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The Large *closo*-Borane Dianions, $B_nH_n^{2-}$ ($n = 13-17$) Are Aromatic, Why Are They Unknown?[†]

Paul von Ragué Schleyer,*[,‡] Katayoun Najafian,[‡] and Alexander M. Mebel[§]

Institut für Organische Chemie der Universität Erlangen−Nürnberg, Henkestrasse 42,
D-91504 Erlangen, Germany, and Institute of Atomic and Molecular Sciences, Academia Sinica,
P.O. Box 23-166, Taipei, Taiwan 10764

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The relative stabilities of the unknown larger *closo*-borane dianions $B_nH_n^{2-}$ ($n = 13-17$), were evaluated at the B3LYP/6-31G* level of density functional theory by comparing the average energies, E/n, and also by the energies using the model equation: $B_{n-1}H_{n-1}^{2-} + B_6H_{10} \rightarrow B_nH_n^{2-} + B_5H_9$ ($n = 6-17$). Starting with the small *closo*-borane, $B_5H_5^{2-}$, the sequential addition of BH groups is represented by formal transfer from B_6H_{10} to build up larger and larger clusters. Most of the energies for these sequential steps are exothermic, but not for the $B_{12}H_{12}^{2-}$ to $B_{13}H_{13}^{2-}$ and the $B_{14}H_{14}^{2-}$ to $B_{15}H_{15}^{2-}$ stages. The cumulative total energies (ΔH_{add}) of these BH group additions, based on $B_5H_5^{2-}$ as the reference zero, tend to increase with increasing cluster size. ΔH_{add} indicates that the larger unknown *closo*-boranes $B_{13}H_{13}^{2-}$ to $B_{17}H_{17}^{2-}$ are more stable than $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{11}H_{11}^{2-}$; this agrees with E/n and with Lipscomb's earlier conclusion based on the PRDDO average energies. $B_{13}H_{13}^{2-}$, $B_{14}H_{14}^{2-}$, and $B_{15}H_{15}^{2-}$ are less stable than $B_{12}H_{12}^{2-}$, which has the lowest average energy on a per vertex basis among the *closo*-borane dianions. However, the total ΔH_{add} treatment indicates the larger $B_{16}H_{16}^{2-}$ and $B_{17}H_{17}^{2-}$ to be favorable relative to $B_{12}H_{12}^{2-}$, because of the larger number of vertexes. The formation of $B_{13}H_{13}^{2-}$ from $B_{12}H_{12}^{2-}$ is especially unfavorable. The further formation of $B_{14}H_{14}^{2-}$ and $B_{15}H_{15}^{2-}$ via BH transfer also is endothermic. These are not the only thermodynamic difficulties in building up large *closo*-borane dianions beyond $B_{12}H_{12}^{2-}$. The highly exothermic disproportionation of larger and smaller *closo*-borane dianions, e.g., $B_{12+n}H_{12+n}^{2-} + B_{12-n}H_{12-n}^{2-} \rightarrow 2B_{12}H_{12}^{2-}$ ($n = 1-5$), also indicate possible synthetic problems in preparing larger *closo*-boranes with more than 12 vertexes under condition where smaller boranes are present. All the larger *closo*-$B_nH_n^{2-}$ ($n = 13-17$) cluster exhibit "three-dimensional aromaticity", judging from the computed Nucleus Independent Chemical Shifts (NICS), which range from −30.9 to −36.5 ppm. The trends in NICS values are similar to the variations in the bond length alternations, Δr. Thus, the qualitative relationships between geometric and magnetic criteria of aromaticity found earlier for the smaller clusters extends to the larger *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 13-17$).

Introduction

The chemistry of boron is dominated by its electron deficient character and three-dimensionally delocalized electronic structures.[1−5] The unusually high stability, bonding and aromaticity of the *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 5-12$), are now well understood.[1−5] The energies of *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 5-12$) generally become more favorable with increasing cluster size, but the relative stabilities of individual members of this class vary in characteristic patterns.[4a,5] Twenty years ago, Lipscomb and co-workers explored the structures and energies of larger *closo*-borane dianions, $B_nH_n^{2-}$ ($n > 12$) computationally.[6,7] The average PRDDO energy per BH unit (E/n), used to compare the relative stabilities of large *closo*-borane dianions with more than 12 vertexes, suggested that there might not be any thermodynamic basis for the nonobservation of *closo*-borane dianions with more than 12 vertexes. Many of these larger clusters were predicted to favor high-symmetry, low-energy structures and were identified as strong "candidates for synthesis". In particular, $B_{14}H_{14}^{2-}$ and $B_{17}H_{17}^{2-}$ were indicated to be more stable than $B_{11}H_{11}^{2-}$, $B_9H_9^{2-}$, and even

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[†] Dedicated to Professor W. N. Lipscomb on the occasion of his 80th birthday.

[‡] Universitat Erlangen−Nürnberg.

[§] Academia Sinica.

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$B_{10}H_{10}^{2-}$.[7] Nevertheless, the parent supraicosahedral clusters (i.e. $B_nH_n^{2-}$, $n \geq 13$), are still unknown,[8,9] even though a number of metallocarboranes with 13 vertexes or more have been reported.[10−20]

Thus, Grimes[11,12] and Hawthorne[13−16] describe a variety of metallocarboranes based on 13- to 15-vertex deltahedra. Thirteen-vertex examples include [*closo*-1,1,1-$(MeCN)_3$-1,2,4-$EuC_2B_{10}H_{12}]_\infty$,[14] [*closo*-1,1,1-$(MeCN)_3$-1,2,4-$SrC_2B_{10}H_{12}]_n$,[15] and *closo*-1,1,1-$(MeCN)_3$-1,2,4-$CaC_2B_{10}H_{12}$.[16] According to the compatibility of orbital overlap of the ring-cap, Jemmis[17] predicted that the six-membered ring in 14-vertex boranes and carboranes should prefer capping groups with orbitals more diffuse than those of BH and CH, e.g., C_5H_5Fe or C_5H_5Co. Indeed, transition metal-based caps stablilize 14-vertex clusters. Both $(C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$[12] and $(C_5H_5)_2Co_2C_2B_{10}H_{12}$[13b] have bicapped hexagonal antiprism (D_{6d}) architecture isoelectronic with $B_{14}H_{14}^{2-}$. *Closed* 15-vertex clusters without substituents are found in BeB_3[18] and in SiB_6.[19] Likewise, 16-vertex geometry is represented experimentally in the discrete In_{16} cluster units in a solid-state compound, $Na_7In_{11.8}$.[20]

Recently, we have taken the most highly symmetric species, $B_{12}H_{12}^{2-}$ and $B_6H_6^{2-}$, as references for the quantitative comparison of the stabilities of individual clusters.[5] On this basis, $B_{10}H_{10}^{2-}$ and $B_7H_7^{2-}$ are not as favorable, $B_9H_9^{2-}$ and $B_8H_8^{2-}$ are less stable, and $B_{11}H_{11}^{2-}$ and $B_5H_5^{2-}$ are the least stable members of this family. We confirmed[5] that not only the total stabilization energies but also the average stability per vertex of *closo*-borane dianions, $B_nH_n^{2-}$ tend generally to increase as the systems become larger from 5 to 12 vertexes. This energetic behavior of the *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 5-12$) is exceptional, when compared to polybenzenoid hydrocarbons and the [*n*]annulenes, and characterizes the three-dimensional aromaticity in such clusters.

We now reexamine the stabilities of the hypothetical 13- to 17-vertex $B_nH_n^{2-}$ ($n = 13-17$) cages employing density functional theory. We also assess the "three-dimensional aromaticity" of these larger *closo*-borane dianions, by applying e.g., magnetic (nucleus independent chemical shifts, NICS)[21] (based on the magnetic shieldings computed in the geometric centers) as well as geometric criteria (the difference between the longest and the shortest bond, Δr).[5] The results are compared with these obtained earlier for the smaller $B_nH_n^{2-}$ ($n = 5-12$) *closo*-dianions, and the problem of the nonobservation of the larger cages is addressed.

Computational Methods

The geometries of *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 13-17$) were optimized within chosen symmetry restrictions using the GAUSSIAN 94 program[22] and the B3LYP/6-31G* and B3LYP/6-311+G** levels of density functional theory (Figure 1). Frequency calculations at B3LYP/6-31G* characterized the stationary points as minima and provided the zero point energies (ZPE).[23]

Lipscomb and co-workers[6,7] found the large *closo*-borane dianions with 13 to 17 vertexes to favor high-symmetry point groups (Figure 1) e.g., $B_{14}H_{14}^{2-}$ (D_{6d}), $B_{15}H_{15}^{2-}$ (D_{3h}), and $B_{17}H_{17}^{2-}$ (D_{5h}). Our less extensive searches confirmed the earlier conclusions, except that $B_{16}H_{16}^{2-}$ has D_{4d} (instead of D_2) symmetry. The T_d form is a triplet, 53.2 kcal/mol higher in energy at B3LYP/6-311+G**. $B_{13}H_{13}^{2-}$ has only C_{2v} symmetry, since this results from the formal addition of a neutral BH unit to any B−B edge of the $B_{12}H_{12}^{2-}$ icosahedron.[6] We were not be able to optimize $B_{15}H_{15}^{2-}$ and $B_{17}H_{17}^{2-}$ fully at B3LYP/6-311+G** due to problems with energy oscillation. Thus, for uniformity the geometries and energies (Table 2) discussed here were obtained at the electron-correlated B3LYP/6-31G* optimized DFT level. The NICS[21] were computed at GIAO−HF/6-31+G*[24] at the cage centers using the B3LYP/6-31G* optimized geometries.

While the smaller *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 5-12$), are unbound toward loss of an electron (many of the highest-occupied orbitals have positive eigenvalues), this is not found for the larger 13- to 17-vertex dianions, where the coulomb repulsion is reduced due to the larger size.

Results and Discussion

Relative Stabilities. We first checked Lipscomb's PRDDO results against our higher level DFT data. The B3LYP/6-31G* functional includes electron correlation which should provide a better description of delocalized bonding. Plots based on Lipscomb's treatment (but employing a different presentation)

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Table 1. Data for *closo*-Borane Dianions, $B_nH_n^{2-}$ ($n = 5-17$): Total Energies in au; Zero-Point Energies (ZPE, in kcal/mol);[a] Average of Our BH Energy ($E_{av} = E$ at B3LYP/6-31G*/n and $E'_{av} = E$ at B3LYP/6-311+G**/n);[c,d] PRDDO Relative Energies (E_L) of Lipscomb and Co-workers[e]

molecule	sym.	B3LYP/6-31G*	ZPE[a]	B3LYP/6-311+G**	E_{av}[c]	E'_{av}[d]	E_L[e]
$B_5H_5^{2-}$	D_{3h}	−127.09274	36.69	−127.17129	0.00	0.00	0.00
$B_6H_6^{2-}$	O_h	−152.65160	47.10	−152.72451	−14.67	−12.44	−23.22
$B_7H_7^{2-}$	D_{5h}	−178.14319	56.29	−178.21180	−19.13	−15.42	−33.89
$B_8H_8^{2-}$	D_{2d}	−203.62086	65.06	−203.68894	−21.37	−16.85	−37.65
$B_9H_9^{2-}$	D_{3h}	−229.12195	74.45	−229.19051	−24.75	−19.68	−44.55
$B_{10}H_{10}^{2-}$	D_{4d}	−254.64388	84.71	−254.71361	−28.77	−23.28	−50.83
$B_{11}H_{11}^{2-}$	C_{2v}	−280.10784	93.22	−280.18060	−28.74	−23.03	−49.57
$B_{12}H_{12}^{2-}$	I_h	−305.69026	104.77	−305.76291	−34.91	−28.86	−61.50
$B_{13}H_{13}^{2-}$	C_{2v}	−331.07633	111.90	−331.15286	−30.66	−24.49	−51.46
$B_{14}H_{14}^{2-}$	D_{6d}	−356.58815	122.45	−356.66553	−32.65	−26.26	−55.22
$B_{15}H_{15}^{2-}$	D_{3h}	−382.03790	131.04	–[b]	−31.78	–	−51.46
$B_{16}H_{16}^{2-}$	D_{4d}	−407.52132	141.02	−407.60511	−32.34	−25.77	−52.71
$B_{17}H_{17}^{2-}$	D_{5h}	−432.99603	149.92	–[b]	−32.51	–	−55.85
B_5H_9	C_{4v}	−129.66272	67.08				
B_6H_{10}	C_s	−155.11714	75.75				

[a] Zero-point energy calculated at B3LYP/6-31G*. [b] Due to oscillation, these energies are not fully optimized. [c] Average energy per BH group at B3LYP/6-31G*. [d] The trend is exactly the same as with the lower basis set as in *c*, however, the energy changes are smoother. [e] From the ref 7 (note that in both cases, *c*, *d*, and *e*, $B_5H_5^{2-}$ is chosen as the reference energy).

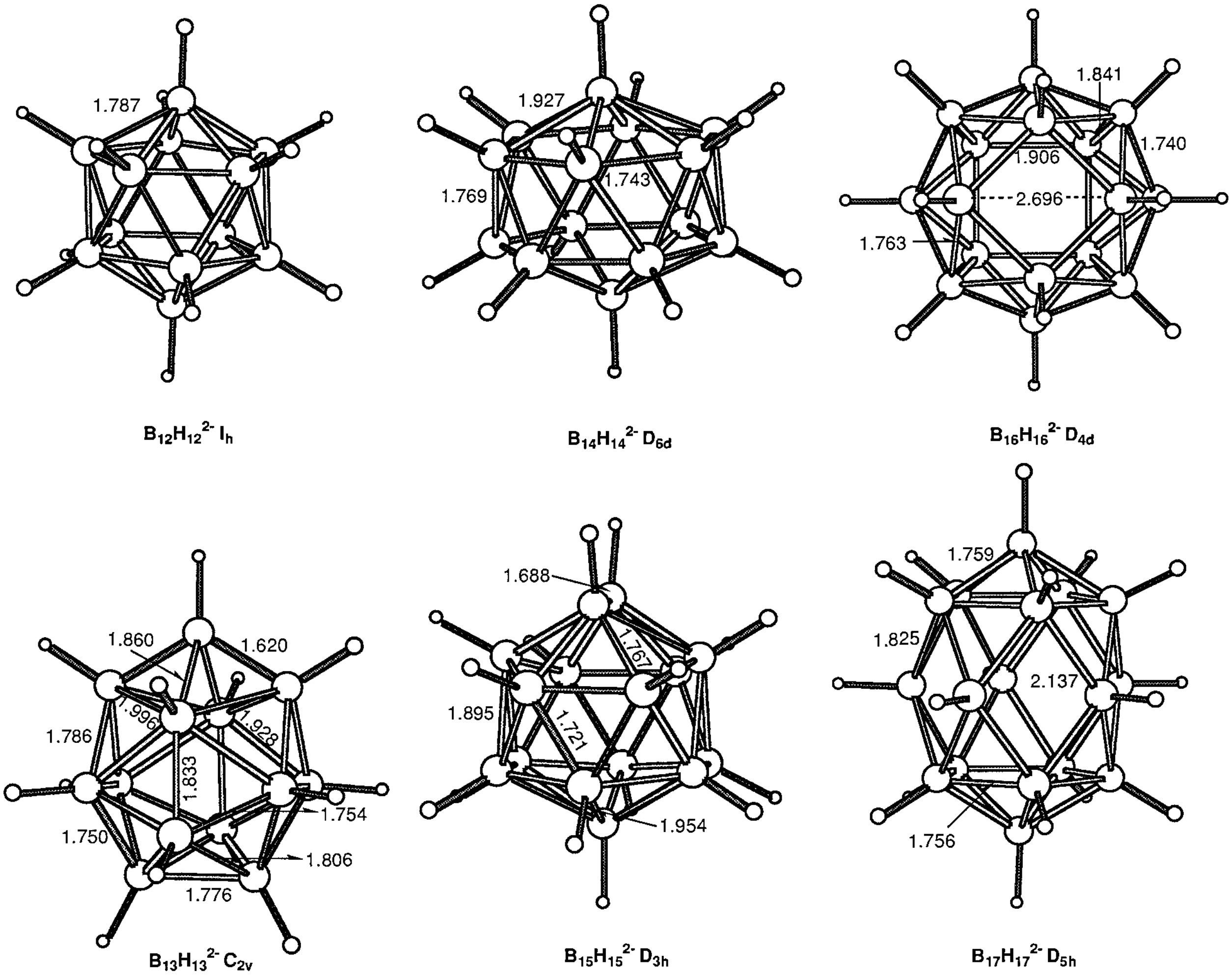

Figure 1. B3LYP/6-31G* optimized geometries for larger *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 12-17$). For the geometries for $B_5H_5^{2-}$ to $B_{11}H_{11}^{2-}$ see ref 5.

of the PRDDO average energies (total PRDDO energy of $B_nH_n^{2-}$ clusters in kcal/mol divided by the number of borons, E/n) and our average B3LYP/6-31G* energies ($E_{av} = E/n$) are compared in Figure 2. In both cases, $B_5H_5^{2-}$ was chosen as the reference species (Table 1). The differences in relative average energies (vs $B_5H_5^{2-}$) are less pronounced at B3LYP/6-31G* than at PRDDO, but both levels show the trend to lower energies as the cluster become larger. The most highly symmetrical cluster, $B_{12}H_{12}^{2-}$, is still indicated to be the most favorable, but not at B3LYP/6-31G* to such a large extent. The larger *closo*-boranes, $B_{13}H_{13}^{2-}$ to $B_{17}H_{17}^{2-}$, are more stable than $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{11}H_{11}^{2-}$. Note that $B_{13}H_{13}^{2-}$ is significantly less favorable than the other larger dianions, $B_{14}H_{14}^{2-}$ and $B_{17}H_{17}^{2-}$ in particular.

Table 2. Data for *closo*-Borane Dianions, $B_nH_n^{2-}$ ($n = 5-17$), All Energies in kcal/mol; Reaction Energies from eq 1 (ΔH);[a] Cumulative BH Addition Energies (${}^{\Delta}H_{\rm add}$);[b] Disproportionation Energies from Eq. 17 (${}^{\Delta}H_{\rm dis}$);[c] Bond Length Alternations (Δr, Å);[d] Nucleus Independent Chemical Shifts (NICS, ppm)[e]

molecule	sym.	ΔH^a	$\Delta H_{\rm add}{}^b$	$\Delta H_{\rm dis}{}^c$	Δr^d	NICS^e
$B_5H_5^{2-}$	D_{3h}		0.00		0.157	−26.48
$B_6H_6^{2-}$	O_h	−63.79	−63.79	+40.99	0.000	−34.26
$B_7H_7^{2-}$	D_{5h}	−22.80	−86.59	+8.31	0.172	−27.52
$B_8H_8^{2-}$	D_{2d}	−14.48	−101.07	−14.07	0.291	−24.22
$B_9H_9^{2-}$	D_{3h}	−28.56	−129.63	−12.21	0.275	−27.38
$B_{10}H_{10}^{2-}$	D_{4d}	−40.77	−170.40	+34.63	0.138	−33.47
$B_{11}H_{11}^{2-}$	C_{2v}	−6.14	−176.54	−71.29	0.356	−32.47
$B_{12}H_{12}^{2-}$	I_h	−77.44	−253.98	+118.79	0.000	−35.82
$B_{13}H_{13}^{2-}$	C_{2v}	+41.36	−212.62	−75.49	0.376	−30.93
$B_{14}H_{14}^{2-}$	D_{6d}	−34.13	−246.75	+37.00	0.184	−32.25
$B_{15}H_{15}^{2-}$	D_{3h}	+2.86	−243.89	−19.74	0.266	−31.59
$B_{16}H_{16}^{2-}$	D_{4d}	−16.88	−260.77	+4.39	0.166	−33.71
$B_{17}H_{17}^{2-}$	D_{5h}	−12.50	−273.27		0.069	−36.54

[a] Equation 1: $B_{n-1}H_{n-1}^{2-} + B_6H_{10} \rightarrow B_nH_n^{2-} + B_5H_9$ ($n = 6-17$) at B3LYP/6-31G*, with ZPE corrections scaled by 0.98 in kcal/mol (ref 23). [b] Note that the $B_5H_5^{2-}$ is used to define the zero point: differences from this basis ($\Delta H_{\rm add}$) is employed for the quantitative comparison of *closo*-borane dianion stabilities. [c] Equation 17:$2B_nH_n^{2-} \rightarrow B_{n-1}H_{n-1}^{2-} + B_{n+1}H_{n+1}^{2-}$ ($n = 6-16$) at B3LYP/6-31G* with ZPE corrections scaled as in *a*. [d] Difference (Å) between the longest and the shortest BB distances in each dianions at B3LYP/6-31G*. [e] At GIAO-HF/6-31+G*//B3LYP/6-31G*.

However, the average energies employed in these evaluations (Figure 2) are somewhat misleading. In the first place, they do not compensate properly for the negative charges which vary fractionally from one cluster size to another. Comparisons of one dianion with another are not charge balanced. More important, E/n evaluates of the average stabilization per vertex but not the total stabilization of a borane dianion cluster. In general, the thermodynamic stability of $B_nH_n^{2-}$ clusters increases as n becomes larger since the coulomb repulsion in the dianions decreases and there is a greater number of favorable multicenter bonding interactions. This trend is shown clearly in Figure 3 which will be discussed in detail below. While the E/n criteria (Figure 2) identifies $B_{12}H_{12}^{2-}$ as being unusually stable on a per vertex basis, the total stability of the larger *closo*-borane dianions clusters is greater than $B_{12}H_{12}^{2-}$ due to the larger number of vertexes (Figure 3).

This can be shown by extending our BH group increment method[5] to examine the energetic relationships among the *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 5-17$). We now employ a variation of our earlier treatment,[5,25] namely eq 1, which is balanced with regard to the negative charges,

$$B_{n-1}H_{n-1}^{\ 2-} + B_6H_{10} \rightarrow B_nH_n^{\ 2-} + B_5H_9\ (n = 6-17), \qquad \Delta H \quad (1)$$

Two *closo*-boranes are compared in eq 1 by employing two well-known neutral boron hydrides, B_5H_9 and B_6H_{10}.[1] In effect, a bonded BH group in B_6H_{10} is transferred to the smaller of the two *closo*-dianions. This simulates the "building up" of borane dianions for which experimental analogies exist. For example, $B_{10}H_{10}^{2-}$, $B_{11}H_{11}^{2-}$, and $B_{12}H_{12}^{2-}$ can be synthesized from smaller systems (even B_2H_6).[26]

Starting with $B_5H_5^{2-}$, the successive application of eq 1, i.e., the sequential addition of BH groups, builds up larger and larger clusters. The reaction energies of each step, ΔH, are given in Table 2, along with the cumulative total energy, $\Delta H_{\rm add}$, (based on $B_5H_5^{2-}$ as the reference zero). These total energies, $\Delta H_{\rm add}$, are plotted as a function of number of vertexes in Figure 3. This provides a more revealing quantitative comparison of the *closo*-borane dianions stabilities than Figure 2, especially for the larger clusters, $B_{13}H_{13}^{2-}$ to $B_{17}H_{17}^{2-}$.

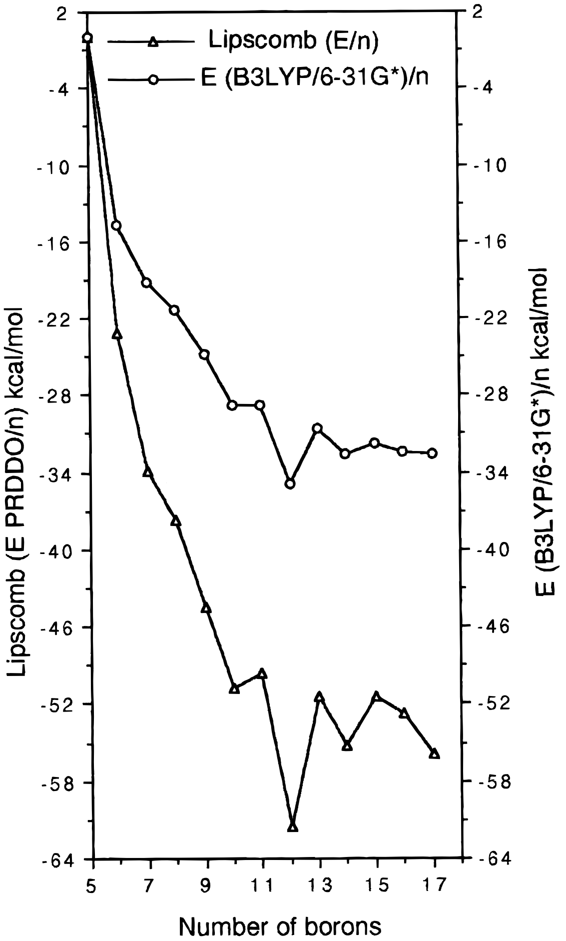

Figure 2. Comparison of results using the same treatment at B3LYP/6-31G* and PRDDO levels of theory. Plots of $E_{\rm av}$ (the B3LYP/6-31G* total energies per vertex; $E_{\rm av} = E/n$ in kcal/mol, Table 1) and Lipscomb's PRDDO energy (E/n, kcal/mol) for large *closo*-borane dianions $B_nH_n^{2-}$ ($n = 5-17$) vs number of boron atoms. Note that in both cases, the $B_5H_5^{2-}$ energy is chosen as the reference.

Figure 3 shows that $\Delta H_{\rm add}$ tends to increase in magnitude with increasing cluster size. The trend is indicated by the dashed line through most of the points in Figure 3. On this basis, $B_{10}H_{10}^{2-}$, $B_{14}H_{14}^{2-}$, and especially $B_{12}H_{12}^{2-}$ are exceptionally stable, and $B_5H_5^{2-}$ and $B_8H_8^{2-}$ are relatively unstable. This plot emphasizes and confirms our earlier conclusions[5] for the $B_5H_5^{2-}$ to $B_{12}H_{12}^{2-}$ clusters: (a) the trend toward increasing stability with cluster size, and (b) the variations among individual *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 5-12$). While most of the reaction energies ΔH (eq 1) are exothermic, this is not found for the $B_{12}H_{12}^{2-}$ to $B_{13}H_{13}^{2-}$ and $B_{14}H_{14}^{2-}$ to $B_{15}H_{15}^{2-}$ steps. $\Delta H_{\rm add}$ decreases sharply from $B_{13}H_{13}^{2-}$ to $B_{14}H_{14}^{2-}$, but

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(25) The relative stabilities of *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 5-12$) based on the following equation: $B_2H_2^{2-} + (n-2)BH_{\rm inc} \rightarrow B_nH_n^{2-}$ ($n = 5-12$). The acetylene-like $B_2H_2^{2-}$ was employed to compensate for the charges and the BH increment was taken as the energy difference between B_3H_5 (C_{2v}, planar) and B_2H_4 (D_{2h}, ethylene-like). The $BH_{\rm inc}$ is electron deficient and does not include any inherent stabilization due to hyperconjugation or to delocalization. Hence, it is higher in energy than the BH increment derived from bonding situations, i.e., the $B_5H_9 - B_6H_{10}$ difference, employed in eq 1.

(26) Middaugh, R. L. In *Boron Hydride Chemistry*; Academic Press: New York, 1975; p 280.

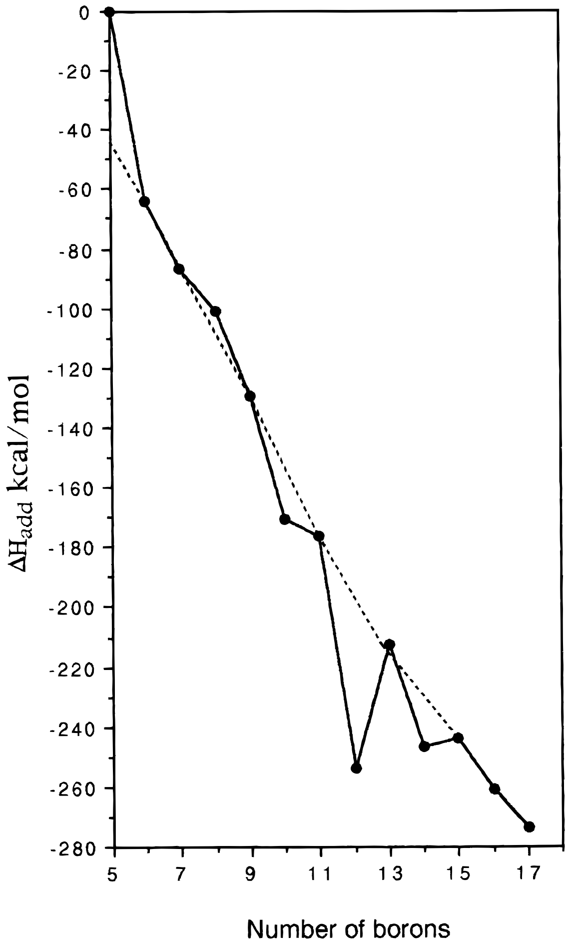

Figure 3. Plot based on ΔH_{add} (cumulative BH addition energy in kcal/mol from Table 2) for the *closo*-borane dianions, $B_nH_n^{2-}$ (n = 5−17), vs number of boron atoms.

increases slightly from $B_{14}H_{14}^{2-}$ to $B_{15}H_{15}^{2-}$. The further steps to $B_{16}H_{16}^{2-}$ and $B_{17}H_{17}^{2-}$ are exothermic and lie on the trend line of Figure 3.

Figure 3 also shows that the overall stabilities of the 13- to 17-boron cages are greater than 9- to 11-boron cages. While this agrees with Lipscomb's conclusion (Figure 2), $B_{12}H_{12}^{2-}$ is not the most stable cluster *closo*-borane dianion, when total energies are considered. At least in the isolated state, the unknown $B_{16}H_{16}^{2-}$ and $B_{17}H_{17}^{2-}$ are more favorable than $B_{12}H_{12}^{2-}$. This also is demonstrated directly by means of eqs 2−6, with increasing cluster size from 12 to 17 vertexes, which evaluate the transfer energies of appropriate number of BH increments from B_6H_{10}[1] to $B_{12}H_{12}^{2-}$. (These reaction energies also can be derived from the ΔH_{add} values of the larger *closo*-clusters in Table 2).

$$B_{12}H_{12}^{2-} + B_6H_{10} \rightarrow B_{13}H_{13}^{2-} + B_5H_9,\ \Delta H_2 = +41.36 \quad (2)$$

$$B_{12}H_{12}^{2-} + 2B_6H_{10} \rightarrow B_{14}H_{14}^{2-} + 2B_5H_9,\ \Delta H_3 = +7.22 \quad (3)$$

$$B_{12}H_{12}^{2-} + 3B_6H_{10} \rightarrow B_{15}H_{15}^{2-} + 3B_5H_9\ \Delta H_4 = +10.09 \quad (4)$$

$$B_{12}H_{12}^{2-} + 4B_6H_{10} \rightarrow B_{16}H_{16}^{2-} + 4B_5H_9,\ \Delta H_5 = -6.79 \quad (5)$$

$$B_{12}H_{12}^{2-} + 5B_6H_{10} \rightarrow B_{17}H_{17}^{2-} + 5B_5H_9,\ \Delta H_6 = -19.29 \quad (6)$$

This alternative presentation indicates that the formation of $B_{14}H_{14}^{2-}$, $B_{15}H_{15}^{2-}$, and especially $B_{13}H_{13}^{2-}$ from $B_{12}H_{12}^{2-}$ are unfavorable energetically (see Figure 3). This rationalizes the failure to observe such large dianions as products of reactions in which larger *closo*-borane dianions are built up from smaller units. Although reactions 5 and 6 are exothermic, the formation of $B_{16}H_{16}^{2-}$ and $B_{17}H_{17}^{2-}$ from $B_{12}H_{12}^{2-}$ may involve too many unfavorable steps along the reaction pathway.

The highly exothermic disproportionation reactions (eqs 7−11), of a larger with a smaller *closo*-borane dianion cluster also point to energetic difficulties in preparing larger *closo*-borane dianions, $B_nH_n^{2-}$ (n = 13−17). Large *closo*-borane dianions cluster could be transformed into e.g. $B_{12}H_{12}^{2-}$, by reaction with smaller boranes, both charged and neutral, if the activation barriers are low enough.

$$B_{13}H_{13}^{2-} + B_{11}H_{11}^{2-} \rightarrow 2B_{12}H_{12}^{2-},\ \Delta H_7 = -118.79 \quad (7)$$

$$B_{14}H_{14}^{2-} + B_{10}H_{10}^{2-} \rightarrow 2B_{12}H_{12}^{2-},\ \Delta H_8 = -90.80 \quad (8)$$

$$B_{15}H_{15}^{2-} + B_9H_9^{2-} \rightarrow 2B_{12}H_{12}^{2-},\ \Delta H_9 = -134.42 \quad (9)$$

$$B_{16}H_{16}^{2-} + B_8H_8^{2-} \rightarrow 2B_{12}H_{12}^{2-},\ \Delta H_{10} = -146.10 \quad (10)$$

$$B_{17}H_{17}^{2-} + B_7H_7^{2-} \rightarrow 2B_{12}H_{12}^{2-},\ \Delta H_{11} = -148.09 \quad (11)$$

Such behavior is known experimentally. While $B_{12}H_{12}^{2-}$ is exceptionally stable toward degradative as well as disproportionation reactions,[27] the cesium salt of $B_{11}H_{11}^{2-}$ disproportionates above 400 °C into a equimolar mixture of $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$.[28] Other cage interconversions are known, e.g., the air oxidation of $B_9H_9^{2-}$ generates $B_8H_8^{2-}$, and small amounts of $B_6H_6^{2-}$ and $B_7H_7^{2-}$.[29] The oxidation of the sodium salt of $B_8H_8^{2-}$ yield $B_7H_7^{2-}$ and large amounts of $B_6H_6^{2-}$; small amounts of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$.[29]

On the other hand, the high stability of $B_{12}H_{12}^{2-}$ is illustrated by the following endothermic reactions:

$$B_{12}H_{12}^{2-} + B_6H_6^{2-} \rightarrow 2B_9H_9^{2-},\ \Delta H_{12} = +58.50 \quad (12)$$

$$B_{12}H_{12}^{2-} + B_8H_8^{2-} \rightarrow 2B_{10}H_{10}^{2-},\ \Delta H_{13} = +14.25 \quad (13)$$

$$B_{12}H_{12}^{2-} + B_{10}H_{10}^{2-} \rightarrow 2B_{11}H_{11}^{2-},\ \Delta H_{14} = +71.29 \quad (14)$$

$$B_{12}H_{12}^{2-} + B_{14}H_{14}^{2-} \rightarrow 2B_{13}H_{13}^{2-},\ \Delta H_{15} = +75.49 \quad (15)$$

$$B_{12}H_{12}^{2-} + B_{16}H_{16}^{2-} \rightarrow 2B_{14}H_{14}^{2-},\ \Delta H_{16} = +21.25 \quad (16)$$

This indicates that larger *closo*-borane dianions, $B_nH_n^{2-}$ (n = 13−17) once formed are not expected to degrade through interaction with $B_{12}H_{12}^{2-}$.

Recently,[5] we deduced the stability of an individual *closo*-borane dianion, $B_nH_n^{2-}$ (n = 5−12) compared with its neighbors, by another type of disproportionation, eq 17. This equation is now applied to the large *closo*-borane dianions, $B_nH_n^{2-}$ (n = 13−17).

$$2B_nH_n^{2-} \rightarrow B_{n-1}H_{n-1}^{2-} + B_{n+1}H_{n+1}^{2-},\ \Delta H_{\mathrm{dis}} \quad (17)$$

$B_{16}H_{16}^{2-}$, $B_{14}H_{14}^{2-}$, and $B_{12}H_{12}^{2-}$ are stable relative to their neighbors (all ΔH_{dis}, eq 17, are endothermic), whereas the corresponding $B_{15}H_{15}^{2-}$ and $B_{13}H_{13}^{2-}$ disproportionations are exothermic (Table 2). The values suggest $B_{13}H_{13}^{2-}$ (ΔH_{dis} = −75.5 kcal/mol) to be the least stable toward disproportionation

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(27) Middaugh, R. L. In *Boron Hydride Chemistry*; Academic Press: New York, 1975; p 282.

(28) Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1966**, *5*, 1955.

(29) Klanberg, F.; Eaton, D. R.; Guggenberger, L. J.; Mutterties, E. L. *Inorg. Chem.* **1967**, *6*, 1271.

in the larger *closo*-family. This is exactly the pattern indicated by Figure 3 where the curve is concave downward. According to eq 17, $B_{14}H_{14}^{2-}$ has the largest endothermic ΔH_{dis} value (+37.0 kcal/mol) among the large clusters (note the upward concave curve in Figure 3).

Three-Dimensional Aromaticity in Large *closo*-Borane Dianions, $B_nH_n^{2-}$ ($n = 13-17$). The main aromaticity criteria employed to characterize two-dimensional molecules[30,31] are energetic (resonance and aromatic stabilization energies, ASE),[32] geometric (bond length equalization, bond order indices, etc.),[33] and magnetic (^{1}H NMR chemical shifts,[34] magnetic susceptibility anisotropies[35] and their exaltations, Λ[36] as well as NICS[21] discussed below). While excellent correlations among the three criteria (e.g., ASE, NICS, Λ, and geometries) for a test set of five-membered heterocycles with wide-ranging properties has been demonstrated,[21,37] such quantitative relationships did not (and cannot be expected to) extend to more complex systems when other effects dominate.[5,38]

Recently, we assessed[5] the average energy per CH groups in two-dimensional aromatic compounds. The Hückel annulenes behave differently from the polybenzenoid hydrocarbons. The average stabilization energy per π electron (or CH group) in the strain-corrected [4n+2] Hückel annulenes decreases when n becomes larger. In contrast, the aromatic stabilization energy per π electron in polybenzenoid hydrocarbons is quite constant. Similar observations have been made by Aihara,[39] by Peck et al.,[40] and recently by Wiberg.[41] We have pointed out that these two-dimensional aromatic systems behave quite differently from the "three-dimensional aromatic" (*closo*-borane-based) clusters.[5]

As shown in Figure 2 (and previously)[5] the stabilization of the *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 5-12$) tends to increase with increasing cluster size. This characterizes the aromaticity in such three-dimensional systems. However, the average stability per vertex of the unknown larger *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 13-17$) are nearly the same and are much less than *closo*-$B_nH_n^{2-}$.

Moreover, all the aromaticity criteria do not serve well for *closo*-borane systems. Thus, the magnetic susceptibility anisotropies (χ_{anis})[35,35] are zero or very small in three-dimensionally delocalized spherical or nearly spherical molecules, and ^{11}B as well as ^{1}H NMR chemical shifts are not informative in this context. While the magnetic susceptibility exaltation, Λ,[36] (ppm, cgs), is a unique aromaticity criteria directly related to ring currents,[36] the magnitude of Λ depends not only on the degree of cyclic electron delocalization, but also on the volume of a cluster to a higher order. Nevertheless, quite large magnetic susceptibility exaltations have been found in *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 5-12$).[1a,4,5] Chemical shifts of encapsulated ^{3}He atoms (computed as well as experimental) have been employed as measure of aromaticity in fullerenes and fullerene derivatives.[42] However, most of the *closo*-systems are too small to accommodate ^{3}He or other elements.[43] Instead, we use the magnetic shieldings computed at chosen points, e.g., at the cage center; these NICS[21] can be obtained readily via widely used quantum chemical programs (the sign of the magnetic shielding is changed to conform with the chemical shift convention). This new magnetic criteria, NICS,[21] evaluates ring current effects and aromaticity and appears not to exhibit a higher order dependence, e.g., on the area of a ring or the volume of a three-dimensional cluser.[5,21]

The NICS and geometric criteria (bond length alternation) confirm long-standing proposals in the literature that *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 5-12$) are spherical aromatics and exhibit three-dimensional aromaticity.[1-5] We have shown cyclic electron delocalization (and the ability to sustain a diamagnetic ring current) to be the defining characteristic of aromaticity for the *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 5-12$);[5] to what extent are larger *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 13-17$) aromatic on this basis?

NICS of the Large *closo*-Borane Dianions, $B_nH_n^{2-}$ ($n = 13-17$). The NICS values, typically between −25 and −35 ppm, have shown *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 5-12$) to be "three-dimensional aromatic" prototypes. The most symmetric $B_{12}H_{12}^{2-}$ (I_h), $B_6H_6^{2-}$ (O_h), and $B_{10}H_{10}^{2-}$ (D_{4d}) species give the largest NICS values and are the most "aromatic" among the *closo*-borane dianions family.

The NICS values computed at the cage centers of the large *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 13-17$) all are quite negative (Table 2) indicating the "three-dimensional aromaticity" in these large clusters. Compound $B_{17}H_{17}^{2-}$ has the largest NICS value (−36.5 ppm) in this family of large clusters. NICS values, −33.7 in the center of $B_{16}H_{16}^{2-}$ and −33.5 in $B_{10}H_{10}^{2-}$, show both dianions to have nearly the same degree of aromatic delocalization. The NICS value for $B_{14}H_{14}^{2-}$, −32.3, is larger in magnitude than the −31.6 for $B_{15}H_{15}^{2-}$. Like the other criteria, the NICS value (−30.9) suggests $B_{13}H_{13}^{2-}$ to be the least aromatic among the larger *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 13-17$), we have considered. However, the variations are not large.

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[43] The energies of reactions 18 and 19 (below) are strongly endothermic at B3LYP/6-31G*.

$$B_{12}H_{12}^{2-}\ (I_h) + \mathrm{He} \rightarrow \mathrm{He}@B_{12}H_{12}^{2-}\ (I_h),\quad E_{18} = +170\ \mathrm{kcal/mol} \quad (18)$$

$$B_{17}H_{17}^{2-}\ (D_{5h}) + \mathrm{He} \rightarrow \mathrm{He}@B_{17}H_{17}^{2-}\ (D_{5h}),\quad E_{19} = +85\ \mathrm{kcal/mol} \quad (19)$$

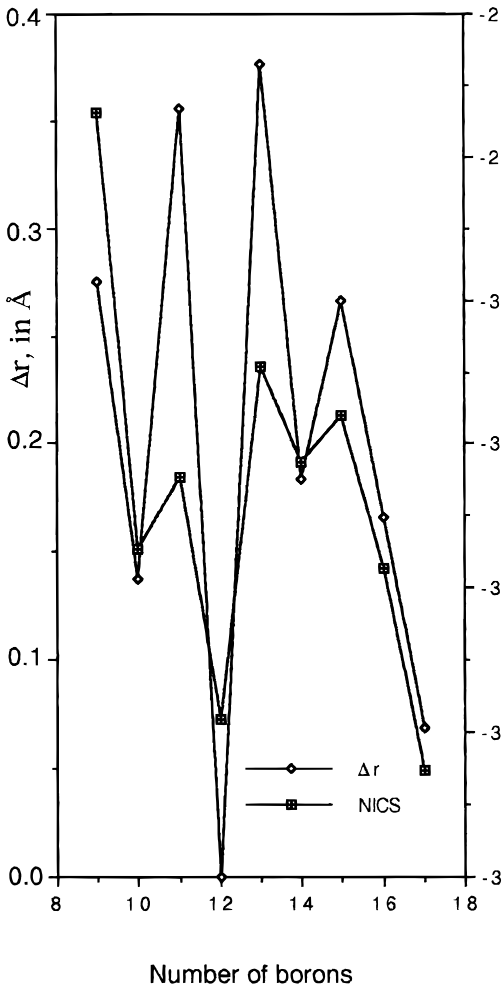

Figure 4. Plots of NICS computed at the centers of the larger *closo*-borane dianions $B_nH_n^{2-}$ (n = 9−17) and the largest bond length difference (Δ*r*, in Å) of each cluster vs the number of boron atoms. Note that both these trends agree qualitatively with the energy trends in Figure 3.

Geometric Criteria. Aromatic compounds are characterized by bond length equalization, whereas antiaromatic compounds show large bond length alternations.[30,31,33] We employed[5] the difference between the longest and shortest skeletal bonds (Δ*r*) in *closo*-borane dianions, $B_nH_n^{2-}$ (n = 5−12), as the simplest geometric criterion. High symmetry and small bond length alternations are associated with more efficient deltahedral skeletal bonding in the *closo*-borane dianions. The variation in the bond distances between the skeleton atoms appears to reflect the extent of delocalization in the cage. The regular $B_{12}H_{12}^{2-}$ icosahedron possesses "perfect" deltahedral bonding; all the bond length are the same (Δ*r* = 0.0 Å) (Figure 4). Among the larger *closo*-borane dianions, $B_{17}H_{17}^{2-}$ has a relatively small bond length alternation Δ*r* = 0.069 Å (compare $B_{10}H_{10}^{2-}$, Δ*r* = 0.138 Å). Both $B_{16}H_{16}^{2-}$ (Δ*r* = 0.166 Å) and $B_{14}H_{14}^{2-}$ (Δ*r* = 0.184 Å) have nearly the same bond length ranges. The Δ*r* of *closo*-$B_{13}H_{13}^{2-}$ (Δ*r* = 0.376 Å), like $B_{11}H_{11}^{2-}$ (Δ*r* = 0.356 Å), is significantly larger. The bond length ranges of *closo*-$B_{15}H_{15}^{2}$ (Δ*r* = 0.266 Å) and $B_9H_9^{2}$ (Δ*r* = 0.275 Å) are intermediate (Table 2).

The patterns of the NICS values and of the bond length alternations (Δ*r*), compared in Figure 4, are remarkably similar, (e.g., low NICS and high Δ*r* for $B_9H_9^{2-}$, $B_{11}H_{11}^{2-}$, $B_{13}H_{13}^{2-}$, and $B_{15}H_{15}^{2-}$; opposite behavior for the rest). While not quantitative, this demonstrates the relationship between geometric and magnetic criteria of aromaticity in large *closo*-borane dianions, $B_nH_n^{2-}$ (n = 9−17). Note that both these trends also agree qualitatively with the energy trends (compare Figures 3 and 4).

Conclusions

Experimentally, $B_{10}H_{10}^{2-}$, $B_{11}H_{11}^{2-}$, and $B_{12}H_{12}^{2-}$ can be prepared from $B_{10}H_{14}$ or even from B_2H_6.[26] The failure to observe $B_{13}H_{13}^{2-}$ or the larger *closo*-borane dianions under such synthetic conditions indicates either that they are relatively unstable thermodynamically, or that there is a "mechanistic bottleneck" (e.g. the $B_{12}H_{12}^{2-}$ to $B_{13}H_{13}^{2-}$ step). The data from eqs 7−11 support these possibilities. However, degradation routes, e.g., starting from the larger metalloboranes with 13 or more borons,[10−20] would appear to offer synthetic opportunities. Professor W. N. Lipscomb pointed out to us that he has long felt that ring closure or addition reactions of cis-conjuncto boranes, e.g. $B_{14}H_{20}$,[44] might serve as routes to the larger *closo*-boranes.

According to our energetic analysis (both Figures 2 and 3) the thermodynamic stabilities of the unknown larger *closo*-boranes, $B_{13}H_{13}^{2-}$ to $B_{17}H_{17}^{2-}$, are greater than e.g., $B_9H_9^{2-}$ and even $B_{10}H_{10}^{2-}$ and $B_{11}H_{11}^{2-}$; this agrees with Lipscomb's conclusions. However, $B_{13}H_{13}^{2-}$, $B_{14}H_{14}^{2-}$, and $B_{15}H_{15}^{2-}$ are less stable than $B_{12}H_{12}^{2-}$ according to both treatments. While Lipscomb's treatment identifies the most highly symmetrical species, $B_{12}H_{12}^{2-}$, as having the lowest average energy per vertex among the *closo*-borane dianions (Figure 2), our cumulative total energies for the sequential addition of BH groups, ΔH_{add} (Figure 3), show that $B_{16}H_{16}^{2-}$ and $B_{17}H_{17}^{2-}$ are more favorable than $B_{12}H_{12}^{2-}$ due to the larger number of vertexes. The endothermic reaction energies (eqs 2−4) also show, the formation of $B_{14}H_{14}^{2-}$, $B_{15}H_{15}^{2-}$, and especially $B_{13}H_{13}^{2-}$ from $B_{12}H_{12}^{2-}$ to be unfavorable. In contrast, the exothermicity of eqs 5 and 6 indicate that formation of the larger $B_{16}H_{16}^{2-}$ and $B_{17}H_{17}^{2-}$ dianions are favorable relative to $B_{12}H_{12}^{2-}$.

According to our quantitative evaluations, the stabilities of the larger *closo*-borane dianions, $B_nH_n^{2-}$ (n = 12−17) decrease in the following sequence:

$$B_{17}H_{17}^{2-} > B_{16}H_{16}^{2-} > B_{12}H_{12}^{2-} > B_{14}H_{14}^{2-} > B_{15}H_{15}^{2-} > B_{13}H_{13}^{2-}$$

Moreover, the highly exothermic disproportionation reactions of larger and smaller *closo*-borane dianions (eqs 7−11) indicate that the larger *closo*-borane dianions, $B_nH_n^{2-}$ (n = 13−17) may not persist under conditions where smaller boranes are present. Hence, $B_{12}H_{12}^{2-}$ is likely to form during attempted synthesis of the larger borane dianions; this may be responsible for the failure to observe the larger species.

Magnetic properties are most closely related to the degree of cyclic electron delocalization. NICS, based on the magnetic shielding in the geometric centers of the cage systems, supports the existence of three-dimensional aromaticity in the large *closo*-borane dianions, $B_nH_n^{2-}$ (n = 13−17). The trends agree qualitatively with the thermodynamic stabilities and with those from the bond length alternation (Δ*r*) (compare Figures 3 and 4). $B_{12}H_{12}^{2-}$ and $B_{17}H_{17}^{2-}$ are more "aromatic" than the other members of the larger dianion family; $B_{13}H_{13}^{2-}$ is the least aromatic.

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