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Ab Initio Study of B_nH_n and $B_n(NH_2)_n$ ($n = 3-6$) Species. A Comparison of Classical and Nonclassical Structures

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For early members of the *hypercloso* boron hydride family, B_nH_n ($n = 3-5$), the lowest energy isomer contains one or more three-membered aromatic BBB rings. Not until B_6H_6 do cage structures become more stable. When hydrogens are replaced by amino groups, the classical nonplanar ring structure is more stable than the nonclassical cage, $B_n(NH_2)_n$ ($n = 4-6$). A disagreement of over 20 kcal/mol is found between MP2/6-31G(2d,p)//MP2/6-31G(d) and B3LYP/6-31G(d)//B3LYP/6-31G(d) for the relative energy of ring and cage structures of $B_6(NH_2)_6$. Calculations on $B_4(NH_2)_4$ including additional electron correlation indicate B3LYP/6-31G(d) is more reliable than MP2/6-31G(2d,p) for relative energies. The lowest energy $B_6(NH_2)_6$ classical structure is a D_{3d} symmetry chair, while a D_{3d} cage is predicted to be 15.0 kcal/mol higher in energy.

Introduction

The number of cage-bonding electron pairs has proven be a very effective indicator of cage geometry in boranes and carboranes.[1] Stable cage structures are predicted for the dianions[2] $B_nH_n^{2-}$ and the neutral carboranes[3] $C_2B_{n-2}H_n$ because the $n+1$ cage electrons are just enough to fill all of the bonding orbitals. In the counting procedure, exocyclic substituents are assumed to bond each boron or carbon with a two-center two-electron (2c-2e) bond. However, some substituents, such as halogens, amines, and to a lesser extent alkyl groups, exert a considerable electronic effect on the cage.

If the cage has halogen or amine substituents, the geometry may be more open than that predicted by cage-counting rules.[4−14] For example, replacing two hydrogens on boron in $C_4B_2H_6$ with fluorine alters the pentagonal pyramidal cage structure of the parent[15] ($C_4B_2H_6$) to a planar structure for the derivative[5] ($C_4B_2F_2H_4$).

The number of π donating groups substituted on boron also affects the nature of the cage. For example, when one BH hydrogen is replaced with an amino group in $C_4B_2H_6$, the nonclassical cage structure is retained. However, when both BH hydrogens are replaced with amino groups, the observed structure is a classical bicyclic compound.[10−14] Likewise, substituting one and two halogens for hydrogen (i.e. B-monohalo and B-dihalo derivatives) in 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$ is not enough to favor the classical planar structure over the nonclassical cage structure.[8] Two recent studies[16,17] on *closo*-1,5-$(CH)_2(BR)_3$ structures found that the bonding pattern in the trigonal bipyramidal cage changed from nonclassical to classical when R was varied from H to NH_2. Other classical structures which are known to be stabilized by amino groups are di-coordinate boron cations ($[B(NR_2)_2]^+$)[18] and polyboranes of formula $B_n(NR_2)_{n+2}$, which have a chainlike structure.[19]

Boron hydrides of formula B_nH_n have n cage-bonding electron pairs and are called *hypercloso*.[20−23] While parent boron hydrides of this formula are quite rare, there are known examples of metalloboranes[24−26] and cages where halides have replaced hydrogens. These polyhedral boron halides,[27−30] B_nX_n (X = F,

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Cl, Br, I), form a well-known class of compounds where cages from four to twelve vertexes have been characterized. All structures are consistent with *closo* cages and the halide substitutent is thought to stabilize the cage by π donation.

In 1963, Urry et al.[31] synthesized $B_4(NMe_2)_4$ from the reaction of dimethylamine with B_2Cl_4. While too little material was obtained to allow extensive characterization, the authors suggested on the basis of IR spectroscopy that the molecule was likely to have a four-membered ring structure rather than a tetrahedral cage structure. In 1980, Nöth and Pommerening[32] reported the X-ray structure of $B_6(NMe_2)_6$. Rather than an octahedral geometry, the aminoborane had a ring geometry with C_2 symmetry in the solid state and a higher symmetry in solution (probably D_{3d}). CNDO/INDO calculations on $B_6(NH_2)_6$ were reported by Neckel et al.[33] who found the planar structure to be more stable than the chair and octahedral structures.

More recently, Baudler et al.[34] reported the synthesis of $B_n(NEt_2)_n$ ($n = 3, 4, 6$) from the reaction of Et_2NBCl_2 with potassium in boiling cyclohexane. Two isomers of $B_6(NEt_2)_6$ were isolated, a classical cyclic polyborane and a nonclassical octahedral cage.[35] The authors found that the classical isomer rearranged to the nonclassical isomer at room temperature in hydrocarbon solution, while the opposite rearrangement was observed to occur in the crystal (cage → cyclic) when heated to 137 °C. It would appear that the classical and nonclassical isomers must have similar gas-phase energies with secondary effects such as solvation, lattice energy, and entropy playing important roles.

Computational Methods

All geometries were fully optimized in the given symmetry at the HF/6-31G(d), MP2/6-31G(d) and B3LYP/6-31G(d) levels.[36] Vibrational frequencies were calculated at the HF/6-31G(d) and B3LYP/6-31G(d) levels to determine the nature of the stationary points and to make zero-point corrections. Single-point calculations were made on MP2/6-31G(d) geometries at QCISD(T)/6-31G(d) and MP2/6-31G(2d,p) in order to estimate[37] relative energies at the [QCISD(T)/6-31G(2d,p)] level. Zero-point corrections were made using scaled HF/6-31G(d) frequencies (0.9 factor). For molecular systems larger than $B_4(NH_2)_4$, QCISD(T)/6-31G(d) calculations were not possible and zero-point corrections were applied to MP2/6-31G(2d,p) relative energies. Density functional optimizations were made using B3LYP/6-31G(d) and relative energies were corrected using unscaled B3LYP/6-31G(d) vibrational frequencies.

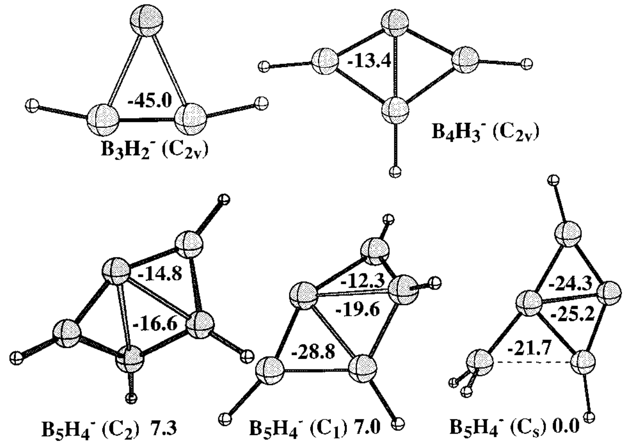

Figure 1. Molecular plots of $B_nH_{n-1}^-$ anions. Negative numbers are NICS values (ppm) at the GIAO/HF/6-311+G(d,p) level. Relative energies (kcal/mol) at the B3LYP/6-31G(d)+ZPC level are provided just following the symmetry designation.

When comparing relative energies of isomers with classical structures (rings) and nonclassical structures (cages), electron correlation is very important.[38] While the [QCISD(T)/6-31G(2d,p)] level is expected to give reliable relative energies, the QCISD(T) method could not be applied to the larger systems. Therefore, the [QCISD(T)/6-31G(2d,p)] method was used to benchmark relative energies for ring versus cage species in the $B_4(NH_2)_4$ system at the MP2/6-31G(2d,p) and B3LYP/6-31G(d) levels to determine which method is more reliable. The stability of the $B_4(NH_2)_4$ cage was overestimated by 8.0 kcal/mol (relative to the ring) at the MP2/6-31G(2d,p) level, and underestimated by 2.0 kcal/mol at the B3LYP/6-31G(d) level (relative to [QCISD(T)/6-31G(2d,p)]). Thus, the B3LYP/6-31G(d) method is more reliable for predicting relative energies between rings and cages. This point becomes even more important in the $B_6(NH_2)_6$ system where the DFT and MP2 methods differ by over 20 kcal/mol.

Aromaticity effects in the B_nH_n systems were estimated by calculating NICS (nucleus independent chemical shifts)[39] values (in units of ppm) in the geometric center of BBB rings at the GIAO/HF/6-311+G(d,p)//B3LYP/6-31G(d) level. NICS values, the negative of the absolute magnetic shielding, have been shown to correlate with a variety of properties related to aromaticity.[39] Wave functions have been analyzed by the NBO method[40] in an attempt to localize the canonical orbitals into lone pairs, two-center bonds, and three-center bonds.

Molecular plots of $B_nH_{n-1}^-$ anions are given in Figure 1, those of B_nH_n boron hydrides in Figure 2, and those of $B_n(NH_2)_n$ aminoboranes in Figure 3. Total energies (hartrees) and zero-point energies (kcal/mol) are given in Tables 1 and 2, and relative energies (kcal/mol) are given in Tables 3 and 4. Cartesian coordinates at the B3LYP/6-31G(d) level of all species are provided as Supporting Information.

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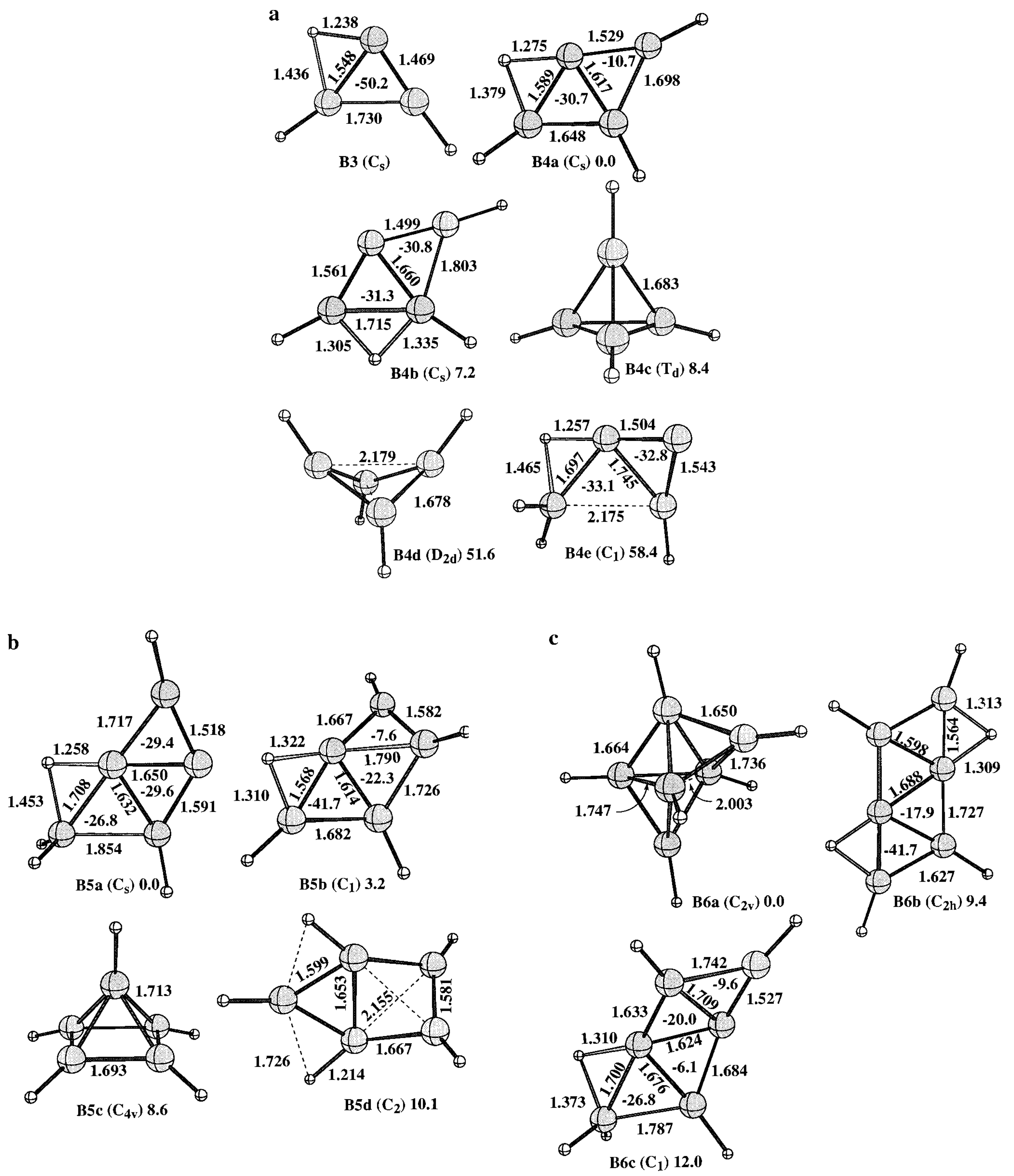
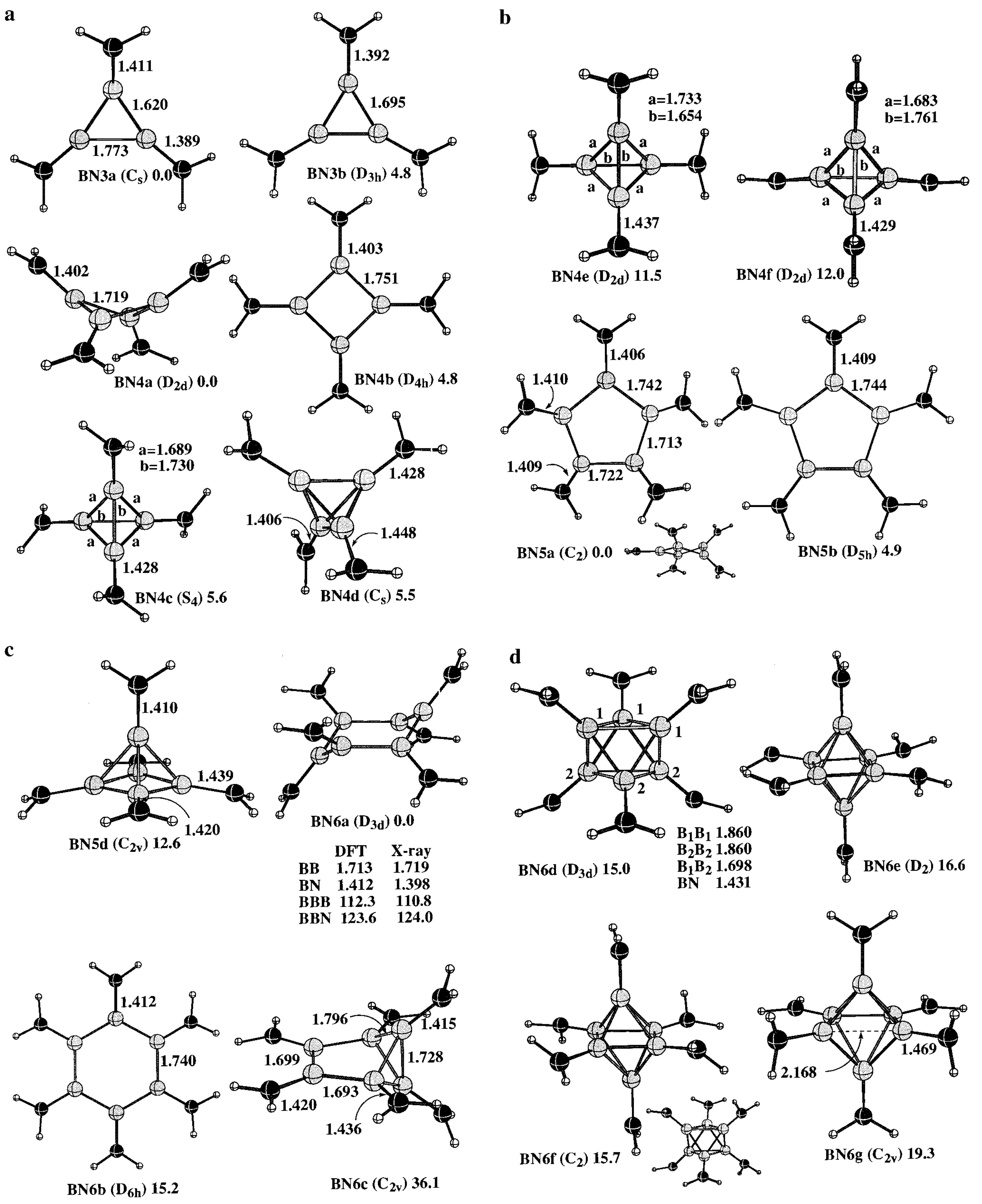


Figure 2. Molecular plots of B_nH_n boron hydrides. Selected distances (Å) are given at the B3LYP/6-31G(d) level. Negative numbers are NICS values (ppm) at the GIAO/HF/6-311+G(d,p) level. Relative energies (kcal/mol) at the B3LYP/6-31G(d)+ZPC level are provided just following the symmetry designation.

Results and Discussion

The nature of the substituent (R = H, NH_2) in B_nR_n (n = 3−6) has such a profound effect on the structure and bonding of the boron hydride, that it is advantageous to divide the discussion into two sections.

Neutral B_nH_n Species (n = 3−6) and $B_nH_{n-1}^-$ Anions (n = 3−5). B_nH_n species, members of the *hypercloso* class, lack enough cage electrons to fill all of the *closo* cage-bonding orbitals. For larger members of this series, the capping principle applies, which suggests that the most stable geometry for a *hypercloso* species is one based on a *closo* cage smaller by one vertex with the extra vertex adopting a capping position.[1] For smaller members of this series, the capping principle may not be as effective in predicting the lowest energy structure since



	DFT	X-ray
BB	1.713	1.719
BN	1.412	1.398
BBB	112.3	110.8
BBN	123.6	124.0

Figure 3. Molecular plots of $B_n(NH_2)_n$ aminoboranes. Selected distances (Å) are given at the B3LYP/6-31G(d) level. Experimental[32] distances (Å) and angles (degrees) for $B_6(NMe_2)_6$ are compared to **BN6a**. An alternative view of **BN6f** (C_2) shows the similarity to **BN6d** (D_{3d}). Relative energies (kcal/mol) at the B3LYP/6-31G(d)+ZPC level are provided just following the symmetry designation.

the even smaller *closo* cage dictated by the capping principle may not yield a stabilizing effect. Instead, there is an alternative stabilizing effect that may lead to low-energy structures. In an extensive study of B_3H_n species, Korkin et al.[41] calculated a number of B_3H_3 species at the QCISD(T)/6-311+G(d,p)//MP2/6-31+G(d) level. The lowest energy structure was a three-membered ring with two terminal BH bonds and one bridging

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Table 1. Absolute Energies (hartrees) and Zero-Point Energies (kcal/mol)[a]

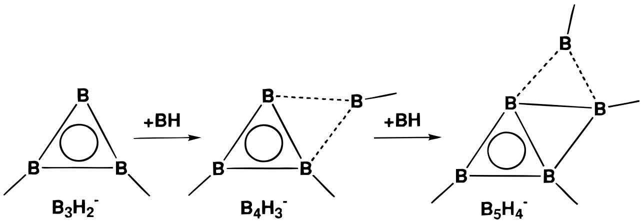
		PG	//HF/a		//MP2/a			//B3LYP/a	
			HF/a	ZPE(NIF)	MP2/a	QCI/a	MP2/b	B3LYP/a	ZPE(NIF)
BH_3		D_{3h}	−26.39001	17.38(0)	−26.46424	−26.48466	−26.49108	−26.61299	16.68(0)
B_2H_4		D_{2h}	−51.61801	25.68(1)	−51.75691	−51.79309	−51.79596	−52.02135	24.57(1)
B_3H_5		C_{2v}	−76.84409	33.61(2)	−77.04852	−77.10047	−77.10000	−77.42826	32.09(2)
$BH_2{=}NH_2$		C_{2v}	−81.48910	31.94(0)	−81.73122	−81.76243	−81.78482	−82.03932	30.14(0)
$BH_2{-}NH_2$		C_s	−81.44219	30.00(1)	−81.67817	−81.70893	−81.73340	−81.98757	28.16(1)
B_3H_3	**B3**	C_s	−75.64668	23.24(0)	−75.89939	−75.94264	−75.93481	−76.23358	22.32(0)
$B_3H_2^-$		C_{2v}	−75.06718	17.22(0)	−75.33065	−75.37206	−75.36317	−75.65697	16.40(0)
B_4H_4	**B4a**	C_s	−100.94408	32.88(0)	−101.27844	−101.33033	−101.32462	−101.72605	31.24(0)
	B4b	C_s	−100.93111	32.93(0)	−101.26768	−101.31880	−101.31515	−101.71486	31.39(0)
	B4c	T_d	−100.92570	32.58(0)	−101.27149	−101.32568	−101.31804	−101.71296	31.44(0)
	B4d	D_{2d}	−100.88955	30.03(0)	−101.17423	−101.23662	−101.22007	−101.63782	27.47(0)
	B4e	C_1	*b*	31.46(0)[c]	−101.18222	−101.24094	−101.23064	−101.63201	30.60(0)
$B_4H_3^-$		C_{2v}	−100.38361	25.60(0)	−100.72127	−100.77131	−100.76478	−101.16206	24.50(0)
B_5H_5	**B5a**	C_s	−126.19532	41.99(0)	−126.61741	−126.68135	−126.67512	−127.17460	40.07(0)
	B5b	C_1	−126.19005	41.18(0)	−126.61078	−126.67458	−126.66856	−127.16808	39.16(0)
	B5c	C_{4v}	−126.16790	40.25(0)	−126.60972	−126.67307	−126.66781	−127.15904	38.90(0)
	B5d	C_2	−126.17542	39.75(1)	−126.59559	−126.65917	−126.65537	−127.15496	37.88(1)
$B_5H_4^-$		C_s	*b*	33.69(0)[c]	−126.07511	−126.13584	−126.13064	−126.62479	33.07(0)
$B_5H_4^-$		C_2	−125.63720	33.32(0)	−126.05586	−126.12016	−126.11205	−126.61076	31.58(1)
$B_5H_4^-$		C_1	*b*	33.12(0)[c]	−126.06386	−126.12422	−126.11899	−126.61178	31.91(0)
B_6H_6	**B6a**	C_{2v}	−151.44795	49.98(0)	−151.99986	−152.06514	−152.06841	−152.64588	47.73(0)
	B6b	C_{2h}	−151.43708	50.74(0)	−151.96974	−152.04097	−152.03884	−152.63169	48.24(0)
	B6c	C_1	−151.43574	50.23(0)	−151.95783	−152.03416	−152.02750	−152.62687	47.86(0)

[a] Basis set "a" is 6-31G(d), and basis set "b" is 6-31G(2d,p). [b] Not a minimum at HF/6-31G(d). [c] Vibrational frequencies calculated at MP2/6-31G(d) level.

BH_bH bond which can be rationalized by the existence of a three-center two-electron (3c-2e) π bond. This 2π-electron aromatic stabilizing effect has been recognized as important by Berndt and Schleyer in a number of carboranes with a C_2B_2 framework.[42] Thus, if one removes two electrons from $B_3H_3^{2-}$, it is conceptually more favorable to remove a 2c-2e σ BB bond (simultaneously converting a 2c-2e BB bond into a 3c-2e BBB bond and a 2c-2e BH bond into a BH_bH bond), rather than remove the two π electrons.

The monoanions $B_nH_{n-1}^-$ ($n = 3-5$) were calculated to give insight into the neutral boron hydrides. The three-membered BBB ring in $B_3H_2^-$ is quite aromatic as shown by the negative NICS value of −45.0 ppm. Using the $B_3H_2^-$ structure[43] as a building block, larger anions can be built up by adding a bridging BH group[44] (Scheme 1). The resulting BBB rings (Figure 1) all have negative NICS values indicating varying degrees of aromaticity. It is interesting to note that $B_5H_4^-$ in C_2 symmetry is a transition state to a C_1 symmetry structure 0.3 kcal/mol lower in energy. Despite the small energy change, the NICS values in the two equivalent rings change significantly (−14.8 → −12.3/−28.8 ppm, Figure 1) indicating that a small structural change can induce large changes in ring currents. However, the lowest-energy $B_5H_4^-$ anion is not the C_1 structure, but a C_s structure with a BH_2 group (Figure 1) which is computed to be 7.0 kcal/mol more stable. The lowest energy structure of B_5H_5 is a protonated form of this anion (see below).

Scheme 1



A number of calculations have been reported for B_4H_4,[45] the next member of the *hypercloso* series. Most studies considered only a planar (or folded) and tetrahedral geometries. However, in a recent study, Mach et al.[46] found that a structure of C_s symmetry was lower in energy than both the folded (**B4d**, D_{2d}) and tetrahedral (**B4c**, T_d) isomers (Figure 2). The C_s structure

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(44) From an analysis of the low-energy B_nH_n structures, a series can be constructed where a BH group is formally added to a BB bond to form the next member of the series. This "adding bridging BH" principle suggests that the added BH unit has minimal impact on the "core" structure. The added BH unit (with two electrons available for bonding) interacts with the BB 2c-2e σ bond to form a BBB ring that is internally bonded by one 2c-2e bond and one 3c-2e bond.

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Table 2. Absolute Energies (hartrees) and Zero-Point Energies (kcal/mol)[a]

		PG	//HF/a		//MP2/a			//B3LYP/a	
			HF/a	ZPE(NIF)	MP2/a	QCI/a	MP2/b	B3LYP/a	ZPE(NIF)
$B_3N_3H_6$	**BN3a**	C_s	−240.88705	61.96(0)	−241.60645	−241.68258	−241.72282	−242.43248	57.61(0)
	BN3b	D_{3h}	−240.88666	61.89(2)	−241.59730	−241.67496	−241.71398	−242.42490	57.58(2)
borazine		D_{3h}	−241.15101	62.01(0)	−241.85540	−241.92485	−241.96353	−242.67016	58.62(0)
$B_4N_4H_8$	**BN4a**	D_{2d}	−321.25298	84.43(0)	−322.20518	−322.30604	−322.36240	−323.30050	78.56(0)
	BN4b	D_{4h}	−321.24899	84.20(1)	−322.19506	−322.29746	−322.35256	−323.29198	78.04(1)
	BN4c	S_4	−321.20147	79.75(1)	−322.20550	−322.29382	−322.36448	−323.28627	75.26(0)
	BN4d	C_s	−321.20385	79.89(0)	−322.20510	−322.29319	−322.36404	−323.28591	74.89(1)
	BN4e	D_{2d}	−321.19300	79.07(3)	−322.19687	−322.28526	−322.35559	−323.27576	74.51(3)
	BN4f	D_{2d}	−321.18967	76.90(8)	−322.19136	−322.27885	−322.35008	−323.27146	72.33(8)
$B_5N_5H_{10}$	**BN5a**	C_2	−401.61043	106.17(0)	−402.79956		−402.99650	−404.16534	98.99(0)
	BN5b	D_{5h}	−401.60513	105.88(2)	−402.78967		−402.98724	−404.15651	98.35(2)
	BN5c	C_{2v}	−401.53355	101.89(0)	−402.79179		−402.99159	−404.13962	95.52(0)
$B_6N_6H_{12}$	**BN6a**	D_{3d}	−481.96202	127.93(0)	−483.39157		−483.62707	−485.02733	119.43(0)
	BN6b	D_{6h}	−481.94000	127.36(3)	−483.36399		−483.60073	−485.00131	118.34(3)
	BN6c	C_{2v}	−481.84450	122.80(3)	−483.34567		−483.58491	−484.96374	115.66(1)
	BN6d	D_{3d}	−481.86433	120.84(2)	−483.38874		−483.62918	−484.99469	113.90(2)
	BN6e	D_2	−481.86563	123.25(0)	−483.39045		−483.63095	−484.99454	115.39(1)
	BN6f	C_2						−484.99500	114.82(0)
	BN6g	C_{2v}	−481.87439	125.40(0)	−483.38277		−483.62285	−484.99207	116.62(0)

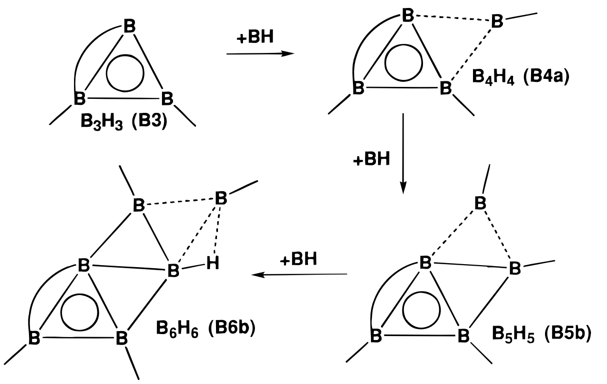
[a] Basis set “a” is 6-31G(d), and basis set “b” is 6-31G(2d,p).

Table 3. Relative Energies (kcal/mol)) for Various Species[a]

		PG	//HF/a	//MP2/a					//B3LYP/a	
			HF/a	MP2/a	QCI/a	MP2/b	[QCI/b]	+ZPC[b]	B3LYP/a	+ZPC
B_3H_3	**B3**	C_s	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$B_3H_2^-$		C_{2v}	363.6	356.9	358.0	358.7	359.8	354.4	361.8	355.9
B_4H_4	**B4a**	C_s	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	B4b	C_s	8.0	6.8	7.2	5.9	6.3	6.3	7.0	7.2
	B4c	T_d	11.5	4.4	2.9	4.1	2.6	2.3	8.2	8.4
	B4d	D_{2d}	34.2	65.4	58.8	65.6	59.0	56.4	55.4	51.6
	B4e	C_1	c	60.4	56.1	59.0	54.7	54.9[d]	59.0	58.4
$B_4H_3^-$		C_{2v}	351.7	349.6	350.8	351.3	352.5	345.9	353.9	347.2
B_5H_5	**B5a**	C_s	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	B5b	C_1	3.3	4.2	4.2	4.1	4.1	3.4	4.1	3.2
	B5c	C_{4v}	17.2	4.8	5.2	4.6	5.0	3.4	9.8	8.6
	B5d	C_2	12.5	13.7	13.9	12.4	12.6	10.6	12.3	10.1
$B_5H_4^-$		C_s	c	340.3	342.3	341.7	343.7	337.8[d]	345.0	338.0
$B_5H_4^-$		C_2	350.2	352.4	352.1	353.3	353.0	345.2	353.8	345.3
$B_5H_4^-$		C_1	c	347.4	349.6	349.0	351.2	344.8[d]	353.2	345.0
B_6H_6	**B6a**	C_{2v}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	B6b	C_{2h}	6.8	18.9	15.2	18.6	14.9	15.6	8.9	9.4
	B6c	C_1	7.7	26.4	19.4	25.7	18.7	18.9	11.9	12.0

[a] Basis set “a” is 6-31G(d), and basis set “b” is 6-31G(2d,p). [b] Scaled (0.9 factor) zero-point correction at HF/6-31G(d) level applied to [QCISD(T)/6-31G(2d,p)] relative energies. [c] Not a minimum at HF/6-31G(d). [d] Zero-point correction taken from MP2/6-31G(d) vibrational frequencies (0.95 scaling factor).

Scheme 2



(**B4a**), which is 8.8 kcal/mol lower in energy than tetrahedral B_4H_4 at the CISD/cc-pVTZ level, has a bridging hydrogen and a 3c-2e π bond. In fact, it can be viewed as the lowest-energy B_3H_3 structure (**B3**) with a bridging BH group (Scheme 2) or as a protonated form of $B_4H_3^-$. An alternative structure (**B4b**) is possible if the bridging hydrogen is moved to a different location. At the standard level, **B4a** is 7.2 kcal/mol lower than **B4b** and 8.4 kcal/mol below **B4c**.

Another bonding motif for B_nH_n species can be envisioned by the association of the BH_2^+ cation and the $B_{n-1}H_{n-2}^-$ anion (Scheme 3). For $n = 4$, a C_1 minimum was found (**B4e**) 58.4 kcal/mol higher than **B4a**.

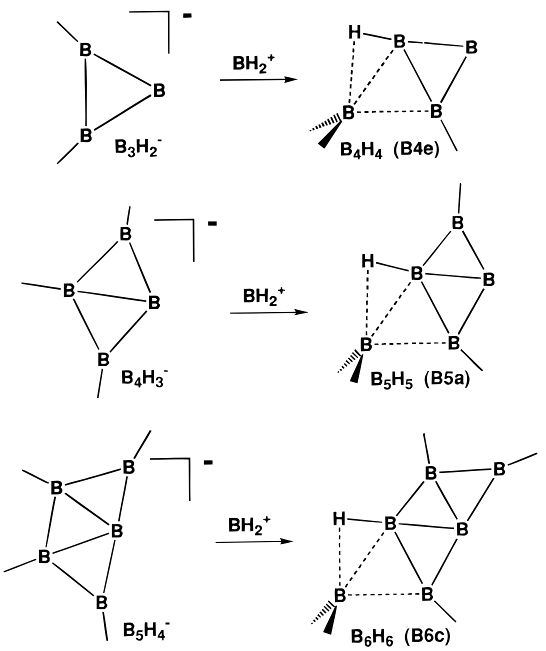
For B_5H_5, three minima were located (**B5a**−**c**). The lowest energy minimum (**B5a**) can be viewed as the association of BH_2^+ and the $B_4H_3^-$ anion (Scheme 3). All three BBB rings are aromatic as indicated by their NICS values (−26.8, −29.6, and −29.4 ppm). The next lowest-energy isomer (**B5b**), 3.2 kcal/mol above **B5a**, can be viewed as a BH bridged **B4a** isomer (Scheme 2). According to NICS values, the BBB ring formed by the added BH is much less aromatic (−7.6 ppm) than the other two BBB rings (−22.3 and −41.7 ppm). Isomer **B5c**, the nonclassical square pyramid, is 8.6 kcal/mol above **B5a**. Further exploration of the B_5H_5 potential energy surface led to **B5d**, a degenerate transition state for the interconversion of **B5b** isomers with a 6.9 kcal/mol activation barrier.

Table 4. Relative Energies (kcal/mol) for Various Species[a]

		PG	//HF/a	//MP2/a					//B3LYP/a	
			HF/a	MP2/a	QCI/a	MP2/b	[QCI/b]	+ZPC[b]	B3LYP/a	+ZPC
$B_3N_3H_6$	**BN3a**	C_s	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	BN3b	D_{3h}	0.2	5.7	4.8	5.5	4.6	4.5	4.8	4.8
borazine		D_{3h}	−165.6	−156.3	−152.0	−151.0	−146.8	−146.8	−149.1	−148.1
$B_4N_4H_8$	**BN4a**	D_{2d}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	BN4b	D_{4h}	2.5	6.4	5.4	6.2	5.2	5.0	5.3	4.8
	BN4c	S_4	32.3	−0.2	7.7	−1.3	6.6	2.4	8.9	5.6
	BN4d	C_s	30.8	0.1	8.1	−1.0	7.0	2.9	9.2	5.5
	BN4e	D_{2d}	37.6	5.2	13.0	4.3	12.1	7.3	15.5	11.5
	BN4f	D_{2d}	39.7	8.7	17.1	7.7	16.1	9.3	18.2	12.0
$B_5N_5H_{10}$	**BN5a**	C_2	0.0	0.0		0.0		0.0	0.0	0.0
	BN5b	D_{5h}	3.3	6.2		5.8		5.5	5.5	4.9
	BN5c	C_{2v}	48.2	4.9		3.1		−0.7	16.1	12.6
$B_6N_6H_{12}$	**BN6a**	D_{3d}	0.0	0.0		0.0		0.0	0.0	0.0
	BN6b	D_{6h}	13.8	17.3		16.5		16.0	16.3	15.2
	BN6c	C_{2v}	73.7	28.8		26.4		21.8	39.9	36.1
	BN6d	D_{3d}	61.3	1.8		−1.3		−7.7	20.5	15.0
	BN6e	D_2	60.5	0.7		−2.4		−6.6	20.6	16.6
	BN6f	C_2							20.3	15.7
	BN6g	C_{2v}	55.0	5.5		2.6		0.3	22.1	19.3

[a] Basis set "a" is 6-31G(d), and basis set "b" is 6-31G(2d,p). [b] Scaled (0.9 factor) zero-point correction at HF/6-31G(d) level applied to [QCISD(T)/6-31G(2d,p)] relative energies for $B_3(NH_2)_3$ and $B_4(NH_2)_4$ species and to MP2/6-31G(2d,p) relative energies for $B_5(NH_2)_5$ and $B_6(NH_2)_6$ species.

Scheme 3



The lowest energy isomer of B_6H_6 is **B6a**, a BH-capped trigonal bipyramid. This is the first member of the *hypercloso* series whose lowest energy structure is given by the capping principle.[1] Thus, it appears that the underlying $B_5H_5^{2-}$ dianion cage has sufficient intrinsic stability to provide the basic scaffolding for the added BH cap. Only 9.4 kcal/mol higher in energy than **B6a** is **B6b**, a C_{2h} structure which can be derived from **B5b** by addition of a bridging BH group[44] plus the conversion of a terminal BH to a bridging BH (Scheme 3). In **B6b**, the two outer BBB rings are more aromatic than the two inner rings (−41.7 and −17.9 ppm, respectively). A third isomer **B6c**, 12.0 kcal/mol higher than **B6a**, is conceptually derived from the BH_2^+ cation and the $B_5H_4^-$ anion (Scheme 2). Of the four BBB rings, rings 1 and 3 (−26.8 and −20.0 ppm) are more aromatic than rings 2 and 4 (−6.1 and −9.6 kcal/mol).

$B_n(NH_2)_n$ Series ($n = 3-6$). The substitution of an amino group for hydrogen in B_nH_n changes the nature of bonding among the boron atoms. Due to the ability of the lone pair on nitrogen to donate electron density into empty orbitals on boron,[47] classical structures with tri-coordinate boron atoms are stabilized relative to nonclassical structures. In fact, if the boron atoms form a ring, the species would be inorganic analogues of radialenes.

The first member of the series, $B_3(NH_2)_3$ (**BN3a**), adopts a C_s symmetry conformation, 4.8 kcal/mol lower in energy than the symmetrical D_{3h} structure (**BN3b**). The three amino groups remain planar (within 0.4°); one is attached to a boron which becomes pyramidal ($\tau = 338.8°$, where τ is the sum of bond angles around nitrogen) while the other two twist out of the BBB plane. In contrast to the NBO analysis (HF/6-31G*//MP2/6-31G(d)) of the D_{3h} structure (**BN3b**) where three 2c-2e BB bonds were found, the NBO analysis of the C_s structure (**BN3a**) revealed only two 2c-2e BB bonds with one very delocalized bond. As a result, the C_s structure has two short BB bonds (1.620 Å) and one long BB bond (1.773 Å). However, the average BB distance is smaller in the C_s structure (1.671 Å) compared to the D_{3h} structure (1.695 Å) indicating stronger bonds. For comparison, the *exo* 2c-2e BB bonds to boron hydrides are in the range 1.66−1.74 Å.[48]

The global minimum on the $B_3N_3H_6$ potential energy surface is borazine,[49] the inorganic analogue of benzene, which has an experimental heat of formation[50] of −121.9 kcal/mol at 298 K. The $B_3(NH_2)_3$ isomer (**BN3a**) is predicted to be 148.1 kcal/mol less stable than borazine and, when combined with a 1.6 kcal/mol contribution from heat capacity, leads to a predicted heat of formation at 298 K of 27.8 kcal/mol. It is interesting to

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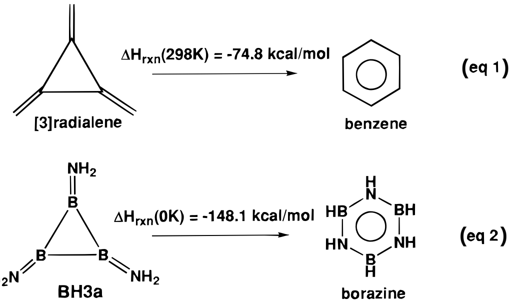

Figure 4. Reaction energies (kcal/mol) for the formation of benzene from [3]radialene in eq 1 (experimental) and the formation of borazine from **BN3a** in eq 2 (calculated, B3LYP/6-31G(d)+ZPC).

compare (Figure 4) the formation of benzene from tris(methylidene)cyclopropane ([3]radialene)[51] (eq 1) with the formation of borazine from **BN3a** (eq 2). The experimental enthalpy of reaction[50,51] in eq 1 is −74.8 kcal/mol which can be compared to a calculated reaction energy in eq 2 of −148.1 kcal/mol. The large difference (73.3 kcal/mol) can be attributed to the much weaker B═N bonds in **BN3a** compared to the C═C bonds in [3]radialene.

The folded $B_4(NH_2)_4$ species (**BN4a**, D_{2d}) is 4.8 kcal/mol lower in energy than the planar species (**BN4b**, D_{4h}). Again, the average BB distance in **BN4a** (1.719 Å) is shorter than the BB distances in **BN4b** (1.751 Å). Four stationary points (**BN4c−f**) were located with amino groups attached to a tetrahedral B_4 core. Two D_{2d} structures were considered with the amino group bisecting (**BN4f**) and in (**BN4e**) the molecular planes. The energies (with respect to **BN4a**) were similar (11.5 and 12.0 kcal/mol, respectively); both had multiple imaginary frequencies. The minimum (**BN4c**) had S_4 symmetry and was 5.6 kcal/mol above **BN4a**. A transition state for amino group rotation was located (**BN4d**, C_s) which (with zero-point correction) is predicted to be slightly lower in energy than the S_4 minimum (**BN4c**). The $D_{2d} \rightarrow S_4$ (**BN4e** → **BN4c**) symmetry lowering allows the four amino groups to become pyramidal ($\tau = 351.5°$) which occurs due to the much smaller conjugation with boron. The BN distances increase 0.026 Å in going from **BN4a** to **BN4c** (1.402 → 1.428 Å). In the amino rotation transition state (**BN4d**), the BN bond to the rotating amino group increases to 1.448 Å.

In $B_5(NH_2)_5$ the planar species (**BN5b**) distorts to a C_2 species (**BN5a**), 4.9 kcal/mol lower in energy. The average BB distance in **BN5a** is shorter than in the planar structure **BN5b** (1.726 Å compared to 1.744 Å). A square pyramidal minimum (**BN5c**, C_{2v}) was located which was 12.6 kcal/mol higher in energy than **BN5a**. The BN distance to the apical amino group is short (1.410 Å) because symmetry forces the amino group into maximum conjugation, while the basal amino groups are longer (1.439 and 1.420 Å) and pyramidal ($\tau = 352.2°$ and 358.9°).

Planar $B_6(NH_2)_6$ (**BN6b**) is predicted to be 15.2 kcal/mol higher in energy than the D_{3d} chair minimum (**BN6a**). While the BN distances are the same in **BN6a** and **BN6b**, the BB distance is considerable shorter in **BN6a** than in planar **BN6b** (1.713 and 1.740 Å, respectively). In contrast to the present work, an earlier theoretical study[33] at the INDO level predicted that the planar geometry was lower in energy than the chair. In addition to **BN6a** and **BN6b**, a classical bicyclic isomer was also considered (**BN6c**), since this is the structure adopted by $(CH)_2(BNR_2)_4$.[52] However, the energy of **BN6c** is significantly above **BN6a** (36.1 kcal/mol).

An X-ray structure has been determined[32] for the chair isomer of $B_6(NMe_2)_6$. If averaged to D_{3d} symmetry, the bond lengths and bond angles are in good agreement with chair $B_6(NH_2)_6$ (**BN6a**) optimized at the B3LYP/6-31G(d) level (Figure 3). The largest deviation (0.014 Å) is an overestimation of the BN bond length which is no doubt due to the replacement of methyl by hydrogen in the calculation.

Three stationary points (**BN6d−f**) were considered for amino groups substituted on an octahedral core. The energy range for the octahedral species with respect to **BN6a** was 15.0 to 19.3 kcal/mol. A D_2 structure (**BN6e**) was computed to be a minimum at HF/6-31G(d) but a transition state at B3LYP/6-31G(d). Following the imaginary mode gave a C_2 minimumm (**BN6f**), 0.3 kcal/mol lower in energy at B3LYP/6-31G(d). Interestingly, the lowest energy octahedral structure (after zero-point correction), is the symmetrical D_{3d} structure (**BN6d**) which has two imaginary frequencies but is only 0.2 kcal/mol less stable than **BN6f** (C_2). The amino groups are relatively planar ($\tau = 357.2°$), but show little conjugation with boron atoms in **BN6d** as evidenced by long BN bonds (1.433 Å). A minimum resembling a distorted octahedron (**BN6g**, C_{2v}) was computed to be 19.3 kcal/mol less stable than **BN6a**.

While all energies reported above are at the B3LYP/6-31G(d)//B3LYP/6-31G(d)+ZPC level ("standard level"), it should be noted that energies at the MP2/6-31G(2d,p)//MP2/6-31G(d)+ZPC/6-31G(d) level give a different relative ordering. Specifically, the octahedral species (**BN6d,e**) are stabilized by over 20 kcal/mol relative to the chair (**BN6a**). In contrast to DFT results, at the MP2 level, the lowest-energy octahedral species (**BN6d**) is 7.7 kcal/mol *lower* in energy than the chair (**BN6a**). As discussed above, additional electron correlation at QCISD(T), would probably reduce the difference between ab initio and DFT. However, it is likely that the DFT difference between **BN6a** and **BN6d** (15.0 kcal/mol) is an upper limit, and the real difference might be 5−10 kcal/mol lower. A smaller difference would be more consistent with experimental results[34] which indicate that the two forms interconvert.

Steric effects may also affect the chair−cage energy separation since the experimental system refers to $B_6(NEt_2)_6$ while the calculations consider $B_6(NH_2)_6$. The ethyl groups would be more crowded in the chair form (**BN6a**) relative to the cage form (**BN6d**) which would destabilize the chair form and reduce the chair−cage energy difference.

Thermodynamic Comparisons

Cage stabilization energies can be calculated from isodesmic reactions involving BH_3, B_2H_4, and B_3H_5. It is important to choose reference geometries in which hyperconjugation is precluded, even though the molecules themselves may not correspond to minima. For that reason, planar B_2H_4 (D_{2h}) and B_3H_5 (C_{2v}) were used as reference compounds even though nonplanar structures are more stable. The reaction energy of eq 3 is close to zero (−0.5 kcal/mol, Table 5), as expected, since

$$B_3H_5(C_{2v}) + BH_3 \rightarrow 2B_2H_4(D_{2h}) \qquad (3)$$

no cage stabilization is present. Equation 4 was used to evaluate

$$B_3H_5 + BH_3 \rightarrow 2B_2H_4 + 1/n(B_nH_n) \qquad (4)$$

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Table 5. Reaction Energies (kcal/mol) from Isomdesmic Reactions (Eqs 3−6)

	//HF/a	//MP2/a					//B3LYP/a	
	HF/a	MP2/a	QCI/a	MP2/b	[QCI/b]	+ZPC[b]	B3LYP/a	+ZPC
eq 3	−1.2	−0.7	−0.6	−0.5	−0.4	−0.1	−0.9	−0.5
eq 4 ($n = 3$)	6.6	−5.1	−4.3	−4.7	−3.9	−4.1	−2.7	−2.6
eq 4 ($n = 4$)	−6.2	−17.6	−15.8	−17.0	−15.2	−14.9	−15.4	−15.2
eq 4 ($n = 5$)	−8.1	−20.0	−18.1	−19.4	−17.5	−17.1	−17.6	−17.1
eq 4 ($n = 6$)	−9.6	−26.2	−23.1	−25.5	−22.4	−22.1	−21.4	−21.0
eq 5 ($n = 3$)	19.7	15.2	15.9	15.3	16.0	14.0	15.0	12.8
eq 5 ($n = 4$)	8.7	5.2	6.1	5.0	5.9	4.3	6.0	4.3
eq 5 ($n = 5$)	3.1	−0.2		−0.4		−1.9	1.0	−0.5
eq 5 ($n = 6$)	0.1	−3.5		−3.7		−5.1	−2.0	−3.4
$BH_2NH_2(C_s \rightarrow C_{2v})$	−29.4	−33.3	−33.5	−32.3	−32.5	−30.8	−32.5	−30.5
eq 6a ($n = 4$)	−24.2	−27.5	−27.0	−27.2	−26.7	−25.8	−25.8	−24.5
eq 6b ($n = 4$)	−10.5	−12.3	−11.1	−12.2	−11.0	−11.7	−11.8	−12.3
eq 6c ($n = 5$)	−13.1	−14.1		−14.1		−14.4	−13.5	−13.7
eq 6d ($n = 6$)	−10.8	−11.0		−11.2		−12.0	−10.6	−11.1

[a] Basis set "a" is 6-31G(d), and basis set "b" is 6-31G(2d,p). [b] Scaled (0.9 factor) zero-point correction at HF/6-31G(d) level applied to [QCISD(T)/6-31G(2d,p)] relative energies for $B_3(NH_2)_3$ and $B_4(NH_2)_4$ species and to MP2/6-31G(2d,p) relative energies for $B_5(NH_2)_5$ and $B_6(NH_2)_6$ species.

Table 6. Calculated ^{11}B Chemical Shifts (ppm) and NICS Values (ppm) for $B_n(NH_2)_n$ Species at GIAO/HF/6-311+G(d,p)//B3LYP/6-31G(d)

ring (classical) form			cage (nonclassical) form		
$B_n(NH_2)_n$	$\delta(^{11}B)$	NICS	$B_n(NH_2)_n$	$\delta(^{11}B)$	NICS
BN3b (D_{3h})	119.6	103.1			
BN3a (C_s)	83.3[a](48)[b]	25.1			
BN4a (D_{2d})	75.3	19.7	**BN4c** (S_4)	25.4	−6.0
BN5a (C_2)	50.7[a]	13.6	**BN5d** (C_{2v})	29.0[a]	3.3
BN6a (D_{3d})	70.1(64)[b]	7.1	**BN6d** (D_{3d})	77.2(40)[b]	10.8

[a] Chemical shift averaged over all boron atoms. [b] Reported experimental values for diethylamine derivative ($B_n(NEt_2)_n$) are given in parentheses (ref 34).

cage stabilization per boron atom for the most stable isomer of each neutral boron hydride B_nH_n ($n = 3-6$) (Table 5). For B_3H_3, the cage stabilization slightly exceeds the strain in the BBB ring giving a net stabilization of 2.6 kcal/mol per boron. From B_3H_3 to B_4H_4, there is a large increase of stabilization per boron (2.6 → 15.2 kcal/mol), while from B_4H_4 to B_6H_6 there is a small gradual increase in stabilization.

Equation 5 is used to calculate cage stabilization per boron

$$BH_2{=}NH_2(C_{2v}) + B_2H_4(D_{2h}) \rightarrow 2BH_3 + 1/n(B_n(NH_2)_n) \quad (5)$$

in the aminoboranes $B_n(NH_2)_n$ ($n = 3-6$) (Table 5). A positive value for $B_3(NH_2)_3$ (12.8 kcal/mol) indicates that cage stabilization does not compensate for ring strain and reduced conjugation with the exocyclic amino groups. Cage stabilization per boron steadily increases as the cage size increases from $n = 4$ (4.3 kcal/mol) to $n = 6$ (−3.4 kcal/mol).

Equation 6 was used to evaluate the degree of conjugation

$$1/n(B_nH_n) + BH_2{-}NH_2(C_s) \rightarrow 1/n(B_n(NH_2)_n) + BH_3 \quad (6)$$

of the amino group with boron (per amino group). Full conjugation of amino with boron is given by the energy change between the $BH_2{-}NH_2$ rotation transition state (C_s symmetry) and the $BH_2{=}NH_2$ minimum (C_{2v} symmetry) which is −30.5 kcal/mol (Table 5). The comparison is made for B_nH_n and $B_n(NH_2)_n$ in the same geometry. Thus, **B4d** and **BN4a** are used in eq 6a (Table 5), where both are in the folded ring geometry to evaluate the degree of NH_2 conjugation in the classical ring structure. The conjugation in eq 6a (−24.5 kcal/mol) is nearly as large as found in BH_2NH_2 (−30.5 kcal/mol). When the NH_2 group is attached to a nonclassical cage, the degree of conjugation is much less. Comparing **B4c** and **BN4c** (eq 6b), where both have tetrahedral cores, the conjugation is only −12.3 kcal/mol (Table 5). When comparing amino conjugation in the square pyramids (**B5c** and **BN5d**, eq 6c) and octahedrons (**B6a** and **BN6d**, eq 6d), the stabilization is only −13.7 kcal/mol and −11.1 kcal/mol, respectively. Thus, the greater the cage stabilization, the smaller the amino conjugation.

Magnetic Comparisons

Comparisons of calculated and measured ^{11}B and ^{13}C chemical shifts have proved to be a valuable tool in establishing structures in electron deficient cages.[53] Experimental ^{11}B chemical shifts have been reported for $B_3(NEt_2)_3$ as well as for the ring and cage form of $B_6(NEt_2)_6$.[34] Calculated ^{11}B chemical shifts (relative to B_2H_6 which is assigned a value of 16.6 ppm[53a]) are reported for the lowest energy ring and cage form in Table 6. The agreement between theory (**BN6a**, $\delta(^{11}B) = 70.1$ ppm) and experiment ($B_6(NEt_2)_6$, $\delta(^{11}B) = 64$ ppm) is acceptable given that the substitutent on nitrogen is different. However, the agreement between the calculated and experimental ^{11}B chemical shifts of the ring form of $B_3(NEt_2)_3$ and the cage form of $B_6(NEt_2)_6$ is poor (Table 6). The calculated $\delta(^{11}B)$ value in $B_3(NH_2)_3$ was found to be very sensitive to geometry. In the symmetric D_{3h} geometry (**BN3b**), the $\delta(^{11}B)$ increased 36.3 ppm to 119.6 ppm (Table 6). The NICS values (Table 6) were positive in all rings and cages except **BN4c** which suggests that aromatic stabilization is not important in the fully amino-substituted B_nR_n derivatives.

Conclusions

The structure of early members of the *hypercloso* series B_nR_n are radically different when R = H and R = NH_2. In the former case (R = H), no back-donation of electron density into the boron hydride cluster is possible, and the lowest energy structure contains one or more 2π aromatic BBB rings. There are two structural types of B_nH_n species, those with a BH_2 group and those without. The next member in each series can be formed by adding a bridging BH group to the member before. B_6H_6 is the first boron hydride in the *hypercloso* series for which the

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structure of the lowest energy isomer is predicted by the capping principle. When the substituents in B_nR_n are amino groups (R = NH_2), significant electron density is transferred from nitrogen to boron. In this case, classical rings (isoelectronic to radialenes) are predicted to be the most stable structure. However, the nonclassical cages for the series $B_n(NH_2)_n$ ($n = 3-6$) are close in energy to the ring structures. The cage is 5.6 kcal/mol higher in $B_4(NH_2)_4$, 12.6 kcal/mol higher in $B_5(NH_2)_5$, and 15.0 kcal/mol higher in $B_6(NH_2)_6$. Density functional theory (B3LYP) is superior to low levels of electron correlation (MP2) for predicting the relative energies between classical and nonclassical isomers.

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Supporting Information Available: Cartesian coordinates for relevant structures optimized at the B3LYP/6-31G(d) level are given in Table S1 (16 pages). See any current masthead page for ordering and Internet access instructions.

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