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Articles

Stability and Three-Dimensional Aromaticity of *closo*-Monocarbaborane Anions, $CB_{n-1}H_n^-$, and *closo*-Dicarboranes, $C_2B_{n-2}H_n$

Paul von Ragué Schleyer*[†,‡] **and Katayoun Najafian**[†]

Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkstrasse 42,
D-91054 Erlangen, Germany, and Department of Chemistry, University of Georgia,
Athens, Georgia 30602

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Comprehensive ab initio calculations RMP2(fc)/6-31G* on the *closo*-monocarbaboranes, $CB_{n-1}H_n^-$ ($n = 5-12$), and the *closo*-dicarboranes, $C_2B_{n-2}H_n$ ($n = 5-12$), show that the relative energies of all the positional isomers agree with the qualitative connectivity considerations of Williams and with the topological charge stabilization rule of Gimarc. The reaction energies (ΔH) of the most stable positional isomers, 1-$CB_4H_5^-$, $CB_5H_6^-$, 2-$CB_6H_7^-$, 1-$CB_7H_8^-$, 5-$CB_8H_9^-$, 1-$CB_9H_{10}^-$, 2-$CB_{10}H_{11}^-$, $CB_{11}H_{12}^-$, as well as 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, 1,7-$C_2B_6H_8$, 4,5-$C_2B_7H_9$, 1,10-$C_2B_8H_{10}$, 2,3-$C_2B_9H_{11}$, and 1,12-$C_2B_{10}H_{12}$ (computed using the equations, $CBH_2^- + (n-1)BH_{\text{increment}} \rightarrow CB_nH_{n+1}^-$ ($n = 4-11$) and $C_2H_2 + nBH_{\text{increment}} \rightarrow C_2B_nH_{n+2}$ ($n = 3-10$)), show that the stabilities of *closo*-$CB_{n-1}H_n^-$ and of *closo*-$C_2B_{n-2}H_n$ generally increase with increasing cluster size from 5 to 12 vertexes. This is a characteristic of three-dimensional aromaticity. There are variations in stabilities of individual *closo*-$CB_{n-1}H_n^-$ and *closo*-$C_2B_{n-2}H_n$ species, but these show quite similar trends. Moreover, there is rough additivity for each carbon replacement. The rather large nucleus independent chemical shifts (NICS) and the magnetic susceptibilities (χ), which correspond well with one another, also show all *closo*-$CB_{n-1}H_n^-$ and *closo*-$C_2B_{n-2}H_n$ species to exhibit "three-dimensional aromaticity". However, the aromaticity ordering based on these magnetic properties does not always agree with the relative stabilities of positional isomers of the same cluster, when other effects such as connectivity and charge considerations are important.

Introduction

The fascinating *closo*-carboranes are a widely studied class of carbon-containing polyhedral boron-clusters.[1−3] Because of their high stability, nonclassical bonding, and the benzene-like reactivity, many members of this class of compounds have long been regarded as being aromatic.,[4,5,12−15,90−93] King and Rouvray[6] introduced a graph-theoretical model based on the Hückel theory for the interpretation of the three-dimensional delocalization in polyhedral borane dianions with n vertexes and containing ($n + 1$) skeletal electron pairs. Using similar graph-theoretical methods, Aihara[7] evaluated the resonance energies of *closo*-$B_nH_n^{2-}$ resulting from three-dimensional delocalization. Accordingly, the most highly symmetric *closo*-$B_{12}H_{12}^{2-}$ (I_h) has the largest resonance stabilization, 1.763β, but *closo*-$B_5H_5^{2-}$ with 0.0β was classified as "non-aromatic". However, our recent ab initio[4,5] studies show three-dimensional delocalization in $B_5H_5^{2-}$ in contrast to Aihara's description.[7] Furthermore, the isoelectronic 1,5-$C_2B_3H_5$ was shown[4] to exhibit nonclassical, delocalized bonding (refuting the widely accepted classical description[8]).

The two carbons in the *closo*-$C_2B_{n-2}H_n$ set can be located in different polyhedral cage vertexes, giving rise to at least two positional isomers for a given cluster nuclearity. The relative stabilities of positional isomers of *closo*-dicarboranes $C_2B_{n-2}H_n$

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* Author for correspondence.

[†] University of Erlangen−Nuremberg.

[‡] University of Georgia.

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($n = 5-12$) have been investigated at lower theoretical levels by Dewar and McKee (modified neglect of diatomic overlap (MNDO)),[9] as well as by Gimarc et al. (three-dimensional Hückel theory[10] and minimal basis set ab initio).[11] One of the goals of the present paper is to reevaluate the stability of the *closo*-dicarboranes $C_2B_{n-2}H_n$ ($n = 5-12$) at electron-correlated theoretical levels higher than have been employed previously.

Due to the unusual stability and benzene-like reactivity (electrophilic substitution) the ortho-icosahedral carborane $C_2B_{10}H_{12}$ and its meta and para isomers have even been described as "superaromatic".[1−2,12] The connection, both physical and conceptual, between the three-dimensional icosahedral carboranes and the classical two-dimensional polybenzenoid aromatic compounds has been fruitful.[13−15]

Moreover, the remarkable stability of the iscosahedral $C_2B_{10}H_{12}$ has led to various uses, e.g., in medicine for boron neutron capture therapy (BNCT) for tumors,[16] in material science (as precursors to boron carbide thin films and other ceramics),[17] and as molecular scaffolds (rigid building units).[18] The chemistry of $C_2B_{10}H_{12}$,[19] $C_2B_9H_{11}$,[20−23] $C_2B_8H_{10}$,[20,21a,24,25] $C_2B_7H_9$,[20,26,27] $C_2B_6H_8$,[8,20,21a,26b,28] $C_2B_5H_7$,[8,20,29−31] $C_2B_4H_6$,[8,20,29,32,33] and $C_2B_3H_5$[4,8,20,29,33,34] have been investigated to the greatest extent.

Recently, *closo*-boranes with only one heteroatom,[35] e.g., $B_{11}H_{11}NH$,[36] $B_{11}H_{11}PR$,[37] $B_{11}H_{11}S$,[38] B_9H_9NH,[39] and B_9H_9S,[40] in 10 and 12 vertex systems have been synthesized. Unlike *closo*-$C_2B_{n-2}H_n$ ($n = 5-12$), the monoanionic analogues, $CB_{n-1}H_n^-$ ($n = 5-12$), have received less attention,[41,43−50,60−74] even though the first member of this family, $CB_{11}H_{12}^-$, was prepared by Knoth 30 years.[42a]

In the $CB_{n-1}H_n^-$ family, $CB_{11}H_{12}^-$ [60−71] and similar anions such as $CB_9H_{10}^-$ [72−74] have been studied extensively experimentally due to their potential use as weakly coordinating anions and as extremely weak nucleophiles with exceptional inertness.

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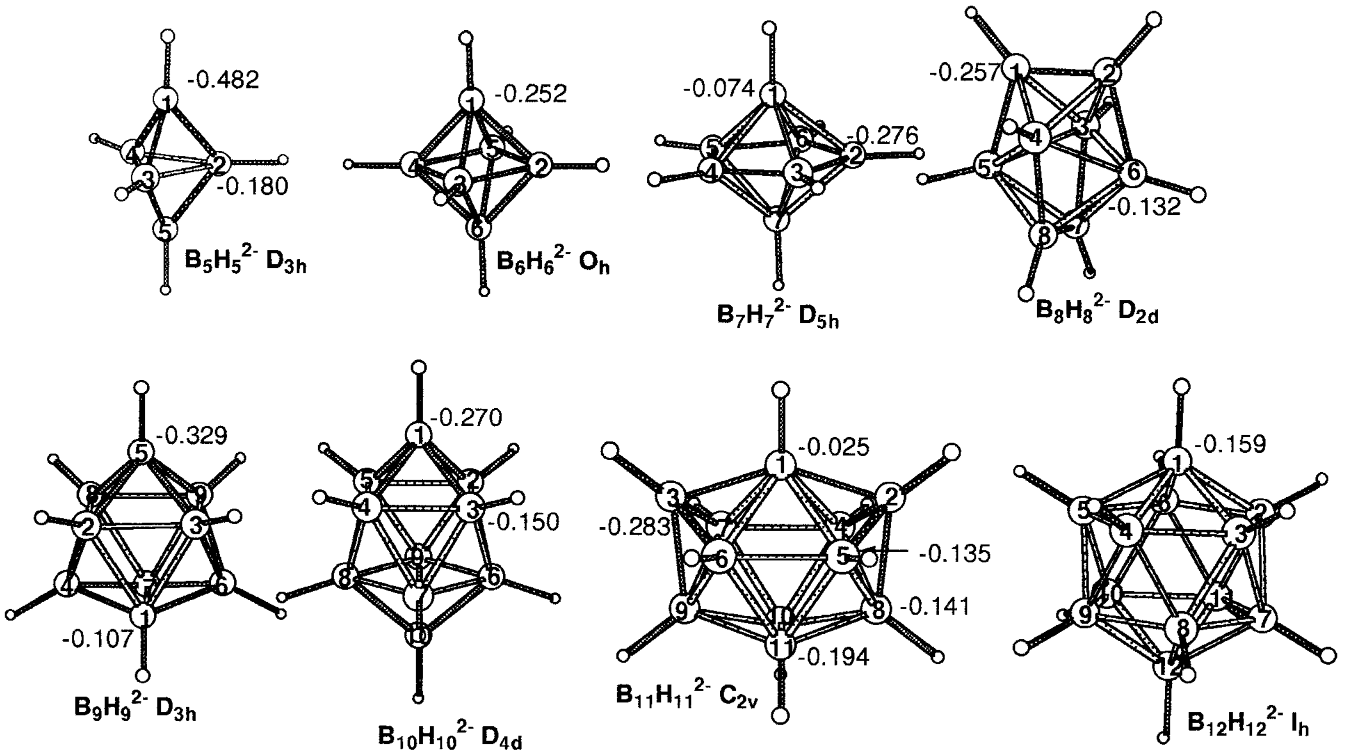

Figure 1. Natural charges obtained at RHF/6-31G* level for *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 5-12$).

Among other members of this *closo*-family, only $CB_{10}H_{11}^{-}$ [42,43] and $CB_7H_8^{-}$ [44,45] have been synthesized and characterized by ^{11}B NMR; their derivatives have not been investigated to any gr(eat extent.[46,47] There has been no report on the synthesis of small vertex *closo*-monocarbaboranes. Likewise, ab initio calculations only on $CB_{11}H_{12}^{-}$,[48,49] $CB_9H_{10}^{-}$,[39b,48b,49] $CB_5H_6^{-}$,[50] and $CB_4H_5^{-}$ [49] have been reported.

Three qualitative considerations rationalize and predict the relative stabilities of *closo*-dicarboranes, $C_2B_{n-2}H_n$ ($n = 5-12$). The first is the empirical valence rules of Williams,[51] which suggest that (a) electronegative atoms such as carbon usually prefer the least connected vertex since such atoms are less prone to electron sharing and consequently form fewer bonds; (b) the carbons in the thermodynamically most stable dicarborane isomers are as far apart as possible. Empirical rule (a) helps rationalize the positional isomers of the neutral *closo*-dicarboranes[52] with two carbons and should be applicable to the *closo*-monocarbaboranes systems as well.

Gimarc's topological charge stabilization[52] rule is based on the perturbation of a homonuclear cage: the electronegative heteroatoms prefer sites with the highest negative charge. This rule successfully predicts the stability order of the *closo*-$C_2B_{n-2}H_n$ ($n = 5-12$) positional isomers and agrees well with the experimental observations.[52]

Jemmis and Schleyer[53] refined their "six interstitial electron rule" for three-dimensional delocalization to consider the compatibility of orbital overlap. The radial extension of the π-orbitals of the capping atom should give the best "fit" to rings of optimum size. Like Williams's connectivity rule, this rationalizes the relative preferences of various positional isomers in a polyhedral skeleton.

Recently, we pointed out[5] that the exceptional behavior of the *closo*-borane family is direct evidence of the "three-dimensional aromaticity" which becomes greater proportionately to increasing cluster size. This was shown by several criteria. The difference between the longest and the shortest bonds (Δr) was proposed as a structural criterion of aromaticity in the *closo*-borane dianions. The deviations from perfectly symmetrical deltahedral bonding (exhibited only by $B_{12}H_{12}^{2-}$ and $B_6H_6^{2-}$) in the other *closo*-borane dianion cages is reflected in higher relative energies.

Magnetic criteria agree that the *closo*-borane dianions are aromatic, in particular, nucleus independent chemical shifts (NICS),[54] which are based on the magnetic shieldings computed in the geometric centers of the *closo*-boranes cage, provide a direct measure of the ring current effects.[5] There is remarkably similar behavior among the NICS values of the *closo*-borane dianions, the Δr geometric criterion, and the average energy.[5] This supports the existence of three-dimensional aromaticity in polyhedral clusters.[7] We now extend our theoretical studies at the ab initio MP2/6-31G* level to the *closo*-monocarbaboranes. The *closo*-monocarbaboranes, $CB_nH_{n+1}^{-}$ ($n = 5-12$), have not been addressed comprehensively in the literature. Hence, another goal of this paper is to predict the relative stabilities of members of this family by using ab initio molecular orbital theory. We compare the results with predictions based on

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Table 1. Data for Positional Isomers of *closo*-Dicarboranes, $C_2B_{n-2}H_n$ ($n = 5-12$), Zero Point (ZPE)[a] and Relative Energies[c]

isomer	symmetry	ZPE[a]	RMP2/6-31G*	relative energies[c]
$C_2B_3H_5$				
1,5-	D_{3h}	47.31(0)	−153.18433	0.00
1,2-	C_s	46.33(0)	−153.12666	35.32
2,3-	C_{2v}	44.26(2)	−153.08896	57.13
$C_2B_4H_6$				
1,6-	D_{4h}	57.37(0)	−178.56238	0.00
1,2-	C_{2v}	57.44(0)	−178.54745	9.43
$C_2B_5H_7$				
2,4-	C_{2v}	67.43(0)	−203.94443	0.00
2,3-	C_{2v}	67.24(0)	−203.91775	16.58
1,2-	C_s	66.33(0)	−203.87669	41.53
1,7-	D_{5h}	65.19(0)	−203.83643	65.78
$C_2B_6H_8$				
1,7-	C_2	76.53(0)	−229.30079	0.00
1,2-	C_{2v}	76.07(0)	−229.26484	22.16
1,6-	C_s	75.41(1)	−229.25930	25.04
1,3-	C_s	75.99(0)	−229.24540	34.28
1,5-	C_s	75.93(0)	−229.23454	41.05
3,4-	C_{2v}	75.14(0)	−229.21452	52.91
$C_2B_7H_9$				
4,5-	C_{2v}	83.29(0)[b]	−254.68224	0.00
3,4-	C_s	85.62(0)	−254.65273	16.43
1,4-	C_1	85.57(0)	−254.62440	34.16
1,8-	C_2	81.85(0)[b]	−254.61166	42.93
1,7-	C_{2v}	81.57(0)[b]	−254.59013	56.18
$C_2B_8H_{10}$				
1,10-	D_{4d}	97.18(0)	−280.09789	0.00
1,6-	C_s	96.59(0)	−280.06276	21.52
1,2-	C_s	96.31(0)	−280.03388	39.39
2,7-	C_2	96.04(0)	−280.02971	41.76
2,4-	C_{2v}	95.80(0)	−280.02326	45.60
2,6-	C_2	95.74(0)	−280.00785	55.21
2,3-	C_s	95.70(0)	−280.00591	56.40
$C_2B_9H_{11}$				
2,3-	C_{2v}	105.84(0)	−305.43626	0.00
2,9-	C_s	105.80(0)	−305.40840	17.46
2,10-	C_1	105.65(0)	−305.40704	18.17
$C_2B_{10}H_{12}$				
1,12-	D_{5d}	117.91(0)	−330.86234	0.00
1,7-	C_{2v}	117.83(0)	−330.85660	3.53
1,2-	C_{2v}	117.54(0)	−330.83138	19.10
C_2H_2	$D_{\infty h}$	18.48(0)	−77.06679	

[a] Zero point energy (ZAE) (kcal/mol), calculated at HF/6-31G(d). In parentheses, number of imaginary frequencies NIMAG. [b] At RMP2/6-31G*. [c] The relative energies with ZPEs corrections scaled by 0.89 (and 0.94 for RMP2/6-31G*) in kcal/mol.

Table 2. Relative Energies of *closo*-Dicarboranes, $C_2B_{n-2}H_n$ (kcal/mol),[a−c] and Nucleus Independent Chemical Shifts[d] (NICS, ppm) and Magnetic Suceptibilities[e] (χ, ppm cgs)

		relative energies				
isomer	symmetry	3D Hückel[a]	STO-3G[b]	RMP2/ 6-31G*[c]	NICS[d]	χ[e]
$C_2B_3H_5$						
1,5-	D_{3h}	0.0	0.0	0.00	−17.06	−37.74
1,2-	C_s	57.4	53.5	35.32	−24.60	−44.10
2,3-	C_{2v}	82.3	85.1	57.13	−35.74	−51.52
$C_2B_4H_6$						
1,6-	D_{4h}	0.0	0.0	0.00	−36.01	−60.07
1,2-	C_{2v}	25.2	9.8	9.43	−34.92	−58.50
$C_2B_5H_7$						
2,4-	C_{2v}	0.0	0.0	0.00	−28.36	−67.33
2,3-	C_{2v}	27.2	24.2	16.58	−28.04	−66.67
1,2-	C_s	48.3	49.8	41.53	−27.72	−65.96
1,7-	D_{5h}	51.3	79.8	65.78	−28.30	−66.90
$C_2B_6H_8$						
1,7-	C_2	0.0	0.0	0.0	−24.01	−74.85
1,2-	C_{2v}	28.4	29.5	22.16	−21.17	−72.36
1,6-	C_s	26.5	27.6	25.04	−22.68	−74.30
1,3-	C_s	48.8	37.1	34.28	−15.90	−65.76
1,5-	C_s	51.4	53.8	41.05	−17.18	−65.89
3,4-	C_{2v}	53.1	63.3	52.91	−24.40	−77.45
$C_2B_7H_9$						
4,5-	C_{2v}	0.0	0.0	0.00	−25.10	−90.85
3,4-	C_s	26.9	19.9	16.43	−25.93	−93.50
1,4-	C_1	51.2	42.6	34.16	−24.21	−91.48
1,8-	C_2	53.9	53.1	42.93	−27.27	−98.46
1,7-	C_{2v}	75.5	75.1	56.18	−26.72	−97.04
$C_2B_8H_{10}$						
1,10-	D_{4d}	0.0	0.0	0.0	−29.61	−109.28
1,6-	C_s	24.5	28.1	21.52	−30.58	−114.96
1,2-	C_s	49.0	54.0	39.39	−29.72	−114.12
2,7-	C_2	48.9	53.2	41.76	−33.84	−122.07
2,4-	C_{2v}	48.9	61.0	45.60	−34.07	−123.64
2,6-	C_2	70.0	73.7	55.21	−34.22	−123.13
2,3-	C_s	70.3	74.0	56.40	−33.48	−122.33
$C_2B_9H_{11}$						
2,3-	C_{2v}	0.0	0.0	0.0	−28.39	−120.47
2,9-	C_s	22.4	19.8	17.46	−28.75	−122.75
2,10-	C_1	24.3	24.5	18.17	−31.42	−127.10
$C_2B_{10}H_{12}$						
1,12-	D_{5d}	0.0	0.0	0.0	−35.40	−148.20
1,7-	C_{2v}	0.0	4.6	3.53	−34.19	−145.87[f]
1,2-	C_{2v}	22.1	35.9	19.10	−34.10	−145.82[g]

[a,b] Relative energies of *closo*-dicarborane isomers, $C_2B_{n-2}H_n$ ($n = 5-12$), as obtained by three-dimensional Hückel theory and ab initio calculations from refs 10, 11. [c] From Table 1. [d] At GIAO-SCF/6-31G*//MP2(fc)/6-31G*. [e] At CSGT-HF/6-31+G*//MP2(fc)/6-31G*. [f] Measured magnetic susceptiblity for 1,7-$C_2B_{10}H_{12}$ $\chi = -144$ ppm cgs, ref 96. [g] Measured magnetic susceptibility for 1,2-$C_2B_{10}H_{12}$ $\chi = -145$ ppm cgs, ref 96.

William's empirical valence rule[51] and on Gimarc's rule of topological charge stabilization.[52] Comparison of the *closo*-borane dianions with the isoelectronic *closo*-dicarboranes and monocarbaboranes reveals the effects of the electronegative carbon atoms in these structures.

Methods

All calculations used the Gaussian94 program package.[55] The structures considered in this paper, *closo*-$B_nH_n^{2-}$ ($n = 5-12$), and *closo*-$CB_{n-1}H_n^-$ ($n = 5-12$), and *closo*-$C_2B_{n-2}H_n$ ($n = 5-12$), were optimized first at HF/6-31G* within the given symmetry restriction. Frequency calculations, carried out at the same level, determined the nature of the stationary points and gave the zero point energies (ZPE).[56] Minima were characterized with zero imaginary frequency and transition states with one imaginary frequency. Further optimizations at MP2(fc)/6-31G* included the effect of electron correlation and gave the relative energies. The natural population analysis (NPA)[57] obtained at HF/6-31G* level for the *closo*-borane dianions are discussed (see Figure 1). Based on the data in Tables 1−4, the relative reaction energies ΔH for three sets of *closo*-clusters in Tables 5−7 include zero point energies scaled by a factor of 0.89. Selected geometry parameters are given in Table 4.

NICS[54] were computed at GIAO-HF/6-31G*[58] and magnetic susceptibilities at CSGT-HF/6-31+G*//MP2/6-31G*,[59] both using the RMP2/6-31G* optimized geometries (Figures 2 and 3).

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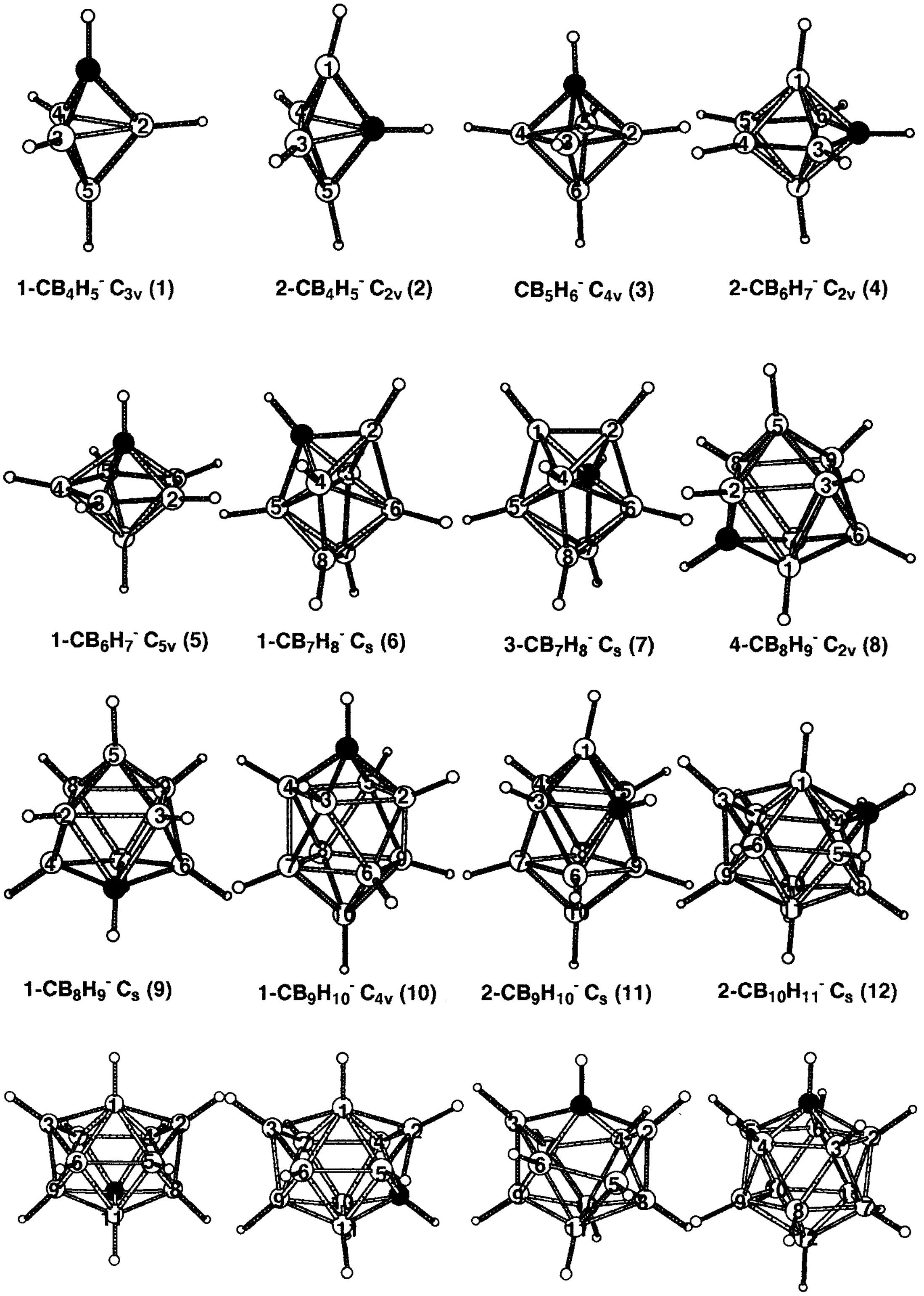

1-CB$_4$H$_5^-$ C_{3v} (1) **2-CB$_4$H$_5^-$ C_{2v} (2)** **CB$_5$H$_6^-$ C_{4v} (3)** **2-CB$_6$H$_7^-$ C_{2v} (4)**

1-CB$_6$H$_7^-$ C_{5v} (5) **1-CB$_7$H$_8^-$ C_s (6)** **3-CB$_7$H$_8^-$ C_s (7)** **4-CB$_8$H$_9^-$ C_{2v} (8)**

1-CB$_8$H$_9^-$ C_s (9) **1-CB$_9$H$_{10}^-$ C_{4v} (10)** **2-CB$_9$H$_{10}^-$ C_s (11)** **2-CB$_{10}$H$_{11}^-$ C_s (12)**

10-CB$_{10}$H$_{11}^-$ C_s (13) **8-CB$_{10}$H$_{11}^-$ C_s (14)** **1-CB$_{10}$H$_{11}^-$ C_2 (15)** **CB$_{11}$H$_{12}^-$ C_{5v} (16)**

Figure 2. RMP2/6-31G* optimized geometries for *closo*-monocarbaboranes CB$_{n-1}$H$_n^-$ (n = 5−12).

Results and Discussion

On the basis of topological charge stabilization[52] and three-dimensional Hückel theory[10] (also quantified using minimal basis set STO-3G ab initio calculations),[11] Gimarc predicted the relative stability of the *closo*-dicarboranes positional isomers (Table 2). We reevaluate the relative energies of this family using higher level (MP2(fc)/6-31G*) data including electron correlation effects. The total energies of all the positional isomers of *closo*-dicarboranes are given in Table 1 along with the zero point energies and the number of imaginary frequencies. Our calculations agree with Gimarc's predictions and also with experimental experience.[10,11]

Relative Energies of *closo*-Monocarbaborane Anions, CB$_{n-1}$H$_n^-$ Isomers (n = 5−12). *closo*-Monocarbaborane anions, CB$_{n-1}$H$_n^-$ (n = 5−12), are closed polyhedral structure with triangular faces (Figure 2). The total coordination number

Table 3. *closo*-Monocarbaboranes, $CB_{n-1}H_n^-$ ($n = 5-12$), Zero Point (ZPE)[a] and Relative Energies[c]

molecules	symmetry	ZPE[a]	RMP2/6-31G*	relative energy[c]
$CB_4H_5^-$				
1-	C_{3v}	43.32(0)	−139.96038	0.00
2-	C_{2v}	40.06(0)[b]	−139.92081	25.53
$CB_5H_6^-$	C_{4v}	54.06(0)	−165.38007	0.00
$CB_6H_7^-$				
2-	C_{2v}	63.66(0)	−190.75884	0.00
1-	C_{5v}	62.74(0)	−190.70896	30.47
$CB_7H_8^-$				
1-	C_s	72.71(0)	−216.12067	0.00
3-	C_s	71.53(1)	−216.08095	23.88
$CB_8H_9^-$				
4-	C_{2v}	78.69(0)[b]	−241.51270	0.00
1-	C_s	81.70(0)	−241.47755	17.65
$CB_9H_{10}^-$				
1-	C_{4v}	93.35(0)	−266.93001	0.00
2-	C_s	92.81(0)	−266.89637	20.63
$CB_{10}H_{11}^-$				
2-	C_s	102.42(0)	−292.27992	0.00
10-	C_s	102.11(0)	−292.25056	18.15
8-	C_s	101.98(0)	−292.24662	20.51
1-	C_2	100.96(1)	−292.22503	33.15
$CB_{11}H_{12}^-$	C_{5v}	114.48(0)	−317.73467	0.00
CBH_2^-	$C_{\infty v}$	15.63(0)	−63.80076	

[a] Zero point energy (kcal/mol), calculated at HF/6-31G(d). In parentheses, number of imaginary frequencies NIMAG. [b] At B3LYP/6-31G*. [c] The relative energies with ZPEs corrections scaled by 0.89 (and 0.98 for B3LYP/6-31G*) in kcal/mol.

(includig the hydrogen) of each boron or carbon, at a cage vertex, range from 4 to 7 and are denoted as B4, B5, B6, and B7. All the different possible carbon sites in each polyhedral cage were considered. Table 3 lists the total and relative energies, along with the ZPE and the number of imaginary frequencies for all 16 positional isomers of the *closo*-monocarbaboranes, $CB_{n-1}H_n^-$ ($n = 5-12$). The $B_nH_n^{2-}$ ($n = 5-12$) set serves as the reference framework for the charge differences between vertexes in a polyhedral cage. The natural charges on each boron vertex, derived from NPA[57] are shown in Figure 1 for the *closo*-borane dianions (along with the numbering scheme, which is generally employed).

$CB_{11}H_{12}^-$. The regular $B_{12}H_{12}^{2-}$ icosahedron possesses indistinguishable BH groups, and the charge distribution is uniform. Hence there is only one $CB_{11}H_{12}^-$ isomer (**16**) (Figure 2). Our ab initio calculations show a stable minimum the C_{5v} geometry.

Although $CB_{11}H_{12}^-$ was first reported by Knöth[42a] in 1967 and its ^{11}B NMR spectra confirm the icosahedral structure, the chemistry of this anion has been developed only recently.[60−71] Reed's group has exploited the low ligand coordinating power of this anion for the complexation of transition metals, for example, in $[(\eta^1\text{-}C_6H_6)Ag(\textit{closo}\text{-}1\text{-}CB_{11}H_{12})]C_6H_6$,[62] $[Fe(TPP)(\textit{closo}\text{-}1\text{-}CB_{11}H_{12})]C_7H_8$,[63] $[(Ir(CO)(PPh_3)_2Ag(\textit{closo}\text{-}1\text{-}CB_{11}H_{12})]$,[64,65] and $[Cp(CO)_2FeCB_{11}H_{12})]$.[65] Structural studies have shown that the most hydridic (negatively charged) hydrogen atom in these complexes (H_{12}, at the boron antipodal to carbon)[66] is always involved in the metal−$CB_{11}H_{12}^-$ bonding. Derivatization of $CB_{11}H_{12}^-$ via electrophilic substitution results in even larger, less nucleophilic, and less coordinating anions which also are more soluble in low dielectric solvents. Examples are 12-$CB_{11}H_{11}X^-$ (X = F^-,[67] Cl^-,[68] Br^-,[68] I^-[69]); 7,12-$CB_{11}H_{10}X_2^-$ (X= Cl^-, Br^-, I^-);[68] 7,8,9,10,12-$CB_{11}H_7Cl_5^-$ and 7,8,9,10,11,-12-$CB_{11}H_6X_6^-$ (X= Cl^-, Br^-).[69a,70] Recently, Michl and coworkers[71] have synthesized the completely methyl-substituted $CB_{11}Me_{12}^-$.

$CB_{10}H_{11}^-$. Although five positional isomers based on $B_{11}H_{11}^{2-}$ (Figure 1) are possible for $CB_{10}H_{11}^-$, only the 2-$CB_{10}H_{11}^-$ isomer has been synthesized[42a] and characterized by ^{11}B NMR.[43] Position 1 of the $B_{11}H_{11}^{2-}$ reference frame, Figure 1, is unique and seven-coordinated (B7). Positions 2 and 3 are five-coordinated (B5); the other 8 vertexes are six-coordinated (B6). The empirical valence rules of Williams predict the 2-$CB_{10}H_{11}^-$ > 10-$CB_{10}H_{11}^-$ > 1-$CB_{10}H_{11}^-$ stability order since the carbons prefer sites with lower connectivity. As shown in Figure 1, the negative charges in $B_{11}H_{11}^{2-}$ follow the connectivity B2 (−0.283) (B5); B10 (−0.194), B8 (−0.141), B5 (−0.135) (B6); and B1 (−0.025) (B7) in agreement with the topological charge stabilization rule; the more electronegative carbons do prefer the locations with the highest negative charges in the homoatomic system. This predicts that the five possible isomeric *closo*-monocarbaboranes should follow the following decreasing order of stability: 2-$CB_{10}H_{11}^-$ > 10-$CB_{10}H_{11}^-$ > 8-$CB_{10}H_{11}^-$ > 5-$CB_{10}H_{11}^-$ > 1-$CB_{10}H_{11}^-$.

Our ab initio calculations on all the positional isomers of $CB_{10}H_{11}^-$ assumed C_s symmetry for 2-$CB_{10}H_{11}^-$ (**12**), 10-$CB_{10}H_{11}^-$ (**13**), and 8-$CB_{10}H_{11}^-$ (**14**) (Figure 2). Frequency calculations indicate that the resulating structures are local minima, but isomers **13** and **14** lie 18.15 and 20.51 kcal/mol, respectively, above **12**, the most stable form (Table 3). In contrast, 1-$CB_{10}H_{11}^-$, with C_{2v} symmetry, possesses one imaginary frequency. Reduction of the symmetry to C_2 (**15**) does not result in a local minimum. Optimization of the remaining positional isomer, 5-$CB_{10}H_{11}^-$, led to the most stable form, 2-$CB_{10}H_{11}^-$ (**12**).

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Table 4. Selected Interatomic Distances (Å) for *closo*-Monocarbaboranes, $CB_{n-1}H_n^-$ ($n = 5-9$), at RMP2/6-31G* (Atom Numbering in Figure 2)

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
1−2	1.555	1.560	1.624	1.726	1.733	1.520	1.606	1.975	1.958	1.603	1.622	1.639	1.774	1.732	1.621	1.702
1−3		1.660		1.820		1.701	1.724				1.694	1.738		1.740		
1−4				1.799			1.804	1.610	1.600		1.693	2.022	1.999			
1−5						1.608	1.699							1.993	2.292	
1−6												2.008	1.996	2.002	1.794	
2−3	1.818	1.699	1.717	1.551	1.638	1.817	1.724	1.958	1.981							
2−4												1.572	1.661			
2−5	1.664							1.698	1.682	1.836	1.747		1.671	1.661	1.712	
2−6			1.726			1.695					1.732					
2−7					1.824											
2−8												1.663	1.749	1.677	1.739	
3−4		1.806		1.645							1.818					
3−5						1.882	1.864	1.710								
3−6						1.907			1.702		1.802	1.670		1.671		
3−7						1.697					1.787					
3−9												1.746		1.756		
4−5				1.664			1.859									
4−7										1.802	1.823	1.842	1.841			
4−8									1.714			1.792	1.785	1.705		
4−10												1.767	1.699			
5−7						1.795	1.771									
5−8									1.721							
6−5													1.863	1.832	1.843	1.776
6−7						1.814	1.827		1.712							
6−9										1.835	1.822	1.794	1.776	1.795	1.806	
6−11												1.781	1.768	1.772	1.791	1.769
7−8									1.906		1.833					
10−8										1.701	1.704	1.774	1.715		1.802	
10−9											1.689	1.781		1.770		1.784
10−11												1.822	1.729	1.809	1.799	
11−8													1.776	1.702	1.793	
12−7																1.781

Our ab initio calculations confirm the predicted stability: 2-$CB_{10}H_{11}^-$ (**12**) > 10-$CB_{10}H_{11}^-$ (**13**) > 8-$CB_{10}H_{11}^-$ (**14**) > 1-$CB_{10}H_{11}^-$ (**15**) (Table 3). The carbons do tend to occupy positions of low coordination and with more negative charge.

$CB_9H_{10}^-$. $CB_9H_{10}^-$ is isoelectronic with $B_{10}H_{10}^{2-}$, a bicapped square antiprism. Two isomers of $CB_9H_{10}^-$ are possible. The 8 antiprism vertexes are equivalent and are six-coordinate (B6). The 2 vertex borons (1 and 10) capping the square face are five-coordinated (B5) and possess a greater negative charge (−0.270) than B6 (−0.150). Therefore, the 1-$CB_9H_{10}^-$ isomer should be the most stable; it is the only isomer which has been synthesized.[42] The structure of **10** deduced from its ^{11}B NMR spectrum[42,43] was confirmed recently by X-ray crystallography.[72] Reed[73] and Strauss[74] synthesized and characterized a set of new 10 vertex *closo*-1-$CB_9H_{10}^-$ derivatives which are exceptionally inert, weakly coordinating carborane anions.

Geometry optimization assumed C_{4v} symmetry for 1-$CB_9H_{10}^-$ (**10**) and C_s for 2-$CB_9H_{10}^-$ (**11**) (Figure 2). Frequency calculations indicate both structures to be minima, but **10** is 20.63 kcal/mol lower in energy than **11** (Table 3). Our ab initio calculations confirm the ordering expected from the coordination and the topological charge stabilization.

$CB_8H_9^-$. Although $CB_8H_9^-$ is not known, its structure should be based on the tricapped trigonal prism favored by the isoelectronic borane, $B_9H_9^{2-}$. As shown in Figure 1, 3 vertexes which cap the rectangular faces of the $B_9H_9^{2-}$ prism are five-coordinated (B5), while the 6 vertexes of the prism are six-coordinated (B6). The charges in $B_9H_9^{2-}$ are larger on B5 (−0.329) than on B6 (−0.107). Hence, isomer 4-$CB_8H_9^-$ should be more stable than 1-$CB_8H_9^-$.

We assumed C_{2v} symmetry for 4-$CB_8H_9^-$ (**8**) and C_s for 1-$CB_8H_9^-$ (**9**) (Figure 2). Frequency calculations indicate both structures to be minima, but **8** is 17.65 kcal/mol lower in energy than **9** (Table 3).

$CB_7H_8^-$. The ^{11}B and ^{1}H NMR behavior[44] of the first 8 vertex *closo*-monocarbaborane, 1-$CB_7H_8^-$, was observed recently.[45] The ^{11}B NMR behavior of this anion shows 4:3 fluxionality at room temperature and is supported by ab initio/IGLO/NMR studies.[21a,28a] A similar fluxional mechanism for 1-$CB_7H_8^-$ as for $B_8H_8^{2-}$ seems likely.[28a,b,75] In the parent dianion $B_8H_8^{2-}$, the five-coordinated sites B1, B2, B7, and B8 are all equivalent as are the six-coordinated B3, B4, B5, and B6. The B5 positions are more negatively charged (−0.257) than the B6 positions (−0.132); hence, 1-$CB_7H_8^-$ is preferred over 3-$CB_7H_8^-$. The RMP2/6-31G* calculations were carried out, assuming C_s symmetry for 1-$CB_7H_8^-$ (**6**) and for 3-$CB_7H_8^-$ (**7**) (Figure 2). According to second derivative analysis, **6** is a minimum, whereas **7** has one imaginary frequency (NIMAG = 1) and is 23.88 kcal/mol higher than **6** (Table 3).

$CB_6H_7^-$. Although $CB_6H_7^-$ has not been reported experimentally, it would be expected to favor a pentagonal bipyramidal structure like that of the isoelectronic $B_7H_7^{2-}$. The charges in the parent dianion $B_7H_7^{2-}$ (Figure 1) are higher on the five-coordinated (B5) B2−B6 (−0.276) in the base, than on the six-coordinated (B6) B1 and B7 in the apical positions (−0.074). As expected, our ab initio computations show the 2-$CB_6H_7^-$

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Table 5. *closo*-Borane Dianions, $B_nH_n^{2-}$ ($n = 5-12$), Zero Point (ZPE)^a and Reaction Energies from Eq 1 (ΔH)^c and Magnetic Susceptibilities (χ, ppm cgs)^d

molecule	symmetry	ZPE^a	RMP2/6-31G*	ΔH^c	χ^d
$B_5H_5^{2-}$	D_{3h}	38.21	−126.52638	−240.82	−69.74
$B_6H_6^{2-}$	O_h	49.56	−151.99072	−346.18	−81.24
$B_7H_7^{2-}$	D_{5h}	59.01	−177.38059	−406.48	−85.37
$B_8H_8^{2-}$	D_{2d}	68.53	−202.75682	−458.18	−94.43
$B_9H_9^{2-}$	D_{3h}	77.93	−228.16066	−527.29	−116.31
$B_{10}H_{10}^{2-}$	D_{4d}	88.69	−253.58919	−610.71	−141.57
$B_{11}H_{11}^{2-}$	C_{2v}	97.89	−278.95172	−654.09	−148.83
$B_{12}H_{12}^{2-}$	I_h	110.21	−304.44474	−776.56	−167.40
B_3H_5	C_{2v}^b	33.61(2)	−77.04852		+1.79
B_2H_4	D_{2h}	25.68(1)	−51.75692		−0.75
$B_2H_2^{2-}$	C_{2h}	11.31(0)	−50.26340		−51.38
$B_2H_2^{2-}$	$D_{\infty h}$	11.07(2)^e	−50.25973		−49.66

[a] Zero point energy (kcal/mol), calculated at HF/6-31G*. In parentheses, number of imaginary frequencies (NIMAG) when these are not zero. [b] Planar form. [c] $B_2H_2^{2-} + (n-2)BH_{inc} \rightarrow B_nH_n^{2-}$ ($n = 5-12$) at MP2/6-31G*, with ZPE corrections (ref 56) scaled by 0.89 in kcal/mol. Note that $B_2H_2^{2-}$ (C_{2h}) data were used and that the BH_{inc} increment was taken as the difference in energy between B_3H_5 (C_{2v}, planar form) and B_2H_4 (D_{2h}, ethylene-like) since no inherent stabilization due to hyperconjugation or to delocalization is absent. [d] At CSGT-HF/6-31+G*//MP2(fc)/6-31G*. [e] Linear $B_2H_2^{2-}$ is a minimum at B3LYP/6-311+G** but not at B3LYP/6-31G*, MP2/6-31G*, and MP2/6-311+G**.

Table 6. Most Stable *closo*-Monocarbaborane Anions, $CB_{n-1}H_n^-$ ($n = 5-12$), Zero Point (ZPE)^a and Reaction Energies in from Eq 2 (ΔH)^c

molecule	symmetry	ZPE^a	RMP2/6-31G*	ΔH^c
$1\text{-}CB_4H_5^-$	C_{3v}	43.32	−139.96038	−175.26
$CB_5H_6^-$	C_{4v}	54.06	−165.38007	−253.13
$2\text{-}CB_6H_7^-$	C_{2v}	63.66	−190.75884	−306.35
$1\text{-}CB_7H_8^-$	C_s	72.71	−216.12067	−349.43
$4\text{-}CB_8H_9^-$	C_{2v}	78.69^b	−241.51270	−407.11
$1\text{-}CB_9H_{10}^-$	C_{4v}	93.35	−266.93001	−487.07
$2\text{-}CB_{10}H_{11}^-$	C_s	102.42	−292.27992	−522.66
$CB_{11}H_{12}^-$	C_{5v}	114.48	−317.73467	−621.35

[a] Zero point energy (kcal/mol), calculated at HF/6-31G*. [b] At B3LYP/6-31G*. [c] $CBH_2^- + (n-1)\ BH_{inc} \rightarrow CB_nH_{n+1}^-$ ($n = 4-11$) at MP2/6-31G*, with ZPE corrections (ref 56) scaled by 0.89 (and 0.98 for B3LYP/6-31G*) in kcal/mol.

Table 7. Most Stable *closo*-Dicarboranes, $C_2B_{n-2}H_n$ ($n = 5-12$), Zero Point (ZPE)^a and Reaction Energies from Eq 3 (ΔH)^c

molecule	symmetry	ZPE^a	RMP2/6-31G*	ΔH^c
$1,5\text{-}C_2B_3H_5$	D_{3h}	47.31	−153.18433	−147.83
$1,6\text{-}C_2B_4H_6$	D_{4h}	57.37	−178.56238	−200.19
$2,4\text{-}C_2B_5H_7$	C_{2v}	67.43	−203.94443	−255.05
$1,7\text{-}C_2B_6H_8$	C_2	76.53	−229.30079	−294.65
$4,5\text{-}C_2B_7H_9$	C_{2v}	83.29^b	−254.68224	−347.91
$1,10\text{-}C_2B_8H_{10}$	D_{4d}	97.18	−280.09789	−424.61
$2,3\text{-}C_2B_9H_{11}$	C_{2v}	105.84	−305.43626	−453.31
$1,12\text{-}C_2B_{10}H_{12}$	D_{5d}	117.91	−330.86234	−534.01

[a] Zero point energy (kcal/mol), calculated at HF/6-31G*. [b] At MP2/6-31G*. [c] $C_2H_2 + n$BHinc $\rightarrow C_2B_nH_{n+2}$ ($n = 3-10$) at MP2/6-31G*, with ZPE corrections (ref 56) scaled by 0.89 (and 0.94 for MP2/6-31G*) in kcal/mol.

minimum (**4**) to be 30.47 kcal/mol more stable than the C_{5v} minimum $1\text{-}CB_6H_7^-$ (**5**).

$CB_5H_6^-$. *closo*-$1\text{-}CB_5H_7$[1b] is the smallest *closo*-monocarbaborane which has been isolated. However, its deprotonated form, *closo*-$1\text{-}CB_5H_6^-$ (**3**), has not yet been reported. All boron atoms and all BB bonds are equivalent in the parent dianion, $B_6H_6^{2-}$, and the charge distribution is uniform (−0.252). Only one isomer of $CB_5H_6^-$ (**3**) with C_{4v} geometry is a stable minimum (Figure 2 and Table 3).

$CB_4H_5^-$. Although $CB_4H_5^-$ has never been prepared, it should have a trigonal bipyramidal structure like that of the isoelectronic *closo*-$1,5\text{-}C_2B_3H_5$, which is familiar as the smallest known *closo*-dicarboranes.[1−3] Two carbon isomers $1\text{-}CB_4H_5^-$ (**1**) and $2\text{-}CB_4H_5^-$ (**2**) are possible. In contrast to $B_7H_7^{2-}$ (see Figure 1), the negative charge on the four-coordinated (B4) apical (−0.482) position of the reference dianion $B_5H_5^2$ is significantly larger than the charge on the five-coordinated (B5) equatorial positions (−0.180). Hence, $1\text{-}CB_4H_5^-$ (**1**) should be preferred over $5\text{-}CB_4H_5^-$ (**2**).

Frequency analyses established $1\text{-}CB_4H_5^-$ (C_{3v}) to be a minimum (**1**), but $2\text{-}CB_4H_5^-$ (C_{2v}, **2**, shown in Figure 2) possessed one imaginary frequency at HF/6-31G*. However, the C_{2v} geometry was a minimum at both B3LYP/6-31G* and MP2/6-31G* levels, where it was 25.53 kcal/mol less stable than **1** (Table 3).

Stability of the *closo*-Monocarbaborane Anions, $CB_{n-1}H_n^-$, and *closo*-Dicarboranes, $C_2B_{n-2}H_n$. Recently, we evaluated the stabilization energies as well as the average energy per CH group in two-dimensional aromatic compounds.[5] The Hückel [*n*]annulenes and the polybenzenoid hydrocarbons behave differently. The strain-corrected total aromatic stabilization energies (ASE) in the [*n*]annulenes do not increase with increasing ring size; more importantly, the average stability per CH group (ASE/*n*) decreases. For example, both the energy and the ASE of $C_{18}H_{18}$ are much less than that of three benzenes. In contrast, the ASEs of benzene, naphthalene, anthracene, and tetracene increase regularly with the number of rings. The ASE per carbon, obtained by dividing the ASE of the molecule by the total number of carbons (ASE/*n*), is nearly constant for the acenes. Similar observations have been made by Aihara,[76] by Peck et al.,[77a] and recently by Wiberg.[77b]

Both the additive stabilization in the polybenzenoid hydrocarbons and the decreasing aromaticity per CH group exhibited by the Hückel [*n*]annulenes are quite different from the exceptional behavior exhibited by the three-dimensional aromatic (*closo*-borane-cased clusters).[5] As we have noted,[5] not only do the stabilization energies of the *closo*-borane dianions tend to increase with increased cluster size, but also the average stability per vertex tends to increase. This characterizes the aromaticity in such three-dimensional systems.

Equations 1−3 and ab initio RMP2/6-31G* data are employed to evaluate the relative stabilities of members of the related families, the *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 5-12$), the *closo*-monocarbaborane anions, $CB_{n-1}H_n^-$ ($n = 5-12$), and the *closo*-dicarboranes, $C_2B_{n-2}H_n$ ($n = 5-12$), respectively. Data

$$B_2H_2^{2-} + (n-2)BH_{inc} \rightarrow B_nH_n^{2-}\ (n = 5-12) \quad \Delta H \tag{1}$$

$$CBH_2^- + (n-1)BH_{inc} \rightarrow CB_nH_{n+1}^-\ (n = 4-11) \quad \Delta H \tag{2}$$

$$C_2H_2 + nBH_{inc} \rightarrow C_2B_nH_{n+2}\ (n = 3-10) \quad \Delta H \tag{3}$$

for the most stable positional isomers are used for the last two sets. Acetylene and its analogues, $B_2H_2^{2-}$ and $HBCH^-$ serve as the isoelectronic reference species. The BH_{inc} increment is

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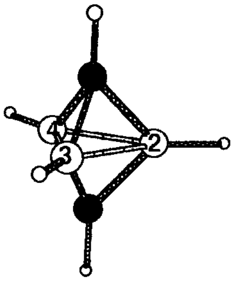
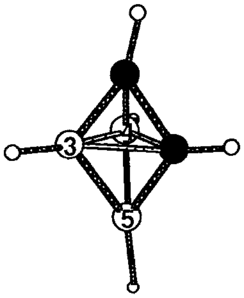
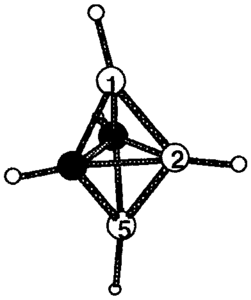
(78) The estimated reaction energies for each *closo*-borane dianions can be evaluated by $\Delta H_{estimated} = 84.199 - 71.73(x)$ (where *x* is the number of vertexes). This equation defines the straight line which connected the two reference species, $B_{12}H_{12}^{2-}$ and $B_6H_6^{2-}$ in Figure 4. Hence, the deviation of the energy of each cluster from this line (ΔH_{dev}) can be estimated by taking the differences between ΔH_{est} and the reaction energies from eq 1 (ΔH_{obs}) (Table 8), $\Delta H_{dev} = \Delta H_{est} - \Delta H_{obs}$.



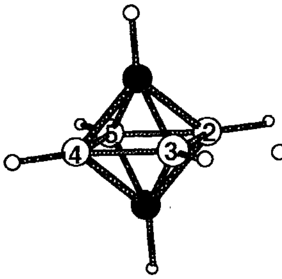
1,5-$C_2B_3H_5$ D_{3h}
(17)



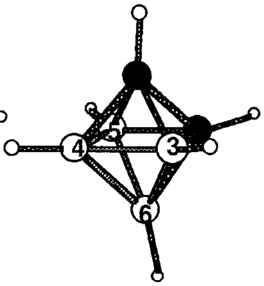
1,2-$C_2B_3H_5$ C_s
(18)



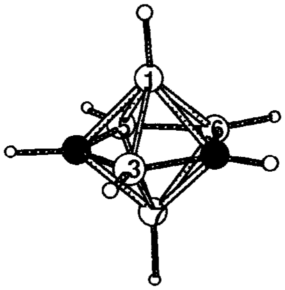
2,3-$C_2B_3H_5$ C_{2v}
(19)



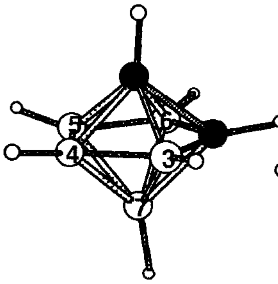
1,6-$C_2B_4H_6$ D_{4h}
(20)



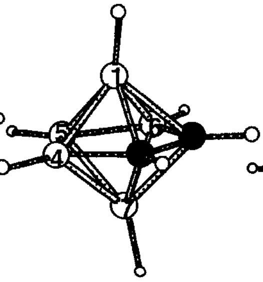
1,2-$C_2B_4H_6$ C_{2v}
(21)



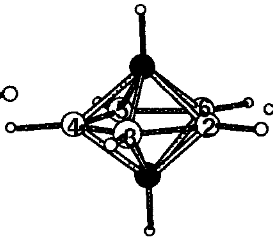
2,4-$C_2B_5H_7$ C_{2v}
(22)



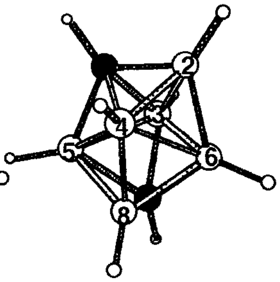
1,2-$C_2B_5H_7$ C_s
(23)



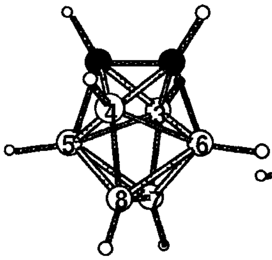
2,3-$C_2B_5H_7$ C_{2v}
(24)



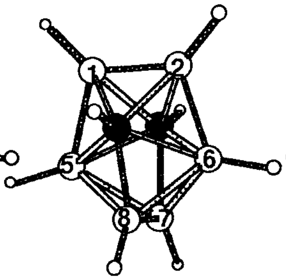
1,7-$C_2B_5H_7$ D_{5h}
(25)



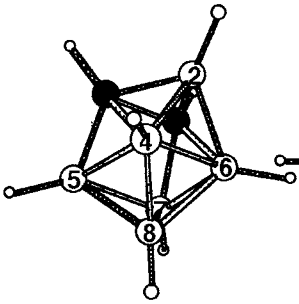
1,7-$C_2B_6H_8$ C_2
(26)



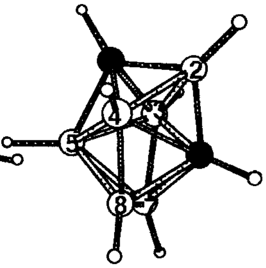
1,2-$C_2B_6H_8$ C_{2v}
(27)



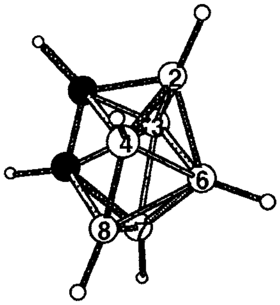
3,4-$C_2B_6H_8$ C_{2v}
(28)



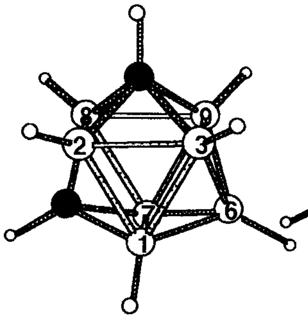
1,3-$C_2B_6H_8$ C_s
(29)



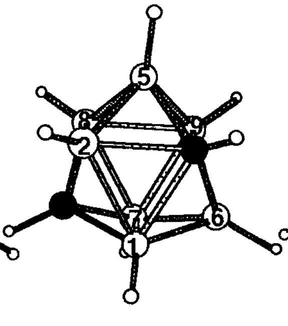
1,6-$C_2B_6H_8$ C_s
(30)



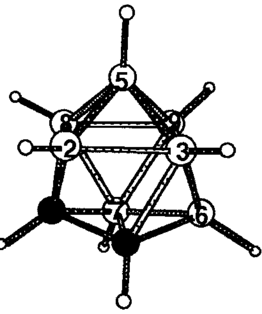
1,5-$C_2B_6H_8$ C_s
(31)



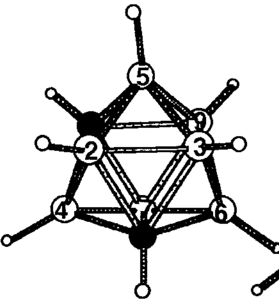
4,5-$C_2B_7H_9$ C_{2v}
(32)



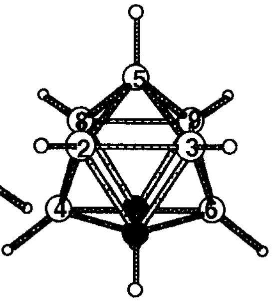
3,4-$C_2B_7H_9$ C_s
(33)



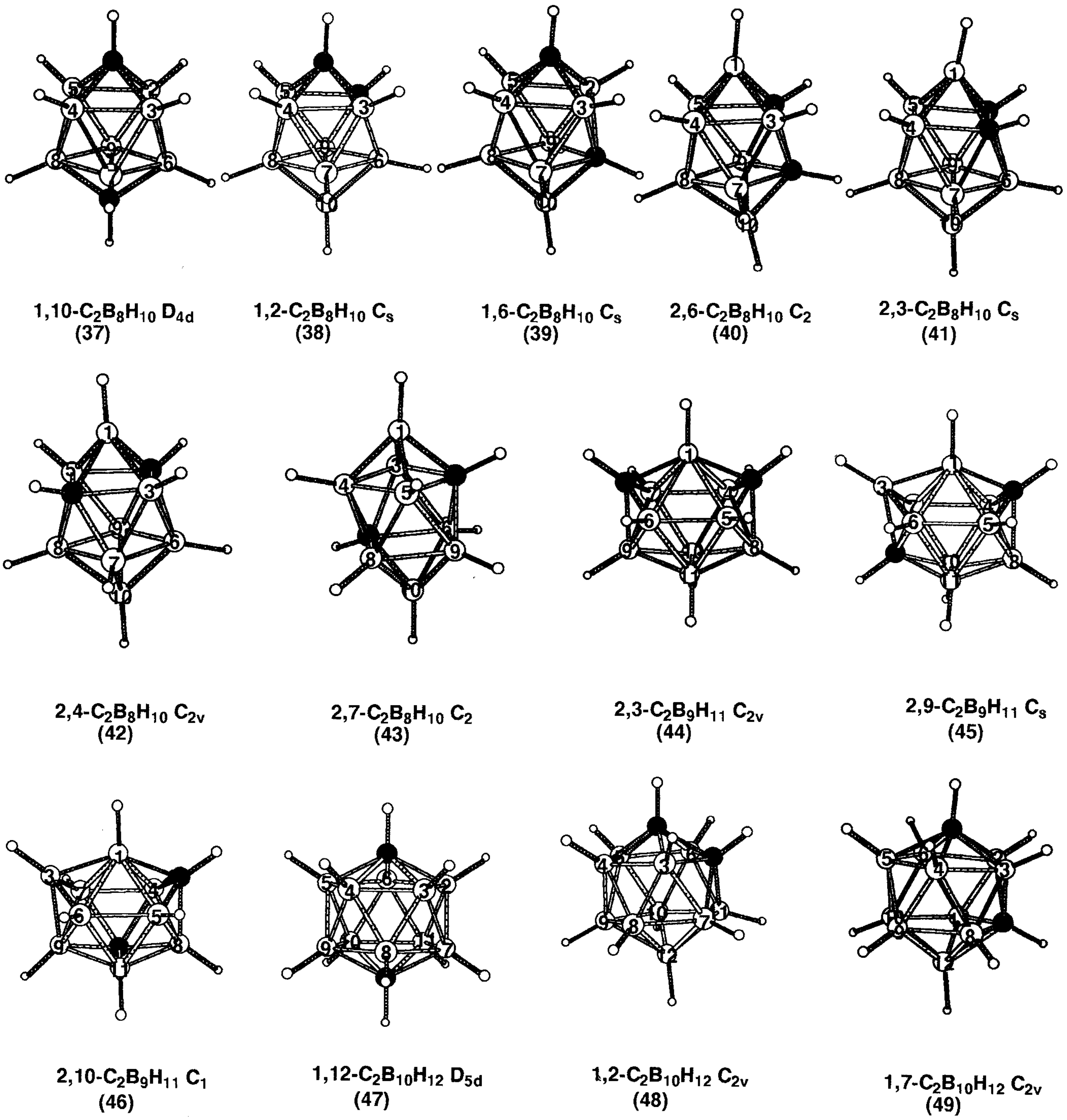
1,4-$C_2B_7H_9$ C_1
(34)



1,8-$C_2B_7H_9$ C_2
(35)



1,7-$C_2B_7H_9$ C_{2v}
(36)



1,10-$C_2B_8H_{10}$ D_{4d} (37)
1,2-$C_2B_8H_{10}$ C_s (38)
1,6-$C_2B_8H_{10}$ C_s (39)
2,6-$C_2B_8H_{10}$ C_2 (40)
2,3-$C_2B_8H_{10}$ C_s (41)
2,4-$C_2B_8H_{10}$ C_{2v} (42)
2,7-$C_2B_8H_{10}$ C_2 (43)
2,3-$C_2B_9H_{11}$ C_{2v} (44)
2,9-$C_2B_9H_{11}$ C_s (45)
2,10-$C_2B_9H_{11}$ C_1 (46)
1,12-$C_2B_{10}H_{12}$ D_{5d} (47)
1,2-$C_2B_{10}H_{12}$ C_{2v} (48)
1,7-$C_2B_{10}H_{12}$ C_{2v} (49)

Figure 3. RMP2/6-31G* optimized geometries for *closo*-dicarboranes $C_2B_{n-2}H_n$ ($n = 5-12$).

taken as the difference in energy between B_3H_5 (C_{2v}, planar) and B_2H_4 (D_{2h}, ethylene-like). (Note that this computed BH_{inc} increment does not possess any inherent stabilization due to hyperconjugation or to delocalization.)

The reaction energies (ΔH) of eqs 1−3 are all exothermic (Tables 5−7). The exothermicity of these reactions tends generally to increase as the size of the cluster increases. However, variations of individual compounds are apparent when the reaction energies (ΔH) are plotted as a function of cluster size (see Figure 4).

These plots are based on the data treatment employed previously[5] to evaluate the relative stability of *closo*-borane dianions, $B_nH_n^{2-}$ ($n = 5-12$), which we have extended to the *closo*-monocarbaborane anion, $CB_{n-1}H_n^-$, and *closo*-dicarborane, $C_2B_{n-2}H_n$, systems. Data from eqs 1−3 for the most symmetrical 6 and 12 vertex species are used to define the reference lines in Figure 4: deviations from the line (ΔH_{dev},[78] Table 8) were employed for the quantitative comparison of the stabilities of individual clusters.

The patterns of variation of corresponding compounds are remarkably similar qualitatively in the *closo*-$B_nH_n^{2-}$, *closo*-$CB_{n-1}H_n^-$, and *closo*-$C_2B_{n-2}H_n$ clusters. As summarized in Table 8, the deviations (ΔH_{dev}) of the *closo*-$B_nH_n^{2-}$ species are the largest of the three sets. $B_7H_7^{2-}$ and $B_{10}H_{10}^{2-}$ have the smallest deviations, $\Delta H_{dev} = 11.4$ and 22.4 kcal/mol, respectively, while the $B_8H_8^{2-}$, $B_9H_9^{2-}$, and $B_5H_5^{2-}$ deviations are larger ($\Delta H_{dev} = 31.5$, 34.1 and 33.6 kcal/mol, respectively, Table 8). The quantitative variations from the defining lines in Figure

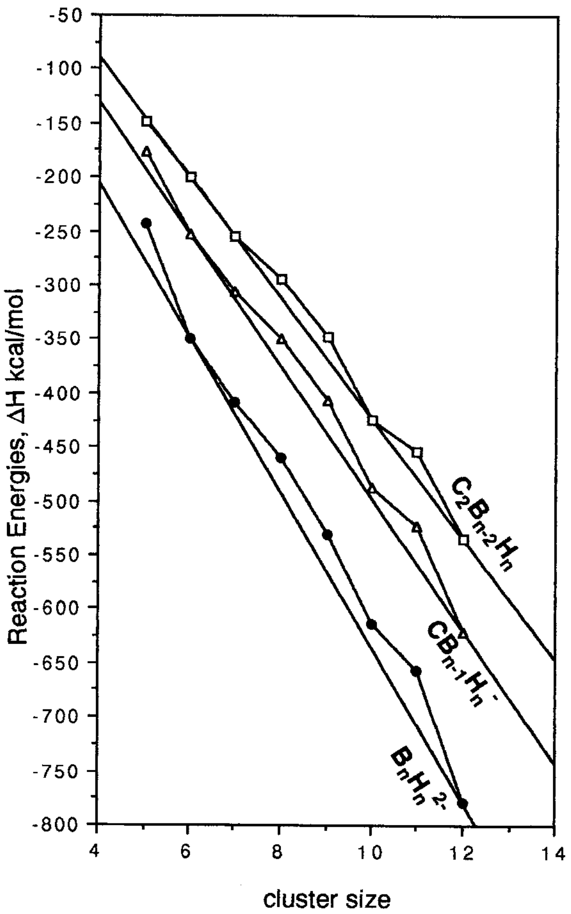


Figure 4. Plots of the reaction energies, ΔH in kcal/mol, of the *closo*-borane dianions ($B_nH_n^{2-}$) and the most stable *closo*-monocarbaborane anion ($CB_{n-1}H_n^-$) and *closo*-dicarborane ($C_2B_{n-2}H_n$) isomers (from Tables 5−7) vs cluster size. The trends to more negative ΔH's are indicated by the lines defined by the 6 and 12 vertex systems in each family. The deviations from the lines are largest for *closo*-$B_nH_n^{2-}$, smallest for *closo*-$C_2B_{n-2}H_n$, and intermediate for *closo*-$CB_{n-1}H_n^-$ set.

Table 8. Deviations (ΔH_{dev}, in kcal/mol) of *closo*-Borane Dianions, $B_nH_n^{2-}$,[a] the Most Stable *closo*-Monocarbaboranes, $CB_{n-1}H_n^-$,[b] and *closo*-Dicarboranes, $C_2B_{n-2}H_n$,[c] from the Lines Defined by the 6 and 12 Vertex Species (See Figure 4)

clusters	ΔH_{dev}[a] $B_nH_n^{2-}$	ΔH_{dev}[b] $CB_{n-1}H_n^-$	ΔH_{dev}[c] $C_2B_{n-2}H_n$
5 vertex	33.63	16.50	−3.25
6 vertex	0.00	0.00	0.00
7 vertex	11.43	8.15	0.78
8 vertex	31.46	26.44	16.81
9 vertex	34.08	30.13	19.20
10 vertex	22.40	11.54	−1.87
11 vertex	50.74	37.32	25.06
12 vertex	0.00	0.00	0.00

[a] Calculated using eq 1. [b] Calculated using eq 2. [c] Calculated using eq 3. (See text also.)

4 (given in Table 8) are greatest for the *closo*-borane dianions, $B_nH_n^{2-}$, less for the *closo*-monocarbaborane anions, $CB_{n-1}H_n^-$ and least for the *closo*-dicarboranes, $C_2B_{n-2}H_n$. This suggests an additive effect due to carbon replacement.

Unlike C_2H_2, $B_2H_2^{2-}$ (used in eq 1) is destabilized due to Coulombic repulsion of the two adjacent negative charges. Equation 1, where the unfavorable ($B_2H_2^{2-}$) is incorporated into larger *closo*-$B_nH_n^{2-}$, gives the largest exothermicities (Figure 4 and Table 5), partly due to the attenuation of the Coulombic repulsions.

The ΔH_{dev} values for species with the same number of vertexes decrease from *closo*-boranes, $B_nH_n^{2-}$, to *closo*-monocarbaboranes, $CB_{n-1}H_n^-$, and from *closo*-monocarbaboranes, $CB_{n-1}H_n^-$, to *closo*-dicarboranes, $C_2B_{n-2}H_n$ (Table 8). For example, the ΔH_{dev} values for the 8 and 7 vertex *closo*-boranes, $B_nH_n^{2-}$ (31.46 and 11.43 kcal/mol, respectively), are more than those of *closo*-monocarbaboranes, $CB_{n-1}H_n^-$ (to 26.44 and 8.15 kcal/mol, respectively) and decrease further in the *closo*-dicarboranes, $C_2B_{n-2}H_n$ (to 16.81 and 0.78 kcal/mol, respectively). This reveals that the incorporation of carbon in clusters results in more regular energetic trends and smaller differentiation with the number of vertexes.

This leveling effect, relative to *closo*-$B_nH_n^{2-}$ and as seen in the *closo*-$CB_{n-1}H_n^-$ and even more in *closo*-$C_2B_{n-2}H_n$ set, evidently is due to the partial electron localization in the vicinity of the more electronegative carbons. The magnitude of this leveling effect (as noted above in describing Figure 4) is about twice as large for the *closo*-$C_2B_{n-2}H_n$ as for the *closo*-$CB_{n-1}H_n^-$ families. It even operates in $C_2B_3H_5$, which has less spherical aromaticity than $B_5H_5^{2-}$. Greater electron localization due to the presence of the more electronegative carbon atoms decreases the electron density available for BB cage bonding. Consequently, the differentiation in ΔH_{dev} among the cages is reduced. As discussed below, the magnetic susceptibility exaltations, also estimated using eqs 1−3, do not show differences as great as those of the energies.

Support for this rationalization is found, e.g., in the decreasing Wiberg bond index (WBI), a measure of the bonding interactions between the B's in the equatorial planes, with increasing number of carbons for the central BB bonds along the $B_6H_6^{2-}$ (0.685), $CB_5H_6^-$ (0.600), $C_2B_4H_6$ (0.485) series. The same trend has been noted in the 5 vertex systems, $B_5H_5^{2-}$, vs the related 5 vertex 1,5-diheteroborane cages, e.g. 1,5-$C_2B_3H_5$, analyzed in detail earlier.[4] The WBI decreases from WBI = 0.452 for $B_5H_5^{2-}$ to WBI = 0.202 for 1,5-$C_2B_3H_5$.

The variations in WBI for the 10 and 12 vertex *closo*-systems show similar trends. The BB WBI in the equatorial planes of the *closo*-$B_{10}H_{10}^{2-}$ is 0.460, while the corresponding BB WBI in *closo*-1-$CB_9H_{10}^-$ is 0.361 (nearest the carbon) and 0.344 in *closo*-1,10-$C_2B_8H_{10}$. The similar decreasing BB WBI is found in 12 vertex systems. The B−B WBI in *closo*-$B_{12}H_{12}^{2-}$ is 0.535, and in $CB_{11}H_{12}^-$ and *closo*-1,12-$C_2B_{10}H_{12}$, B2−B3 WBIs are 0.439 and 0.423, respectively.

Three-Dimensional Aromaticity in *closo*-Monocarborane Anions, $CB_{n-1}H_n^-$ ($n = 5−12$), and *closo*-Dicarboranes, $C_2B_{n-2}H_n$ ($n = 5−12$). The main criteria employed to illustrate and characterize aromaticity[79,80] in two-dimensional molecules are energetic (resonance and aromatic stabilization energies),[76,81] geometric (bond length equalization, bond order indexes, etc.),[82]

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and magnetic (^{1}H NMR chemical shifts,[83] magnetic susceptibility anisotropies,[84] and their exaltations,[85] as well as NICS, discussed below).[54] While strong correlations among the above three criteria for sets of five-membered heterocycles with wide-ranging[86] properties was demonstrated, such parallel behavior is not found in more complex systems where other effects dominate.[87]

We now extend these criteria (with special emphasis on the magnetic properties) to investigate the aromaticity of the *closo*-monocarbaborane anions, $CB_{n-1}H_n^-$ ($n = 5-12$), as well as the *closo*-dicarboranes, $C_2B_{n-2}H_n$ ($n = 5-12$). However, the magnetic susceptibility anisotropies (χ_{anis})[84] 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. The magnetic susceptibility exaltation, Λ (ppm cgs), is a unique aromaticity criteria since it is directly related to ring currents.[85] For the three-dimensional *closo*-systems, the ring currents can be regarded as flowing in the three principal dimensions. While quite large magnetic susceptibility exaltations Λ are found in *closo*-borane dianions, $B_nH_n^{2-}$,[1a,4] *closo*-monocarbaborane anions, $CB_{n-1}H_n^-$, as well as *closo*-dicarboranes, $C_2B_{n-2}H_n$, comparisons among the $n =$ 5 to 12 vertex systems are inherently complex since such exaltations are known in monocyclic systems to depend on the square of the ring area as well as on the degree of electron delocalization.

Chemical shifts of encapsulated ^{3}He atoms now serve as experimental and computed measures of aromaticity in fullerenes and fullerene derivatives.[88] Since most of the *closo*-systems are too small to accommodate ^{3}He or other elements,[89] we employ an alternative simple and efficient aromaticity/antiaromaticity criterion: NICS[54] based on the negative of the absolute magnetic shieldings computed, for example, at the geometrical centers of rings or cages. At such positions, negative NICS values (given in ppm) imply aromaticity (diatropic ring currents), and positive NICS values correspond to antiaromaticity (paratropic ring currents). The quantitative relationship of NICS with ASE, magnetic susceptibility exaltation Λ, and geometric criteria has been demonstrated recently for the calibrating set of five-membered rings.[54]

Magnetic Susceptibility Exaltation, Λ. As pointed out by Lipscomb in 1963,[1a] further evidence for three-dimensional aromaticity in *closo*-clusters can be obtained from the evaluation of magnetic susceptibility exaltation, Λ. Generally, Λ is defined as $\Lambda = \chi_m - \chi_m'$ where χ_m is the bulk magnetic susceptibility of a cyclically conjugated compound and χ_m' the susceptibility estimated via an increment system for the same structure without a ring current contribution. A negative χ value for a compound implies that it is aromatic; antiaromatic compounds have positive χ's. As noted above, the magnitude of the exaltation can be expected to depend on the volume of cluster.[85] Equations 1−3 can also be applied to evaluate the magnetic susceptibility exaltation (Λ), of *closo*-borane dianions, *closo*-monocarbaborane anions, and *closo*-dicarboranes, using CSGT-SCF/6-31+G*//MP2/6-31G* data (Table 9). As anticipated by Lipscomb,[1a] the Λ's are all negative, indicating the three-dimensional aromaticity in these three sets of clusters. The plots (Figure 5) of the Λ values of *closo*-borane dianions, $B_nH_n^{2-}$, *closo*-monocarbaborane anions, $CB_{n-1}H_n^-$, and *closo*-dicarboranes, $C_2B_{n-2}H_n$ vs cluster size are quite similar. The Λ's of all three sets tend to increase with increasing cluster size from 5 to 12 vertexes, although individual deviations are apparent. Also as shown in Figure 5, the differences in magnetic susceptibility exaltations between *closo*-monocarbaboranes, $CB_{n-1}H_n^-$, and the corresponding *closo*-boranes, $B_nH_n^{2-}$, are larger than those between the exaltations of corresponding *closo*-monocarbaboranes, $CB_{n-1}H_n^-$, and *closo*-dicarboranes, $C_2B_{n-2}H_n$.

Table 9. Magnetic Susceptibility Exaltations (Λ, ppm cgs) of *closo*-Boranes, $B_nH_n^{2-}$,[a] and the Most Stable Isomers of *closo*-Monocarbaboranes, $CB_{n-1}H_n^-$,[b] and of the *closo*-Dicarboranes, $C_2B_{n-2}H_n$[c]

custers	$B_nH_n^{2-}$ [a]	$CB_{n-1}H_n^-$ [b]	$C_2B_{n-2}H_n$[c]
5 vertex[d]	−25.98	−29.29	−27.62
6 vertex	−40.02	−50.00	−52.49
7 vertex	−46.69	−59.80	−62.29
8 vertex	−58.29	−70.59	−72.35
9 vertex	−82.71	−91.19	−90.89
10 vertex	−110.51	−115.50	−111.86
11 vertex	−120.31	−127.80	−125.59
12 vertex	−141.42	−153.48	−155.86

[a] Calculated using eq 1, CSGT-HF/6-31+G*//MP2(fc)/6-31G*. [b] Calculated using eq 2, CSGT-HF/6-31+G*//MP2(fc)/6-31G*. [c] Calculated using eq 3, CSGT-HF/6-31+G*//MP2(fc)/6-31G*. [d] Calculated Λ using eqs 1−3 in 5 vertex cages are different from those values in 1,5-diheteroatoms cages in ref 4 due to different used equations.

NICS of *closo*-Monocarbaborane Anions, $CB_{n-1}H_n^-$ ($n = 5-12$), and *closo*-Dicarboranes, $C_2B_{n-2}H_n$ ($n = 5-12$). We have reported that *closo*-borane dianions, $B_nH_n^{2-}$, which serve well as three-dimensional aromatic prototypes, have large NICS values typically in the range between −25 and −35 ppm.[5] The most symmetric $B_{12}H_{12}^{2-}$ (I_h), $B_6H_6^{2-}$ (O_h), and $B_{10}H_{10}^{2-}$ (D_{4d}) are the most aromatic among the *closo*-borane dianion family, also based on NICS. The NICS values indicated that $B_7H_7^{2-}$, $B_8H_8^{2-}$, $B_9H_9^{2-}$, and $B_5H_5^{2-}$ have less aromatic delocalization and agreed qualitatively both with the bond length alternation (Δr) and with the energy trends.

The NICS values computed at the cage centers of *closo*-monocarbaborane anions and *closo*-dicarboranes all are negative (Table 10), indicating the three-dimensional delocalization and aromaticity in these clusters. The unusual stability and low reactivity, especially of icosahedral carboranes, $C_2B_{10}H_{12}$[1,2,12−15] and $CB_{11}H_{12}^-$ [1,2,67−70] (electrophilic substitution like that of benzene), has long suggested that at least such members of the respective *closo*-sets may be described as aromatic. Unlike the Λ's (Figure 5), the NICS values do not show a volume dependence, and there is no trend to larger values with cluster size.

The plot of the NICS values of *closo*-$B_nH_n^{2-}$, *closo*-$CB_{n-1}H_n^-$, and *closo*-$C_2B_{n-2}H_n$ vs cluster size (Figure 6) shows strikingly similar patterns. The NICS behavior distinguishes between two sets of cluster sizes. The first set has the most

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(89) The energy of the reaction, $B_{12}H_{12}^{2-}$ (I_h) + He → He@$B_{12}H_{12}^{2-}$ (I_h) is strongly endothermic, 170 kcal/mol, at B3LYP/6-31G*//B3LYP/6−31G*.

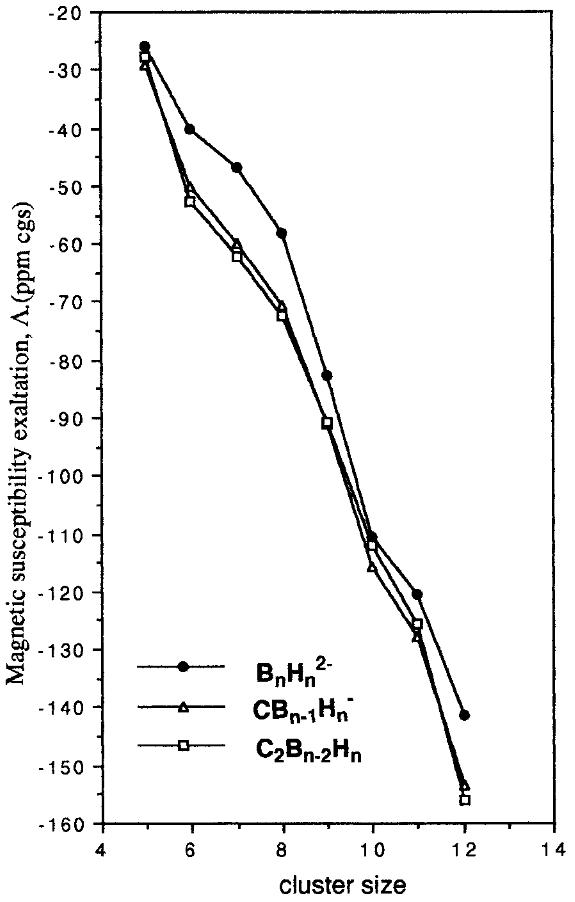

Figure 5. Plots of the magnetic susceptibility exaltations, Λ (ppm cgs, Table 9), of *closo*-$B_nH_n^{2-}$ and the most stable *closo*-$CB_{n-1}H_n^-$ and *closo*-$C_2B_{n-2}H_n$ isomers vs the number of vertexes (cluster size). Note the closely parallel behavior.

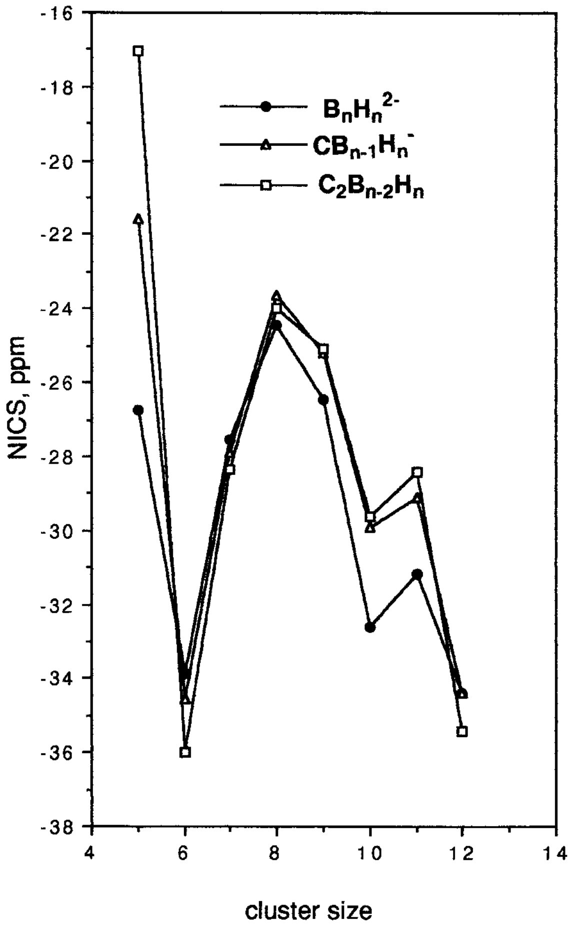

Figure 6. Plots of NICS at the center of *closo*-boranes and the most stable *closo*-monocarbaborane and *closo*-dicarborane isomers (in ppm, from Table 10) vs the cluster size.

Table 10. Nucleus Independent Chemical Shifts (NICS, ppm) of *closo*-Boranes, $B_nH_n^{2-}$,[a] and the Most Stable of *closo*-Monocarbaboranes, $CB_{n-1}H_n^-$,[b] and of the *closo*-Dicarboranes, $C_2B_{n-2}H_n$[c] Isomers

custers	$B_nH_n^{2-\,a}$	$CB_{n-1}H_n^{-\,b}$	$C_2B_{n-2}H_n^{\,c}$
5 vertex	−26.76	−21.57	−17.06
6 vertex	−33.84	−34.57	−36.01
7 vertex	−27.57	−27.90	−28.36
8 vertex	−24.47	−23.62	−24.01
9 vertex	−26.43	−25.21	−25.10
10 vertex	−32.60	−29.91	−29.61
11 vertex	−31.15	−29.12	−28.39
12 vertex	−34.40	−34.36	−35.40

[a−c] At GIAO-SCF/6-31G*//MP2(fc)/6-31G*.

diatropic NICS values and comprises the 6 and 12 vertex polyhedral species, i.e., the *closo*-monocarborane anions, $CB_5H_6^-$ (−34.57) and $CB_{11}H_{12}^-$ (−34.36), as well as the corresponding *closo*-dicarboranes, 1,12-$C_2B_{10}H_{12}$ (−35.40) and 1,6-$C_2B_4H_6$ (−36.01). These, like their isoelectronic counterparts, $B_{12}H_{12}^{2-}$ (I_h) and $B_6H_6^{2-}$ (O_h), are more aromatic than the other members of each family (Table 10).

Our support for the three-dimensional aromaticity of at least some 5 vertex cage systems[4] was based on the quantitative evaluations of the ASE, magnetic susceptibility exaltations (Λ), and the NICS values. Among the 5 vertex $B_3X_2H_5$ deltahedra (X = N, CH, P, SiH, BH^-), $B_5H_5^{2-}$ has the largest ASE (−34.8 kcal/mol), the largest Λ (−46.1), and the most strongly diatropic NICS (−28.1). The isoelectronic 1,5-$C_2B_3H_5$ exhibits smaller ASE (−19.8 kcal/mol), Λ (−6.9), and NICS (−17.1) values. The trends in the NICS, ASE, and Λ results agree.[4]

The NICS values shown in Table 10 suggest that 2,3-$C_2B_9H_{11}$ (−28.39), 1,10-$C_2B_8H_{10}$ (−29.61), and 2,4-$C_2B_5H_7$ (−28.36) as well as 2-$CB_{10}H_{11}^-$ (−29.12), 1-$CB_9H_{10}^-$ (−29.91), and 2-$CB_6H_7^-$ (−27.90) have nearly the same aromatic delocalization, somewhat lower than in the 12 and 6 vertex sets. Note that "Friedel-Crafts type" alkylation[90] and halogenation[91,92] have been observed for 2,4-$C_2B_5H_7$[90−93] and 1,10-$C_2B_8H_{10}$.[93]

Consistent with the behavior of their isoelectronic 9 and 8 vertex *closo*-borane dianions, $B_9H_9^{2-}$ and $B_8H_8^{2-}$,[5] 4,5-$C_2B_7H_9$ and 1,7-$C_2B_6H_8$ (NICS = −25.10 and −24.01, respectively) are the least aromatic dicarboranes (except for 1,5-$C_2B_3H_5$), and the same is true for their monoanion analogues, 4-$CB_8H_9^-$ and 1-$CB_7H_8^-$ (NICS = −25.21 and −23.62, respectively).

Magnetic Susceptibility, χ, and NICS of Positional Isomers of *closo*-Dicarboranes, $C_2B_{n-2}H_n$ (n = 5−12), and *closo*-Monocarbaboranes, $CB_{n-1}H_n^-$ (n = 5−12). The aromaticities

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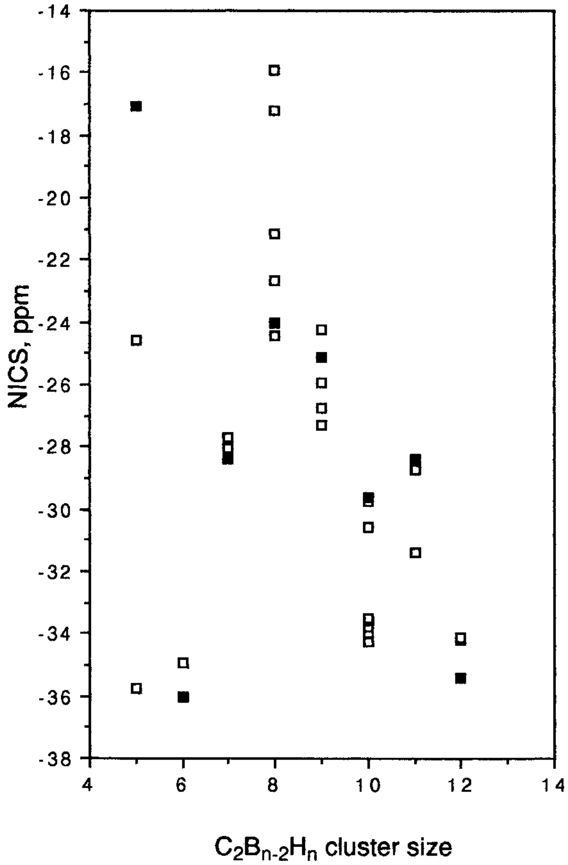

Figure 7. NICS computed at the center of all positional isomers of *closo*-dicarboranes $C_2B_{n-2}H_n$ (n = 5−12) (in ppm, from Table 2) vs the cluster size. This figure emphasizes that the most stable isomers (shown by *n*; these points are plotted in Figures 4−6) often do not have the largest NICS values.

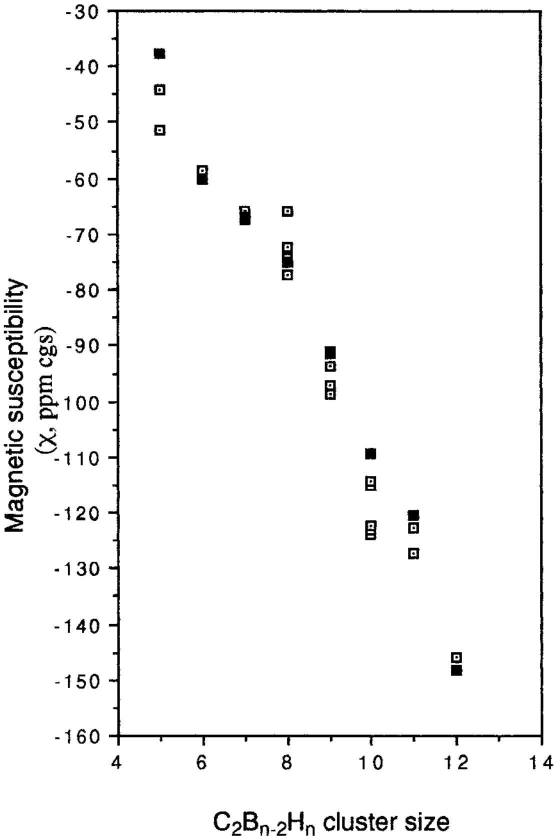

Figure 8. Magnetic susceptibilities χ (ppm cgs, from Table 2) computed for all positional isomers of *closo*-dicarboranes, $C_2B_{n-2}H_n$ (n = 5−12) vs the cluster size. This figure emphasizes that the most stable isomers (shown by *n*; these points are plotted in Figures 4−6) often do not have the largest χ values.

of the various positional isomers of *closo*-$CB_{n-1}H_n^-$ (n = 5−12) and *closo*-$C_2B_{n-2}H_n$ (n = 5−12) were also evaluated by comparing their magnetic susceptibilities (χ) and nucleus independent chemical shifts (NICS) directly. Since the estimated magnetic susceptibility (χ_m') depends primarily on the number of atoms and groups in a molecule (i.e., the group increments) and less on the connectivity,[94] χ_m data of isomers of the aromatic carbon-substituted boranes can be compared directly in order to evaluate their relative aromaticity. All positional isomers of *closo*-dicarboranes have large χ values (Table 2) (their exaltations, Λ, have been discussed above). Both NICS and χ give the same orderings (see Table 2) and characterize the degree of three-dimensional aromaticity of all positional isomers of the *closo*-carboranes, $C_2B_{n-2}H_n$ (n = 5−12) (see Figures 7 and 8).

However, such aromaticity measures and the thermodynamic stability of *closo*-dicarboranes (Table 2) are not always related. In the 5, 8, 9, and 10 vertex cages, NICS and relative χ values of isomers do not follow the thermodynamic stability trends. The NICS and the χ order for the $C_2B_3H_5$ isomers 2,3- > 1,2- > 1,5- are just the opposite from the relative energy ordering (1,5- > 1,2- > 2,3-). Both the magnetic susceptibility χ values (−51.52) and the NICS value (−35.74) of the least stable 2,3-$C_2B_3H_5$ isomer are much larger than χ = −37.74 and NICS = −17.06 of the lowest energy 1,5- form. As has been shown earlier,[87,95] the most stable isomer in more complex systems does not need to be the most aromatic, on the basis of magnetic criteria, since the overall bonding energies may depend on other factors such as connectivity and topological charge stabilizations. When built into borane cages (or other kinds of polycyclic systems), electronegative atoms such as carbon tend to localize the electrons, and this may decrease the aromaticity.

The stabilities of the $C_2B_6H_8$ isomers decrease in the 1,7- > 1,2- > 1,6- > 1,3- > 1,5- > 3,4- sequence (Table 2). However, both the NICS and the χ values increase with decreasing stability in the opposite order: 3,4- > 1,7- > 1,6- > 1,2- > 1,5- > 1,3- (see Figures 7 and 8). This extends earlier conclusions that there does not need to be any direct relationship between the thermodynamic stability and aromaticity when other factors such as topological charge stabilization dominate, e.g., in [5,5] and [5,6] fused diheteroannulenes.[87,95]

Dramatic differences are also found between the sequence of relative energies 1,10- > 1,6- > 1,2- > 2,7- > 2,4- > 2,6- > 2,3- of the $C_2B_8H_{10}$ isomers and the ordering of the magnetic properties. Both the NICS and magnetic susceptibilities of the least stable isomers, 2,6-, 2,4-, 2,7-, and 2,3- are nearly the same and are more negative than those of the most stable 1,10- form (Table 2). The values for the 1,6- and 1,2- isomers, NICS = −30.58 and −29.72, χ = −114.96 and −114.12, respectively, are also larger in magnitude than those for the most stable 1,10- isomer, NICS = −29.61 and χ = −109.28 (see Figures 7 and 8).

Similarly, the most stable isomers are not the most aromatic in the 9 vertex system. The relative stability order of $C_2B_7H_9$

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(94) Note that χ for the 1,2- and 1,7- isomers of $C_2B_{10}H_{12}$ (both experimental and computed, Table 2) are nearly the same.

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Table 11. Relative Energies of *closo*-Monocarbaborane Anions, $CB_{n-1}H_n^-$ ($n = 5-12$) (kcal/mol),[a] Nucleus Independent Chemical Shifts (NICS, ppm),[b] and Magnetic Suceptibilities (χ, ppm cgs)[c]

molecules	symmetry	relative energy[a]	NICS[b]	χ[c]
$CB_4H_5^-$				
1-	C_{3v}	0.00	−21.57	−49.47
2-	C_{2v}	25.53	−31.33	−58.03
$CB_5H_6^-$	C_{4v}	0.00	−34.57	−67.64
$CB_6H_7^-$				
2-	C_{2v}	0.00	−27.90	−74.90
1-	C_{5v}	30.47	−27.79	−74.42
$CB_7H_8^-$				
1-	C_s	0.00	−23.62	−83.15
3-	C_s	23.88	−23.55	−83.73
$CB_8H_9^-$				
4-	C_{2v}	0.00	−25.21	−101.21
1-	C_s	17.65	−26.73	−105.76
$CB_9H_{10}^-$				
1-	C_{4v}	0.00	−29.91	−122.98
2-	C_s	20.63	−33.30	−131.05
$CB_{10}H_{11}^-$				
2-	C_s	0.00	−29.12	−132.74
10-	C_s	18.15	−33.69	−140.31
8-	C_s	20.51	−30.66	−135.69
1-	C_2	33.15	−31.67	−138.18
$CB_{11}H_{12}^-$	C_{5v}	0.00	−34.36	−155.88

[a] From Table 3. [b] At GIAO-SCF/6-31G*//MP2/6-31G*. [c] At CSGT-HF/6-31+G*//MP2/6-31G*.

isomers is 4,5- > 3,4- > 1,4- > 1,8- > 1,7-. The least stable (1,8- and 1,7-) isomers have very large χ's (−98.46 and −97.04, respectively) and NICS values (−27.27 and −26.72, respectively) relative to the other isomers. The magnetic susceptibility $\chi = -93.50$ and the NICS $= -25.93$ of the 3,4- isomer also are larger than $\chi = -90.85$ and NICS $= -25.10$ of the most stable 4,5- isomer (see Table 2, Figures 7 and 8).

In contrast to these cases, some systems do exhibit direct correlations between the aromaticity trends based on NICS and magnetic susceptibilities and the relative stabilities of *closo*-dicarboranes positional isomers. For example, the computed NICS and magnetic susceptibility aromaticity ordering 1,12- > 1,7- ≈ 1,2- for the $C_2B_{10}H_{12}$ isomers does follow the stability trend: the most stable positional isomer also is the most aromatic. A similar result is found for the 6 vertex systems where the magnetic aromaticity decreases with decreasing relative stability: the least stable 1,2-$C_2B_4H_6$ isomer is the least aromatic. Likewise, in the 7 vertex $C_2B_5H_7$ system, the most stable 2,4- isomer has both the largest magnetic susceptibility, −67.33, and NICS, −28.36 (Table 2).

The behavior of the *closo*-monocarbaboranes, $CB_{n-1}H_n^-$ ($n = 5-12$) (Table 11), also emphasizes the contrasts between the relative thermodynamic stabilities and magnetic properties of isomers.

In the 5 vertex cage 2-$CB_4H_5^-$, for example, the χ and NICS values, −58.03 and −31.33, respectively, are larger than those of 1-$CB_4H_5^-$ ($\chi = -49.47$ and NICS $= -21.57$). This magnetic property order is the opposite of that of the relative energies (1-$CB_4H_5^-$ > 2-$CB_4H_5^-$). Likewise, the values for χ and NICS, −105.76 and −26.73, respectively, in the less stable 1-$CB_8H_9^-$ isomer are larger in magnitude than those of 4-$CB_8H_9^-$ ($\chi = -101.21$ and NICS $= -25.21$). A similar trend is found in the 10 vertex, $CB_9H_{10}^-$ isomers, where the magnetic aromaticity[79b] increases with decreasing thermodynamic stability. The least stable isomer, 2-$CB_9H_{10}^-$ has the largest NICS and the largest χ values (Table 11). There also are differences in aromaticity and stability ordering of the 11 vertex cages. The relative stabilities show the sequences 2- > 10- > 8- > 1- the aromaticity ordering (based on the magnetic criteria) is: 10- > 1- > 8- > 2-.

Conclusions

There is excellent agreement among the relative stabilities of all the positional isomers of the *closo*-monocarbaborane anions, $CB_{n-1}H_n^-$, and of the *closo*-dicarboranes, $C_2B_{n-2}H_n$ ($n = 5-12$), with the qualitative connectivity considerations of Williams,[51] with Gimarc's topological charge[52] stabilization rule, and with available experimental experience. The carbons occupy sites of the lowest connectivity and the highest negative charge preferentially: When two carbons are present, these prefer nonadjacent sites, since B−C bonds are inherently stronger than C−C bonds.

The stabilities of the most stable positional isomers of *closo*-monocarbaboranes, $CB_{n-1}H_n^-$ and of the *closo*-dicarboranes, $C_2B_{n-2}H_n$, were compared with those of the isoelectronic, *closo*-borane dianions. The most symmetrical 6 and 12 vertex *closo*-species, $B_{12}H_{12}^{2-}$ and $B_6H_6^{2-}$, $CB_{11}H_{12}^-$ and $CB_5H_6^-$, as well as 1,12-$C_2B_{10}H_{12}$ and 1,6-$C_2B_4H_6$, define the lines shown in Figure 4 and serve as the basis for the quantitative comparison of the members of the *closo*-$CB_{n-1}H_n^-$ and *closo*-$C_2B_{n-2}H_n$ families. The energies of reaction, ΔH, eq 1 for *closo*-$B_nH_n^{2-}$, eq 2 for *closo*-$CB_{n-1}H_n^-$, and eq 3 for *closo*-$C_2B_{n-2}H_n$, tend to increase as the *closo*-systems become larger from $n = 5$ to $n = 12$. Deviations of individual species from the lines in Figure 4 (defined by the 6 and 12 vertex data) are qualitatively similar for the three families but decrease from *closo*-$B_nH_n^{2-}$ to *closo*-$CB_{n-1}H_n^-$ and from *closo*-$CB_{n-1}H_n^-$ to *closo*-$C_2B_{n-2}H_n$. When individual species deviate from the these correlation lines in Figure 4, the magnitude tends to be largest for the *closo*-$B_nH_n^{2-}$ set, smallest for *closo*-$C_2B_{n-2}H_n$, and intermediate for *closo*-$CB_{n-1}H_n^-$.

The energies of reaction, ΔH, are about twice as large from *closo*-boranes, $B_nH_n^{2-}$, to *closo*-monocarbaboranes, $CB_{n-1}H_n^-$, as those from *closo*-monocarbaboranes, $CB_{n-1}H_n^-$, to *closo*-dicarboranes, $C_2B_{n-2}H_n$, i.e., each carbon replacement is roughly additive. The incorporation of carbon in clusters results in more regular energetic trends and smaller deviations from the cor-

Table 12. Selected Interatomic Distances (Å) for *closo*-Borane Dianions, $B_nH_n^{2-}$ ($n = 5-12$), at RMP2/6-31G* (Atom Numbering in Figure 1)

	$B_5H_5^{2-}$ (D_{3h})	$B_6H_6^{2-}$ (O_h)	$B_7H_7^{2-}$ (D_{5h})	$B_8H_8^{2-}$ (D_{2d})	$B_9H_9^{2-}$ (D_{3h})	$B_{10}H_{10}^{2-}$ (D_{4d})	$B_{11}H_{11}^{2-}$ (C_{2v})	$B_{12}H_{12}^{2-}$ (I_h)
1−2	1.674	1.731	1.822	1.614	1.968	1.702	1.746	1.782
1−4							2.004	
2−3	1.813		1.655	1.811		1.831		
3−6				1.894	1.709	1.814	1.670	
3−9					1.790		1.753	
4−7							1.856	
4−8				1.713			1.791	
11−5							1.780	
11−8							1.785	
11−10							1.814	

Table 13. Selected Interatomic Distances (Å) for *closo*-$C_2B_3H_5$, *closo*-$C_2B_4H_6$, *closo*-$C_2B_5H_7$, and *closo*-$C_2B_6H_8$ at RMP2/6-31G* (Atom Numbering in Figure 3)

	17	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**
1−2	1.553	1.509	1.559	1.622	1.535	1.708	1.634	1.744	1.737	1.523	1.440	1.589	1.597	1.525	1.571
1−3		1.527			1.619	1.829	1.751			1.693			1.652		1.720
1−4			1.653		1.626		1.713	1.812		1.703			1.753	1.668	
1−5						1.797		1.784		1.593	1.584		1.583	1.641	1.480
2−3	1.843	1.728	1.593	1.709		1.544	1.545	1.463	1.627						
2−4			1.694								1.726	1.727		1.857	1.689
2−5		1.514													
2−6						1.562				1.691		1.696	1.735	1.571	1.745
3−4		1.828			1.728		1.640	1.542							
3−5		1.692								1.884			2.406	1.848	
4−6					1.711					1.939	1.915	1.804	1.834	1.897	1.854
5−6						1.619	1.646	1.659							
7−2							1.757								
7−4							1.791								
8−4											1.694	1.621	1.761	1.681	1.666
8−5										1.806			1.669	1.785	1.868
8−6										1.832	1.809	1.786		1.734	1.854
8−7											1.622	1.614		1.620	1.689

	32	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**	**41**	**42**	**43**
1−2	1.968	2.008	2.123	1.866	1.893	1.599	1.530	1.591	1.608	1.627	1.613	1.629
1−3	1.981	1.954	1.969	1.935			1.606				1.691	1.684
1−4	1.610	1.583	1.506	1.607	1.619		1.604	1.606	1.697	1.693		1.686
1−6	1.706	1.694	1.570	1.619								
2−3			2.030	1.920	1.961	1.844	1.777	1.859	1.775	1.655	1.733	1.741
2−4	1.602		1.606	1.704	1.711							
2−5			1.662		1.695			1.827	1.732	1.744		1.751
2−6							1.712		1.677	1.746	1.746	1.701
3−5		1.602	1.685	1.689								
3−6			1.718	1.719		1.806	1.812	1.727	1.725		1.778	1.800
4−5							1.831	1.836	1.820	1.803		1.801
7−1	1.784	1.788	1.708	1.692	1.594							
7−3							1.779	1.783	1.777	1.704		
7−4		1.628	1.639				1.806	1.789	1.801	1.818		1.750
7−6		1.714	1.730				1.836	1.748		1.828	1.821	
8−2	1.803		1.783	1.692	1.775							
8−4			1.649					1.818	1.838	1.796		1.811
8−7		1.935	1.885				1.841	1.828		1.830		
9−3	1.748	1.695	1.798									
9−5		1.718	1.742									
9−6			1.713				1.828					1.823
9−8		1.893	1.900						1.816			1.810
10−6							1.698	1.627		1.674	1.694	
10−7							1.706	1.698	1.700	1.699		
10−8								1.694				1.699

	44	**45**	**46**	**47**	**48**	**49**
1−2	1.626	1.633	1.639	1.703	1.619	1.688
1−3		1.729	1.746		1.714	
1−5	2.055	2.027	2.029		1.692	
1−6		2.013	2.016			1.709
2−5	1.573	1.571	1.574			
3−4		1.662	1.667	1.781	1.773	1.765
3−9		1.672	1.739			
5−6	1.862	1.853	1.859			1.780
8−2	1.660	1.666	1.651			
8−7	1.792	1.798	1.799		1.776	1.709
9−4		1.705	1.788	1.762		
10−6					1.761	
10−8	1.776	1.766	1.699			
10−9		1.699	1.710		1.786	
11−6	1.771		1.769			1.766
11−10	1.835		1.743			1.775
12−7					1.774	1.706
12−8					1.786	1.778
12−10						1.773

relation lines (Figure 4). The replacement of boron by the more electronegative carbon in polyhedra results in leveling which is about twice as large for the *closo*-$C_2B_{n-2}H_n$ as for the *closo*-$CB_{n-1}H_n^-$ families.

The magnetic criteria, NICS values as well as magnetic susceptibilities, reveal the three-dimensional aromaticity in both the *closo*-monocarbaboranes, $CB_{n-1}H_n^-$, and the *closo*-dicarboranes, $C_2B_{n-2}H_n$. The NICS values of *closo*-boranes, $B_nH_n^{2-}$, *closo*-monocarbaboranes, $CB_{n-1}H_n^-$, and *closo*-dicarboranes, $C_2B_{n-2}H_n$, show strikingly similar patterns as a function of cluster size (Figure 6). The $B_nH_n^{2-}$ NICS values tend to be the largest among the three sets but not in all cases. The differences in the 5 vertex species are remarkably large, reflecting the "classical-delocalized" dichotomy of the bonding. As expected, the 6 and 12 vertex polyhedra are more aromatic than the other members of their families (Figure 6). On the basis of the unusual stability and low reactivity, $C_2B_{10}H_{12}$[1,2,12−15] and $CB_{11}H_{12}^-$ [1,2,67−70] (which both undergo benzene-like electrophilic substitution) have long been described as aromatic and serve as standards. The 10 and 7 vertex systems have nearly the same degree of aromatic delocalization and follow next. Indeed, Friedel-Crafts type alkylation[90] and halogenation[91,92] have been observed for 2,4-$C_2B_5H_7$[90−93] and 1,10-$C_2B_8H_{10}$[93] as well.

Tables 2 and 11 suggest that the most stable positional isomers indeed need not be the most aromatic. There are many discrepancies between the energetic and the magnetic (NICS and χ) orderings. The relative stabilities of the positional isomers in *closo*-carboranes are consistent with connectivity and topological charge stabilization considerations. Electronegative heteroatoms such as carbon prefer positions with the lowest connectivity and the largest charge density. On the other hand, aromaticity,[79,80] defined as a consequence of cyclic electron delocalization, can be characterized most directly by magnetic criteria.[54,83−85] There need not be any direct relationship between the thermodynamic stability of *closo*-carboranes and their aromaticity based on NICS and χ measures although this may be found in favorable cases where other factors do not dominate. Direct relationships between the relative stability of positional isomers and three-dimensional delocalization only are to be expected when other energy contributions (e.g., due to the connectivity and the topological charge stabilization) are not important.

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