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Heats of Formation of Boron Hydride Anions and Dianions and Their Ammonium Salts $[B_nH_m^{y-}][NH_4^+]_y$ with $y = 1–2$

Minh Tho Nguyen,*,[†,‡] Myrna H. Matus,[‡] and David A. Dixon*,[†]

Department of Chemistry, The University of Alabama, Shelby Hall, Tuscaloosa, Alabama 35487-0336, and Department of Chemistry, University of Leuven, B-3001 Leuven, Belgium

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Thermochemical parameters of the closo boron hydride $B_nH_n^{2-}$ dianions, with $n = 5–12$, the $B_3H_8^-$ and $B_{11}H_{14}^-$ anions, and the B_5H_9 and $B_{10}H_{14}$ neutral species were predicted by high-level ab initio electronic structure calculations. Total atomization energies obtained from coupled-cluster CCSD(T)/complete basis set (CBS) extrapolated energies, plus additional corrections were used to predict the heats of formation of the simplest $B_nH_m^{y-}$ species in the gas phase in kcal/mol at 298 K: $\Delta H_f(B_3H_8^-) = -23.1 \pm 1.0$; $\Delta H_f(B_5H_5^{2-}) = 119.4 \pm 1.5$; $\Delta H_f(B_6H_6^{2-}) = 64.1 \pm 1.5$; and $\Delta H_f(B_5H_9) = 24.1 \pm 1.5$. The heats of formation of the larger species were evaluated by the G3 method from hydrogenation reactions (values at 298 K, in kcal/mol with estimated error bars of ± 3 kcal/mol): $\Delta H_f(B_7H_7^{2-}) = 51.8$; $\Delta H_f(B_8H_8^{2-}) = 46.1$; $\Delta H_f(B_9H_9^{2-}) = 24.4$; $\Delta H_f(B_{10}H_{10}^{2-}) = -12.5$; $\Delta H_f(B_{11}H_{11}^{2-}) = -11.8$; $\Delta H_f(B_{12}H_{12}^{2-}) = -86.3$; $\Delta H_f(B_{11}H_{14}^-) = -57.3$; and $\Delta H_f(B_{10}H_{14}) = 18.7$. A linear correlation between atomization energies of the dianions and energies of the BH units was found. The heats of formation of the ammonium salts of the anions and dianions were predicted using lattice energies (U_L) calculated from an empirical expression based on ionic volumes. The U_L values (0 K) of the $B_nH_n^{2-}$ dianions range from 319 to 372 kcal/mol. The values of U_L for the $B_3H_8^-$ and $B_{11}H_{14}^-$ anions are 113 and 135 kcal/mol, respectively. The calculated lattice energies and gas-phase heats of formation of the constituent ions were used to predict the heats of formation of the ammonium crystal salts $[B_nH_m^{y-}][NH_4^+]_y$. These results were used to evaluate the thermodynamics of the H_2 release reactions from the ammonium hydro-borate salts.

Introduction

Compounds formed from nitrogen, boron, and hydrogen such as ammonia borane derivatives have been considered as potential hydrogen sources for use in the H_2 chemical storage systems due to their high percent of hydrogen by weight.[1−4] Critical issues for such hydrogen storage materials are H_2 uptake and release. For example, it has recently been reported that the oxidative hydrolysis of triborane amine, $B_3H_7NH_3$, in aqueous solution leads to the release of up to 8 equiv of H_2 upon addition of either acids or metal catalysts (such as $RhCl_3$).[5] N-Heterocyclic carbene metal complexes have been shown to afford long-lived catalysts leading to substantial hydrogen release from ammonia borane (<2.5 equiv or 18 chemical wt %).[6] We have recently predicted the thermodynamic and kinetic parameters for various H_2 release processes of borane derivatives up to $B_3N_3H_{14}$.[7−13] We found that the borane molecule (BH_3) can act as a

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* To whom correspondence should be addressed. E-mail: dadixon@bama.ua.edu (D.A.D.).

[†] The University of Alabama.

[‡] University of Leuven.

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bifunctional Lewis acid catalyst greatly accelerating the H_2 formation from either BH_3NH_3[9] or P_2H_4.[10] We also predicted that molecular ammonia borane (BH_3NH_3) and its corresponding salt [BH_4^-/NH_4^+] can serve as good hydrogen storage systems that release H_2 in near-thermoneutral processes.[7]

The simplest ionic salt [BH_4^-/NH_4^+] can be prepared from mixtures containing $NaBH_4$ and various ammonium salts such as $(NH_4)_2SO_4$.[14] The heat of formation of the $(BH_4)^-$ anion in the gaseous phase has been predicted to be $\Delta H_f(BH_4^-) = -11.6 \pm 0.7$ kcal/mol at 0 K and -13.5 ± 0.7 kcal/mol at 298 K.[7] The lattice energy of [BH_4^-/NH_4^+] was predicted to be 146.1 ± 5.0 kcal/mol by using a volume-based approach.[15] Together with the heat of formation of the gaseous $(NH_4)^+$ cation (153.6 ± 0.5 at 0 K and 150.9 ± 0.7 at 298 K), the heat of formation of the [BH_4^-/NH_4^+] salt is predicted to be -4.1 ± 5.0 kcal/mol at 0 K[7] and -11.1 ± 5.0 kcal/mol at 298 K. The reaction from the ionic crystal to form gas-phase products (eq 1) is close to thermoneutral with $\Delta H_r = -5.0$ kcal/mol at 0 K and -2.4 at 298 K.

$$[BH_4^-/NH_4^+](s) \rightarrow H_3BNH_3(g) + H_2(g) \qquad (1a)$$

$$[BH_4^-/NH_4^+](s) \rightarrow H_3BNH_3(s) + H_2(g) \qquad (1b)$$

Formation of solid ammonia borane (reaction 1b) leads to an exothermic reaction with $\Delta H_r = -25.5$ at 298 K.[4,7,12]

Many boron hydrides form cages or cagelike structures often as the anion or dianion. The additional electrons are needed to fill the incomplete degenerate orbital levels of the boron hydride cage so as to avoid structural distortion and leading to increased stabilization. The bonding in these compounds has been studied in detail.[16−24] The anions will form stable crystal salts with appropriate counterions, as is well known for the $B_nH_n^{2-}$ dianions for $n = 6$, 8, 9, 10, and 12.[16,17,25−28] The molecules $B_7H_7^{2-}$ and $B_{11}H_{11}^{2-}$ have been partially characterized by ^{11}B NMR.[29,30] The crystal structures for the $B_3H_8^-$ and $B_{11}H_{14}^-$ anions are also available.[31,32] $B_3H_8^-$ is a fluxional molecule on the NMR time scale down to 137 K with a single proton peak in the NMR spectrum.[33,34]

We are especially interested in the use of ammonium salts of boron hydride anions, $[B_nH_m^{y-}][NH_4^+]_y$ with $y = 1$ and 2, as H_2 storage materials. The ionic salts with ammonium derivatives of hexahydro-*closo*-decaborate, $[B_6H_6^{2-}][Me_4N^+]_2$, decahydro-*closo*-decaborate, $[B_{10}H_{10}^{2-}][Bu_4N^+]_2$, and dodecahydro-*closo*-dodecaborate, $[B_{12}H_{12}^{2-}][Bu_4N^+]_2$, are known.[25,35] As part of our continuing efforts in predicting accurate thermodynamic properties of relevant compounds using high-level molecular orbital theory,[12,36,37] we have predicted the thermodynamic properties of the $B_3H_8^-$ and $B_{11}H_{14}^-$ anions and the $B_nH_n^{2-}$ dianions, for $n = 5-12$, in the gas and solid salt phases. As far as we are aware, there is no experimental determination for the thermochemical parameters of the ions under study. In order to benchmark our approach, we have also predicted the heats of formation of two neutral boron hydrides, B_5H_9 and $B_{10}H_{14}$, whose available experimental gas-phase heats of formation deviate significantly from calculated values.

Computational Methods

Calculations were performed using the Gaussian03[38] and MOLPRO[39] suites of programs. Due to the relatively large size of the species considered, two different types of calculations were carried out; the first was applied to the $B_3H_8^-$ anion, the $B_5H_5^{2-}$ and $B_6H_6^{2-}$ dianions, and B_5H_9, and the second type was applied to all structures.

For $B_3H_8^-$, $B_5H_5^{2-}$, $B_6H_6^{2-}$, and B_5H_9, geometry parameters were initially optimized using second-order perturbation theory (MP2)[40] in conjunction with the correlation consistent aug-cc-pVDZ basis set[41] (denoted hereafter as aV*n*Z, with n = D, T, and Q). The structures were characterized by calculations of the harmonic vibrational frequencies at the same level. Geometry parameters of the most stable equilibrium structures were then reoptimized using the MP2 method with the larger aVTZ basis set. The latter optimized geometries were subsequently used for single-point electronic energies using coupled-cluster theory at the CCSD(T)

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level.[42] In the MP2 and CCSD(T) calculations, the core orbitals were kept frozen. The ZPEs were evaluated using MP2/aug-cc-pVDZ vibrational frequencies and scaled by a factor of 0.9787 from our previous analysis of boron hydride derivatives.[7,8,43] The final total valence electronic energies were extrapolated to the complete basis set (CBS) limit at the CCSD(T) level using the following expression (eq 2):[44]

$$E(n) = A_{\mathrm{CBS}} + B \exp[-(n-1)] + C \exp[-(n-1)^2] \qquad (2)$$

with $n = 2$, 3, and 4 for the aVnZ, n = D, T, and Q basis sets, respectively.

Additional smaller energetic corrections including core−valence and relativistic corrections were also calculated following our previous work on calculating heats of formation based on total atomization energies (ΣD_0).[7,8,12] Core−valence corrections (ΔE_{CV}) were obtained at the CCSD(T)/cc-pwCVTZ level of theory.[45] Scalar relativistic corrections (ΔE_{SR}), which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were included at the CISD (configuration interaction singles and doubles) level of theory using the cc-pVTZ basis set. ΔE_{SR} is taken as the sum of the mass-velocity and 1-electron Darwin (MVD) terms in the Breit−Pauli Hamiltonian.[46] Most calculations using available electronic structure computer codes do not correctly describe the lowest energy spin multiplet of an atomic state as spin−orbit in the atom is usually not included. Instead, the energy is a weighted average of the available multiplets. The spin−orbit correction is 0.03 kcal/mol for B, from the excitation energies of Moore.[47] The total atomization energy (ΣD_0 or TAE) of a compound is given by the expression (eq 3):

$$\Sigma D_0 = \Delta E_{\mathrm{elec}}(\mathrm{CBS}) - \Delta E_{\mathrm{ZPE}} + \Delta E_{\mathrm{CV}} + \Delta E_{\mathrm{SR}} + \Delta E_{\mathrm{SO}} \qquad (3)$$

By combining computed ΣD_0 values with the known heats of formation at 0 K for the elements ($\Delta H_{\mathrm{f}}(\mathrm{B}) = 136.2 \pm 0.2$ kcal/mol[48] and $\Delta H_{\mathrm{f}}(\mathrm{H}) = 51.63$ kcal/mol[49]), we can derive ΔH_{f} values for the species under study in the gas phase. To obtain the heats of formation at 298 K, we followed the procedure by Curtiss et al.[50]

For the second type of calculations, we used the composite G3[51] and G3B3[52] methods.

The lattice energy U_{L} of the ionic salts resulting from ionic interactions was evaluated using the volume approach proposed by Jenkins et al.[15] following previous work from the N. Bartlett group.[53] U_{L} is calculated from the empirical expression (eq 4a):

$$U_{\mathrm{L}} = 2I[\alpha V_{\mathrm{m}}^{-1/3} + \beta] \qquad (4a)$$

where I is the ionic strength ($I = 1$ for MX (1:1) salts and $I = 3$ for $\mathrm{M_2X}$ (2:1) salts) and V_{m} is the molecular (formula unit) volume of the lattice involved which is equal to the sum of the individual ion volumes of the cation, V_+ and anion, V_-. The electron densities were calculated using the B3LYP/6-311++G(d,p) level of density functional theory, and the volume corresponds to that inside the 0.001 au contour of the electron density. This choice of contour level was made on the basis of volumes used in free energy of solvation calculations.[54] For the empirical parameters in eq 4,[15] the following values were used: for MX salts, $\alpha = 28.0$ kcal/mol·nm and $\beta = 12.4$ kcal/mol; and for $\mathrm{M_2X}$ salts, $\alpha = 39.55$ kcal/mol·nm and $\beta = -7.12$ kcal/mol. The lattice energies can be corrected to standard conditions at 298 K using eq 4b.[15]

$$U_{\mathrm{L}}(298\ \mathrm{K}) = U_{\mathrm{L}} + [p(n_{\mathrm{M}}/2 - 2) + q(n_{\mathrm{X}}/2)]RT \qquad (4b)$$

for $\mathrm{M}_p\mathrm{X}_q$ salts, where $n_{\mathrm{M}} = n_{\mathrm{X}} = 6$ for nonlinear polyatomic ions.

Results and Discussion

Total energies and optimized geometries (Cartesian coordinates) are given in the Supporting Information. Selected geometry parameters for $\mathrm{B_3H_8^-}$, $\mathrm{B_5H_9}$, $\mathrm{B_{10}H_{14}}$, and $\mathrm{B_{11}H_{14}^-}$ are shown in Table 1. Figure 1 shows the two different isomers for $\mathrm{B_3H_8^-}$ optimized at the MP2/aVTZ level. The lowest energy conformation (Figure 1a) has two B−H−B bridges in C_{2v} symmetry. These bridges are asymmetric with B_{b1}−H_b and B_{b2}−H_b distances of 1.469 and 1.192 Å,

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Table 1. Comparison between Calculated and Experimental Values for the Selected Bond Distances (Å) and Angles (deg) for $B_3H_8^-$, B_5H_9, $B_{10}H_{14}$, and $B_{11}H_{14}^-$

$B_nH_m^{y-}$	parameter	calculated	experimental	deviation[a]
$B_3H_8^-$ (ref 31)	$B_{b1}-H_b$	1.469	1.50	−0.03
	$B_{b2}-H_b$	1.192	1.20	−0.01
	B_b-H_r[b]	1.206 ± 0.001[c]	1.05−1.20	[h]
	$B_{b1}-B_{b2}$	1.787	1.77	0.02
	$B_{b2}-B_{b2}$	1.831	1.80	0.03
	$\angle(B_{b1}-H_b-B_{b2})$	81.3	−	
B_5H_9 (ref 55)	B_b-H_b	1.341	1.352 ± 0.002	−0.011
	B_b-H	1.180	1.186 ± 0.002	−0.006
	B_a-H_a	1.177	1.181 ± 0.002	−0.004
	B_b-B_b	1.790	1.803 ± 0.002	−0.013
	B_a-B_b	1.696	1.690 ± 0.002	0.006
	$\angle(B_b-H_b-B_b)$	83.8	−	
	$\angle(B_a-B_b-H)$	132.0	128.72 ± 0.55	3.3
	$\angle(B_a-B_b-B_b-H_b)$	192.6	193.1 ± 2.9	−0.5
$B_{10}H_{14}$[d] (ref 56)	B1−H6	1.317	1.298 (0.005)	0.019
	B3−H6	1.332	1.337 (0.007)	−0.005
	B1−B3	1.776	1.775 (0.004)	0.001
	B−H[e]	1.189	1.180 (0.006)	0.009
	B−B[e]	1.769	1.773 (0.005)	−0.004
	∠B1−H6−B3	84.2	84.8[f]	−0.6
$B_{11}H_{14}^-$[g]	B_b-H_b	1.314	1.19−1.38 1.30 (9)	[h]
(ref 32a)	B_b-B_b	1.838	−	
	B−B (within the cage)	1.765	1.747−1.775 1.762 (10)	0.003
	B−B (open face of the cage)	1.899	1.875−1.895 1.886 (8)	0.013
	B−H (exo terminal)	1.197	0.99−1.16 1.08 (5)	[h]
	B−H (endo terminal)	1.210	1.13	[h]
	$\angle(B_b-H_b-B_b)$	88.7	−	

[a] Deviation of calculated value from experiment. [b] B_b-H_r stands for any $B_{b1}-H_{r1}$ or $B_{b2}-H_{r2}$ distance. [c] Average of $B_{b1}-H_{r1}$ and $B_{b2}-H_{r2}$ calculated values (explicit values in Table S1). [d] Average of the reported experimental values. [e] Average distance values of unbridged atoms. [f] Estimated from Table IV of ref 56. [g] Averaged calculated values and averaged experimental values. [h] Deviation not reported due to shortening of B−H distances in the X-ray analysis. See Halgren, T. A.; Anderson, R. J.; Jones, D. S.; Lipscomb, W. N. *Chem. Phys. Lett.* **1971**, *8*, 547.

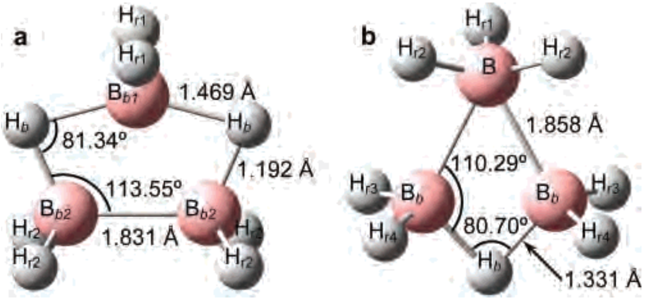

Figure 1. Optimized structures of $B_3H_8^-$ at the MP2/aVTZ level. (a) Lowest energy C_{2v}-symmetric structure. (b) Transition-state C_s-symmetric structure.

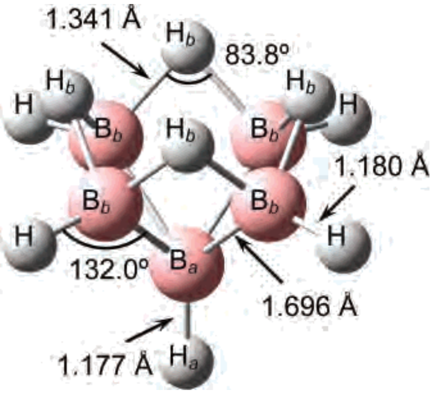

Figure 2. Optimized structure of B_5H_9 in C_{4v} symmetry at the MP2/cc-pVTZ level.

respectively, in good agreement with the experimental values from the X-ray crystal structure of 1.50 and 1.20 Å, The calculated $B_{b1}-B_{b2}$ distances of 1.787 Å is in good agreement with the experimental value of 1.77 Å. The unique $B_{b2}-B_{b2}$ bond distance is predicted to be 1.831 Å in comparison to the experimental value of 1.80 Å.[31]

We calculated the geometry for a second $B_3H_8^-$ conformer (Figure 1b) with C_s symmetry and one B−H−B bridge (see Supporting Information, Table S1). This conformer has been considered to be the transition state enabling fluxional motion in $B_3H_8^-$.[33] This structure is not a minimum energy conformation and has an imaginary frequency, $-222i$ cm^{-1}. This is consistent with the observed solid-state structure and the previous work showing that $B_3H_8^-$ is a fluxional molecule on the NMR time scale even at temperatures of 137 K.[33,34] The calculated energy difference at the CCSD(T)/CBS level including all corrections is 1.7 kcal/mol at 0 K and 1.4 kcal/mol at 298 K favoring the C_{2v} structure. This is in agreement with calculations at much lower levels (an estimated MP3/6-31G(d) value of 0.8 kcal/mol).[33b]

The B_5H_9 structure, optimized with MP2/cc-pVTZ, is shown in Figure 2, and the geometry parameters in Table 1. B_5H_9 has C_{4v} symmetry with four B−H−B bridges. The calculated values are in good agreement with experimental values obtained by microwave spectra.[55]

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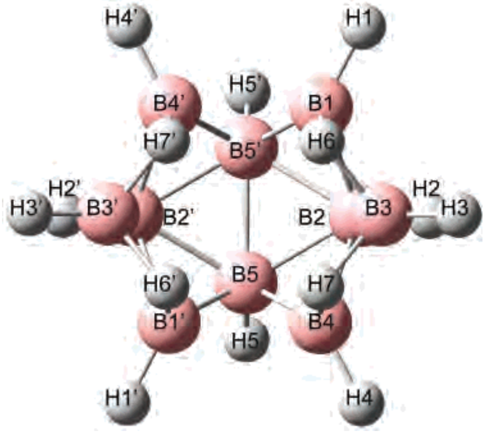

Figure 3. Optimized structure of $B_{10}H_{14}$ in C_{2v} symmetry at the MP2-(full)/6-31G(d) level from the G3 calculations. Atom labels from ref 56. Note that the sets (B1, B1′, B4, B4′), (H1, H1′, H4, H4′), and (H6, H6′, H7, and H7′) are the same in the C_{2v} symmetry predicted by the calculations.

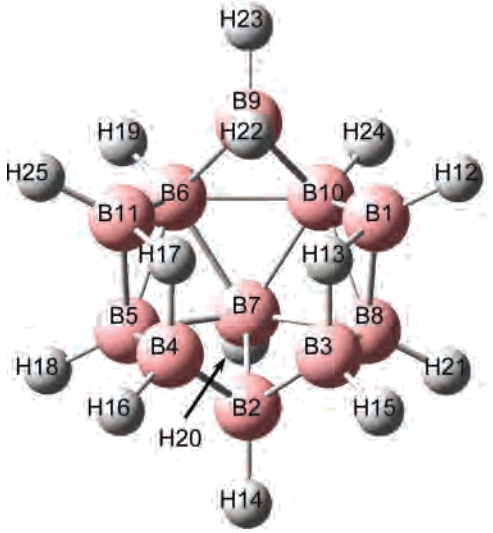

Figure 4. Optimized structure of $B_{11}H_{14}^-$ in C_s symmetry at the MP2-(full)/6-31G(d) level from the G3 calculations.

The $B_{10}H_{14}$ structure (optimized at the MP2(full)/6-31G-(d) level from the G3 calculations) is shown in Figure 3. $B_{10}H_{14}$ has four B−H−B bridges in a C_{2v}-symmetric structure. A neutron diffraction crystal structure[56] (space group C_2/a) for $B_{10}H_{14}$ has been determined. A comparison of selected experimental and calculated values is shown in Table 1 (a comparison of the experimental and calculated bond distances and angles is shown in detail in Table S2 of the Supporting Information). The experimental results were averaged for comparison with the calculated values. In general, the calculated values are in very good agreement with the experimental values with maximum differences of 0.012 Å for the B1−B5′ distance and 2.3° for the B5′−B1−H1 angle (see Table S2).

The optimized structure (MP2(full)/6-31G(d) from the G3 calculation) of $B_{11}H_{14}^-$ is shown in Figure 4. Selected experimental and calculated values are shown in Table 1 (a complete list of parameters is shown in Table S3). $B_{11}H_{14}^-$ has C_s symmetry and only two asymmetric B−H−B bridges with B_b−H_b distances of 1.279 and 1.349 Å (average 1.314 Å). The B−B distances within the cage range from 1.740 to 1.794 Å, with an average value of 1.765 Å. The B−B distances about the open face of the cage range from 1.838 to 1.946 Å, with an average of 1.899 Å. The exo terminal B−H distances range from 1.196 to 1.200 Å, with an average of 1.197 Å. There is a unique endo terminal boron−hydrogen distance, B9−H22, equal to 1.210 Å. X-ray studies[32a] exhibit pseudo-C_s symmetry, and our calculated values are in good agreement with the experimental values.

The molecular structure and electron distribution of the closo boron hydride dianions have previously been investigated in detail by several authors.[18−24] In particular, McKee et al.[19] studied the hypercloso dianions $B_nH_n^{2-}$, with n ranging from 5 to 13, using geometries optimized at the B3LYP/6-31G(d) level of theory and Schleyer and Najafian[24] have reported MP2/6-31G* results for the $B_nH_n^{2-}$ in their study of closo-monocarborane anions and closo-dicarboranes. We briefly summarize our calculated results. The geometries from the study of McKee et al. were used as our starting points. In general, optimizations at the MP2 level with the B3LYP starting point rapidly converged after two or three iterations, consistent with the high symmetry of most structures and the fact that the B3LYP and MP2 geometrical parameters do not differ significantly from each other. There is some geometry dependence on the basis set. For example, for $B_6H_6^{2-}$ with the 6-31G(d) basis set, the calculated B−B distances are 1.736 and 1.727 Å at the B3LYP and MP2 levels, respectively. With the larger aug-cc-pVDZ basis set, this distance is 1.746 and 1.766 Å at the B3LYP and MP2 levels, respectively. At the MP2/aug-cc-pVTZ level, it becomes 1.744 Å. All are longer than the value of 1.69 ± 0.01 Å reported from the crystal, consistent with the fact that the free dianion is not stabilized by counterions and hence should be larger.[25] For the largest dianion, $B_{12}H_{12}^{2-}$, the B−B distance is 1.786 and 1.777 Å at the B3LYP and MP2 levels, respectively, with the 6-31G(d) basis set. Both predicted distances compare well with the corresponding experimental value of 1.781 Å determined in a recent neutron scattering crystal structure.[57]

Heats of Formation. We can use a number of different approaches to predict the gas-phase heats of formation. First, we can calculate the total atomization energies given by eq 5a for the dianions, eq 5b for the $B_3H_8^-$ and $B_{11}H_{14}^-$ anions, and eq 5c for the neutral systems, B_5H_9 and $B_{10}H_{14}$.

$$B_nH_n^{2-} \rightarrow nB + nH + 2e \qquad (5a)$$

$$B_nH_m^{-} \rightarrow nB + mH + e \qquad (5b)$$

$$B_nH_m \rightarrow nB + mH \qquad (5c)$$

A second approach is to use isodesmic or other similar types of reactions with known heats of formation of reactants and products and the calculated reaction energy to predict the unknown heat of formation. Due to the novel bonding in

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Table 2. Atomization Energies of the $B_5H_5^{2-}$ and $B_6H_6^{2-}$ Dianions, $B_3H_8^-$ Isomers, and B_5H_9 Calculated with CCSD(T)/CBS Total Energies and Different Corrections (kcal/mol)

$B_nH_m^{y-}$	CBS[a]	ΔE_{ZPE}[b]	ΔE_{CV}[c]	ΔE_{SR}[d]	ΔE_{SO}[e]	ΣD_0(0 K)
B_5H_9	1173.74	65.72	7.22	−0.44	−0.15	1114.64
$B_3H_8^-$	886.69	51.06	4.06	−0.27	−0.09	839.38
$B_3H_8^-$ (1b)	884.71	50.68	4.00	−0.27	−0.09	837.67
$B_5H_5^{2-}$	846.77	35.51	6.76	−0.48	−0.15	817.40
$B_6H_6^{2-}$	1097.27	45.68	8.29	−0.58	−0.18	1059.12

[a] From CCSD(T)/CBS energies extrapolated using eq 2, with aV*n*Z basis sets, where n = D, T, and Q, based on MP2/aVTZ optimized geometries. Total energies are given Table S4 (Supporting Information). [b] Calculated zero-point energies (see Table S4). A scaling factor of 0.9787 for the dianions was obtained from B_2H_6 experimental and MP2/aVDZ values. A scaling factor of 0.9730 for the monoanion was obtained from B_2H_6 experimental and MP2/aVTZ values. [c] Core−valence corrections obtained at the CCSD(T/cc-pwCVTZ basis set level. [d] Scalar relativistic corrections (MVD) from CISD/aVTZ calculations. [e] Atomic spin−orbit correction taken from ref 47.

Table 3. Gas-Phase Heats of Formation of the $B_nH_n^{2-}$ (n = 5 and 6) Dianions, the $B_3H_8^-$ Anion, and the B_3H_7 and B_5H_9 Neutral Species Calculated Using CCSD(T)/CBS + Corrections (kcal/mol)

$B_nH_m^{y-}$	ΔH_f (0 K)[a]	ΔH_f (298 K)[b]
B_3H_7[c]	37.1	32.5
B_5H_9	31.0 (24.4 ± 1.6[d])	24.1 (17.5 ± 1.6[d])
$B_3H_8^-$	−17.7	−23.1
$B_3H_8^-$ (1b)	−16.0	−21.7
$B_5H_5^{2-}$	121.8	119.4
$B_6H_6^{2-}$	67.9	64.1

[a] Heat of formation at 0 K derived from atomization energy ΣD_0 and heats of formation of B (136.2 kcal/mol) and H (51.63 kcal/mol). [b] Heats of formation at 298 K were obtained by the same procedure of ref 52. [c] Previously calculated in ref 11. [d] Experimental values, ref 49.

boron hydrides, it is not straightforward to find suitable bond separation reactions.[58,59,64] We chose to use the hydrogenation reactions[60−62] given by eq 6a for the dianions, eqs 6b and 6c for the anions, and eq 6d for the neutral systems:

$$B_nH_n^{2-} + (n+1)H_2 \rightarrow 2BH_4^- + (n-2)BH_3 \qquad (6a)$$

$$B_3H_8^- + H_2 \rightarrow BH_4^- + 2BH_3 \qquad (6b)$$

$$B_{11}H_{14}^- + 10H_2 \rightarrow BH_4^- + 10BH_3 \qquad (6c)$$

$$B_nH_{n+4} + (n-2)H_2 \rightarrow nBH_3 \qquad (6d)$$

We first consider $B_5H_5^{2-}$, $B_6H_6^{2-}$, $B_3H_8^-$, and B_5H_9 for which CCSD(T)/CBS results were obtained. Table 2 lists the total atomization energies ΣD_0(0 K) derived from the extrapolated CCSD(T)/CBS total energies and the smaller corrections given in eq 2. Table 3 lists the composite CCSD(T)/CBS heats of formation. Estimated error bars are ±1.5 kcal/mol for $B_5H_5^{2-}$, $B_6H_6^{2-}$, and B_5H_9 and ±1.0 kcal/mol for $B_3H_8^-$, based on the performance of the CBS procedure for boranes,[7,61] plus the uncertainties due to the zero-point energies of the anions. Only the heat of formation of B_5H_9 is known from experiment and is 17.5 ± 1.6 kcal/mol at 298 K.[49] Our calculated value of 24.1 kcal/mol differs from the experimental value by 6.6 kcal/mol, which is far outside our normal error limits of ±1−2 kcal/mol for this size of compound. The T_1 diagnostic[63] for B_5H_9 at the CCSD(T)/aVTZ level is 0.0114, which is small and indicates that this molecule is not dominated by multireference character. This suggests that the heat of formation of B_5H_9 needs to be remeasured.

Table 4. Atomization Energies and Hydrogenation Reactions of $B_nH_m^{y-}$ (y = 1−2) Ions and (y = 0) Neutral Species Calculated with the G3 and G3B3 Methods Using Different Approaches (kcal/mol)[a]

	eqs 5 ΣD_0(0 K)		ΔH_r(6) (0 K)		ΔH_r(6) (298 K)	
$B_nH_m^{y-}$	G3	G3B3	G3	G3B3	G3	G3B3
B_3H_7	731.2	730.4	40.6	40.8	42.3	42.6
B_5H_9	1111.4	1110.0	98.9	99.0	100.8	101.0
$B_{10}H_{14}$	2051.9	2050.2	234.4	235.6	235.6	236.9
$B_3H_8^-$	839.5	838.1	58.9	58.6	60.5	60.0
$B_{11}H_{14}^-$	2263.5	2261.5	298.7	300.0	298.0	299.3
$B_5H_5^{2-}$	817.3	816.4	−63.9	−63.3	−68.5	−67.7
$B_6H_6^{2-}$	1058.1	1057.6	15.9	17.2	11.8	13.1
$B_7H_7^{2-}$	1255.5	1254.6	52.3	53.4	48.0	49.3
$B_8H_8^{2-}$	1448.0	1446.6	83.8	84.8	79.2	80.4
$B_9H_9^{2-}$	1656.2	1654.7	131.0	132.2	126.3	127.7
$B_{10}H_{10}^{2-}$	1879.1	1877.4	192.9	194.1	188.6	190.0
$B_{11}H_{11}^{2-}$	2065.3	2063.6	218.0	219.6	213.4	215.1
$B_{12}H_{12}^{2-}$	2325.5	2323.6	317.3	318.9	313.3	315.1

[a] Heats of formation for H_2, BH_3, and BH_4^-, with G3 and G3B3, in kcal/mol $\Delta H_{f,0K(298K),G3}(H_2) = -0.5$ (−0.5); $\Delta H_{f,0K(298K),G3B3}(H_2) = -0.5$ (−0.4); $\Delta H_{f,0K(298K),G3}(BH_3) = 26.3$ (25.4); $\Delta H_{f,0K(298K),G3B3}(BH_3) = 26.6$ (25.7); $\Delta H_{f,0K(298K),G3}(BH_4^-) = -12.0$ (−13.9); and $\Delta H_{f,0K(298K),G3B3}(BH_4^-) = -11.6$ (−13.5). G3 and G3B3 total energies for the $B_nH_m^{y-}$ species are given in Table S5 (Supporting Information).

Table 4 gives the results obtained from TAEs (eqs 5) and eqs 6 for all species considered using the G3 and G3B3 methods at 0 and 298 K. The heats of formation of the different species using the G3 and G3B3 methods are given in Table 5. The G3 values (Table 4) for the TAEs for $B_3H_8^-$ and $B_5H_5^{2-}$ are in excellent agreement with the corrected CCSD(T)/CBS values (Table 2), and for $B_6H_6^{2-}$, the G3 TAE is 1.0 kcal/mol lower than the more accurate value. For B_5H_9, the G3 and G3B3 heats of formation (Table 5) at 298 K derived from the TAEs (eqs 5) are 3.5 and 4.8 kcal/mol too high, respectively (Table 3). The G3B3 values for the TAE's (eqs 5, Table 4) are systematically smaller than the corresponding G3 values, with deviations varying from 0.4 to 2.0 kcal/mol with the largest difference found for the largest molecule. Our calculated values are higher in energy than the reported experimental values, exactly as found for borane amines up to $B_3N_3H_{12}$ using the G3(MP2) method.[12]

The use of eqs 6 to predict the heat of formation of $B_3H_8^-$ at the G3 and G3B3 levels (Table 5) are in even better agreement with the composite CCSD(T)/CBS results (Table 3). For B_5H_9, the agreement is also improved with heats of formation obtained from eqs 6 being about 2 kcal/mol too high. The use of eqs 6 for the heats of formation of $B_5H_5^{2-}$ and $B_6H_6^{2-}$ leads to values that are more stable (less positive) than the CCSD(T)/CBS values by 2−3 kcal/mol with the

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Table 5. Gas-Phase Heats of Formation of the $B_nH_n^{2-}$ (n = 5−12) Dianions, the $B_3H_8^-$ and $B_{11}H_{14}^-$ Anions, and the B_3H_7, B_5H_9, and $B_{10}H_{14}$ Neutral Species Calculated Using Different Approaches (kcal/mol)

$B_nH_m^{y-}$	G3(5)[a] (0 K)	G3B3(5)[a] (0 K)	G3(6)[b] (0 K)	G3B3(6)[b] (0 K)	G3(5)[c] (298 K)	G3B3(5)[c] (298 K)	G3(6)[c] (298 K)	G3B3(6)[c] (298 K)
B_3H_7	38.8	39.6	34.3	35.1	38.6	38.3	34.1	33.9
B_5H_9	34.2	35.7	33.0	32.9	27.6	28.9	26.4	26.2
$B_{10}H_{14}$	32.9	34.6	29.4	28.2	22.1	23.7	18.7	17.4
$B_3H_8^-$	−17.8	−16.5	−17.8	−17.4	−23.1	−21.6	−23.1	−22.6
$B_{11}H_{14}^-$	−42.5	−40.5	−46.6	−47.9	−53.3	−51.4	−57.3	−58.6
$B_5H_5^{2-}$	121.9	122.8	119.7	119.1	119.6	120.4	117.5	116.7
$B_6H_6^{2-}$	68.9	69.4	66.3	65.0	65.2	65.7	62.7	61.4
$B_7H_7^{2-}$	59.3	60.3	56.3	55.2	54.8	55.7	51.8	50.6
$B_8H_8^{2-}$	54.6	56.0	51.1	50.1	49.5	50.7	46.1	44.9
$B_9H_9^{2-}$	34.2	35.7	30.3	29.1	28.2	29.6	24.4	23.0
$B_{10}H_{10}^{2-}$	−0.8	0.9	−5.2	−6.4	−8.1	−6.6	−12.5	−13.9
$B_{11}H_{11}^{2-}$	0.9	2.5	−4.0	−5.6	−7.1	−5.5	−11.8	−13.5
$B_{12}H_{12}^{2-}$	−71.5	−69.6	−76.9	−78.5	−81.1	−79.4	−86.3	−88.1

[a] Heat of formation at 0 K derived from atomization energy D_e and heats of formation of B (136.2 kcal/mol) and H (51.63 kcal/mol). [b] Heat of formation at 0 K derived from reaction energy $\Delta H_r(6)$ and heats of formation of BH_4^- (−11.4 kcal/mol) and BH_3 (26.4 kcal/mol). [c] Heats of formation at 298 K were obtained by the same procedure of ref 52.

G3B3 values having the larger differences. We have previously calculated the heat of formation of B_3H_7 with high accuracy.[11] To further benchmark our approach, we calculated its heat of formation at the G3 and G3B3 levels. The G3B3 results differ from the CCSD(T)/CBS results for B_3H_7 by ≤2.6 kcal/mol, whereas G3 results reduce this difference to ≤1.8 kcal/mol when using eqs 5. With eqs 6, the differences are even smaller, ≤1.6 kcal/mol for G3 and ≤1.4 kcal/mol for G3B3. On the basis of these comparisons, we chose to use the heats of formation for the dianions obtained from eqs 6 in our predictions of the behavior of the salts.

The calculated values for $B_{10}H_{14}$, at the G3 level using eq 5 at 298 K is 10.8 kcal/mol higher than the experimental value of 11.3 ± 4.5 kcal/mol, and the value using eqs 6 is 7.4 kcal/mol higher.[49] On the basis of the above discussion for B_5H_9, we suggest that the experimental value is probably a little too low, as doubling the error from B_5H_9 of 2 kcal/mol as compared to the CCSD(T) results would lead to a value of 14.7 (18.7 − 4) kcal/mol at the G3 level using eqs 6 for $\Delta H_f(B_{10}H_{14})$ at 298 K, which is within the experimental error limits.

The heats of formation of the two neutral boron hydrides were recently predicted by Chen et al. using the G3 method.[64] Their reported 298 K values of 13.1 kcal/mol for B_5H_9 and −6.8 kcal/mol for $B_{10}H_{14}$ from the G3 total atomization energies differ substantially from our results of 27.6 and 22.1 kcal/mol, respectively, due to the use by Chen et al.[64] of an older, incorrect value of $\Delta H_f°(B)$ = 134.5 kcal/mol at 298 K.[48,49]

The heats of formation obtained using both eqs 5 and 6 are compared in Table 5. For each species, the values obtained by the two approaches differ by up to 5 kcal/mol at the G3 level. The deviations in the G3B3 values are even larger (up to 8 kcal/mol). Such behavior reflects the inherent difficulty in splitting the excess electrons in the hydrogenation reactions.

Although $B_{11}H_{14}^-$ is a stable anion, no thermochemical information is available. The difference between the heats of formation derived from eqs 5b and 6c amounts up to 4.1 and 7.2 kcal/mol at the G3 and G3B3 levels, respectively. Much of this difference is probably due to errors in the calculated heat of formation of H_2. Even though the heat of formation for H_2 at is just −0.5 kcal/mol at 0 or 298 K, this value can add up to a substantial correction that becomes significant with respect to the number of hydrogens in the system.

Using an MO-bond index method, Laurie and Perkins[65] estimated the heats of formation of the dianions $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{12}H_{12}^{2-}$ from total dissociation energies to be 10.9, 18.7, and 17.1 kcal/mol, respectively, using a value of 133.8 kcal/mol for $\Delta H_f°(B)$ at 298 K. Our calculated heats of formation at 298 K differ from their values, using a correct $\Delta H_f°(B)$, by 54.3, −26.8, and −98.2 kcal/mol, respectively (Table 5). This simple index approach is thus too crude to be useful. Estimates for the atomization energies of B_5H_9 and $B_{10}H_{14}$ from empirical resonance energies[66] are in reasonable agreement with our values considering the simplicity of the approach.

One can consider that each dianion consists of n units of BH plus two electrons and the energy increment of this unit is simply equal to $E(BH) = TAE/n$. When plotting E(BH) as a function of n, the resulting function is not well behaved if the small value for $n = 5$ (163.5 kcal/mol) is included. We also did not include $B_{11}H_{11}^{2-}$ which has a non-closo structure. If the value for $n = 5$ (E(BH) is 163.5 kcal/mol from G3 and 163.3 kcal/mol from G3B3) is removed from the fit, an excellent linear correlation can be found for E(BH) with respect to n. Both the G3 and G3B3 data result in a nearly identical fit (Figure 5). This suggests that the larger cages lead to better stabilization of the additional two electrons, leading to a more stable boron hydride dianion, as expected as the two additional charges can be further separated in the larger cage. Except for the $B_5H_5^{2-}$ dianion, which has not been observed, the other dianions from n = 6 to 12, have been structurally characterized.[16,17,25−28,67] $B_{11}H_{11}^{2-}$ has an E(BH) of 187.8 kcal/mol from G3 and of

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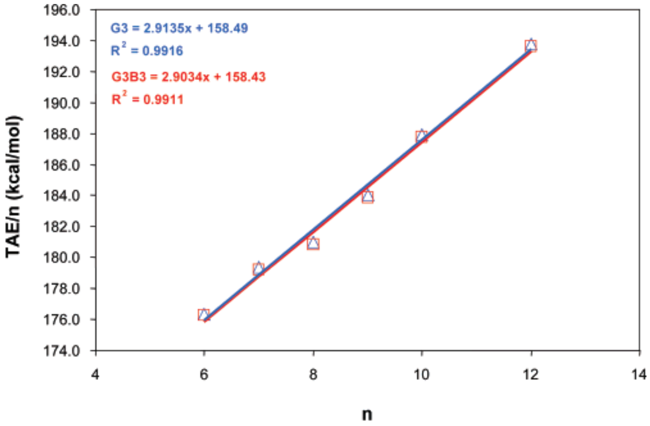

Figure 5. Correlation between n and the normalized TAE (TAE/n) for the $B_nH_n^{2-}$ dianions from $n = 6$ to 12 excluding $n = 11$. TAE values calculated at the G3 (blue triangles) and G3B3 (red squares) methods. The linear fitting equations, as well as the R^2 values for each method, are also shown.

Table 6. Calculated Volumes and Lattice Energies (kcal/mol) of $[B_nH_n^{2-}][NH_4^+]_2$ ($n = 5-12$), $[B_3H_8^-][NH_4^+]$, and $[B_{11}H_{14}^-][NH_4^+]$ Salts

$B_nH_m^{y-}$	ionic volume[a] V_- (nm^3/molecule)	salt volume[b] V (nm^3/molecule)	lattice energy[c] U_L(0 K)	lattice energy[d] U_L (298 K)
$B_3H_8^-$	0.111	0.132	135.1	137.4
$B_{11}H_{14}^-$	0.233	0.254	113.3	115.7
$B_5H_5^{2-}$	0.145	0.187	371.8	375.9
$B_6H_6^{2-}$	0.151	0.193	367.5	371.6
$B_7H_7^{2-}$	0.171	0.213	354.2	358.3
$B_8H_8^{2-}$	0.189	0.231	343.6	347.7
$B_9H_9^{2-}$	0.201	0.243	337.1	341.3
$B_{10}H_{10}^{2-}$	0.217	0.259	329.1	333.3
$B_{11}H_{11}^{2-}$	0.232	0.274	322.2	326.4
$B_{12}H_{12}^{2-}$	0.239	0.281	319.2	323.3

[a] Volumes of the $[B_nH_n^{2-}]$ ($n = 5-12$) dianions and $[B_{11}H_{14}^-]$ anion. [b] Total volumes of the salts taking $[NH_4^+]$ volume = 0.021 ± 0.015 nm^3/molecule (ref 15). [c] Lattice energy at 0 K calculated using eq 4a, see text. [d] Lattice energy at 298 K calculated using eq 4b.

Table 7. Calculated Heats of Formation in kcal/mol for $[B_3H_8^-][NH_4^+]$, $[B_5H_5^{2-}][NH_4^+]_2$, and $[B_6H_6^{2-}][NH_4^+]_2$ Salts from CCSD(T)/CBS Results

$[B_nH_m^{y-}][NH_4^+]_y$	ΔH_f (0 K)	ΔH_f (298 K)
$[B_3H_8^-][NH_4^+]$	0.8	−9.6
$[B_5H_5^{2-}][NH_4^+]_2$	57.2	45.2
$[B_6H_6^{2-}][NH_4^+]_2$	7.6	−5.7

Table 8. Calculated Heats of Formation for $[B_nH_n^{2-}][NH_4^+]_2$ ($n = 5-12$), $[B_3H_8^-][NH_4^+]$, and $[B_{11}H_{14}^-][NH_4^+]$ Salts in kcal/mol[a]

$[B_nH_m^{y-}][NH_4^+]_y$	G3 (0 K)	G3 (298 K)
$[B_3H_8^-][NH_4^+]$	0.8	−9.6
$[B_{11}H_{14}^-][NH_4^+]$	−6.4	−22.1
$[B_5H_5^{2-}][NH_4^+]_2$	55.2	43.3
$[B_6H_6^{2-}][NH_4^+]_2$	6.0	−7.1
$[B_7H_7^{2-}][NH_4^+]_2$	9.3	−4.7
$[B_8H_8^{2-}][NH_4^+]_2$	14.7	0.1
$[B_9H_9^{2-}][NH_4^+]_2$	0.3	−15.1
$[B_{10}H_{10}^{2-}][NH_4^+]_2$	−27.2	−44.0
$[B_{11}H_{11}^{2-}][NH_4^+]_2$	−19.0	−36.4
$[B_{12}H_{12}^{2-}][NH_4^+]_2$	−88.8	−107.9

[a] Calculated heats of formation of the ionic salts using eq 7. G3 and G3B3 values were taken from heats of formation obtained by atomization eqs 6. The heat of formation of the gaseous NH_4^+ cation is 153.6 and 150.9 kcal/mol at 0 and 298 K, respectively (ref 7).

187.6 kcal/mol from G3B3 and falls slightly below the line. The lack of a non-closo structure makes this dianion effectively less stable than the closo dianions. The heats of formation of the dianions in the gas phase are upper limits because it is not clear how many of the isolated dianions are stable with respect to loss of an electron to form the monoanion radical. Only $B_{12}H_{12}^{2-}$ has been predicted to be stable with respect to loss of an electron.[19] The high stability of $B_{12}H_{12}^{2-}$ is consistent with the structural stability of the cage to rearrangements.[68] We estimate an error of ±3 kcal/mol for the heats of formation of the dianions.

Schleyer and Najafian[24] have reported another approach to predict the relative stability of the *closo*-$B_nH_n^{2-}$ molecules. They calculated the energy $\Delta H = E(B_nH_n^{2-}) - (n - 2)(E(B_3H_5) - E(B_2H_4) - E(B_2H_2^{2-})$ at the MP2/6-31G* (note the lack of diffuse functions) level to estimate the stability of the *closo*-$B_nH_n^{2-}$ molecules. The term multiplied by ($n - 2$) is an estimate of an incremental B−H energy. These authors then use the energies for the highly symmetric species $n = 6$ and 12 to draw an ideal line and looked at deviations from this line. The calculated energy values are all negative and the absolute energy gets larger with increasing n. Their plot (Figure 4 in ref 24) exhibits similar behavior to our Figure 5. As found by Schleyer and Najafian[24] and by us, the compounds with $n = 8$ and 9 show a larger deviation from the line in the direction of being destabilized than the compounds with $n = 7$ and 10. They find the largest destabilization for $n = 11$ as we do if $B_{11}H_{11}^{2-}$ is included as discussed above and we note that $B_{11}H_{11}^{2-}$ does not have a closo structure. The essential difference in the approach taken by Schleyer and Najafian and by us in Figure 5 is that we have not constrained our fit to only $n = 6$ and 12 but rather have let all of the molecules determine the fit. We reach essentially the same conclusions in terms of the stabilities of the different molecules as a function of n, but we have not used a definition tied to a nonexistent, highly unstable species, $B_2H_2^{2-}$, nor any approximations such as an estimate for a B−H bond increment.

Lattice Energies and Heats of Formation of the Ammonium Salts of Boron Hydride Ions. The calculated volumes of the anions and dianions and the resulting ammonium salts are given in Table 6 together with U_L. The volume of the $[NH_4^+]$ cation was taken as $V_+ = 0.021$ nm^3/molecule.[7,15] Using the volume approach,[15] the lattice energies from the interaction between ions were evaluated using the empirical eqs 4a and 4b for temperatures at 0 and 298 K, respectively. The lattice energies of the dianion salts at 0 K fall in the range of 315−375 kcal/mol, consistent with other values. The U_L of the anions is about one-third of the latter, consistent with other values.

A comparison of the lattice energies derived using eq 4 with those obtained from experimental data based on the Born−Haber cycle indicated that they are good to ±5 kcal/mol.[15,69] Following a Born−Haber cycle, the heats of

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formation of the ammonium salts were calculated using eq 7:

$$\Delta H_f(\text{salt}) = \Sigma\Delta H_f(\text{gaseous ions}) - U_L(\text{salt}) \quad (7)$$

The results are summarized in Table 7 (CCSD(T)/CBS results) and in Table 8 (G3 results).

Having determined the basic thermochemical parameters of the solid salts, we can now evaluate the energies of their H_2 release.

$$[B_nH_n^{2-}][NH_4^+]_2(s) \rightarrow (^n/_2 + 4)H_2 + nB(s) + N_2 \quad (8a)$$

$$[B_3H_8^-][NH_4^+](s) \rightarrow 6H_2 + 3B(s) + {}^1/_2N_2 \quad (8b)$$

$$[B_{11}H_{14}^-][NH_4^+](s) \rightarrow 9H_2 + 11B(s) + {}^1/_2N_2 \quad (8c)$$

$$[B_nH_n^{2-}][NH_4^+]_2(s) \rightarrow (^n/_2 + 4)H_2 + 2BN(s) + (n-2)B(s) \quad (9a)$$

$$[B_3H_8^-][NH_4^+](s) \rightarrow 6H_2 + BN(s) + 2B(s) \quad (9b)$$

$$[B_{11}H_{14}^-][NH_4^+](s) \rightarrow 9H_2 + BN(s) + 10B(s) \quad (9c)$$

$$[B_nH_n^{2-}][NH_4^+]_2(s) \rightarrow (^n/_2 - 2)H_2 + (n-2)B(s) + 2H_3BNH_3(s) \quad (10a)$$

$$[B_3H_8^-][NH_4^+](s) \rightarrow 3H_2 + 2B(s) + H_3BNH_3(s) \quad (10b)$$

$$[B_{11}H_{14}^-][NH_4^+](s) \rightarrow 6H_2 + 10B(s) + H_3BNH_3(s) \quad (10c)$$

$$[B_nH_n^{2-}][NH_4^+]_2(s) \rightarrow (^n/_2 + 2)H_2 + (n-2)B(s) + {}^2/_3B_3N_3H_6(l) \quad (11a)$$

$$[B_3H_8^-][NH_4^+](s) \rightarrow 5H_2 + 2B(s) + {}^1/_3B_3N_3H_6(l) \quad (11b)$$

$$[B_{11}H_{14}^-][NH_4^+](s) \rightarrow 8H_2 + 10B(s) + {}^1/_3B_3N_3H_6(l) \quad (11c)$$

Table 9. Calculated Heats of Reaction for the H_2 Release from the Salts at 298 K in kcal/mol[a]

H_2 release reactions	G3	G3B3
Reaction 9		
$[B_3H_8^-][NH_4^+](s) \rightarrow 6H_2 + BN(s) + 2B(s)$[b]	−50.4	−50.9
$[B_{11}H_{14}^-][NH_4^+](s) \rightarrow 8H_2 + BN(s) + 10B(s)$	−37.9	−36.5
$[B_5H_5^{2-}][NH_4^+]_2(s) \rightarrow {}^{13}/_2H_2 + 2BN(s) + 3B(s)$[c]	−163.3	−162.5
$[B_6H_6^{2-}][NH_4^+]_2(s) \rightarrow 7H_2 + 2BN(s) + 4B(s)$[d]	−112.8	−111.5
$[B_7H_7^{2-}][NH_4^+]_2(s) \rightarrow {}^{15}/_2H_2 + 2BN(s) + 5B(s)$	−115.2	−114.0
$[B_8H_8^{2-}][NH_4^+]_2(s) \rightarrow 8H_2 + 2BN(s) + 6B(s)$	−120.0	−118.9
$[B_9H_9^{2-}][NH_4^+]_2(s) \rightarrow {}^{17}/_2H_2 + 2BN(s) + 7B(s)$	−104.8	−103.5
$[B_{10}H_{10}^{2-}][NH_4^+]_2(s) \rightarrow 9H_2 + 2BN(s) + 8B(s)$	−76.0	−74.6
$[B_{11}H_{11}^{2-}][NH_4^+]_2(s) \rightarrow {}^{19}/_2H_2 + 2BN(s) + 9B(s)$	−83.5	−81.8
$[B_{12}H_{12}^{2-}][NH_4^+]_2(s) \rightarrow 10H_2 + 2BN(s) + 10B(s)$	−12.1	−10.3
Reaction 10		
$[B_3H_8^-][NH_4^+](s) \rightarrow 3H_2 + 2B(s) + H_3BNH_3(s)$[e]	−27.0	−27.5
$[B_{11}H_{14}^-][NH_4^+](s) \rightarrow 6H_2 + 10B(s) + H_3BNH_3(s)$	−14.5	−13.2
$[B_5H_5^{2-}][NH_4^+]_2(s) \rightarrow {}^1/_2H_2 + 3B(s) + 2H_3BNH_3(s)$[f]	−116.5	−115.8
$[B_6H_6^{2-}][NH_4^+]_2(s) \rightarrow H_2 + 4B(s) + 2H_3BNH_3(s)$[g]	−66.1	−64.8
$[B_7H_7^{2-}][NH_4^+]_2(s) \rightarrow {}^3/_2H_2 + 5B(s) + 2H_3BNH_3(s)$	−68.5	−67.3
$[B_8H_8^{2-}][NH_4^+]_2(s) \rightarrow 2H_2 + 6B(s) + 2H_3BNH_3(s)$	−73.3	−72.2
$[B_9H_9^{2-}][NH_4^+]_2(s) \rightarrow {}^5/_2H_2 + 7B(s) + 2H_3BNH_3(s)$	−58.1	−56.8
$[B_{10}H_{10}^{2-}][NH_4^+]_2(s) \rightarrow 3H_2 + 8B(s) + 2H_3BNH_3(s)$	−29.2	−27.9
$[B_{11}H_{11}^{2-}][NH_4^+]_2(s) \rightarrow {}^7/_2H_2 + 9B(s) + 2H_3BNH_3(s)$	−36.8	−35.1
$[B_{12}H_{12}^{2-}][NH_4^+]_2(s) \rightarrow 4H_2 + 10B(s) + 2H_3BNH_3(s)$	34.7	36.4
Reaction 11		
$[B_3H_8^-][NH_4^+](s) \rightarrow 5H_2 + 2B(s) + {}^1/_3B_3N_3H_6(l)$[h]	−31.3	−31.8
$[B_{11}H_{14}^-][NH_4^+](s) \rightarrow 8H_2 + 10B(s) + {}^1/_3B_3N_3H_6(l)$	−18.8	−17.4
$[B_5H_5^{2-}][NH_4^+]_2(s) \rightarrow {}^9/_2H_2 + 3B(s) + {}^2/_3B_3N_3H_6(l)$[i]	−125.1	−124.3
$[B_6H_6^{2-}][NH_4^+]_2(s) \rightarrow 5H_2 + 4B(s) + {}^2/_3B_3N_3H_6(l)$[j]	−74.6	−73.3
$[B_7H_7^{2-}][NH_4^+]_2(s) \rightarrow {}^{11}/_2H_2 + 5B(s) + {}^2/_3B_3N_3H_6(l)$	−77.0	−75.8
$[B_8H_8^{2-}][NH_4^+]_2(s) \rightarrow 6H_2 + 6B(s) + {}^2/_3B_3N_3H_6(l)$	−81.8	−80.7
$[B_9H_9^{2-}][NH_4^+]_2(s) \rightarrow {}^{13}/_2H_2 + 7B(s) + {}^2/_3B_3N_3H_6(l)$	−66.6	−65.3
$[B_{10}H_{10}^{2-}][NH_4^+]_2(s) \rightarrow 7H_2 + 8B(s) + {}^2/_3B_3N_3H_6(l)$	−37.8	−36.4
$[B_{11}H_{11}^{2-}][NH_4^+]_2(s) \rightarrow {}^{15}/_2H_2 + 9B(s) + {}^2/_3B_3N_3H_6(l)$	−45.3	−43.6
$[B_{12}H_{12}^{2-}][NH_4^+]_2(s) \rightarrow 8H_2 + 10B(s) + {}^2/_3B_3N_3H_6(l)$	26.1	27.9

[a] The heats of formation of H_2 and B are 0 kcal/mol, as they are the form of the element. The heat of formation of BN (crystal) was taken from ref 49, −59.97 ± 0.4 kcal/mol at 298 K. The heats of formation at 298 K of $BH_3NH_3(s)$ and $B_3N_3H_6(l)$ are −36.6 and −122.6 kcal/mol, respectively (ref 12). [b] Value obtained using the CCSD(T)/CBS heat of formation of the anion is −50.4 kcal/mol at 298 K. [c] Value obtained using the CCSD(T)/CBS heat of formation of the dianion is −165.2 kcal/mol at 298 K. [d] Value obtained using the CCSD(T)/CBS heat of formation of the dianion is −114.2 kcal/mol at 298 K. [e] Value obtained using the CCSD(T)/CBS heat of formation of the anion is −27.0 kcal/mol at 298 K. [f] Value obtained using the CCSD(T)/CBS heat of formation of the dianion is −118.4 kcal/mol at 298 K. [g] Value obtained using the CCSD(T)/CBS heat of formation of the dianion is −67.5 kcal/mol at 298 K. [h] Value obtained using the CCSD(T)/CBS heat of formation of the anion is −31.3 at 298 K. [i] Value obtained using the CCSD(T)/CBS heat of formation of the dianion is −127.0 kcal/mol at 298 K. [j] Value obtained using the CCSD(T)/CBS heat of formation of the dianion is −76.0 kcal/mol at 298 K.

Equations 8 are just the negative of the heat of formation of the salt. The only exothermic process for decomposition will be for $n = 5$. Table 9 shows the heats of reaction for eqs 9−11 at 298 K. The elimination of H_2 from the salt to give solid BN and elemental boron, eqs 9, is exothermic in all cases. The exothermicity decreases with the increasing size of the dianion, reflecting the increasing stability of the larger dianions. There is a large difference between $n =$ 11 and 12 with the overall reaction only differing by 10−12 kcal/mol from thermoneutral for $n = 12$ whereas the value for $n = 11$ differs by 82−84 kcal/mol. Thus, $B_{12}H_{12}^{2-}$ is an extremely stable dianion. The exothermicity for $n =$ 10 is less than that for $n = 11$, consistent with the closo structure for $B_{10}H_{10}^{2-}$ and enhanced stability for $n = 10$ as compared to the open structure for $n = 11$ with decreased stability. There is still a large difference in the stability of the $n = 10$ and 12 structures. Release of H_2 from the salts to give solid H_3BNH_3 and elemental boron (eqs 10) are quite exothermic processes, except for $B_{12}H_{12}^{2-}$ which, as expected from its enhanced stability, is an endothermic process. Equations 11 forming cyclic $B_3N_3H_6(l)$ show the same behavior as eqs 10. In general, eq 9 is the most exothermic set of reactions followed by eqs 11, with eqs 10 being the least exothermic. This is clearly related to the quantity of H_2 released.

Concluding Remarks

Electronic structure calculations have been used to predict the thermochemical parameters of the boron hydride $B_nH_n^{2-}$ dianions, for $n = 5−12$, the $B_3H_8^-$ and $B_{11}H_{14}^-$ anions, and the B_5H_9 and $B_{10}H_{14}$ neutral species. At the composite coupled-cluster CCSD(T)/CBS level, the heats of formation in the gas phase of the simplest species are $\Delta H_f(B_3H_8^-) = -17.7 \pm 1.0$ kcal/mol at 0 K and $-23.1 \pm$

1.0 kcal/mol at 298 K; $\Delta H_f(B_5H_5^{2-}) = 121.8 \pm 1.5$ kcal/mol at 0 K and 119.4 ± 1.5 kcal/mol at 298 K; $\Delta H_f(B_6H_6^{2-}) = 67.9 \pm 1.5$ kcal/mol at 0 K and 64.1 ± 1.5 kcal/mol at 298 K; and $\Delta H_f(B_5H_9) = 31.0 \pm 1.5$ kcal/mol at 0 K and 24.1 ± 1.5 kcal/mol at 298 K. For B_5H_9, the calculated heat of formation is 6.6 kcal/mol above the experimental heat of formation. The lack of substantial multireference character in B_5H_9 suggests that our calculated values are reasonable and that the experimental value needs to be redetermined. The heats of formation of the larger ions were evaluated using the composite G3 and G3B3 methods and hydrogenation reactions. The lattice energies of the ammonium hydroborate salts were derived from an empirical expression based on the ionic volumes. The heats of formation of the $[B_nH_m^{y-}][NH_4^+]_y$ ($y = 1-2$) salts were predicted by combining the calculated lattice energies and the gas-phase heats of formation of the constituent ions. These values were then used to calculate the heats of reaction for the H_2 release from the salts. As expected, $B_{12}H_{12}^{2-}$ has a special stability, and the reaction

$$[B_{12}H_{12}^{2-}][NH_4^+]_2(s) \rightarrow 10H_2 + 2BN(s) + 10B(s)$$

differs by only 10 to 12 kcal/mol from being thermoneutral at 298 K.

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Supporting Information Available: Calculated and experimental geometry parameters for $B_3H_8^-$, $B_{10}H_{14}$, and $B_{11}H_{14}^-$; CCSD(T) total energies, unscaled MP2 zero point energies and thermal corrections for B_5H_9, $B_3H_8^-$ (both isomers), $B_5H_5^{2-}$, and $B_6H_6^{2-}$; G3 and G3B3 energies and enthalpies for all species considered; heats of reaction (eqs 10) at 0 K for the H_2 release from the salts; and optimized geometries (Cartesian coordinates) at different levels of calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

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