5876 *Inorg. Chem.* **1999,** *38,* 5876−5878

B−H Bond Protonation in Mono- and Diprotonated Borane Complexes H_3BX (X = N_2H_4, NH_2OH, and H_2O_2) Involving Hypercoordinate Boron[1]

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Received August 5, 1999

Structures of mono- and diprotonated borane complexes H_3BX (X = N_2H_4, NH_2OH, and H_2O_2) as well as their neutral analogues were calculated using the density functional theory method at the B3LYP/6-311+G** level. Global minimum structures (**3**, **9**, and **14**) for all of the monocations H_4BX^+ are B−H protonated with a three-center two-electron bond. Remarkably, in the case of monoprotonated hydrazine−borane $H_3BNH_2NH_2$ (**1**), the B−H protonated $H_4BNH_2NH_2^+$ (**3**) was calculated to be 6.3 kcal/mol more stable than the N-protonated $H_3BNH_2NH_3^+$ (**2**), unexpectedly indicating that the bonded electron pair of the B−H bond is a better donor than the nonbonded nitrogen electron pair in hydrazine−borane complex **1**.

Introduction

Recently we reported[2] the ab initio calculated structures of protonated borane−Lewis base complexes H_4BX^+ (X = NH_3, PH_3, OH_2, SH_2, and CO). All of the H_4BX^+ complexes were found to be B−H protonated, involving hypercoordinate boron with a three-center two-electron (3c-2e) bond. The protonation energies of H_3BX to form H_4BX^+ were calculated to be highly exothermic.[2] The neutron diffraction structure of BH_3NH_3 has recently been reported by Crabtree et al., which shows that the molecules tend to have close N−H···H−B contacts as a result of a novel type of intermolecular hydrogen or dihydrogen bonding.[3a] In continuation of our study we have now extended our investigations to mono- and diprotonated borane complexes H_3BX (X = N_2H_4, NH_2OH, and H_2O_2) as well as their neutral analogues using density functional theory (DFT) calculations.

Calculations

Calculations were carried out with the Gaussian 98 program system.[3b] The geometry optimizations were performed using the DFT[4] method at the B3LYP[5]/6-311+G** level.[6] Vibrational frequencies at the B3LYP/6-311+G**//B3LYP/6-311+G** level were used to characterize stationary points as minima (number of imaginary frequencies (NIMAG) = 0) and to evaluate zero point vibrational energies (ZPE), which were scaled by a factor of 0.96. Final energies were calculated at the B3LYP/6-311+G**//B3LYP/6-311+G** + ZPE level. Calculated energies are given in Table 1. B3LYP/6-311+G** geometrical parameters and final energies will be discussed throughout, unless stated otherwise.

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

	B3LYP/6-311+G**// B3LYP/6-311+G**	ZPE	rel energy
$H_3BNH_2NH_2$ (**1**)	138.583 80	52.7	263.1
$H_3BNH_2NH_3^+$ (**2**)	138.893 13	60.7	77.0
$H_4BNH_2NH_2^+$ (**3**)	138.900 00	58.7	70.7
$H_2BNH_2NH_2^+$ (**4**)	137.701 94	46.8	
$H_4BNH_2NH_3^{2+}$(**5**)	139.024 78	66.3	0.0
$H_5BNH_2NH_2^{2+}$ (**6**)	138.947 01	62.8	45.3
H_3BNH_2OH (**7**)	158.439 03	44.6	217.9
H_3BOHNH_2 (**8**)	158.402 97	43.7	239.6
$H_4BNH_2OH^+$ (**9**)	158.740 95	50.6	34.0
$H_2BNH_2OH^+$ (**10**)	157.542 37	38.8	
$H_4BNH_2OH_2^{2+}$ (**11**)	158.805 37	56.6	0.0
$H_5BNH_2OH^{2+}$ (**12**)	158.783 51	55.1	12.2
H_3BOHOH (**13**)	178.245 28	35.8	187.8
H_4BOHOH^+ (**14**)	178.540 35	41.5	8.4
H_2BOHOH^+ (**15**)	177.353 15	30.5	
H_5BOHOH^{2+} (**16**)	178.560 56	45.8	0.0
H_2	1.179 57	6.1	

[a] Zero point vibrational energies at B3LYP/6-311+G**//B3LYP/6-311+G** scaled by a factor of 0.96. [b] At the B3LYP/6-311+G**//B3LYP/6-311+G** + ZPE level.

Results and Discussion

Mono- and Diprotonated Hydrazine−Borane Complex $H_3BNH_2NH_2$. The calculated structure of hydrazine−borane $H_3BNH_2NH_2$ (**1**) is depicted in Figure 1. Two possible structures of monoprotonated **1**, **2**, and **3** were calculated. Both structures, terminal N-protonated $H_3BNH_2NH_3^+$ (**2**) and B−H protonated $H_4BNH_2NH_2^+$ (**3**), are minima on the potential energy surface (PES). Remarkably **3** is 6.3 kcal/mol more stable than **2**. This indicates that the bonded electron pair of the B−H bond is a

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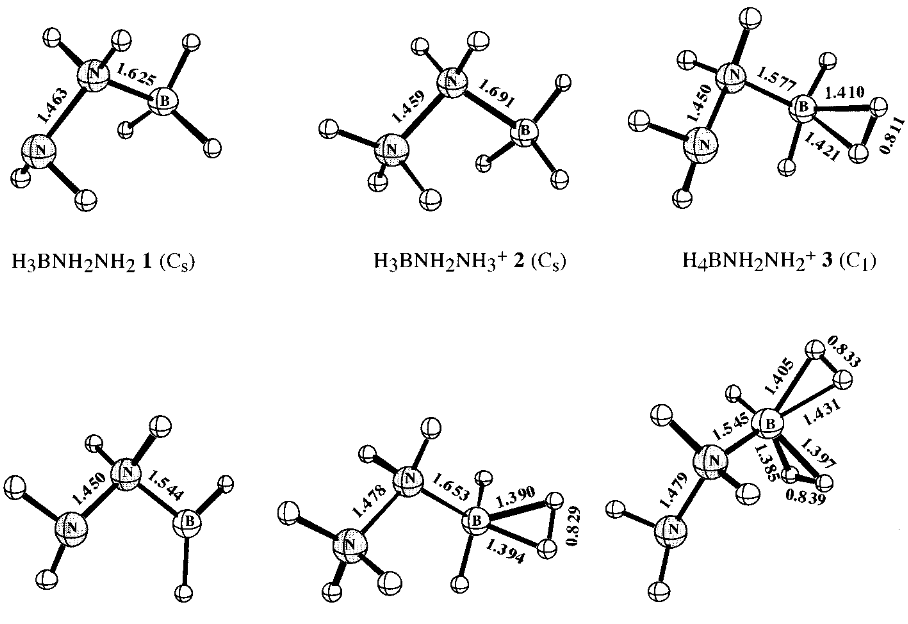

$H_3BNH_2NH_2$ **1** (C_s) $H_3BNH_2NH_3^+$ **2** (C_s) $H_4BNH_2NH_2^+$ **3** (C_1)

$H_2BNH_2NH_2^+$ **4** (C_1) $H_4BNH_2NH_3^{2+}$ **5** (C_1) $H_5BNH_2NH_2^{2+}$ **6** (C_1)

Figure 1. B3LYP/6-311+G** structures of **1**−**6**.

better donor than the nitrogen nonbonded electron pair in the hydrazine−borane complex **1**. Other possible conformers of $H_4BNH_2NH_2^+$ were found to be less stable than **3**. Cation **3** is characterized as having a five-coordinate boron atom with a three-center two-electron (3c-2e) bond (Figure 1). The B−N bond distance of **3** is 1.577 Å, 0.048 Å shorter than that in **1**, indicating stronger B−N bonding in **3** than in **1**. The cation can be considered as a complex between hydrazine N_2H_4 and superelectrophile[7] BH_4^+. Tetracoordinate boronium ion BH_4^+ can be readily prepared[8,9] in the gas phase. Protonation of BH_3 was shown to be exothermic by 137.9 kcal/mol.[10] Structure **2** is an analogue of hydrazinium dication $NH_3NH_3^{2+}$. Leban et al. reported[11] the X-ray crystal structure of hydrazinium salt $NH_3NH_3^{2+}GeF_6^{2-}$. The N−N bond length of 1.428 Å in $NH_3NH_3^{2+}GeF_6^{2-}$ is slightly shorter than the calculated N−N bond length of 1.459 Å in **2**. However, the N−N bond length of 1.459 Å in **2** is close to the HF/6-31G* calculated N−N bond length of 1.442 Å in $NH_3NH_3^{2+}$.[12]

Protonation of **1** to form **3** was calculated to be highly exothermic by 192.4 kcal/mol (Table 1). In comparison protonation of N_2H_4 was calculated to be exothermic by 204.4 kcal/mol. The dissociation of **3** into $H_2BNH_2NH_2^+$ (**4**) and molecular H_2 was found to be endothermic by 5.8 kcal/mol (Table 2). On the other hand, dissociation of **3** into BH_4^+ and N_2H_4 was calculated to be highly endothermic by 82.1 kcal/mol (Table 2).

Table 2. Calculated Δ*H* for Various Dissociations[a]

dissociation process	Δ*H* (kcal/mol)
$H_3BNH_2NH_2$ (**1**) → $H_2NNH_2 + BH_3$	+27.8
$H_3BNH_2NH_3^+$ (**2**) → $H_2NNH_3^+ + BH_3$	+9.4
$H_4BNH_2NH_2^+$ (**3**) → $BH_4^+ + H_2NNH_2$	+82.1
$H_4BNH_2NH_2^+$ (**3**) → $H_2BNH_2NH_2^+$ (**4**) + H_2	+5.8
H_3BNH_2OH (**7**) → $H_2NOH + BH_3$	+27.5
$H_4BNH_2OH^+$ (**9**) → $BH_4^+ + H_2NOH$	+72.8
$H_4BNH_2OH^+$ (**9**) → $H_2BNH_2OH^+$ (**10**) + H_2	+6.2
H_3BOHOH (**13**) → $HOOH + BH_3$	+9.2
H_4BOHOH^+ (**14**) → $BH_4^+ + HOOH$	+51.0
H_4BOHOH^+ (**14**) → H_2BOHOH^+ (**15**) + H_2	−0.1

[a] At the B3LYP/6-311+G**//B3LYP/6-311+G** + ZPE level.

The reported X-ray structure[13] of $H_3BNH_2NH_2$ showed a B−N bond distance of 1.56 Å, which is significantly shorter than the calculated B−N distance of **1** (1.625 Å). On the basis of our present calculations, it is now probable that the Lewis acid or protolytic interaction (protosolvolytic activation[7]) with the B−H bond of $H_3BNH_2NH_2$ is responsible for the observed shorter B−N distance in the solid state. This type of interaction is also suggested to be responsible for the shorter B−N distance of H_3BNH_3 in the solid state compared to the gas-phase calculated data.[2]

Further protonation of **3** can take place on the terminal nitrogen atom to give $H_4BNH_2NH_3^{2+}$ (**5**) or on the B−H bond to give $H_5BNH_2NH_2^{2+}$ (**6**) (Figure 1). **5** was found to be 45.3 kcal/mol more stable than **6**. Dication **5** also contains a 3c-2e bond and can be considered as a complex of BH_4^+ and hydrazinium ion $N_2H_5^+$. Interestingly, protonation of **3** to form **5** was also calculated to be significantly exothermic by 70.7 kcal/mol.

Mono- and Diprotonated Hydroxylamine−Borane Complex H_3BNH_2OH. The structures of both N-coordinated borane−hydroxylamine complex H_3BNH_2OH (**7**) and O-coordinated borane−hydroxylamine complex $H_2NO(H)BH_3$ (**8**) were calculated (Figure 2). Complex **7** was found to be 21.7 kcal/mol more stable than complex **8**. Protonation of **7** can take place either on oxygen or on the B−H bond. No minimum structure could be located for the oxygen protonated structure at the B3LYP/6-311+G** level because of its immediate dissociation into $H_2BNH_3^+$ and H_2O. B−H protonation of **7** leads to $H_4BNH_2OH^+$ (**9**), which was calculated to be a stable minimum at the B3LYP/6-311+G** level. Cation **9** also contains a five-coordinate boron atom with a 3c-2e bond (Figure 2) and can

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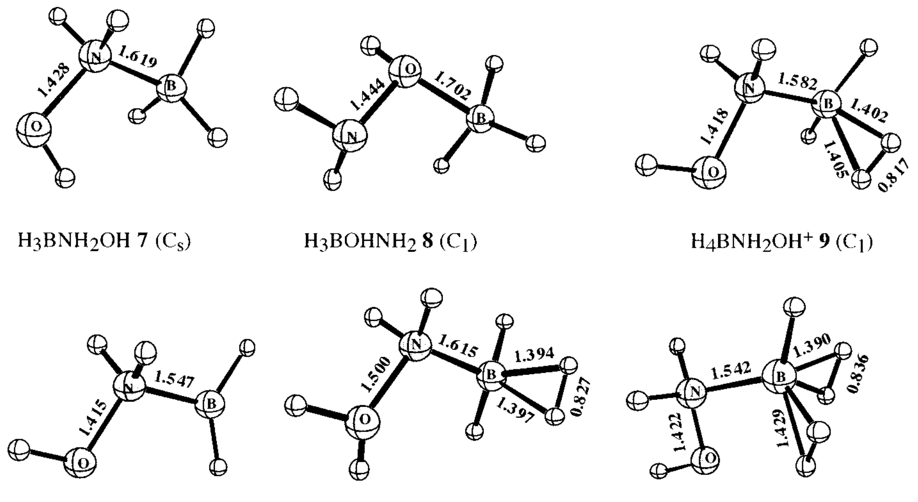
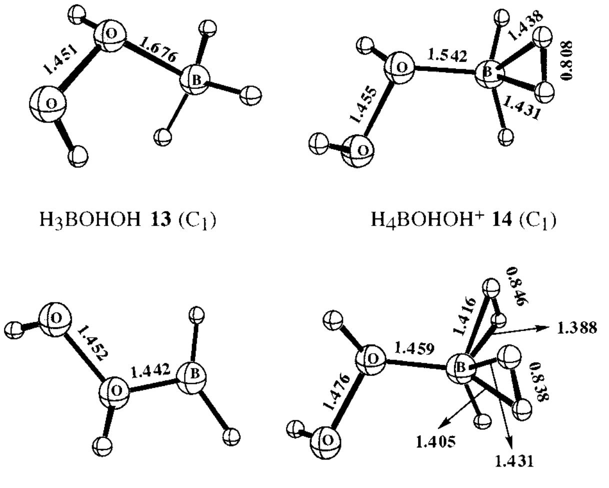


H_3BNH_2OH **7** (C_s) H_3BOHNH_2 **8** (C_1) $H_4BNH_2OH^+$ **9** (C_1)

$H_2BNH_2OH^+$ **10** (C_s) $H_4BNH_2OH_2^{2+}$ **11** (C_1) $H_5BNH_2OH^{2+}$ **12** (C_1)

Figure 2. B3LYP/6-311+G** structures of **7**−**12**.



H_3BOHOH **13** (C_1) H_4BOHOH^+ **14** (C_1)

H_2BOHOH^+ **15** (C_1) H_5BOHOH^{2+} **16** (C_1)

Figure 3. B3LYP/6-311+G** structures of **13**−**16**.

also be considered as a complex between NH_2OH and BH_4^+. Structure **9** is also characterized by a significant shortening of the B−N bond (1.582 Å) as compared to that of the parent **7** (1.702 Å).

Protonation of **7** to form **9** was also calculated to be highly exothermic by 205.2 kcal/mol (Table 1), which is even more exothermic than the protonation of hydrazine analogue **1** (192.4 kcal/mol). The dissociation of **9** into **10** and molecular H_2 was calculated to be endothermic by 6.2 kcal/mol (Table 2). This indicates that the 3c-2e BHH bond is rather weak. Dissociation of **9** into BH_4^+ and NH_2OH was calculated to be endothermic by 72.8 kcal/mol (Table 2).

Further protonation of **9** can take place on oxygen to give $H_4BNH_2OH_2^{2+}$ (**11**) or on the B−H bond to give $H_5BNH_2OH^{2+}$ (**12**) (Figure 2). Structure **11** is, however, 12.2 kcal/mol more stable than **12**. Protonation of **9** to form **11** was also calculated to be exothermic by 34.4 kcal/mol.

Mono- and Diprotonated Hydrogen Peroxide−Borane Complex H_3BOHOH. The calculated structure of hydrogen peroxide−borane complex H_3BOHOH (**13**) is depicted in Figure 1. Protonation of **13** can take place either on terminal oxygen or on the B−H bond. Similar to the hydroxylamine complex **7**, no minimum structure could be located for the terminal O-protonated structure at the B3LYP/6-311+G** level because of its immediate dissociation into $H_2BOH_2^+$ and H_2O. B−H protonation of **13** leads to H_4BOHOH^+ (**14**) (Figure 3), which was calculated to be a stable minimum at the B3LYP/6-311+G** level. Protonation of **13** to form **14** was calculated to be exothermic by 179.4 kcal/mol (Table 1). Further protonation on **14** seems to occur primarily on the B−H bond to give H_5BOHOH^{2+} (**16**) (Figure 3) since on PES the terminal oxygen protonated structure $H_4BOHOH_2^{2+}$ was not a true minimum. The structure $H_4BOHOH_2^{2+}$ was found to dissociate into $HOOH_2^+$ and BH_4^+ upon optmization at the B3LYP/6-311+G** level.

Conclusion

The structures and stabilities of mono- and diprotonated borane complexes H_3BX ($X = N_2H_4$, NH_2OH, and H_2O_2) and their neutral analogues were calculated using the density functional theory method at the B3LYP/6-311+G** level. All three global minimum structures of the monoprotonated H_3BX, **3**, **9**, and **14**, were found to be B−H protonated H_4BX^+ and were characterized as containing a hypercoordinate boron with a 3c-2e bond. The protonation energies of H_3BX to form H_4BX^+ were calculated to be highly exothermic. For hydrazine analogues, although both terminal N-protonated $H_3BNH_2NH_3^+$ (**2**) and B−H protonated $H_4BNH_2NH_2^+$ (**3**) are minima on the PES of monoprotonated $H_3BNH_2NH_2$, **3** is significantly more stable than **2** by 6.3 kcal/mol. This indicates that the bonded electron pair of the B−H bond is a better donor than the nonbonded nitrogen electron pair in hydrazine−borane complex **1**.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

IC990939P