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Proton Affinities of Borane−Amines: Consequences on Dihydrogen Bonding

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The calculated proton affinities of four borane−amines using Gaussian-2 theory have been found to be comparable to conventional bases such as water, methanol, and ammonia. On the other hand the structure of protonated borane−ammonia, $[HBH_3-NH_3]^+$, is found to be drastically different from that of protonated ammonia, $[HNH_3]^+$, and can appropriately be described as a η^2-H_2 complex with $[BH_2-NH_3]^+$ molecular cation. Further, the proton affinities of borane−amines are related to the ease of H_2 elimination.

Hydrogen bonding is ubiquitous in nature and has profound impact on structure and reactivity. The majority of hydrogen bonding observed, both in chemistry and biology, is the interaction between an acidic hydrogen, such as an O−H or a N−H group, and a lone pair of electrons on an electronegative element, such as O, N, or a halogen. Apart from the above-mentioned conventional hydrogen bonds, interactions analogous to hydrogen bonding involving unconventional donors and/or acceptors have also been reported.[1] In numerous cases hydrogen bonding between acidic hydrogens and π-bond electrons have also been observed, of which benzene−water complex is the most celebrated example.[2] Further examples include hydrogen bonds involving methyl groups and boron/metal hydrides.

The two most important factors that influence the structure and energetics of hydrogen bonding are (1) the acidity of the donor and (2) the proton affinity of the acceptor. It is well-known that the hydrogen bonds involving π-bond electrons are rather weak compared to those involving lone pair electrons, with typical stabilization energies roughly half of the latter. This is due to lower proton affinities of π-bond electrons at hydrogen bonding sites. If these results are extrapolated, straightforwardly, one could infer that a σ-bond will be an extremely weak hydrogen bond acceptor. Surprisingly, however, it has been observed in the outer coordination sphere of numerous transition metal complexes, that the metal−hydrogen (M−H) σ-bonds act as proton acceptors to acidic groups, such as N−H or O−H, forming an unconventional hydrogen bond of the type M−H···H−X (X = N, O), termed as the “dihydrogen bond”.[3]

Borane−amines are another important class of compounds, which exhibit dihydrogen bonding.[4] The borane−ammonia dimer, $[BH_3-NH_3]_2$, forms two identical dihydrogen bonds between amine proton and borane hydride of the type B−H····H−N, when two BH_3-NH_3 molecules are aligned head−tail in an antiparallel fashion.[5] The calculated interaction energy for the dimer is as large as 47 kJ mol^{-1}, corresponding to 23.5 kJ mol^{-1} for each dihydrogen bond. This clearly indicates that the strength of the dihydrogen bond is greater than hydrogen bond involving π-bond electrons and is in the same energy range as conventional hydrogen bonds involving lone pair electrons. Experimentally, on the basis of electronic and vibrational spectral shifts, Mikami’s group[6] has shown for several dihydrogen bonded complexes between borane−amines and molecules containing acidic hydrogens, such as phenol, aniline, and 2-pyridone, the stabilization energy of dihydrogen bonded complexes are comparable to conventional hydrogen bonded complexes. Several authors, based on ab initio and DFT calculations, drew similar conclusions.[7]

The interaction energies for the dihydrogen bonding involving borane−amines, derived from experiments as well as theory, suggest that the proton affinities of borane−amines are of the same order as conventional proton acceptors such as H_2O, MeOH, and NH_3. Unfortunately, however, there is no direct experimental evaluation of gas-phase proton affinities of borane−amines. The motivation for the present investigation is to calculate the proton affinities of borane−amines, (which are very well-known to form dihydrogen bonds, to understand the role of B−H bonds as dihydrogen bond acceptors), using Gaussian-2 (G2) theory and to compare with the known proton affinities of conventional bases. The G2 theory is a reliable method for calculating the molecular energies,[8] and has been successfully applied in calculating the absolute proton affinities of several bases, with an accuracy of 10 kJ mol^{-1}.[8,9] The proton affinities of four different borane−amines viz., borane−ammonia, borane−methylamine, borane−dimethylamine, and borane−trimethylamine have been calculated using Gaussian-98.[10] The four borane−amines investigated here are formed by progressive methyl substitution on ammonia moiety of borane−ammonia. This will allow the observation of the effect of methyl groups in the proton affinities and further comparison of it with the same effect in methylamines.

In the case of protonated borane−amines the HF/6-31G(*d*) structure is not a bound minimum and the G2 enthalpy is erroneous. To overcome this bottleneck, the protonated borane−amines are first optimized at MP2/6-31G(*d*) level of theory followed by a frequency calculation. G2 calculations are then performed using the MP2/6-31G(*d*) frequencies with STARTMP2 option. To maintain consistency, all the reported G2 calculations have been carried out using initial MP2/6-31G(*d*) geometries and frequencies. Figure 1 shows the plot of

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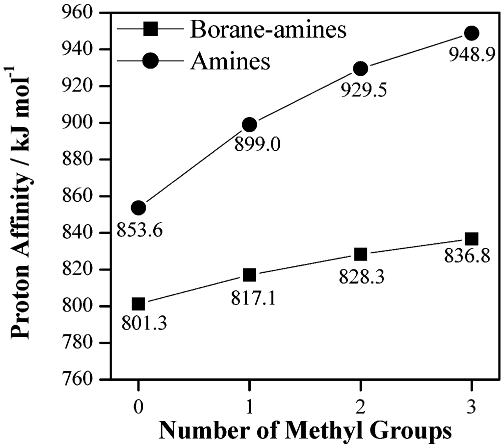

Figure 1. Plot showing the calculated proton affinities of borane−amines vs number of amine methyl groups. Also plotted are the evaluated gas-phase proton affinities of amines[11] vs the number of methyl groups.

calculated G2 proton affinities of borane−amines against the number of amine methyl groups. The proton affinity of borane−ammonia is 801.3 kJ mol^{-1}, being higher than H_2O (691.0 kJ mol^{-1}) and MeOH (754.3 kJ mol^{-1}) and lower than NH_3 (853.6 kJ mol^{-1}),[11] and is in accord with the comparable stabilization energies of dihydrogen and hydrogen bonded complexes. From Figure 1 it is also evident that the proton affinity of borane−amines increases with number of substituted methyl groups (801.3 kJ mol^{-1} for borane−ammonia to 836.8 kJ mol^{-1} in the case of borane−trimethylamine), with marginal stepwise decrease with successive addition of a methyl group. A comparison between the experimentally evaluated proton affinities of amines is also shown in Figure 1. Clearly, the proton affinity of an amine is higher than the corresponding borane−amine. Further, the quantum of increase for successive methyl group addition in the case of amines is higher than those of borane−amines. This can be attributed to the fact that the charge stabilizing methyl groups are directly attached to the protonated center in amines, while in the case of borane−amines the methyl groups are added in the α position.

It is well-known that the stabilization energy of a hydrogen bonded complex depends on the acidity of the donor and the proton affinity on the acceptor. This implies that for a given donor, the stabilization energy depends entirely on the proton affinity of the acceptor. For example, Mikami's group has shown for several hydrogen bonded complexes of phenol that the lowering of the O−H stretching vibration of the phenol moiety depends on the strength of the hydrogen bonded interaction and not the type hydrogen bonding (σ vs π).[12] Figure 2 shows the plot of lowering of O−H stretching frequency of the phenol moiety in hydrogen-bonded complexes with ethylene, acetylene, water, methanol, ammonia, and trimethylamine against the gas-phase proton affinities of the acceptors.[13] It is evident from Figure 2 that the lowering of O−H stretching frequency of the phenol moiety is linearly correlated with proton affinities of the bases. The observed linear correlation (Figure 2) implies that the stabilization of the hydrogen bonded complex is proportional to the proton affinity of the base. Assuming that the same linear correlation holds even for dihydrogen bonded complexes, the lowering of the O−H stretching vibration of the phenol moiety in the dihydrogen bonded phenol−borane−trimethylamine complex by 143 cm^{-1},[6b] can be used to estimate the proton affinity of borane−trimethylamine as 710 kJ mol^{-1} (■, Figure 2). However, this estimated value is about 125 kJ mol^{-1} lower than the G2 value of 836.8 kJ mol^{-1}. Since the G2 theory is known to be accurate within 10 kJ mol^{-1}, this implies that the above assumed linear correlation may not be applicable for dihydrogen bonded complexes. Several reports in the literature, including those by the author, routinely state that dihydrogen bonding is hydrogen bonding between oppositely charged hydrogens. From the results presented here, one can infer that the premise of the dihydrogen bond being another type of hydrogen bond might be incorrect.

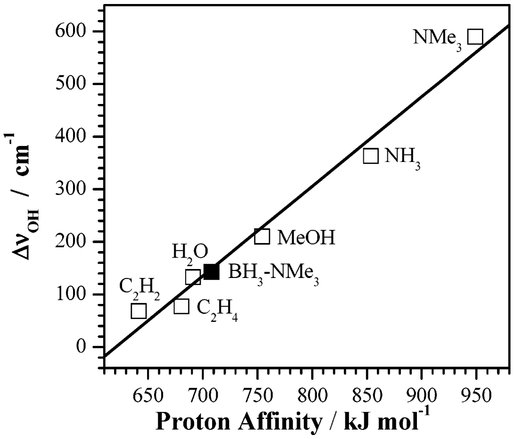

Figure 2. Plot of lowering of the O−H stretching frequency (☐) of phenol moiety in various hydrogen bonded systems vs proton affinities of the acceptors. The straight line is a linear least-squares fit to the data points, excluding the BH_3−NMe_3 (■). From the fit the proton affinity of borane−trimethylamine can be estimated as 710 kJ mol^{-1}.

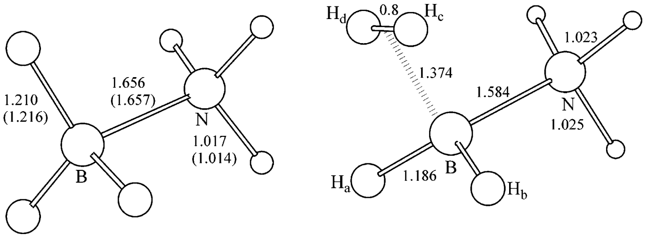

Figure 3. MP2/6-311++G(*d*,*p*) calculated structures of borane−ammonia and its protonated form. Distances are given in Å. The values shown in parentheses are for the experimental gas-phase structure of borane−ammonia.

G2 theory uses the structures calculated at MP2/6-31G(*d*) for the energy calculations, which are usually quite adequate.[8] To understand the origin of this large difference in the proton affinities between the calculated and estimated values from linear relationship (Figure 2), the structures of the protonated and deprotonated borane−amines have been recalculated at MP2/6-311++G(*d*,*p*) level. Figure 3 depicts the calculated structures of borane−ammonia and its protonated species. The structure of borane−ammonia is in good agreement with the gas-phase structure. The protonation occurs at the borane site, which induces drastic structural changes. In this case boron is pentacoordinate with two pairs of B−H bonds with and a considerably shortened B−N bond. Significantly the distance between hydrogens H_c and H_d is only 0.8 Å, comparable to the bond length of H_2 (0.746 Å). An alternate way of looking at this structure will be as a η^2-H_2 complex with $[BH_2-NH_3]^+$ molecular cation. Table 1 lists the relevant geometric parameters for all the four borane−amines and their protonated forms. The most interesting feature that can be noted is, the increase in the B−H_c and decrease in the H_c−H_d distances down the series. Short H−H distances have been observed in the case of pentacoordinated boranes, for instance, the one set of H−H distance (0.796 Å) in BH_5 is shorter than the other sets.[14] It has now been fairly established that protonated methane CH_5^+ can

TABLE 1: Selected Bond Distances, in Å, for the MP2/6-311++G (*d,p*) Calculated Structures of Borane−Amines and Their Protonated Forms

	deprotonated		protonated			
base	B−N	B−H	B−N	$B-H_a$	$B-H_c$	H_c-H_d
BH_3-NH_3	1.656	1.209	1.584	1.186	1.431	0.800
BH_3-NH_2Me	1.640	1.211	1.573	1.187	1.442	0.798
BH_3-NHMe_2	1.636	1.212	1.567	1.188	1.448	0.796
BH_3-NMe_3	1.641	1.212	1.566	1.189	1.452	0.796

TABLE 2: H_c-H_d Distances and the Stretching Frequencies in the Protonated Borane−Amines, Methane and Diborane, Calculated at the MP2/6-311++G(*d,p*) Level of Theory[a]

	H_c-H_d/Å	ν_{H-H}/cm^{-1}
$H^+BH_3-NH_3$	0.800	3682
$H^+BH_3-NH_2Me$	0.798	3709
$H^+BH_3-NHMe_2$	0.796	3726
$H^+BH_3-NMe_3$	0.796	3733
H^+CH_4	0.975	3279
$H^+B_2H_6$	0.800	3735
H_2	0.738	4533

[a] The corresponding value for H_2 is also given for comparison.

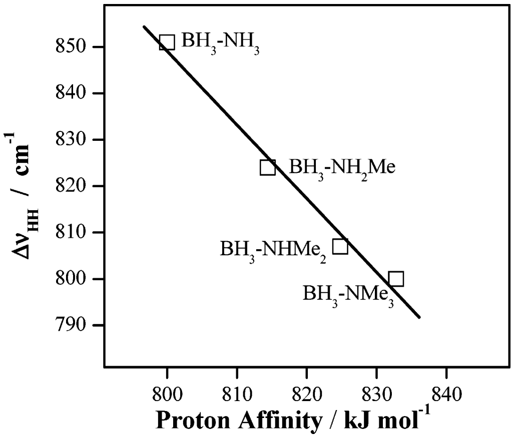

Figure 4. Plot of lowering of the H_c-H_d stretching frequency, calculated at MP2/6-311++G(*d,p*) level of theory, relative to H_2 in protonated forms of (1) BH_3-NH_3, (2) BH_3-NH_2Me, (3) BH_3-NHMe_2, and (4) BH_3-NMe_3. The straight line is a linear least-squares fit to the data points.

be conceived as a complex between H_2 and CH_3^+.[15] Therefore, as a control, the G2 proton affinity of methane has been calculated to be 533.6 kJ mol^{-1}, comparable to experimental value of 543.5 kJ mol^{-1}.[11] Interestingly, the H_c-H_d distance in CH_5^+ calculated at MP2/6-311++G(*d,p*) is 0.975 Å. Table 2 lists the H_c-H_d distances and stretching frequency, calculated at MP2/6-311++G(*d,p*) level of theory, and Figure 4 plots the H_c-H_d stretching frequency of protonated bases relative to free H_2 ($\Delta\nu_{HH}$) against MP2/6-311++G(*d,p*) proton affinities. It is evident from Figure 4 that the $\Delta\nu_{HH}$ goes down linearly with the increase in proton affinity. This clearly demonstrates that for borane−amines the proton affinity can be related to the ease of formation of H_2. The H_c-H_d stretching frequency of protonated form of B_2H_6 does not correlate favorably; this might be due to the fact that B_2H_6 is not a closed shell system and has a nonclassical structure.

Dehydrogenation from a dihydrogen bonded intermediate is well-known in the case of metal hydrides, and has been investigated both experimentally[16] and theoretically.[17] Dehydrogenation from dihydrogen bonded complexes of borane−amines has only been reported by Patwari et al. in the gas phase,[18] and no theoretical perspective has been reported so far. The present investigation on proton affinities of borane−amines clearly brings out the fact that dehydrogenation is a natural manifestation of the protonation of borane−amines.

In summary, the calculated gas-phase proton affinities of the borane−amines are comparable to the conventional bases such as water, methanol, and ammonia. The structure of the protonated borane−ammonia can be viewed η^2-H_2 complex with $[BH_2-NH_3]^+$ molecular ion, which eventually may lead to H_2 elimination. Furthermore, the proton affinities of the borane−amines are related to the ease of elimination of H_2.

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Supporting Information Available: Text describing methodology, a figure showing a plot of the red shift in electronic transition vs proton affinity, and tables of selected geometrical parameters and vibrational frequencies of borane−amines and their protonated forms calculated at various levels of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For example, see: Fujii, A.; Patwari, G. N.; Ebata, T.; Mikami, N. *Int. J. Mass. Spectrom.* **2002**, *202*, 289.

(2) Suzuki, S.; Green, P. G.; Baumgarner, R. E.; Dasgupta, S.; Goddard, W. A., III; Blake, G. A. *Science* **1992**, *257*, 942.

(3) (a) Stevans, R. C.; Bau, R.; Milstein, R.; Blum, O.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1990**, 1429. (b) Vander Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4381.

(4) (a) Klooster, W. T.; Koetzle, T. F.; Siegbahn, P. E. M.; Richardson, T. B.; Crabtree, R. H. *J. Am. Chem. Soc.* **1999**, *121*, 6337. (b) Richardson, T. B.; Gala, S. D.; Crabtree, R. H.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1995**, *117*, 12875.

(5) Merino, G.; Bakhmutov, V. I.; Vela, A. *J. Phys. Chem. A* **2002**, *106*, 8491.

(6) (a) Patwari, G. N.; Ebata, T.; Mikami, N. *J. Chem. Phys.* **2000**, *113*, 9885. (b) Patwari, G. N.; Ebata, T.; Mikami, N. *J. Chem. Phys.* **2001**, *114*, 8877. (c) Patwari, G. N.; Ebata, T.; Mikami, N. *J. Phys. Chem. A* **2001**, *105*, 8642. (d) Patwari, G. N.; Ebata, T.; Mikami, N. *J. Chem. Phys.* **2002**, *116*, 6056. (e) Patwari, G. N.; Ebata, T.; Mikami, N. *Chem. Phys.* **2002**, *283*, 193.

(7) (a) Kulkarni, S. A. *J. Phys. Chem. A* **1998**, *102*, 7704. (b) Kulkarni, S. A.; Srivastava, A. K. *J. Phys. Chem. A* **1999**, *103*, 2836. (c) Grabowski, S. J. *Chem. Phys. Lett.* **2000**, *327*, 203. (d) Popelier, P. L. A. *J. Phys. Chem. A* **1998**, *102*, 1873.

(8) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(9) (a) Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 4885. (b) East, A. L. L.; Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1997**, *118*, 9014.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; et al. *GAUSSIAN 98 (Revision A.11.1.1)* Gaussian, Inc.: Pittsburgh, PA, 2001.

(11) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.

(12) (a) Iwasaki, A.; Fujii, A.; Ebata, T.; Mikami, N. *J. Phys. Chem.* **1996**, *100*, 16053. (b) Fujii, A.; Ebata, T.; Mikami, N. *J. Phys. Chem. A* **2002**, *106*, 8554.

(13) The phenol−benzene complex, which though π-hydrogen bonded falls off the correlation line, however, is an exception. See ref 12b for a complete discussion.

(14) (a) Tague,, T. J., Jr.; Andrews, L. *J. Am. Chem. Soc.* **1994**, *116*, 4790. (b) Schreiner, P. R.; Schaefer, H. F.; Schleyer, P. R. *J. Chem. Phys.* **1994**, *101*, 7625. (c) Kim K. H.; Kim Y. *J. Chem. Phys.* **2004**, *120*, 623.

(15) (a) Bunker, P. J.; Ostojic, B.; Yurchenko, S. *J. Mol. Struct.* **2004**, *695*, 253. (b) Schreiner, P. R.; Kim, S. J.; Schaefer, H. F., III; Schleyer, P. V. R. *J. Chem. Phys.* **1993**, *99*, 3716.

(16) (a) Atwood, J. L.; Koutsantonis, G. A.; Lee, F.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1994**, 91. Gruet, K.; Clot, E.; Eisenstein, O.; Lee, D. H.; Patel, B.; Macchioni, A.; Crabtree, R. H. *New J. Chem.* **2003**, *27*, 80. (c) Custelcean, R.; Jackson, J. E. *Chem. Rev.* **2001**, *101*, 1963.

(17) (a) Kulkarni, S. A. *J. Phys. Chem. A* **1999**, *103*, 9330. (b) Liu, Q.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, *117*, 10108. (c) Rozas, I.; Alkorta, I.; Elguero. J. *Chem. Phys. Lett.* **1997**, *275*, 423.

(18) Patwari, G. N.; Ebata, T.; Mikami, N. *J. Phys. Chem. A* **2001**, *105*, 10753.