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Fundamental Thermochemical Properties of Ammonia Borane and Dehydrogenated Derivatives (BNH$_n$, $n = 0-6$)

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The heats of formation for BN, HBNH, H$_2$BNH$_2$, and H$_3$BNH$_3$ and their radicals, anions, cations, and protonated species were predicted using the CCSD(T) method with correlation consistent basis sets extrapolated to the complete basis set and core−valence, scalar relativistic, spin−orbit, and zero-point energy corrections. Chemical accuracy (±1 kcal/mol) is obtained for these heats of formation, allowing reliable results for electron and hydride affinities, ionization energies, basicities (neutral proton affinities), acidities (anion proton affinities), and bond dissociation energies of the BNH$_n$ ($n = 0-6$) molecules. The closed shell BNH$_n$ molecules, except for H$_3$BNH$_3$ (double diffuse functions on B and N required), do not bind an electron and behave as nitrogen acids and bases. Protonation of H$_3$BNH$_3$ leads to nearly spontaneous H$_2$ release. The closed shell BNH$_n$ species exhibit ionization energies similar or smaller than those of hydrocarbons, and for the H$_2$BNH radical, its ionization energy (∼5.9 eV) is close to that of the alkali elements. Except for H$_3$BNH$_3$, the NH bonds are systematically stronger than the BH bonds, and the BDE(NH) values tend to increase with increasing multiple character of the BN bonds. Trends and comparisons between properties obtained through reactions on the N and B atoms are given. Comparisons with properties of hydrocarbons show similarities and differences between the two isoelectronic series.

Introduction

Because of it low molecular weight (30.7 g/mol) and high gravimetric hydrogen capacity (19.6 wt %), ammonia borane (H$_3$BNH$_3$, **AB**)[1,2] has emerged as a promising material for use in chemical hydrogen storage.[3] The use of chemicals to store H$_2$ and release it when needed for use at the anode of a hydrogen-based fuel cell enables the safe use of H$_2$ for on-board transportation systems.[4] A number of experimental and theoretical studies have thus been devoted to the determination of the molecular structure, electronic properties, and thermochemical and kinetic parameters of **AB**.[5−15]

Wolf and co-workers[6] employed thermo-analytical techniques to determine the kinetics of the stepwise thermal decompositions of **AB** at temperatures as low as 410 K. We calculated the standard heat of formation of **AB** and a variety of BNH$_n$ derivatives ($n = 0, 2,$ and 4) in the gas phase and estimated the value of the corresponding salt [BH$_4^-$][NH$_4^+$] in the solid state by using high-accuracy ab initio electronic structure theory calculations of thermodynamic parameters at the coupled-cluster CCSD(T) theory with energies extrapolated to the complete basis set (CBS) limit.[7,8] We also predicted the kinetics and mechanism of the processes releasing H$_2$ and regenerating the compounds in different molecular forms.[13−15] Patwari[16] evaluated the proton affinities of **AB** and some methylated derivatives with the composite G2 method.[17] Rablen and Hartwig reported the B−H bond dissociation energy (BDE) in BH$_3$NH$_3$ at the G2 and

CBS-4 levels.[18] Average B−H and N−H BDEs for a range of main group compounds obtained from isodesmic reactions have been reported from MP4(SDTQ)/6-311++G(3df,2p) calculations.[19] Grein and co-workers have reported the electron affinity and ionization potential of BN from multireference configuration interaction (MR-CI) calculations with a 6s5p3d1f valence basis set.[20] Kirwan and Roberts estimated the B−H and N−H BDEs for BH$_3$NH$_3$ from MP3/6-31G** calculations.[21] Apart from these results, a consistent set of other basic thermochemical parameters of the BNH$_n$ compounds such as ionization energies, electron affinities, basicities, and acidities are not known. Because of this lack of data, we have performed electronic structure calculations at the same high-accuracy level to evaluate the missing quantities. A goal is to probe further the reaction thermodynamics of the H$_2$-release from BNH$_n$ materials. This is of special interest with relation to the formation of M^{n+}($^-$NH$_2$BH$_3$)$_n$ or M^{n+}($^-$BH$_2$NH$_3$)$_n$ species.

Computational Methods

Calculations were performed using the Gaussian 03[22] and MOLPRO 2002[23] suites of programs. Geometry parameters of the stationary points were initially optimized using Møller−Plesset second-order perturbation theory (MP2)[24] with the correlation consistent aug-cc-pVTZ basis set.[25] Improved optimizations were obtained by using coupled-cluster theory[26] [CCSD(T)] with the aug-cc-pVDZ and aug-cc-pVTZ basis sets for systems containing more than 2 atoms. For diatomic systems, we optimized up to the CCSD(T)/aug-cc-pVQZ level of calculation. Single-point calculations were also carried out at the CCSD(T)/aug-cc-pVQZ level (and aug-cc-pV5Z for diatomic and triatomic systems). Extrapolation to the CBS limit, based on electronic energies obtained with CCSD(T) and the correlation consistent

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aug-cc-pVnZ basis sets, n = D, T, Q, and 5 (referred to hereafter as aVnZ) was done using the following expressions[27]

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

where x = 2, 3, and 4 for the aVnZ bases, D, T, and Q, respectively, and[28]

$$E(x) = E_{CBS} + B/x^3 \quad (2)$$

where x = 4 and 5 for aVQZ and aV5Z, respectively.

Smaller corrections are also required for high-accuracy total atomization energies ($\sum D_0$) and include core–valence and relativistic corrections. Core–valence corrections, ΔE_{CV}, were obtained at the CCSD(T)/cc-pwCVTZ level.[29] Douglas–Kroll–Hess (DKH) scalar relativistic corrections (ΔE_{SR}), which account for changes in the relativistic contributions to the total energies of the molecule and constituent atoms, were calculated using the spin-free, one-electron DKH Hamiltonian.[30–32] ΔE_{SR} is defined as the difference in the atomization energy between the results obtained from basis sets recontracted for DKH calculations[31] and atomization energy obtained with the normal valence basis set of the same quality. Thus, DKH calculations were carried out at the CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVTZ-DK levels of theory.

The spin–orbit correction is 0.03 kcal/mol for B from the excitation energies of Moore.[33] Zero-point energy (ZPE) corrections were also included at the MP2/aVTZ level of calculation. We applied a scaling factor of 0.9743 to the B–H stretches; this value was calculated from the MP2/aVTZ (2607.1 and 2743.2 cm^{-1}) and experimental (2475[34] and 2601.6[35,36] cm^{-1}) values of the a_1' and e' vibrational modes of BH$_3$. For the N–H stretches, we obtained a scaling factor of 0.9733 from NH$_3$ (MP2/aVTZ, a_1 = 3502.6 and e = 3649.6 cm^{-1}; experiment, a_1 = 3337.0 and e = 3444.0 cm^{-1}).[37]

For the diatomic species, BN$^+$ and BN$^-$, harmonic frequencies and anharmonic constants were calculated from a fifth-order fit[38] of the potential energy curves at the CCSD(T)/aVQZ level. The ZPE was calculated including the anharmonic constant. For BN$^+$, we obtained a harmonic frequency of 1077.2 cm^{-1} with a respective anharmonic constant of 26.2 cm^{-1}. For BN$^-$, we obtained 1698.8 and 11.9 cm^{-1} harmonic and anharmonic values, respectively.

By combining our computed $\sum D_0$ values with the known heats of formation at 0 K for the elements [ΔH_f(B) = 135.1 ± 0.2 kcal/mol,[39] ΔH_f(N) = 112.53 ± 0.02 kcal/mol,[40] and ΔH_f(H) = 51.63 ± 0.001 kcal/mol[40]], we can derive ΔH_f values at 0 K for the systems under study in the gas phase. We obtain heats of formation at 298 K by following the procedures outlined by Curtiss et al.[41] We used the following heats of formation for H$^+$: at 0 K, ΔH_f(H$^+$) = 365.22 kcal/mol and at 298 K, ΔH_f^0(H$^+$) = 365.7 kcal/mol.[40,42]

Results and Discussion

Tables S1 and S2 of the Supporting Information list the total energies calculated at different levels of theory and vibrational modes for each system. Table 1 summarizes the geometrical parameters calculated at the CCSD(T)/aVTZ level. Table 2 tabulates $\sum D_0$ and the different components used to evaluate them. Table 3 records the predicted enthalpies of formation at 0 and 298 K. From the calculated heats of formation, the

fundamental thermochemical parameters can be evaluated, including electron affinities (EA, Table 4), hydride affinities (HA, Table 5), ionization energies (IE, Table 6), proton affinities (PA, Table 7), bond dissociation energies (BDE, Table 8), and acidities (Table 9).

Electron and Hydride Affinities. The electronic structure of neutral diatomic BN has extensively been investigated.[7,43,44] BN has a X$^3\Pi$ ground state, which is only ~0.4 kcal/mol below the a$^1\Sigma^+$ state,[43] in agreement with the experiment. Taking the previously determined value $\sum D_0$(BN) = 102.36 kcal/mol[43] and the new value for ΔH_f(B) = 135.1 kcal/mol, we obtain an updated value ΔH_f(BN) = 145.3 kcal/mol at 0 K. The BN$^-$ anion is predicted to have a $^2\Sigma^+$ ground state, with B–N bond distance shortening by ~0.04 Å upon electron attachment. Our calculated value of EA(BN) = 3.17 eV {73.2 kcal/mol, difference between ΔH_f[BN$^-$($^2\Sigma^+$)] and ΔH_f[BN($^3\Pi$)] at 0 K} is in excellent agreement with the experimental value of 3.160 ± 0.005 eV determined from anion photoelectron spectroscopy[45] and the earlier less accurate value of 2.90 ± 0.30 eV from charge inversion spectrometry.[46] The value of 3.10 eV from an MR-CI/6s5p3d1f valence basis set calculation is in good agreement with our value.[20] For the sake of comparison, Table 4 gives the experimental electron affinities (EAs) for some isoelectronic hydrocarbon radicals. The EA(BN) is about 0.1 eV less than that of the isoelectronic dicarbide, EA(C$_2$) of 3.273 ± 0.008 eV.[47]

For the triatomic (BNH) species, the neutral radical BNH($^2\Sigma^+$) is 19.8 kcal/mol more stable than the NBH($^3\Pi$) isomer, and a reverse energy ordering is found for the corresponding anions. The BNH$^-$ anion is 10.8 kcal/mol less stable than the alternative NBH$^-$ anion. With EA(NBH) = 3.14 eV (72.5 kcal/mol), the N radical has a markedly larger capacity for capturing an electron than the B radical, which has EA(BNH) = 1.82 eV (41.9 kcal/mol) (Table 4). The average of the two EAs of BNH and HBN is close to the experimental value of the isoelectronic ethynyl radical, EA(C$_2$H) = 2.969 eV.[48]

In principle, these triatomic anions can be generated from the reaction of BN with H$^-$. The hydride affinity (HA) is defined as the negative of the enthalpy for the reaction A + H$^- \rightarrow$ AH$^-$. Using the experimental value for ΔH_f(H$^-$) = 34.2 kcal/mol at 0 K, the calculated HAs of BN are 149.5 and 160.3 kcal/mol for the N and B sites, respectively (Table 5). This is consistent with the expected polarity of the B–N bond. Both values are smaller than the corresponding experimental value of the isoelectronic C$_2$ molecule with HA = 168.8 kcal/mol.[40] The B site HA is much larger than the 72.2 kcal/mol previously evaluated for BH$_3$.[7a] The HA can be considered a measure of the Lewis acidity of a site, so both sites in BN are quite Lewis acidic.

The EA of HBNH is negative so the molecule does not bind an electron. In the case where the HA of AH$^-$ is negative, the HA (Table 5) is given by the energy of the reaction A + H$^- \rightarrow$ AH + e$^-$. The HAs of HBN and BNH are much smaller than that of BN, but they are still large compared to that of BH$_3$. The preference for H$^-$ is dominated by the stabilities of the BNH versus NBH, with the BNH being more stable and having a lower HA.

The aminoboryl radical HBNH$_2$ is 7.2 kcal/mol more stable than the borylamino radical H$_2$BNH.[49] Again, the relative energy ordering is reversed upon electron attachment. The B-centered radical is unbound with respect to electron attachment, whereas the parent boryl radical has a small but significant EA, EA(BH$_2$) = 0.39 eV.[50] Even use of a double diffuse set of basis functions did not make the EA positive for HBNH$_2$. The N-centered

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TABLE 1: CCSD(T)/aVTZ Optimized Structures

system	symmetry	r_{BN} (Å)	r_{BH} (Å)	r_{NH} (Å)	θ_{H-B-N} (deg)	θ_{B-N-H} (deg)	$\theta_{H-B-N-H}$ (deg)
BN$^+$	$C_{\infty v}$	1.4548					
BN$^-$	$C_{\infty v}$	1.2894					
BNH$^+$	$C_{\infty v}$	1.2153		1.0096		180.0	
NBH$^+$	$C_{\infty v}$	1.4223	1.1745		180.0		
BNH	$C_{\infty v}$	1.2470		0.9939		180.0	
NBH	$C_{\infty v}$	1.3204	1.1723		180.0		
BNH$^-$	$C_{\infty v}$	1.2947		0.9967		180.0	
NBH$^-$	$C_{\infty v}$	1.2810	1.1896		180.0		
HBNH$^+$	$C_{\infty v}$	1.3133	1.1705	1.0150	180.0	180.0	^{a}
HBNH$^-$	C_s	1.3507	1.2274	1.0262	135.5	115.1	0.0
HBNH$_2^+$	C_{2v}	1.3219	1.1709	1.0198	155.6	123.1	^{b}
				1.0198		123.1	
HBNH$_2^-$	C_s	1.4299	1.2301	1.0216	109.8	125.1	0.0
				1.0022		122.0	180.0
H$_2$BNH$^-$	C_s	1.3876	1.2403	1.0242	124.8	109.6	0.0
			1.2312		120.6		180.0
H$_2$BNH$_2^+$	C_{2v}	1.4772	1.1920	1.0249	116.8	123.2	90.0
			1.1920	1.0249	116.8	123.2	-90.0^c
H$_2$BNH$_2^-$	C_{2v}	1.3911	1.1980	1.0112	119.5	123.9	0.0
							180.0^b
H$_2$BNH$_3^+$	C_s	1.5588	1.1786	1.0296	115.2	108.7	89.3, −89.3
			1.1786	1.0235	115.2	113.4	153.2, −153.2
H$_2$BNH$_3$	C_s	1.6267	1.1986	1.0213	109.7	113.4	69.5. −69.5
				1.0158		110.3	120.6, −120.6
H$_3$BNH$_2$	C_s	1.4476	1.1943	1.0086	117.0	123.6	0.0, 180.0
			1.2641	1.0089	110.3	122.8	136.5, −136.5
H$_3$BNH$_2^-$	C_s	1.5838	1.2538	1.0191	113.5	109.4	56.7, −56.7
			1.2406	1.0191	109.1	109.4	63.7, −63.7
			1.2406		109.1		
H$_3$BNH$_3^+$	C_s	1.5592	1.1743	1.0219	119.9	114.8	180.0
			1.2706	1.0246	113.3	110.6	29.1, −29.1
			1.2706	1.0246	113.3	110.6	58.5, −58.5
H$_3$BNH$_3$	C_{3v}	1.6568	1.2111	1.0157			
H$_3$BNH$_3^-$	C_{3v}	1.6356	1.2163	1.0234	106.6	113.0	180.0
							60.0, −60.0
H$_4$BNH$_3^+$	C_s	1.5854	1.4155	1.0239	105.3	107.1	162.8, −162.8
			1.4155	1.0215	105.3	114.5	69.8, −69.8
			1.1877	1.0215	113.3	114.5	45.4, −45.4
			1.1877		113.3		

^{a} Linear structure. ^{b} Planar structure. ^{c} BH$_2$ perpendicular to NH$_2$.

TABLE 2: Components for Atomization Energies and Thermal Corrections (TC) for BNH$_n$ ($n = 0-7$) Species^a

structure	ΔE_{CBS} (DTQ)/[(Q5)] (kcal/mol)	ΔE_{DKH-SR} (kcal/mol)	ΔE_{CV} (kcal/mol)	ΔE_{ZPE} (kcal/mol)	ΣD_0 (DTQ)/[(Q5)] (kcal/mol)	TC
BN$^+$ ($^4\Sigma^+$)	−158.16 [−158.19]	−0.04	−0.02	1.52	−159.77 [−159.80]	2.08
BN$^-$ ($^2\Sigma^+$)	176.79 [176.92]	−0.19	1.30	2.42	175.45 [175.57]	2.07
BNH$^+$ ($^1\Sigma^+$)	−37.69 [−37.86]	−0.34	1.55	9.14	−45.64 [−45.82]	2.41
BNH ($^2\Sigma^+$)	235.74 [235.65]	−0.30	1.70	9.69	227.41 [227.33]	2.37
BNH$^-$ ($^1\Sigma^+$)	276.25 [276.27]	−0.27	1.45	8.15	269.25 [269.27]	2.72
NBH$^+$ ($^1\Sigma^+$)	−74.72 [−74.61]	−0.07	0.31	7.75	−82.25 [−82.15]	2.25
NBH ($^2\Pi$)	215.14 [215.21]	−0.15	1.31	8.79	207.47 [207.55]	2.21
NBH$^-$ ($^1\Sigma^+$)	284.89 [284.98]	1.27	1.67	7.88	279.93 [280.02]	2.26
HBNH$^+$ ($^2\Pi$)	91.29	−0.25	1.28	13.88	78.40	2.79
HBNH$^-$ ($^2A'$)	323.50	−0.29	1.54	15.11	309.61	2.52
HBNH$_2^+$ ($^1A_1$)	227.68	−0.32	1.52	22.36	206.50	2.67
H$_2$BNH$^-$ ($^1A'$)	425.25	−0.29	1.62	20.30	406.24	2.51
H$_2$BNH$_2^+$ ($^2B_1$)	252.31	−0.29	1.49	27.16	226.32	3.04
H$_2$BNH$_2^-$ ($^2A_1$)	489.76	−0.25	1.84	29.57	461.75	2.62
H$_2$BNH$_3^+$ ($^1A'$)	373.26	−0.34	1.57	37.56	336.90	3.10
H$_2$BNH$_3$ (^2A)^b	501.99 [502.14] (501.93)	−0.35	1.75	36.44	466.91 [467.06] (466.86)	3.00
H$_2$BNH$_3^-$ ($^1A'$)^b	499.54 (502.18)	−0.28	1.56	35.00	465.79 (468.43)	2.96
H$_3$BNH$_2$ ($^2A''$)	504.83 [504.89]	−0.34	2.00	32.94	473.53 [473.59]	2.95
H$_3$BNH$_2^-$ ($^1A'$)	557.43	−0.34	1.70	33.22	525.54	2.93
H$_3$BNH$_3^+$ ($^2A''$)	394.30	−0.36	1.90	42.40	353.41	3.07
H$_3$BNH$_3^-$ ($^2A_1$)^b	608.30 (610.80)	−0.26	1.83	42.93	566.91 (569.41)	2.97
H$_4$BNH$_3^+$ ($^1A'$)	493.51	−0.36	1.90	50.27	444.75	3.15

^{a} $\Delta E_{SO} = -0.3$ kcal/mol for every system. ^{b} Values in parentheses were calculated using double diffuse functions on B and N.

TABLE 3: Heats of Formation at 0 and 298 K for BNH$_n$ (n = 0−7) Species

structure	ΔH_{0K} (DTQ)/[(Q5)] (kcal/mol)	ΔH_{298K} (DTQ)/[(Q5)] (kcal/mol)
BN$^+$ ($^4\Sigma^+$)	407.4 [407.4]	408.2 [408.2]
BN ($^3\Pi$)^a	145.3	146.0
BN$^-$ ($^2\Sigma^+$)	72.2 [72.1]	72.9 [72.8]
BNH$^+$ ($^1\Sigma^+$)	344.9 [345.1]	345.0 [345.2]
BNH ($^2\Sigma^+$)	71.8 [71.9]	71.9 [72.0]
BNH$^-$ ($^1\Sigma^+$)	30.0 [30.0]	30.4 [30.4]
NBH$^+$ ($^1\Sigma^+$)	381.5 [381.4]	381.4 [381.3]
NBH ($^2\Pi$)	91.8 [91.7]	91.7 [91.6]
NBH$^-$ ($^1\Sigma^+$)	19.3 [19.2]	19.3 [19.2]
HBNH$^+$ ($^2\Pi$)	272.5	271.9
HBNH ($^1\Sigma^+$)^a	12.5	11.7
HBNH$^-$ ($^2A'$)	41.3	40.5
HBNH$_2^+$ ($^1A_1$)	196.0	194.3
HBNH$_2$ ($^2A'$)^b	36.0 [36.0]	34.3 [34.3]
H$_2$BNH (^2A)^b	43.2 [43.2]	42.1 [42.1]
H$_2$BNH$^-$ ($^1A'$)	−3.7	−5.6
H$_2$BNH$_2^+$ ($^2B_1$)	227.8	225.5
H$_2$BNH$_2$ ($^1A_1$)^a	−17.0	−19.7
H$_2$BNH$_2^-$ ($^2A_1$)	−7.6	−10.4
H$_2$BNH$_3^+$ ($^1A'$)	168.9	165.6
H$_2$BNH$_3$ ($^2A'$)^{b,c}	38.9 [38.7] (38.9)	35.5 [35.3] (35.5)
H$_2$BNH$_3^-$ ($^1A'$)^c	40.0 (37.4)	36.6 (33.9)
H$_3$BNH$_2$ ($^2A''$)^b	32.2 [32.2]	28.8 [28.8]
H$_3$BNH$_2^-$ ($^1A'$)	−19.8	−23.2
H$_3$BNH$_3^+$ ($^2A''$)	204.0	199.7
H$_3$BNH$_3$ ($^1A_1$)^{a,c}	−10.2 (−10.1)	−14.6 (−14.5)
H$_3$BNH$_3^-$ ($^2A_1$)^c	−9.5 (−12.0)	−13.9 (−16.4)
H$_4$BNH$_3^+$ ($^1A'$)	164.3	159.0

^{a} Obtained from ΣD_0 values in ref 7a and the new value for the heat of formation of B; 135.1 ± 0.02 kcal/mol (ref 39). ^{b} Obtained from ΣD_0 values in ref 49 with ZPEs calculated at the MP2/aVTZ level. ^{c} Values in parentheses were calculated with double diffuse functions on B and N.

TABLE 4: Calculated EA at 0 K for BNH$_n$ (n = 0−6) Species

molecule	EA (eV)
BN	3.17
BNH	1.82
NBH	3.14
HBNH	−1.25
HBNH$_2$	−0.10/−0.07^a
H$_2$BNH	2.03
H$_2$BNH$_2$	−0.41
H$_3$BNH$_2$	2.25
H$_2$BNH$_3$	−0.05/0.07^a
H$_3$BNH$_3$	−0.03/0.08^a
C$_2$	3.273 ± 0.008^b
C$_2$H	2.9690 ± 0.0060^c
C$_2$H$_3$	0.667 ± 0.024^d
C$_2$H$_5$	−0.260 ± 0.089^e

^{a} Calculated with double diffuse functions on B and N. ^{b} Ref 47. ^{c} Ref 48. ^{d} Ref 52. ^{e} Ref 53.

radical has EA(H$_2$BNH) = 2.03 eV (46.9 kcal/mol), far larger than that of the parent amino radical EA(NH$_2$) = 0.771 ± 0.005 eV from the experiment.[51] The electron-deficient BH$_2$ substituent considerably increases the ability of the NH$_2$ radical to accept an electron, whereas the electron-rich NH$_2$ group tends to reduce the ability of the BH$_2$ radical to accept an electron. The EA(H$_2$BNH) is substantially larger than the corresponding value for the isoelectronic vinyl radical, EA(H$_2$CCH) = 0.667 ± 0.024 eV.[52] The HA of HBNH is 50.4 kcal/mol for binding to B, which is lower than that for HA(BH$_3$). Addition of H$^-$ to N leads to loss of the electron and a very low HA. H$_2$BNH$_2$ does not bind

TABLE 5: Calculated Hydride Affinities at 0 K for BNH$_n$ (n = 0−6) Species

reaction	0 K (kcal/mol)
BN + H$^-$ → NBH$^-$	160.3
BN + H$^-$ → BNH$^-$	149.5
BNH + H$^-$ → HBNH + e$^-$	93.6
NBH + H$^-$ → HBNH + e$^-$	113.4
HBNH + H$^-$ → H$_2$BNH$^-$	50.4
HBNH + H$^-$ → HBNH$_2$ + e$^-$	10.7
HBNH$_2$ + H$^-$ → H$_2$BNH$_2$ + e$^-$	87.2
H$_2$BNH + H$^-$ → H$_2$BNH$_2$ + e$^-$	94.4
H$_2$BNH$_2$ + H$^-$ → H$_3$BNH$_2^-$	37.0
H$_2$BNH$_2$ + H$^-$ → H$_2$BNH$_3^-$	−20.2
H$_2$BNH$_3$ + H$^-$ → H$_3$BNH$_3^-$	84.9
H$_3$BNH$_2$ + H$^-$ → H$_3$BNH$_3^-$	78.4

TABLE 6: Calculated Adiabatic Ionization Potentials at 0 K for BNH$_n$ (n = 0−6) Species

molecule	IE (eV)	Expt. (eV)
BN	11.37	
BNH	11.85	
NBH	12.56	
HBNH	11.27	
HBNH$_2$	6.94	
H$_2$BNH	6.63	
H$_2$BNH$_2$	10.62	11.0 ± 0.1^a
H$_2$BNH$_3$	5.65	
H$_3$BNH$_3$	9.29	9.44 ± 0.02^b
C$_2$		11.4 ± 0.3^c
C$_2$H		11.61 ± 0.07^d
C$_2$H$_2$		11.403 ± 0.003,^{e} 11.400 ± 0.002^f
C$_2$H$_3$		8.25^g
C$_2$H$_4$		10.5138 ± 0.0006^h
C$_2$H$_5$		8.117 ± 0.008^i
C$_2$H$_6$		11.52 ± 0.04^f

^{a} Ref 63. ^{b} Ref 64. ^{c} Ref 59. ^{d} Ref 60. ^{e} Ref 61. ^{f} Ref 62. ^{g} Ref 66. ^{h} Ref 65. ^{i} Ref 67.

TABLE 7: Calculated Proton Affinities at 298 K for BNH$_n$ (n = 0−6) Species

Reaction	298 K (kcal/mol)
BN + H$^+$ → NBH$^+$	130.4
BN + H$^+$ → BNH$^+$	166.5
BNH + H$^+$ → HBNH$^+$	165.8
NBH + H$^+$ → HBNH$^+$	185.4
HBNH + H$^+$ → HBNH$_2^+$	183.1
HBNH$_2$ + H$^+$ → H$_2$BNH$_2^+$	174.5
H$_2$BNH + H$^+$ → H$_2$BNH$_2^+$	182.3
H$_2$BNH$_2$ + H$^+$ → H$_2$BNH$_3^+$	180.4
H$_2$BNH$_3$ + H$^+$ → H$_3$BNH$_3^+$	201.3
H$_3$BNH$_2$ + H$^+$ → H$_3$BNH$_3^+$	194.8
H$_3$BNH$_3$ + H$^+$ → H$_4$BNH$_3^+$	192.1
C$_2$ + H$^+$ → C$_2$H$^+$	180.0^a
C$_2$H$_2$ + H$^+$ → C$_2$H$_3^+$	153.3^a
C$_2$H$_3$ + H$^+$ → C$_2$H$_4^+$	180.5^a
C$_2$H$_4$ + H$^+$ → C$_2$H$_5^+$	162.6^a
C$_2$H$_5$ + H$^+$ → C$_2$H$_6^+$	147.0^a
C$_2$H$_6$ + H$^+$ → C$_2$H$_7^+$	142.5^a

^{a} Ref 69.

an electron, so the addition of H$^-$ to H$_2$BNH or BHNH$_2$ leads to loss of the electron. The HAs are much larger than for those for HBNH, and the difference in HA of H$_2$BNH and BHNH$_2$ is due to the difference in the stabilities of the two radicals.

For the BNH$_5$ radicals, the borane-substituted ammonia H$_3$BNH$_2$ ($^2A''$), a derivative of BH$_4$, is calculated to be 6.5 kcal/mol lower in energy than the alternative borylammonium radical H$_2$BNH$_3$ ($^2A'$, derived from NH$_4$).[49] The B radical has a

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TABLE 8: Calculated Adiabatic Bond Dissociation Energies at 0 and 298 K for BNH$_n$ ($n = 0-6$) Species and Experimental BDEs for C$_2$H$_n$ ($n = 0-6$) Species at 298 K

reaction	0 K (kcal/mol)	298 K (kcal/mol)
HBN → BN + H	105.2	106.5
BNH → BN + H	125.0	126.1
HBNH → BNH + H	111.0	112.4
HBNH → HBN + H	130.8	132.0
H$_2$BNH → HBNH + H	20.9	21.7
HBNH$_2$ → HBNH + H	28.1	29.5
H$_2$BNH$_2$ → HBNH$_2$ + H	104.6	106.1
H$_2$BNH$_2$ → H$_2$BNH + H	111.8	113.9
H$_3$BNH$_2$ → H$_2$BNH$_2$ + H	2.4	3.6
H$_2$BNH$_3$ → H$_2$BNH$_2$ + H	−4.1	−2.9
H$_3$BNH$_3$ → H$_2$BNH$_3$ + H	100.5	102.0
H$_3$BNH$_3$ → H$_3$BNH$_2$ + H	94.0	95.5
C$_2$H → C$_2$ + H		111.8 ± 2[a]
C$_2$H$_2$ → C$_2$H + H		133.3 ± 0.07[a]
C$_2$H$_3$ → C$_2$H$_2$ + H		35.0 ± 0.9[a]
C$_2$H$_4$ → C$_2$H$_3$ + H		110.9 ± 0.6[a]
C$_2$H$_5$ → C$_2$H$_4$ + H		36.2 ± 0.3[a]
C$_2$H$_6$ → C$_2$H$_5$ + H		100.5 ± 0.3[a]

[a] Ref 70.

TABLE 9: Calculated Acidities at 0 and 298 K for BNH$_n$ ($n = 0-6$) Species

reaction	0 K (kcal/mol)	298 K (kcal/mol)
HBN → BN$^-$ + H$^+$	345.6	346.9
BNH → BN$^-$ + H$^+$	365.4	366.5
HBNH → BNH$^-$ + H$^+$	382.7	384.4
HBNH → NBH$^-$ + H$^+$	371.9	373.2
H$_2$BNH → HBNH + H$^+$ + e$^-$	334.5	335.3
HBNH$_2$ → HBNH + H$^+$ + e$^-$	341.7	343.1
H$_2$BNH$_2$ → HBNH$_2$ + H$^+$ + e$^-$	418.2	419.7
H$_2$BNH$_2$ → H$_2$BNH$^-$ + H$^+$	378.5	379.8
H$_3$BNH$_2$ → H$_2$BNH$_2$ + H$^+$ + e$^-$	316.0	317.2
H$_2$BNH$_3$ → H$_2$BNH$_2$ + H$^+$ + e$^-$	309.5	310.7
H$_3$BNH$_3$ → H$_2$BNH$_3^-$ + H$^+$	412.7	414.1
H$_3$BNH$_3$ → H$_3$BNH$_2^-$ + H$^+$	355.5	357.0
C$_2$H$_2$ → C$_2$H$^-$ + H$^+$		379.0 ± 5.0[a]
C$_2$H$_4$ → C$_2$H$_3^-$ + H$^+$		409.40 ± 0.60[b]

[a] Ref 71. [b] Ref 72.

significant EA, EA(H$_3$BNH$_2$) = 2.25 eV (52.0 kcal/mol), due to the high stability of the parent BH$_4^-$ anion, whereas an electron is not bound to the tetracoordinated N radical. The behavior of the latter is thus similar to that of the isoelectronic ethyl radical, which is characterized by a negative EA.[53] However, given that the EA of H$_2$BNH$_3$ is very close to zero, we have recalculated it with a double diffuse basis set on B and N.[25,54] At the latter level, H$_2$BNH$_3$ now binds an electron by 0.07 eV (1.5 kcal/mol). The addition of H$^-$ to H$_2$BNH$_2$ at B has a positive HA, but one that is 35 kcal/mol less than that of HA(BH$_3$). This is comparable to the B–N adiabatic donor–acceptor π bond energy of 30 kcal/mol in H$_2$BNH$_2$.[55] As expected, one cannot add an H$^-$ to the N in H$_2$BNH$_2$ as this is an endothermic process.

The EAs of the closed shell molecules BNH$_n$, with $n = 2, 4$, and 6, are all negative so they do not bind electrons at the CBS level with just the aug-cc-pVnZ basis sets (heats of formation of the anions are not included in Table 3). The EA of H$_3$BNH$_3$ is very close to zero, so we recalculated it with a double diffuse basis set.[54] At the latter level, H$_3$BNH$_3$ now binds an electron by 0.08 eV (1.9 kcal/mol). Compared with the experimental value for borane EA(BH$_3$) = 0.038 ± 0.015 eV,[56] we find the

presence of NH$_3$ does not induce a significant effect. The HA of H$_2$BNH$_3$ and H$_3$BNH$_2$ are again reasonably large, and the difference is due to the difference in the stabilities of the parent radicals. Comparing the HA of the radicals BNH/HBN, HBNH$_2$/H$_2$BNH, and H$_2$BNH$_3$/H$_3$BNH$_2$, we see that HA decreases as n increases for the BNH$_n$ radicals.

Ionization Energies. The results are given in Table 6. The spin density of the diatomic calculated at the density functional theory B3LYP/DZVP2 level[57,58] clearly shows that the electron is removed from the π orbital of the X$^3\Pi$ ground state of BN predominantly from the B. The MR-CI value[20] of 11.40 eV is in excellent agreement with our value. The IE(BN) is nearly identical to the experimental value for C$_2$[59] (Table 6). Similarly, the N-centered radical NBH has a higher IE than that of the B radical BNH, whose IE is comparable to that of C$_2$H.[60] Of the two resulting cations, BNH$^+$ is 36.3 kcal/mol more stable than NBH$^+$. The triply bonded closed shell species HBNH has an IE of 11.27 eV, approximately 0.1 eV below that of BN or acetylene.[61,62] Whereas the IEs of C$_2$H$_n$ for $n = 1$ and 2 are nearly the same within 0.2 eV (Table 6), there is a larger variation (1.29 eV) in the values of BNH$_n$ for $n = 1$ and 2.

Ionization of H$_2$BNH and HBNH$_2$ led to the same ion HBNH$_2^+$ as a structure starting from H$_2$BNH$^+$ rearranged to HBNH$_2^+$. The calculated IEs of H$_2$BNH$_2$ (10.62 eV) and H$_3$BNH$_3$ (9.29 eV) are lower than the available experimental data[63,64] determined in the early 1970s (Table 6). They are also lower than the experimental value of BH$_3$ (12.03 eV)[50] but closer to that of NH$_3$ (10.07 eV).[50] Although there is a strong electron delocalization from the N lone pair to B, the boryl BH$_2$ substituent increases the IE of ammonia by making a stronger π bond in the neutral, whereas the borane BH$_3$ has the opposite effect by stabilizing the ammonia cation. Compared with H$_3$BNH$_3^+$, the ethane cation is less stabilized by interaction of a CH$_3$ radical with a CH$_3^+$ cation. This is the likely reason for the difference between the two series of isoelectronic species, in which the IE of ethane[62] is about 1 eV higher than that of ethylene,[65] whereas the IE is actually decreased by 1.3 eV going from H$_2$BNH$_2$ to H$_3$BNH$_3$.

Both B centered radicals, HBNH$_2$ and H$_2$BNH$_3$, are predicted to have remarkably low IEs of ~6.9 and ~5.7 eV, respectively. These are even lower than the values for the boryl radical H$_2$B (9.8 eV) or the boron atom (8.3 eV).[50] The vinyl[66] and ethyl[67] radicals are also characterized by IEs, which are around 3 eV lower than those of the corresponding closed shell parent. The IE of 5.65 eV for H$_2$BNH$_3$ is approaching the values of the alkali elements, lithium (5.39 eV)[68] and sodium (5.14 eV).[68] The presence of the amine group contributes to a strong stabilization of the corresponding HBNH$_2^+$ and H$_2$BNH$_3^+$ cations. The alternative N cations, H$_2$BNH$^+$ and H$_3$BNH$_2^+$, do not exist as stable equilibrium structures.

Proton Affinities. The relevant data in Table 7 include the experimentally determined values for the hydrocarbon systems.[69] The PA is defined as the ability of a neutral molecule to bind a proton and is an index of the molecular basicity and, hence, its nucleophilic capability. As noted above, NBH$^+$ is 36.3 kcal/mol higher in energy than its isomer BNH$^+$, so there is a clear preference for N -protonation of BN. Compared with PA(N$_2$) = 118.0 kcal/mol,[50] we find the markedly larger PA of 166.5 kcal/mol predicted for BN arises from a high polarity of the diatomic species. PA(BN) is smaller than the value of ~180 kcal/mol for PA(C$_2$) (Table 7).

For HBNH and H$_2$BNH$_2$, N protonation is the only possible product. Taking PA(NH$_3$) = 204.0 kcal/mol[50] as a reference, we find the basicities of HBNH and H$_2$BNH$_2$ are significantly

reduced (Table 7). The PA of triply bonded HBNH is ~3 kcal/mol larger than the PA of doubly bonded H_2BNH_2. A reverse trend is observed for acetylene and ethylene, in which the PA at the triply bonded C atom is ~9 kcal/mol smaller than that of the doubly bonded counterpart.

Patwari[16] predicted that protonation of **AB** leads to a weak η^2-H_2 complex with an H_2 bonded to the $H_2BNH_3^+$ molecular cation, with H_2 interacting with the B-center; this is geometrically similar to the structure of the BH_5 species where H_2 interacts with the BH_3 core. The value for PA(**AB**) determined using the G2 approach[16] is 191.5 kcal/mol, close to our CCSD(T)/CBS value of 192.1 kcal/mol. The binding energy of the η^2-H_2 complex is calculated to be 4.6 kcal/mol, suggesting a nearly spontaneous generation of H_2 upon protonation of **AB**. This is consistent with the experimental observation of the relative ease of H_2 release from H_3BNH_3 in different acidic media.[10b]

Bond Dissociation Energies. Table 8 collects the calculated BDEs of the BNH_n species, together with the experimental values for the corresponding hydrocarbons from Luo's compilation.[70] The CBS-4 and G2 values[18] for the B−H BDE in BH_3NH_3 are in good agreement with our higher level value. Except for **AB**, a BH bond is in general weaker than an NH bond. The difference in the B−H and N−H BDEs can be as large as 38.5 kcal/mol in the separate BNH systems but is reduced to 20 kcal/mol in HBNH and to ~7 kcal/mol in the remaining molecules. Kirwan and Roberts[21] estimated a B−H BDE of 103.0 kcal/mol and an N−H BDE of 100.6 kcal/mol for H_3BNH_3. These are somewhat larger than our values of 102.0 and 95.5 kcal/mol at 298 K, and our difference is somewhat larger. As expected, the BDEs of the radicals are markedly smaller than those in the closed shell molecules. The H_3BNH_2 radical is barely stable with respect to loss of H to form H_2BNH_2, and the H_2BNH_3 radical is unstable with respect to loss of H to form H_2BNH_2.

A reverse trend is predicted for H_3BNH_3 with the BH bond being 6.5 kcal/mol stronger than the NH bond. For the B−H and N−H bonds, the BDE decreases with a decrease in the bond order. This parallels the trend of the CH bonds in hydrocarbons (Table 8). The B−H and N−H BDEs are much larger than the BDE of 26.5 kcal/mol obtained for the dative B−N bond.[13] In view of the high instability of the resulting radicals, an alternative pathway for hydrogen generation from **AB** could be initiated by an H abstraction reaction by a strong radical, leading to the H_3BNH_2 radical, which rapidly loses an H atom giving rise to aminoborane H_2BNH_2. Molecular H_2 could be formed by the abstraction of an H atom from BH_3NH_3, which would give a BNH_5 radical that will readily lose an H atom to continue the radical chain reaction.

Gas Phase Acidities. The gas phase acidity is the free energy representation of the deprotonation energy (DPE) of a neutral species (AH $\rightarrow$ A$^-$ + H$^+$). We focus on the enthalpic contribution to the DPE. The relative enthalpic contribution to the gas phase acidity of the B and N sites is primarily determined by the relative stability of the forming anions described above; the more stable the anion, the lower the gas phase acidity of the molecule leading to a stronger acid. The DPE values of the three closed shell molecules, HBNH, H_2BNH_2, and H_3BNH_3, which formally could be described as having triple, double, and single boron−nitrogen bonds, respectively, are given in Table 9, together with the relevant values for acetylene[71] and ethylene.[72] We also include the acidity of the radicals. When the anion is unbound, the acidity is determined by the energy of a neutral radical plus a free electron.

SCHEME 1
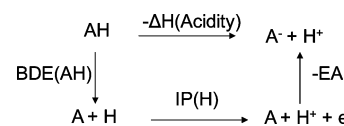
All three BN systems behave as N acids. The acidity beginning with the triply bonded HBNH (DPE $= \sim373$ kcal/mol) decreases for the doubly bonded H_2BNH_2 (DPE $= \sim380$ kcal/mol) and then increases for the singly bonded H_3BNH_3 (DPE $= \sim357$ kcal/mol). The decrease of ~7 kcal/mol in DPE going from HBNH to H_2BNH_2 is much smaller than the change from acetylene (DPE $= \sim379$ kcal/mol), which is much more acidic than ethylene (DPE $= \sim409$ kcal/mol) (Table 9). The higher polarity of B−N compounds better stabilizes the resulting anions.

The bonding of BH_3 with a dative bond substantially decreases the N acidity of **AB** as compared with the experimental gas phase acidity of 403.4 kcal/mol of NH_3.[50] The anion $H_3BNH_2^-$ formed upon deprotonation is stabilized by 46 kcal/mol relative to the isolated parent NH_2^- anion due to the B−N dative bond. However, the DPE(B site) values of 419.7 and 414.1 kcal/mol of H_2BNH_2 and H_3BNH_3, respectively, are larger than the experimental value of 411.8 kcal/mol of BH_3.[50] The B acidity of substituted boranes is reduced by a small amount when substituting an H in borane by an amino group or complexation of ammonia to borane. The borane derivatives behave in both cases as nitrogen acids; a qualitatively similar effect has been found for methylborane (H_2BCH_3), which is a carbon acid, and is predicted to have an intrinsic acidity of ~48 kcal/mol stronger than borane.[73]

The various components of the Born−Haber cycle for acidity are shown in Scheme 1. The relative acidities of HBN and BNH are determined by the strength of the B−H or N−H bonds, and the stronger N−H bond leads to the weaker acid. In HBNH, the acidity is dominated by the EA step, so the molecule is an N acid. For H_2BNH_2, the N acidity is due to the EA(H_2BNH) ~2 eV. The same is true for the N acidity of H_3BNH_3, which is dominated by EA(H_3BNH_2). Because EA(HBNH) < 0, the difference in the acidities of H_2BNH and $HBNH_2$ are determined by the BDEs. The high acidities of H_2BNH_3 and H_3BNH_2 are due to the very low BDEs.

Concluding Remarks

The heats of formation at 0 and 298 K for a series of small BNH_n compounds, including BN, HBNH, H_2BNH_2, and H_3BNH_3, and their radicals, anions, cations, and protonated forms were predicted on the basis of valence electronic energies computed at the coupled-cluster CCSD(T) method with correlation consistent basis sets extrapolated to the complete basis set. Total atomization energies were obtained by including the smaller core−valence, scalar relativistic, spin−orbit, and zero-point energy corrections. On the basis of our extensive evaluations of the thermochemical parameters of B−N compounds, chemical accuracy (±1.0 kcal/mol) is expected for these heats of formation, thus allowing reliable results for the fundamental thermochemical parameters of the BNH_n ($n = 0-6$) molecules. These include electron and hydride affinities (EAs and HAs), ionization energies (IEs), basicities, acidities, and bond dissociation energies (BDEs). Most of these parameters are not yet known experimentally. Comparison with properties of relevant hydrocarbons shows similarities and differences between the two isoelectronic series. The closed shell BNH_n compounds, except for H_3BNH_3 (double diffuse functions on

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B and N required), do not bind an electron and behave as nitrogen acids. The N acids have intrinsic acidities much stronger than the corresponding carbon acids from hydrocarbons. They also act as nitrogen bases, but their basicities are significantly reduced with respect to ammonia and in fact are similar to the isoelectronic hydrocarbons. Protonation of ammonia borane leads to nearly spontaneous H_2 release. The closed shell BNH_n species exhibit ionization energies similar or smaller than those of hydrocarbons. The H_2BNH radical has a low ionization energy (~5.9 eV), close to that of the alkali elements. Except for H_3BNH_3, the NH bonds are systematically stronger than the BH bonds, irrespective of the molecular system considered. The BDE(NH) values tend to increase with increasing multiple character of the BN bonds. All three BN systems behave as N acids.

Supporting Information Available: Total CCSD(T) electronic energies (a.u.) as a function of basis set extrapolated to the complete basis set limit, calculated vibrational modes (cm^{-1}), and calculated electron affinities (kcal/mol) as a function of basis set at 0 K with and without double diffuse functions on B and N for $HBNH_2$, H_2BNH_3 and H_3BNH_3. This material is available free of charge via the Internet at http://pubs.acs.org.

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