Protonated Borane−Lewis Base Complexes BH_4X^+ ($X = NH_3, PH_3, H_2O, H_2S, CO$)[1]

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Structures of protonated borane−Lewis base complexes H_4BX^+ ($X = NH_3$, PH_3, OH_2, SH_2, CO) as well as their neutral parents were calculated using ab initio method at the MP2/6-31G** level. All of the monocations H_4BX^+ are B−H protonated involving hypercoordinate boron with a three-center two-electron (3c-2e) bond. Protonation energies of H_3BX to form H_4BX^+ were calculated with the G2 theory and were found to be highly exothermic. The ^{11}B NMR chemical shifts of the compounds were also calculated by the GIAO-MP2 method.

Introduction

Lewis acid−base interactions are at the heart of our understanding of many catalytic reactions. Donor−acceptor complexes of Lewis acid BH_3 have been the subject of many theoretical studies.[2] Recently Anane et al. reported a G2 molecular orbital study of a series of donor−acceptor complexes of BH_3 including BH_3X ($X = NH_3$, PH_3, H_2O, H_2S).[2a] Previously, we reported[3] on the calculated structures and energies of the parent hexa-, hepta-, and octacoordinate boronium ions, BH_6^+, BH_7^{2+}, and BH_8^{3+}. In continuation of our study of onium ions and dications[4] we have now extended our investigations to the structures and energetics of protonated BH_3X ($X = NH_3$, PH_3, H_2O, H_2S, CO) by ab initio calculations and found some very intriguing results.

Calculations

Calculations were carried out with the Gaussian 94 program system.[5] The geometry optimizations and frequency calculations were performed at the MP2/6-31G** level.[6] From calculated frequencies, the optimized structures were characterized as minima (NIMAG = 0) or transition structure (NIMAG = 1). For improved energy, the Gaussian-2 (G2) energies[7] were computed. Calculated energies are given in Table 1.

Table 1. Total Energies (−au), ZPE,[a] and Relative Energies (kcal/mol)[b]

		MP2/6-31G**//MP2/6-31G**	G2	rel. energy (kcal/mol)
H_3BNH_3	**1a**	82.92320 (42.2)	83.02504	0.0
$H_4BNH_3^+$	**1b**	83.24289 (48.2)	83.33242	192.9
$H_2BNH_3^+$	**1c**	82.07360 (36.1)	82.15705	
H_3BPH_3	**2a**	369.10145 (34.8)	369.23661	0.0
$H_4BPH_3^+$	**2b**	369.40858 (40.7)	369.53012	184.2
$H_2BPH_3^+$	**2c**	368.23001 (28.9)	368.34683	
H_3BOH_2	**3a**	102.73427 (33.4)	102.87328	0.0
$H_4BOH_2^+$	**3b**	103.04298 (39.3)	103.17224	187.6
$H_2BOH_2^+$	**3c**	101.88426 (28.4)	102.00400	
H_3BSH_2	**4a**	425.31670 (29.4)	425.47470	0.0
$H_4BSH_2^+$	**4b**	425.61816 (35.5)	425.76149	180.0
$H_2BSH_2^+$	**4c**	424.44714 (24.1)	424.58502	
H_3BCO	**5a**	139.54693 (22.1)	139.73668	0.0
H_4BCO^+	**5b**	139.81674 (28.3)	139.99280	160.7
H_2BCO^+	**5c**	138.63025 (16.4)	138.80159	
H_2		1.15766 (6.6)	1.16636	

[a] Zero point vibrational energies (ZPE) at MP2/6-31G**//MP2/6-31G** scaled by a factor of 0.93. [b] Relative energy based on G2 energies.

Table 2. Calculated[a] and Experimental[b] ^{11}B NMR Chemical Shifts

		GIAO-MP2/tzp/dz	expt
H_3BNH_3	**1a**	−19.3	−22.3
$H_4BNH_3^+$	**1b**	−17.9	
$H_2BNH_3^+$	**1c**	76.4	
H_3BPH_3	**2a**	−44.6	−42.5
$H_4BPH_3^+$	**2b**	−36.3	
$H_2BPH_3^+$	**2c**	92.5	
H_3BOH_2	**3a**	7.1	2.5[c]
$H_4BOH_2^+$	**3b**	−3.5	
$H_2BOH_2^+$	**3c**	57.7	
H_3BSH_2	**4a**	−20.4	−20.1[d]
$H_4BSH_2^+$	**4b**	−24.1	
$H_2BSH_2^+$	**4c**	81.4	
H_3BCO	**5a**	−50.9	−48.5
H_4BCO^+	**5b**	−36.1	
H_2BCO^+	**5c**	75.3	

[a] ^{11}B NMR chemical shifts were referenced to $F_3B{:}O(C_2H_6)_2$. [b] Experimental values were taken from refs 16 and 17. [c] For $H_3B{:}O(CH_3)_2$. [d] For $H_3B{:}S(CH_3)_2$.

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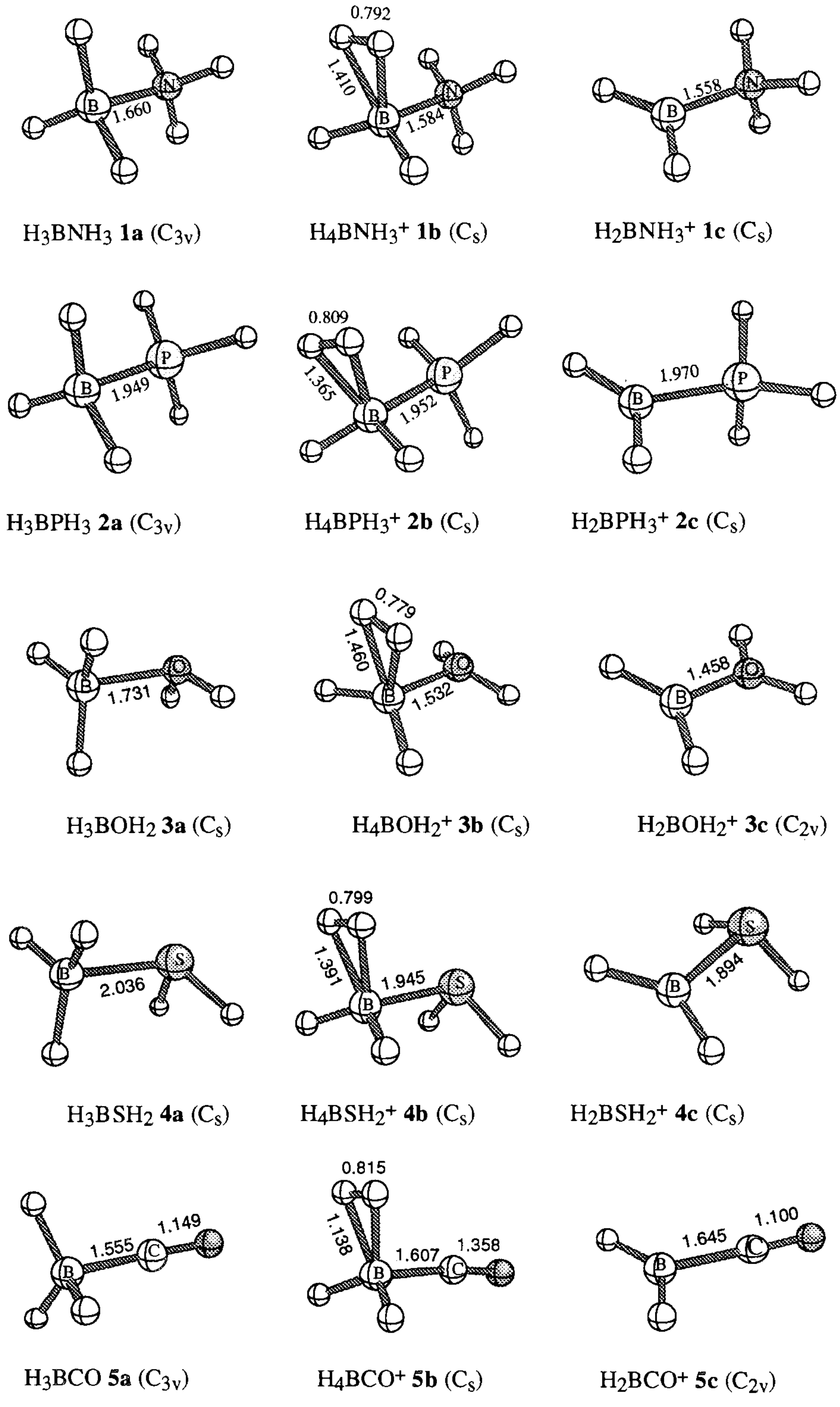

H_3BNH_3 **1a** (C_{3v}) $H_4BNH_3^+$ **1b** (C_s) $H_2BNH_3^+$ **1c** (C_s)

H_3BPH_3 **2a** (C_{3v}) $H_4BPH_3^+$ **2b** (C_s) $H_2BPH_3^+$ **2c** (C_s)

H_3BOH_2 **3a** (C_s) $H_4BOH_2^+$ **3b** (C_s) $H_2BOH_2^+$ **3c** (C_{2v})

H_3BSH_2 **4a** (C_s) $H_4BSH_2^+$ **4b** (C_s) $H_2BSH_2^+$ **4c** (C_s)

H_3BCO **5a** (C_{3v}) H_4BCO^+ **5b** (C_s) H_2BCO^+ **5c** (C_{2v})

Figure 1. MP2/6-31G** structures of **1**−**5**.

MP2/6-31G** geometrical parameters and G2 calculated energies will be discussed throughout, unless stated otherwise. NMR chemical shifts were calculated by the GIAO[8,9] method. GIAO-MP2 calculations using the tzp/dz basis set[8,9] have been performed with the ACES II program.[10] Calculated chemical shifts are listed in Table 2.

Results and Discussion

Protonated H_3BNH_3 and H_3BPH_3 ($H_4BNH_3^+$ and $H_4BPH_3^+$). B−H protonation of the H_3BNH_3 (**1a**) leads to monocation $H_4BNH_3^+$ (**1b**) which was calculated to be a stable minimum at the MP2/6-31G** level. The C_s symmetry structure **1b** is isoelectronic and isostructural with dication $H_4CNH_3^{2+}$.[11] Monocation **1b** contains a five-coordinate boron atom with a three-center two-electron (3c-2e) bond (Figure 1). Ion **1b** can be considered as $-NH_3^+$ substituted BH_5. BH_5, which is isoelectronic with CH_5^+, is C_s symmetrical with a 3c-2e bond

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Table 3. Thermodynamics of the Dissociation of **1**−**5b**[a]

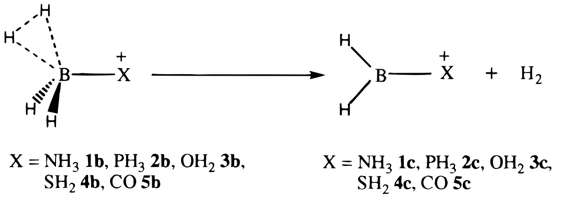
dissociation process	ΔH (kcal/mol)
$H_4BNH_3^+$ (**1b**) → $H_2BNH_3^+$ (**1c**) + H_2	+5.7
$H_4BNH_3^+$ (**1b**) → BH_4^+ + NH_3	+81.0
$H_4BPH_3^+$ (**2b**) → $H_2BPH_3^+$ (**2c**) + H_2	+10.6
$H_4BPH_3^+$ (**2b**) → BH_4^+ + PH_3	+66.8
$H_4BOH_2^+$ (**3b**) → $H_2BOH_2^+$ (**3c**) + H_2	+1.2
$H_4BOH_2^+$ (**3b**) → BH_4^+ + H_2O	+59.9
$H_4BSH_2^+$ (**4b**) → $H_2BSH_2^+$ (**4c**) + H_2	+6.3
$H_4BSH_2^+$ (**4b**) → BH_4^+ + H_2S	+54.0
H_4BCO^+ (**5b**) → H_2BCO^+ (**5c**) + H_2	+15.6
H_4BCO^+ (**5b**) → BH_4^+ + CO	+44.3

[a] With the G2 theory.

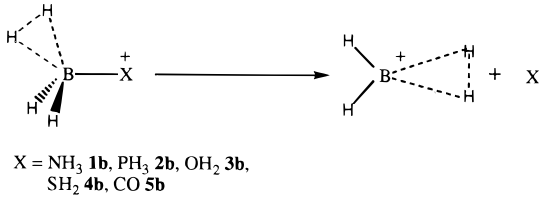
based on high level ab initio calculations.[11,13] The B−N bond distance of **1b** is 1.584 Å, 0.076 Å shorter than that found in H_3BNH_3 at the same MP2/6-31G** level which indicates stronger B−N bonding in **1b** than in **1a**.

Protonation of H_3BNH_3 **1a** to form **1b** was calculated to be highly exothermic by 192.9 kcal/mol (Table 1), which is more exothermic by 28 kcal/mol than the protonation of water. The dissociation of **1b** into **1c** and molecular H_2 (Scheme 1) is endothermic by 5.7 kcal/mol (Table 3). In comparison, dissociation of BH_5 into BH_3 and H_2 is indicated to be exothermic by 6.8 kcal/mol.[12] The experimental gas phase observation (by infrared spectroscopy) of BH_5 has recently been reported.[14] On the other hand, dissociation of **1b** into BH_4^+ and NH_3 (Scheme 2) is calculated to be even more endothermic by 81.0 kcal/mol (Table 3). BH_4^+ which is isoelectronic with CH_4^{2+} is of C_{2v} symmetry and contains a 3c-2e bond.[3]

Scheme 1



Scheme 2



The X-ray structure of H_3BNH_3 showed a B−N bond distance of 1.564 Å, which is significantly shorter than the gas-phase B−N distance of 1.672 Å (determined by microwave spectroscopy).[2h] The gas-phase value, however, agrees rather well with the calculated value of 1.660 Å. Based on self-consistent reaction field (SCRF) calculations it was concluded that the reduction of B−N distance in the crystal is due to the dipolar field effect of the crystal. In fact, on the basis of our present calculations, it is now probable that protosolvation of H_3BNH_3 is responsible for the observed shorter B−N distance in the solid state.

Protonation of the H_3BPH_3 (**2a**) leads to the monocation $H_4BPH_3^+$ (**2b**). Similar to ammonium cation **1b**, the calculated structure **2b** also contains a 3c-2e bond. However, unlike **1b**, the B−P bond distance of **2b** (1.952 Å) is 0.003 Å longer than that of H_3BNH_3. Protonation of H_3BPH_3 **2a** was also calculated to be highly exothermic by 184.2 kcal/mol (Table 1). The dissociation of **2b** into **2c** and H_2 (Scheme 1) and into BH_4^+ and NH_3 (Scheme 2) were calculated to be endothermic by 10.6 and 66.8 kcal/mol (Table 3), respectively. These results indicate that the cations **1b** and **2b** should be observable experimentally.

Protonated H_3BOH_2 and H_3BSH_2 ($H_4BOH_2^+$ and $H_4BSH_2^+$). We have also calculated the structures of B−H protonated H_3BOH_2 (**3a**) and H_3BSH_2 (**4a**) leading to $H_4BOH_2^+$ (**3b**) and $H_4BSH_2^+$ (**4b**), respectively, at the MP2/6-31G** level. Each of the structures **3b** and **4b** was characterized by a 3c-2e bond. Structure **3a** is isoelectronic as well as isostructural with the carbon analogue $H_4COH_2^{2+}$.[11] The oxygen in **3b** and the sulfur in **4b** are pyramidal. The B−O and B−S bond lengths of **3b** (1.532 Å) and **4b** (1.945 Å) are shorter than those of neutral **3a** (1.731 Å) and **4b** (2.036 Å), respectively.

Cation **3b** is endothermic by only 1.2 kcal/mol (Table 3) toward dissociation into **3c** and H_2 (Scheme 1). Similar dissociation of **4b** into **4c** and H_2 (Scheme 2), however, is more endothermic by 6.3 kcal/mol (Table 3).

Protonated H_3BCO (H_4BCO^+). The borane−carbon monoxide complex H_3BCO (**5a**) is isoelectronic with the acetyl cation H_3CCO^+. Protonation of the H_3BCO (**5a**) leads to B−H protonated monocation H_4BCO^+ (**5b**) containing a HBH 3c-2e bond. In comparison, the calculated structure of C−H protonated acetyl dication H_4CCO^{2+} is C_{4v} symmetrical with no localized 3c-2e bond.[15] The B−C bond distance of **5b** (1.607 Å) is 0.052 Å longer than that of H_3BCO (**5a**). The possible O-protonated structure H_3BCOH^+ is not a minimum on the potential energy surface as the cation dissociates into BH_3 and isoformyl cation COH^+ when optimized at the MP2/6-31G** level. In contrast, O-protonated acetyl dication H_3CCOH^{2+} is more stable by 18.9 kcal/mol than the C−H protonated H_4CCO^{2+}.[11] This is consistent with the superior donor ability of the BH_3 group in H_3BCO **5a** compared to that of the CH_3 group in H_3CCO^+. Protonation of H_3BCO **5a** was calculated to be less exothermic (160.7 kcal/mol) compared to that of other borane complexes (Table 1). The dissociation of **5b** into **5c** and H_2 (Scheme 1) and into BH_4^+ and CO (Scheme 2) were calculated to be endothermic by 15.6 and 44.3 kcal/mol (Table 3), respectively.

NMR Chemical Shifts. We have also calculated the ^{11}B NMR chemical shifts of **1**−**5** by the correlated GIAO-MP2 method[7,8] using MP2/6-31G** geometries (Table 2). The calculated $\delta^{11}B$ of H_3BNH_3 (**1a**) is −19.3, which agrees very well the experimental value of −22.3. For monocation $H_4BNH_3^+$ (**1b**), the calculated $\delta^{11}B$ of −17.9 is only 1.4 ppm deshielded from the $\delta^{11}B$ value of neutral **1a**. The GIAO-MP2 calculated $\delta^{11}B$ of H_3BPH_3 **2a** is −44.6, which also agrees very well the experimental value of −42.5. Calculated $\delta^{11}B$ of H_3BOH_2 (**3a**) and H_3BSH_2 (**4a**) are 7.1 and −20.4 ppm, respectively, can be compared with the experimentally obtained values of 2.5 for $H_3BO(CH_3)_2$ and −20.1 for $H_3BS(CH_3)_2$. The ^{11}B NMR chemical shifts of the neutral complexes **1**−**5a** by noncorrelated IGLO method have been reported previously.[2h]

Conclusion

In conclusion, present ab intio calculations at the MP2/6-31G** level indicate that the B−H protonated H_3BX (X = NH_3,

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PH_3, OH_2, SH_2, CO), **1−5b**, are stable minima and should be eventually observable experimentally. The optimized structures show that **1−5b** all contain a 3c-2e bond. Protonations of H_3BX to form H_4BX^+ were found to be highly exothermic as calculated with the G2 theory. G2 theory was also employed to calculate the possible dissociation of the cations (**1−5b**) into H_2BX^+ (**1−5c**) and H_2 and into BH_4^+ and X. The ^{11}B NMR chemical shifts of the compounds were also calculated by GIAO-MP2 method.

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