86
9-8-13	0.73	0.69	0.58	22.8	22.8	27.1	24.40
12-11 (delocalized toward 13; to lesser extent also 6,7,10)							
5-2 (delocalized toward 4,7)							
14(D_{6d}, b)							
1-H_t	1.07	0.96		35.7			9.71
2-H_t	1.10	0.97		26.3			13.27
13-12-14	0.69	0.69	0.58	27.0	27.0	30.0	23.98
(also, 9-8-14 and 11-10-14)							
3-8-2	0.75	0.66	0.57	25.9	24.7	28.5	24.96
(also, 3-9-4, 7-12-6, 5-10-4, 7-13-2, and 5-11-6)							
9-10-4	0.77	0.77	0.33	24.2	24.3	18.6	24.89
(also, 11-12-6 and 13-8-2)							
1-3 (delocalized toward 2 and 4)							
(also, 1-5 and 1-7 with similar delocalizations)							
15(D_{3h}, c)							
1-H_t	1.07	0.96		36.4			9.66
4-H_t	1.08	0.95		38.5			9.83
7-H_t	1.10	0.97		26.7			13.69
11-6-9	0.73	0.73	0.51	23.8	23.8	29.4	22.08
10-15-13	0.79	0.62	0.54	27.1	22.2	22.6	22.29
(also, 5-2-3)							
15-7-12	0.69	0.68	0.58	30.6	28.8	25.7	25.46
(also, 2-7-4)							
8-3-6	0.75	0.62	0.54	28.1	31.5	24.0	26.41
(also, 8-13-11)							
8-5-10	0.75	0.56	0.56	26.9	24.1	24.1	24.81
1-4-9	0.75	0.68	0.47	27.2	25.8	29.9	26.70
(also, 14-12-9)							
6-1-3	0.76	0.73	0.29	25.4	24.5	16.6	25.88
(also, 11-14-13)							
4-12-9	0.78	0.78	0.32	21.2	21.2	27.8	23.83
7-5-10	0.71	0.60	0.60	27.8	23.0	23.0	24.79
1-2-3	0.75	0.69	0.55	21.9	24.5	26.8	24.73
(also, 14-15-13)							
16(D_2, d)							
1-H_t	1.10	0.96		29.4			13.56
5-H_t	1.07	0.96		37.9			10.43
9-H_t	1.07	0.95		36.6			9.63
13-H_t	1.08	0.95		38.1			9.80
14-15-2	0.69	0.66	0.61	26.9	24.8	26.9	21.95
16-13-4	0.72	0.67	0.56	25.9	24.6	27.1	22.11
12-14-7	0.75	0.69	0.50	25.9	26.6	24.7	24.19
1-2-5	0.70	0.65	0.54	31.4	32.1	28.1	24.64
3-4-8	0.72	0.59	0.56	30.8	32.7	27.7	25.24
9-16-6	0.76	0.72	0.41	24.6	26.5	22.9	24.79
9-7-4	0.66	0.66	0.63	25.1	27.1	29.1	24.42
2-12-6	0.70	0.64	0.58	28.5	24.2	27.0	25.14
1-13-11	0.70	0.63	0.59	27.6	26.1	28.2	25.76
3-15-10	0.72	0.64	0.53	27.3	25.6	28.5	26.24
12-9-6	0.75	0.73	0.32	24.7	25.0	27.4	27.74
8-10-11	0.76	0.71	0.50	24.4	25.3	24.0	24.44
3-7-14	0.75	0.64	0.52	26.1	26.7	21.3	25.04
1-6-16	0.74	0.64	0.56	26.1	27.5	21.3	25.09
15-5-10	0.78	0.76	0.31	22.3	24.0	27.8	25.84
16(D_2, d)							
5-11-10	0.77	0.73	0.45	23.8	24.3	23.1	24.66
8-13-11	0.78	0.78	0.24	23.5	22.3	26.9	26.40
17(D_{5h}, e)							
1-H_t	1.07	0.96		36.0			9.08
2-H_t	1.08	0.96		38.2			10.22
7-H_t	1.10	0.95		33.5			13.15
13-12-7	0.67	0.66	0.64	26.3	27.3	26.0	22.60
10-15-16	0.67	0.66	0.62	26.0	25.2	27.8	23.02
9-15-14	0.70	0.64	0.58	26.0	24.0	27.4	23.83
8-13-14	0.73	0.61	0.56	25.9	23.5	26.2	24.47
11-12-16	0.74	0.58	0.56	25.9	23.8	24.7	24.76
8-9-3	0.68	0.67	0.54	29.1	29.4	26.2	22.88
11-10-5	0.68	0.65	0.55	28.7	29.6	26.1	22.92
11-7-6	0.68	0.64	0.57	28.5	29.6	26.0	22.99
8-7-2	0.67	0.64	0.58	28.4	29.4	25.9	23.08
9-10-4	0.66	0.64	0.59	28.6	29.0	25.9	23.13
17-12-16	0.73	0.64	0.57	25.6	27.7	27.6	25.53
17-13-14	0.74	0.69	0.45	24.7	27.6	26.6	26.61
17-15-14	0.74	0.72	0.32	23.9	27.6	24.3	27.98
6-5-1	0.75	0.75	0.45	24.5	24.5	26.6	25.10
2-3-1	0.76	0.75	0.43	24.4	24.5	26.5	25.21
4-3-1	0.76	0.75	0.41	24.3	24.5	26.3	25.36
4-5-1	0.76	0.76	0.39	24.2	24.4	26.2	25.54
2-6-1	0.77	0.76	0.38	24.2	24.3	26.0	25.63
17(C_{2v}, f)							
1-H_t	1.10	0.94		33.3			12.77
2-H_t	1.09	0.96		29.9			13.54
4-H_t	1.07	0.96		38.2			10.39
8-H_t	1.07	0.96		36.7			9.48
10-H_t	1.07	0.95		38.4			9.71
14-H_t	1.09	0.97		28.5			13.37
16-H_t	1.08	0.95		39.4			10.41
2-1-5	0.70	0.67	0.50	30.8	29.0	29.5	23.44
16-10-14	0.72	0.69	0.55	26.8	23.5	26.9	22.88
12-17-3	0.75	0.69	0.53	25.1	26.2	27.9	23.15
1-6-3	0.70	0.61	0.57	27.9	27.6	33.1	24.51
11-5-9	0.80	0.63	0.53	26.6	23.8	24.6	23.04
8-13-14	0.72	0.66	0.56	28.0	25.0	28.7	25.03
15-11-16	0.76	0.57	0.52	26.1	23.3	26.9	25.45
7-13-3	0.73	0.65	0.58	27.0	27.4	28.2	25.93
2-11-16	0.71	0.68	0.50	27.2	23.9	26.0	25.80
10-8-4	0.79	0.71	0.32	23.7	24.7	21.2	25.63
1-7-4	0.78	0.61	0.47	25.0	23.7	25.4	24.44
2-10-4	0.74	0.62	0.52	27.1	26.1	30.5	27.41
15-14-17	0.76	0.63	0.48	30.9	33.8	24.4	26.56
15-9-12	0.74	0.62	0.55	26.7	30.0	22.7	25.14
8-7-4	0.71	0.71	0.56	23.1	25.8	26.3	25.66
12-6-9	0.77	0.75	0.33	26.2	23.9	19.2	26.25
6-5-9	0.77	0.73	0.48	22.9	24.1	26.9	24.79
13-17 (delocalized toward 3,14)							
18(D_{3d}, g)							
1-H_t	1.07	0.96		36.8			9.68
4-H_t	1.08	0.96		39.6			10.96
7-H_t	1.09	0.93		33.1			13.66
16-15-17	0.74	0.65	0.58	26.4	26.8	27.9	23.41
8-10-4	0.68	0.65	0.54	29.4	30.5	28.2	22.95
12-7-13	0.69	0.65	0.52	29.3	30.0	28.4	23.12
1-5-3	0.76	0.65	0.54	26.0	26.6	27.9	23.67
2-4-3	0.79	0.63	0.53	24.9	25.7	27.8	24.12
18-13-17	0.78	0.60	0.56	25.2	25.5	27.8	24.18
7-5-11	0.67	0.63	0.56	27.0	26.1	33.3	23.84
12-18-14	0.75	0.63	0.49	25.0	24.4	30.4	25.22
8-2-6	0.74	0.62	0.54	25.2	24.4	29.6	24.66
10-15-9	0.69	0.66	0.51	26.4	25.1	33.7	24.24
7-6-1	0.73	0.65	0.58	25.4	26.8	24.6	23.63
2-1-6	0.75	0.73	0.34	26.7	27.3	18.1	27.80
18-16-14	0.76	0.71	0.38	26.2	27.2	19.4	27.39
10-14-16	0.74	0.66	0.56	25.0	25.9	24.8	23.78
15-11-17	0.76	0.73	0.31	18.8	25.0	25.2	27.03
13-11-17	0.74	0.72	0.45	20.1	22.6	25.1	25.74
5-9-3	0.77	0.72	0.36	18.5	24.8	25.1	26.73

Table VI (*Continued*)

LMO	populations			% s^b			
A-B-C	A	B	C	A	B	C	% *d*
(A) Doubly Negative Structures ($c = -2$) (*Continued*)							
18(D_{3d}, g)							
4-9-3	0.75	0.71	0.45	19.6	22.6	24.9	25.99
8-12 (delocalized toward 6,14)							
19(C_s, h)							
1-H$_t$	1.07	0.96		38.0			9.52
2-H$_t$	1.07	0.96		38.3			10.20
4-H$_t$	1.08	0.96		39.3			11.00
6-H$_t$	1.09	0.94		33.8			13.38
7-H$_t$	1.09	0.95		32.7			13.17
8-H$_t$	1.09	0.95		32.3			13.11
10-H$_t$	1.09	0.95		32.3			13.19
12-H$_t$	1.08	0.96		39.1			10.98
13-H$_t$	1.07	0.95		38.8			9.75
15-H$_t$	1.07	0.96		40.2			10.37
17-H$_t$	1.08	0.95		40.0			10.35
19-H$_t$	1.08	0.98		27.1			13.38
6-9-4	0.69	0.68	0.46	29.0	26.4	29.6	23.69
6-10-5	0.69	0.68	0.42	28.3	26.2	29.4	24.46
1-3-4	0.77	0.62	0.54	25.2	26.8	26.7	25.73
2-3-7	0.68	0.67	0.62	26.7	27.2	24.0	22.50
1-2-5	0.77	0.65	0.49	25.3	27.0	25.6	26.64
13-18-12	0.75	0.75	0.32	28.6	28.7	13.9	26.88
10-11-14	0.71	0.68	0.49	30.6	30.5	27.1	24.60
9-8-17	0.71	0.68	0.50	30.5	30.5	27.1	24.71
18-17-19	0.79	0.70	0.44	24.6	25.5	29.7	24.21
13-14-19	0.79	0.70	0.45	24.4	25.6	29.8	24.21
10-12-13	0.75	0.62	0.58	26.2	30.6	21.7	24.91
9-12-18	0.75	0.63	0.57	26.3	30.3	21.7	24.72
8-7-16	0.70	0.69	0.53	29.1	30.3	23.5	23.79
11-7-15	0.69	0.68	0.54	29.1	30.3	23.5	23.88
11-2-5	0.73	0.63	0.57	24.1	25.1	24.5	24.31
8-3-4	0.73	0.62	0.58	24.1	25.5	23.4	24.42
15-16-19	0.76	0.76	0.38	25.5	25.6	28.1	26.22
14-15-19	0.79	0.78	0.34	22.0	24.4	29.5	25.22
17-16-19	0.79	0.78	0.34	21.8	24.5	29.6	25.18
1-6 (delocalized toward 4,5)							
20(D_{6h}, i)							
1-H$_t$	1.08	0.98		28.1			13.00
2-H$_t$	1.07	0.96		40.1			10.40
8-H$_t$	1.09	0.96		32.2			12.94
19-14-8	0.69	0.69	0.58	26.6	26.6	23.4	22.25
(also, 15-16-10 and 17-18-12)							
9-15-14	0.71	0.59	0.59	24.7	24.8	24.8	24.95
(also, 11-17-16 and 13-19-18)							
5-6-1	0.75	0.75	0.43	26.7	26.7	28.8	25.59
(also, 2-7-1 and 3-4-1)							
20-15-14	0.74	0.56	0.56	26.9	28.4	28.4	27.52
(also, 20-17-16 and 20-19-18)							
9-10-4	0.72	0.67	0.50	29.5	31.6	23.0	24.39
(also, 11-12-6, 9-8-3, 11-10-5, 13-12-7, and 13-8-2)							
2-3-1	0.78	0.78	0.27	25.0	25.0	28.2	26.59
(also, 5-4-1 and 7-6-1)							
20(D_{3h}, j)							
1-H$_t$	1.10	0.95		33.2			13.36
2-H$_t$	1.08	0.96		40.5			10.81
5-H$_t$	1.09	0.95		32.5			12.81
20(D_{3h}, j)							
8-H$_t$	1.07	0.96		38.8			10.17
7-2-1	0.66	0.63	0.62	27.8	27.0	29.0	22.72
(also, 5-3-1, 14-17-20, 6-4-1, 15-18-20, and 16-19-20)							
7-14-8	0.67	0.67	0.53	30.2	30.2	28.4	23.99
(also, 6-16-12 and 5-15-10)							
14-19-13	0.77	0.61	0.51	25.6	24.5	27.1	25.04
(also, 5-2-9, 15-17-9, 7-4-13, 6-3-11, and 16-18-11)							
2-8-9	0.77	0.74	0.43	23.3	24.2	26.5	25.80
(also, 17-8-9, 3-10-11, 4-12-13, 19-12-13, and 18-10-11)							
21(D_3, k)							
1-H$_t$	1.09	0.95		32.8			13.82
4-H$_t$	1.08	0.96		40.0			10.90
7-H$_t$	1.08	0.96		38.7			10.11
10-H$_t$	1.09	0.94		34.0			12.70
3-12-6	0.68	0.64	0.57	28.0	29.3	27.8	22.65
(also, 2-11-15, and 1-10-4)							
12-15-21	0.67	0.62	0.60	28.1	28.7	29.4	23.97
(also, 10-13-19 and 11-14-20)							
2-1-3	0.62	0.62	0.62	30.5	30.5	30.5	22.72
21-19-17	0.68	0.64	0.57	27.9	29.0	25.8	23.73
(also, 19-20-18 and 20-21-16)							
17-13-7	0.77	0.73	0.40	26.2	23.7	26.0	26.26
(also, 16-15-9 and 18-14-8)							
10-18-8	0.75	0.61	0.53	25.1	24.9	27.6	25.57
(also, 11-16-9 and 12-17-7)							
3-4-7	0.78	0.57	0.56	25.4	23.0	27.2	24.42
(also, 2-6-9 and 1-5-8)							
14-5-8	0.75	0.74	0.44	23.0	27.0	24.0	27.01
(also, 15-6-9 and 13-4-7)							
22(D_{5d}, l)							
1-H$_t$	1.07	0.95		35.9			9.03
2-H$_t$	1.08	0.96		38.0			10.12
7-H$_t$	1.11	0.93		37.1			14.13
10-14-15	0.65	0.51	0.47	28.1	30.4	31.1	28.96
8-7-3	0.71	0.71	0.52	31.0	31.4	28.5	23.12
13-14-18	0.72	0.69	0.53	30.2	32.2	28.3	23.19
16-15-20	0.72	0.68	0.54	29.7	32.5	28.2	23.27
10-11-6	0.72	0.65	0.57	29.0	32.8	27.8	23.60
10-9-5	0.72	0.64	0.58	28.6	32.7	27.6	23.89
16-12-21	0.71	0.61	0.61	28.1	32.3	27.2	24.55
13-17-12	0.70	0.62	0.60	27.9	27.0	31.9	24.89
8-4-9	0.69	0.63	0.59	27.9	26.8	30.9	25.41
7-2-11	0.67	0.64	0.60	28.1	26.7	30.3	25.61
14-19-15	0.64	0.64	0.62	28.7	26.7	29.2	25.80
5-6-1	0.73	0.73	0.50	25.4	25.4	27.5	25.04
21-20-22	0.74	0.72	0.50	25.4	25.2	27.4	25.16
17-18-22	0.75	0.72	0.49	25.3	25.2	27.2	25.26
4-3-1	0.75	0.72	0.46	25.1	25.1	27.0	25.50
2-3-1	0.76	0.73	0.45	24.9	25.1	26.8	25.64
19-18-22	0.76	0.74	0.40	24.6	25.1	26.6	25.98
19-20-22	0.77	0.75	0.38	24.4	25.0	26.4	26.20
2-6-1	0.77	0.76	0.33	24.2	24.8	26.0	26.52
4-5-1	0.77	0.76	0.32	24.2	24.6	25.8	26.63
17-21-22	0.77	0.77	0.31	24.3	24.4	25.7	26.74
13-8-9 (delocalized toward 12)							
16-7-11 (delocalized toward 12)							
(B) Neutral Structures ($c = 0$)							
16(T_d, m)							
1-H$_t$	1.16	0.91		27.1			13.02
5-H$_t$	1.16	0.87		40.2			10.41
5-6-7	0.67	0.67	0.67	27.2	27.2	27.2	22.58
(also, 8-9-10, 11-12-13, and 14-15-16)							
1-5-8	0.78	0.55	0.55	27.3	26.6	26.6	24.96
(also, 11 other three-center bonds related to 1-5-8 by symmetry)							
19(C_{3v}, n)							
1-H$_t$	1.15	0.89		31.0			15.10
4-H$_t$	1.15	0.86		41.8			11.27
7-H$_t$	1.15	0.87		40.4			10.17
13-H$_t$	1.15	0.88		40.7			11.51
19(C_{3v}, n)							
16-H$_t$	1.14	0.87		32.5			15.17
19-H$_t$	1.17	0.87		36.4			13.36
8-7-14	0.70	0.70	0.60	26.2	26.2	30.4	24.01
(also, 9-10-15 and 12-11-13)							
3-8-4	0.74	0.61	0.59	26.2	25.6	26.9	24.01
(also, 3-7-6, 1-9-4, 1-10-5, 2-12-6, and 2-11-5)							
3-2-1	0.65	0.65	0.65	34.6	34.6	34.6	23.75
19-16 (delocalized toward 14,15; also to a lesser extent 13)							
(also, 19-17 and 19-18 with similar delocalizations)							
8-16 (delocalized primarily toward 4,14)							
(also, 9-16, 10-17, 11-17, 12-18, and 7-18 with similar delocalizations)							

Table VI (*Continued*)

LMO	populations			% s[b]				LMO	populations			% s[b]			
A-B-C	A	B	C	A	B	C	% *d*	A-B-C	A	B	C	A	B	C	% *d*
(B) Neutral Structures ($c = 0$) (*Continued*)															
$22(T_d, \mathrm{o})$								$22(T_d, \mathrm{o})$							
1-H_t	1.15	0.89		42.0			11.36	4-5-6	0.69	0.69	0.65	27.7	27.6	25.4	26.03
13-H_t	1.15	0.89		34.9			13.14	8-7-9	0.69	0.69	0.65	27.7	27.7	25.3	26.07
17-H_t	1.12	0.85		38.7			15.11	19-15-3	0.73	0.64	0.45	27.0	28.8	28.9	24.43
11-10-12	0.71	0.67	0.66	29.3	27.1	27.0	24.93	22-13-11	0.73	0.62	0.47	26.6	28.9	28.7	24.46
3-2-1	0.70	0.67	0.67	29.3	27.1	27.0	24.94	17-15-3	0.73	0.62	0.47	27.0	27.0	29.6	24.50
17-13-1	0.73	0.62	0.49	27.0	30.6	30.7	23.48	18-13-11	0.73	0.61	0.49	26.7	27.1	29.3	24.52
21-15-7	0.73	0.64	0.47	27.2	30.5	30.5	23.50	22-9-8	0.84	0.47	0.46	18.6	31.1	28.0	27.00
19-14-2	0.73	0.61	0.51	27.1	28.8	31.4	23.56	17-9-7	0.84	0.47	0.45	18.6	30.4	28.7	26.98
22-16-12	0.73	0.63	0.50	27.3	28.8	31.3	23.68	21-5-6	0.84	0.48	0.45	18.7	28.2	30.7	27.08
21-16-8	0.73	0.62	0.51	27.0	28.8	31.1	23.59	19-4-6	0.84	0.48	0.45	18.4	28.0	31.0	27.14
18-14-10	0.73	0.63	0.49	27.2	28.8	31.1	23.74	18-1-2	0.84	0.48	0.46	18.9	29.6	28.9	27.24
20-14-4	0.73	0.63	0.50	27.0	28.9	30.8	23.64	20-10-12	0.84	0.47	0.47	19.0	29.2	29.2	27.26
20-16-5	0.73	0.63	0.50	27.0	28.9	30.7	23.67								

[a] The labels for the structures correspond to the ordering in Figure 1. Inner shells are not listed. Only one of each type of symmetry-related B-H_t LMO's is listed. When several framework LMO's have the same values for all the quantities to be specified, the later ones are listed within parentheses below the first one: (also, . . .). Some LMO's are too delocalized to fall properly into any of the categories of the center-type analysis. In these cases, no numerical values are given, but atoms making the major contributions, as well as those making the secondary ones, are listed, i.e., 5-2 (delocalized toward 4,7). [b] % s character. Since the hydrogen atoms are represented by a 1s orbital in the basis set, the value of this quantity is always 100.0 for them, and it is not listed in the table.

of them are positive. (vi) As a result of the previous two trends, a very interesting charge separation takes place, with all of the seven-coordinate B–H_t group charges being negative and all of the six-coordinate B–H_t group charges being positive. (vii) The valencies of seven-coordinate borons are, on the average, as large as those in the doubly negative structures. (viii) However, the six-coordinate borons have much lower valencies in the neutral structures.

Table V gives the degrees of bonding[5a] and overlap populations for all of the distinct bonding interactions in the molecules. The values for the degree of bonding correlate well with the overlap populations and show similar trends, in particular justifying the "standard bond lengths" given in Table I: (i) In general, the shorter B–B distances have higher degrees of bonding. In 7–7 coordination most degrees of bonding fall between 0.401 and 0.450, in 7–6 bonds between 0.451 and 0.500, and in 6–6 bonds between 0.501 and 0.600. (ii) The degrees of bonding and overlap populations for B–H_t bonds fall into extremely narrow ranges for the doubly negative and quite narrow ranges for the neutral structures, justifying the assumption[3,23] of fixed B–H_t bond lengths.

Localized molecular orbital (LMO) analyses, which have been very illuminating[6c,d] in the areas of boron hydride and carborane chemistry, have been carried out by the Boys criterion[6a,b] on the 15 selected structures. Some of the results of this analysis are listed in Table VI. Among these are (i) populations for the LMO's at the major contributing atoms, 0.20 e being considered as the minimum required to be listed; (ii) % s character, related at the hybridization at a given atom (sp^x) by $x = (100.0 - \% \text{ s})/\% \text{ s}$; (iii) the percentage of delocalization, $\% d = 100[{}^1/_2\int[\phi^L - \phi^T]^2 \, dv]^{1/2}$, where ϕ^L is a localized orbital and ϕ^T can be obtained from ϕ^L by truncating all nonlocal contributions and renormalizing. The LMO's for which none of these quantities are given have extremely large delocalizations. From the coefficients of all basis set orbitals in these LMO's, it is seen that most of them are two-center bonds with enormous amounts of donation to the two atoms attached to both ends of the bond. The rest are extremely delocalized three-center bonds.

It can be seen from Table VI that very few of the LMO structures satisfy the full molecular symmetry, two such cases being $B_{16}H_{16}$ (T_d) and $B_{19}H_{19}$ (C_{3v}). It was to be expected that for most of these large, complicated, highly symmetrical structures the LMO's would have less than the full molecular symmetry.

The concept of a "topologically allowed" (TA) valence structure has been used in the past to choose reasonable valence structures. Since the topological approach assumes that the bonding in a molecule may be expressed as a linear combination of a number of valence structures which conform to a set of well-defined rules, while localization calculations attempt to find a *single* localized structure which best describes the bonding,[24] one cannot in general expect the LMO structures to be TA. For B_nH_n a TA structure will have n three-center and no two-center bonds, while for $B_nH_n^{2-}$ there will be $(n - 2)$ three-center and three two-center bonds.[11] Thus, most of the LMO structures listed in Table VI are topologically forbidden. Some (such as $B_{14}H_{14}^{2-}$ (D_{6d}), $B_{16}H_{16}$ (T_d), and $B_{22}H_{22}$ (T_d)) are TA. There is a third group having $(n - 2)$ clearly three-center LMO's and three LMO's in which the third atom has far less electron population than the first two. In these, it is mainly a matter of definition whether the structure is TA: If the cutoff population for being considered a major contributing atom is slightly increased from 0.20 (for example, to 0.33 for $B_{15}H_{15}^{2-}$ (D_{3h})), the three LMO's mentioned above become two-center bonds with a large amount of donation to a third atom, and the structure becomes TA.

Other observations of interest in Table VI include (i) the presence of a higher electron population at B in all B–H_t bonds, consistent with the relative positive charges of terminal hydrogens revealed by a comparison of the atomic and group charges in Table IV, (ii) the fact that for both B–H_t and (where available) framework LMO's the % s character at B varies greatly and that no limit is approached for large n for either of these, and (iii) the fact that, on the average, B–H_t bond boron % s characters are slightly larger than those in the framework bonds.

Figure 4 depicts the LMO's for $B_{14}H_{14}^{2-}$ (D_{6d}), $B_{16}H_{16}$ (T_d), $B_{17}H_{17}^{2-}$ (D_{5h}), and $B_{20}H_{20}^{2-}$ (D_{3h}). Only the first two are topologically allowed, and the symmetries manifested by the LMO structures are C_{3v}, T_d, C_1, and C_{3h}, respectively. Two further independent localizations were attempted on $B_{14}H_{14}^{2-}$ (D_{6d}), giving LMO structures equivalent by symmetry to the one shown. It is strongly probable that this structure is unique, and it is almost certain that the one for $B_{16}H_{16}$ (T_d) is unique.

IV. Conclusions

For the closo series, structures are known for $B_nH_n^{2-}$ ($6 \leq n \leq 12$), for $C_2B_{n-2}H_n$ ($5 \leq n \leq 12$) and for metallocarboranes

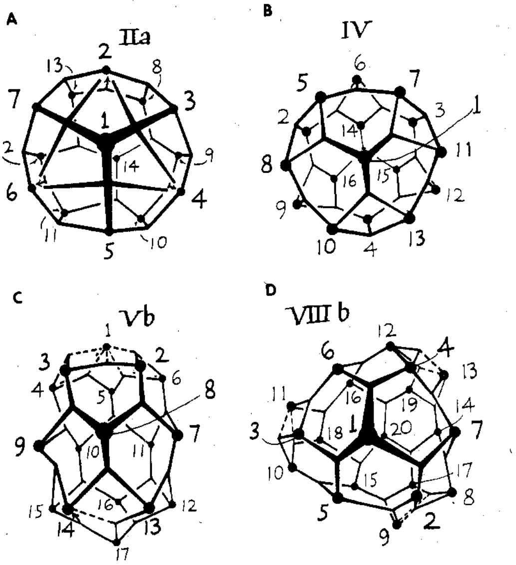

Figure 4. Some LMO structures. Bonding conventions for populations are (—) >0.50 e, (- - -) 0.35–0.50 e, (→) 0.25–0.35 e, and (+) for an extremely delocalized two-center bond with donation to the two atoms attached to both ends of the bond. The thick line is the major part of the bond. (A) LMO's for $B_{14}H_{14}^{2-}$ (D_{6d}); (B) LMO's for $B_{16}H_{16}$ (T_d); (C) LMO's for $B_{17}H_{17}^{2-}$ (D_{5h}); (D) LMO's for $B_{20}H_{20}^{2-}$ (D_{3h}).

up to 14 vertices.[1,2,16a] This extensive theoretical study of large $B_nH_n^c$ structures was aimed at exploring the possibility of the existence of stable $B_nH_n^{2-}$ structures for $n \geq 13$, as well as some B_nH_n molecules. The possible structures seem to be of comparable stability for even and odd n, with $n = 22$ being perhaps an upper stability limit. They are also comparable with the best subicosahedral $B_nH_n^{2-}$ structures: Our calculations show $B_{17}H_{17}^{2-}$ (D_{5h}) and $B_{14}H_{14}^{2-}$ (D_{6d}) to be surpassed only by $B_{12}H_{12}^{2-}$ (I_h) and to be even better than $B_{10}H_{10}^{2-}$ (D_{4d}) in stability. These results are clearly encouraging.

The static reactivity indices for these structures show well-defined trends which could be checked against experimental observations once such stable supraicosahedral structures are synthesized.

Each reasonable structure is expected to have some nido and arachno derivatives which may be quite stable, as well as carborane and metallocarborane relatives, with different numbers of carbons and metal atoms. Synthetic pathways are suggested to obtain some new supraicosahedral systems. Clearly, the synthetic possibilities are immense. When this is added to the extensive substitution reactions these "superaromatic" molecules can be expected to undergo, the wealth of new chemistry open to the experimentalist in this area becomes clear.

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Registry No. $B_9H_9^{2-}$, 12430-24-9; $B_{10}H_{10}^{2-}$, 12356-12-6; $B_{11}H_{11}^{2-}$, 12430-44-3; $B_{12}H_{12}^{2-}$, 12356-13-7; $B_{13}H_{13}^{2-}$, 64175-33-3; $B_{14}H_{14}^{2-}$, 12430-58-9; $B_{15}H_{15}^{2-}$, 64175-23-1; $B_{16}H_{16}^{2-}$, 64175-24-2; $B_{17}H_{17}^{2-}$, 64175-25-3; $B_{18}H_{18}^{2-}$, 64175-26-4; $B_{19}H_{19}^{2-}$, 64175-27-5; $B_{20}H_{20}^{2-}$, 64175-28-6; $B_{21}H_{21}^{2-}$, 64175-29-7; $B_{22}H_{22}^{2-}$, 64175-30-0; $B_{23}H_{23}^{2-}$, 64175-31-1; $B_{24}H_{24}^{2-}$, 64175-32-2; $B_{16}H_{16}$, 67761-34-6; $B_{19}H_{19}$, 67761-35-7; $B_{22}H_{22}$, 67761-36-8.

Supplementary Material Available: Three-dimensional Cartesian coordinates of molecules and ions studied in this article (19 pages). Ordering information is given on any current masthead page.

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