Proton Affinity Correlations between Hydrogen and Dihydrogen Bond Acceptors

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Several series of hydrogen- and dihydrogen-bonded complexes with HCN, C_2H_2, HF, H_2O, CH_3CONH_2, and CH_3COOH as donors and H_2O, MeOH, EtOH, MeOMe, NH_3, NH_2Me, $NHMe_2$, NMe_3, $NEtMe_2$, and BH_3-NMe_3 as acceptors were investigated using the MP2/6-311++G(d,p) level of theory. The total lowering of the X−H stretching frequencies in the hydrogen-bonded complexes were linearly correlated with the proton affinities of the accepting bases. From comparison of hydrogen- and dihydrogen-bonded complexes, a scaling factor to estimate the exact proton affinity of a dihydrogen bond acceptor was developed. Further, the scaling factor involving linear donors (1.204) is marginally higher than that involving nonlinear donor molecules (1.162). Finally, it was found that, given identical conditions, a hydrogen bond will be about 16−20% stronger than a corresponding dihydrogen bond.

Introduction

Dihydrogen bonding essentially is an interaction analogous to hydrogen bonding, between two oppositely charged hydrogen atoms, and can be represented as $E-H^{\delta-}\cdots{}^{\delta+}H-X$, where E and X are less and more electronegative than hydrogen, respectively.[1] The existence of dihydrogen bonding has been well established, and the early examples came from the crystal structures of some transition metal complexes wherein a metal hydride was found to be in close contact with acidic hydrogen in the outer coordination sphere. Apart from metal hydrides, borane amines have played an important role in understanding the dihydrogen bonds. For instance, the neutron diffraction structure of borane−ammonia has been able to pinpoint the exact positions of the two oppositely charged hydrogen atoms, and unequivocally established the formation of dihydrogen bonding.[2] The X-ray and neutron diffraction studies on crystals provide exquisite details of intra- and intermolecular dihydrogen-bonded structures; however, in most of the cases the energetics of interaction were derived using ab initio/DFT calculations.[3,4] Once again borane−ammonia has played a crucial role to this end. Several authors have investigated the formation of the borane−ammonia dimer, $[BH_3-NH_3]_2$, which forms two pairs of symmetrically bifurcated dihydrogen bonds between amine proton and borane hydride of the type N−H···H−B, when two BH_3-NH_3 molecules are aligned head−tail in an antiparallel fashion.[4] The strength of the dihydrogen bond is 23.5 kJ mol^{-1} for each dihydrogen bond, which is comparable to conventional hydrogen bonds.[4c]

Mikami's group has reported the formation of several dihydrogen-bonded complexes, of the type B−H···H−X, (X = O, N), between borane amines and molecules containing acidic hydrogens, such as phenol,[5] aniline,[6] and 2-pyridone,[7] in the gas phase. On the basis of observed spectral shifts in the electronic and vibrational transitions, it was inferred that strength of the dihydrogen-bonded complexes are in the same range as conventional hydrogen bonds. Several authors drew similar conclusions following investigation of a variety of dihydrogen-bonded systems using ab initio and DFT methods.[3−7] Further, a sizable number of reports exist in the literature, which, through the atoms in molecules (AIM) approach, have shown the existence of a favorable noncovalent interaction between the two oppositely charged hydrogen atoms in the dihydrogen-bonded systems.[8]

The two most crucial factors that influence the structure and the energetics of hydrogen bonding are the acidity of the donor and the proton affinity of the acceptor. This implies that, for a given donor, the stabilization energy should be proportional to the proton affinity of the acceptor. It has been long realized that IR spectroscopy in the X−H (X = O, N, C) stretching region is the most important spectroscopic tool for the identification of hydrogen bonding.[9] This is due to the fact that these groups being involved directly are very sensitive to hydrogen-bonded structures and exhibit a characteristic shift to a lower frequency upon hydrogen bonding, which depends upon the strength of interaction. This implies that the lowering of the donor stretching frequency upon hydrogen bonding should be linearly correlated with the proton affinity of the acceptor. Graton et al. investigated the complex formation between *p*-fluorophenol with a wide variety of secondary amines in CCl_4 and showed that the $\Delta\nu_{OH}$ for *p*-fluorophenol is linearly correlated to the equilibrium constant for the hydrogen bond formation.[10] 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 is linearly correlated to the proton affinity of the acceptor.[11] Further, it was also shown that, in the lowering of the O−H stretching frequency of the phenol moiety, the strength of the interaction depends solely on the proton affinity of the hydrogen bond acceptor and not on the type of interaction (σ vs π). In the event dihydrogen bonding can be classified as just another mode of hydrogen-bonded interaction, the same correlation should hold. Recently, we have shown in the case of dihydrogen-bonded complexes of phenol and acetylene with borane−trimethylamine that the shifts in the stretching frequencies of the donors (phenol, acetylene) do not correlate with the proton affinity of borane−trimethylamine.[12] Furthermore, it was also shown that the linear correlation between frequency shifts and the proton affinities involving hydrogen-bonded species grossly underestimates the

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proton affinity of borane−trimethylamine, a dihydrogen bond acceptor. On the basis of the estimated proton affinity of borane−trimethylamine, it was inferred that the premise of dihydrogen bonding as another type of hydrogen bonding may be incorrect.

In this article, we extend the investigation to understand the quantitative relationship between the interaction energies of dihydrogen-bonded and hydrogen-bonded systems and to develop a scaling law between these two sets of interactions. To this end, we investigated, using ab initio methods, several series of hydrogen- and dihydrogen-bonded complexes with hydrogen cyanide (HCN), acetylene (C_2H_2), hydrogen fluoride (HF), water (H_2O), acetamide (CH_3CONH_2), and acetic acid (CH_3COOH) as donors and water (H_2O), methanol (MeOH), ethanol (EtOH), dimethyl ether (MeOMe), ammonia (NH_3), methylamine (NH_2Me), dimethylamine ($NHMe_2$), trimethylamine (NMe_3), *N*,*N*-dimethylethylamine ($NEtMe_2$), and borane−trimethylamine ($BH_3{-}NMe_3$; BTMA) as acceptors. Finally, the experimentally observed spectral shifts in the dihydrogen-bonded complexes of phenol with borane−trimethylamine (BTMA) and diethylmethylsilane (DEMS) were used as test cases to verify the scaling law.

Methodology

The equilibrium structures of the monomers and various complexes were calculated at the MP2(FC)/6-311++G(d,p) level. The nature of the stationary points obtained was verified by calculating the vibrational frequencies at the same level of theory. The calculated vibrational frequencies were scaled for the monomers to match with the experimental values, wherever available, and the same scaling factor was used for the corresponding complexes. The stabilization energies were calculated and in each case were corrected for the zero point vibrational energy (ZPVE). Since the primary motivation of this work is to correlate the shifts in the stretching frequencies of the (di)hydrogen bond donors with the proton affinity of the acceptors, the proton affinities, wherever unavailable, were calculated using G2 theory.[13] All calculations were carried out on a Linux-based PC using the Gaussian 98 suite of programs.[14]

Results and Discussion

The H···H distance of less than 2.4 Å, twice the van der Waals radius of the hydrogen atom (1.2 Å), is the most used geometrical criterion to identify the formation of dihydrogen bonds. However, due to the electrostatic nature of (di)hydrogen bonding, the van der Waals cutoff criterion is strongly criticized, as electrostatic interaction acts beyond this distance.[15] Moreover, it has been reported recently that, for C−H bonds, the van der Waals radius of hydrogen atom is marginally greater than 1.2 Å.[16] However, to be inline with the existing reports in the literature, we have considered 2.4 Å as the cutoff for the formation of dihydrogen bonds. Figure 1 depicts the calculated structures of BTMA with hydrogen cyanide (HCN), acetylene (C_2H_2), hydrogen fluoride (HF), water (H_2O), acetamide (CH_3CONH_2), and acetic acid (CH_3COOH). In each case the positively charged hydrogen of the donor interacts with the two negatively charged hydrogens on BTMA, forming a dihydrogen-bonded complex with a pair of bifurcated dihydrogen bonds. Interestingly, it was observed that, with the linear donors, C_2H_2 and HCN, the dihydrogen bonds are symmetrically bifurcated, while for the nonlinear donors, H_2O, CH_3CONH_2, and CH_3COOH, they are asymmetrically bifurcated. This may be rationalized on the basis of symmetry/asymmetry in the electron density around the positively charged hydrogen approaching the two negatively charged hydrogens of the BH_3 group. Though HF is a linear molecule, it forms an asymmetrical bifurcated structure, which may be attributed to the fluoro effect. The B−H···H angles are the range of 84°−99°, while X−H···H angles, comparatively more linear, are in the range of 140°−157°, in agreement with results reported in the literature.[1−8] Table 1 lists the relevant intermolecular geometrical parameters and ZPVE corrected stabilization energies for the dihydrogen-bonded complexes.

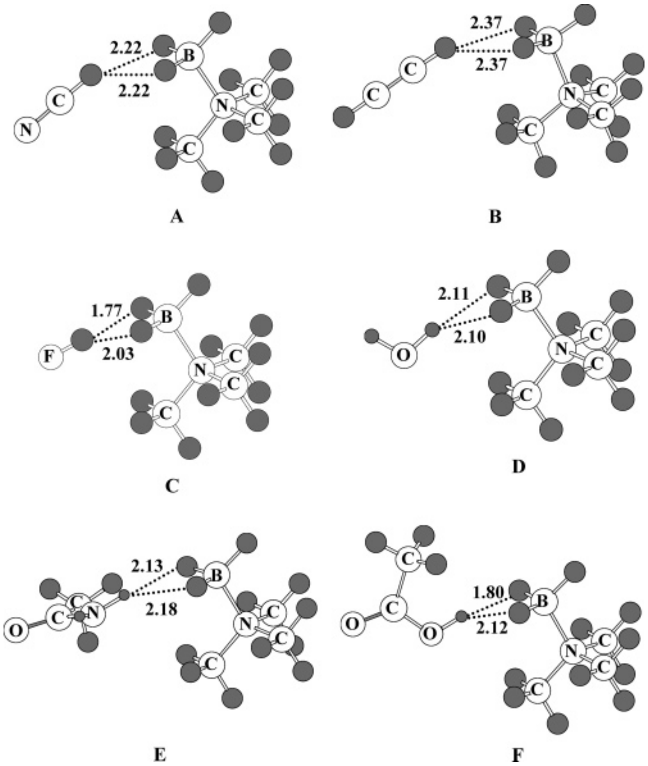

Figure 1. Structures of dihydrogen-bonded complexes of BTMA with (A) HCN, (B) C_2H_2, (C) HF, (D) H_2O, (E) CH_3CONH_2, and (F) CH_3COOH calculated at MP2/6-311++G(d,p) level. Hydrogen atoms are shown in gray, and distances are given in Å.

Since the primary motivation of this work is to compare the energetics of hydrogen- and dihydrogen-bonded complexes, several hydrogen-bonded complexes of hydrogen cyanide (HCN), acetylene (C_2H_2), hydrogen fluoride (HF), water (H_2O), acetamide (CH_3CONH_2), and acetic acid (CH_3COOH) as donors and water (H_2O), methanol (MeOH), ethanol (EtOH), dimethyl ether (MeOMe), ammonia (NH_3), methylamine (NH_2Me), dimethylamine ($NHMe_2$), trimethylamine (NMe_3), and *N*,*N*-dimethylethylamine ($NEtMe_2$) as acceptors were investigated along with the dihydrogen-bonded complexes of borane−trimethylamine (BTMA). Table 2 lists the ZPVE corrected stabilization energies for all the complexes. According to Pimentel and McClellan, the IR spectroscopy of the X−H stretching vibration of the donor provides a quantitative index of the physical and chemical properties of the hydrogen-bonded systems.[9] Therefore, the X−H stretching frequencies of the donor molecules were examined for all the complexes. Table 3 lists the X−H stretching frequencies of all the donors and their shifts upon hydrogen/dihydrogen bonded complex formation. For each donor the shift in X−H stretching frequencies were correlated with the proton affinity of the acceptor. In the cases of C_2H_2, H_2O, and CH_3CONH_2, being donors, we have used the total lowering of the X−H stretching frequencies [$\sum(\Delta\nu_{XH})$] to correlate with the proton affinities of the acceptors. This can be justified due to the fact that, even though the hydrogen bond

TABLE 1: Optimized H···H Distances (Å), B−H···H and X−H···H Angles (deg), and ZPVE Corrected Stabilization Energies (kJ mol^{-1}) for Various Dihydrogen-Bonded Complexes of BTMA

	HCN	C_2H_2	HF	H_2O	CH_3CONH_2	CH_3COOH
H···H	2.21	2.37	1.77, 2.03	2.12, 2.09	2.17, 2.13	2.12, 1.80
−B−H···H	95.8	97.0	96.5, 84.3	92.0, 93.3	93.5, 95.6	83.6, 98.8
−X−H···H	142.2	143.9	150.6, 140.6	145.8,146.8	139.8,157.6	137.8,155.8
ΔE	16.5	13.5	26.6	19.6	23.9	36.8

TABLE 2: ZPVE Corrected Stabilization Energies (kJ mol^{-1}) for Various Hydrogen- and Dihydrogen-Bonded Complexes Calculated at MP2/6-311++G(d,p) Level

	HCN	C_2H_2	HF	H_2O	CH_3CONH_2	CH_3COOH
H_2O	14.3	8.9	28.6	15.5	19.7	29.4
MeOH	17.0	11.4	34.1	19.1	24.1	35.4
EtOH	18.2	12.2	35.9	19.7	26.3	38.6
MeOMe	17.8	13.5	36.4	20.4	26.4	38.3
NH_3	18.8	12.2	43.3	21.1	24.3	38.6
NH_2Me	21.6	14.4	48.6	24.9	26.7	44.8
$NHMe_2$	25.1	16.4	52.0	26.7	29.9	48.8
NMe_3	24.9	17.3	54.1	27.6	32.5	52.3
$NEtMe_2$	25.7	18.7	55.6	29.9	33.5	55.2
BTMA	16.5	13.5	26.6	19.6	23.9	36.8

TABLE 3: X−H Stretching Frequencies and Their Shifts[a] in Various Hydrogen- and Dihydrogen-Bonded Complexes Calculated at MP2/6-311++G(d,p) Level

	HCN	C_2H_2		HF	H_2O		CH_3CONH_2		CH_3COOH
	3311	3373	3288	4138	3756	3656	3550	3437	3582
H_2O	3207	3353	3246	3826	3728	3584	3522	3403	3421
	(104)	(20)	(42)	(312)	(28)	(72)	(28)	(34)	(161)
MeOH	3169	3350	3230	3691	3721	3543	3514	3385	3351
	(142)	(23)	(58)	(447)	(35)	(113)	(36)	(52)	(231)
EtOH	3166	3350	3229	3663	3721	3534	3507	3372	3331
	(145)	(23)	(59)	(475)	(35)	(122)	(43)	(64)	(251)
MeOMe	3136	3348	3215	3622	3718	3509	3506	3362	3297
	(175)	(25)	(73)	(516)	(38)	(147)	(44)	(75)	(285)
NH_3	3098	3347	3197	3426	3719	3464	3496	3314	3178
	(213)	(26)	(91)	(712)	(37)	(190)	(54)	(123)	(404)
NH_2Me	3037	3342	3171	3267	3714	3393	3489	3268	3056
	(274)	(31)	(117)	(871)	(42)	(263)	(61)	(169)	(526)
$NHMe_2$	2976	3340	3143	3128	3749	3342	3486	3230	2961
	(335)	(33)	(145)	(1010)	(7)	(314)	(64)	(207)	(621)
NMe_3	2934	3339	3117	3042	3707	3306	3485	3198	2906
	(377)	(34)	(171)	(1096)	(49)	(352)	(65)	(239)	(676)
$NMeEt_2$	2931	3338	3124	3012	3704	3283	3502	3207	2883
	(380)	(35)	(164)	(1126)	(52)	(373)	(48)	(230)	(699)
BTMA	3237	3355	3257	3869	3720	3589	3513	3400	3420
	(74)	(18)	(31)	(269)	(36)	(67)	(37)	(37)	(162)

[a] The shifts are listed in parentheses.

formation is with only one of the X−H bonds, the other X−H bond gets perturbed as a consequence of decoupling.

Figure 2A shows the plot of the total lowering of C−H stretching frequencies of HCN moiety in various hydrogen-bonded complexes against the gas-phase proton affinities of the acceptors. It can be seen that shifts in the C−H stretching frequency ($\Delta\nu_{CH}$) of the HCN moiety are linearly correlated with the proton affinities of the acceptors. The HCN−MeOMe complex, however, was not included in the correlation. Using the shift of 175 cm^{-1} for the HCN−MeOMe complex (see Table 3), the proton affinity of MeOMe can be estimated as 778 kJ mol^{-1} (left-pointing solid triangle; Figure 2A), from the correlation. Further, from the same correlation, using $\Delta\nu_{CH}$ of 74 cm^{-1} for the HCN−BTMA dihydrogen-bonded complex, the proton affinity of BTMA can be estimated as 726 kJ mol^{-1} (●; Figure 2A). Similarly, the total lowering of the X−H stretching frequencies for each of the remaining five donors, viz., C_2H_2, HF, H_2O, CH_3CONH_2, and CH_3COOH upon formation of hydrogen-bonded complexes with the acceptors H_2O, MeOH, EtOH, NH_3, NH_2Me, $NHMe_2$, NMe_3, and $NEtMe_2$ was plotted against the proton affinities of the acceptors, shown in Figure 2B−F. Once again, in each case a linear correlation was observed. Using the calculated frequency shift for the donor−MeOMe complex, the proton affinity of MeOMe was estimated from each correlation and the results are tabulated in Table 4. Additionally, the proton affinity of BTMA was also estimated, in each case, from the same correlation, and the values are once again listed in Table 4.

The hydrogen-bonded interactions with six different donors, viz., HCN, C_2H_2, HF, H_2O, CH_3CONH_2, and CH_3COOH with a large spread in acid dissociation constants and eight acceptors, viz., H_2O, MeOH, EtOH, NH_3, NH_2Me, $NHMe_2$, NMe_3, and $NEtMe_2$ with proton affinities ranging from 600 to 980 kJ mol^{-1} were investigated. Figure 2 clearly shows that the total lowering in the X−H stretching frequencies of each donor is linearly correlated with the proton affinity of the acceptors. Further, in each case, the proton affinity of MeOMe was estimated from the correlation (see Table 4), and the average estimated proton affinity of MeOMe from the six linear correlations is 781.5 kJ mol^{-1}, which is in excellent agreement with the experimental value of 792 kJ mol^{-1}.[17] Similarly, the proton affinity of BTMA was also estimated from the six linear correlations. An interest-

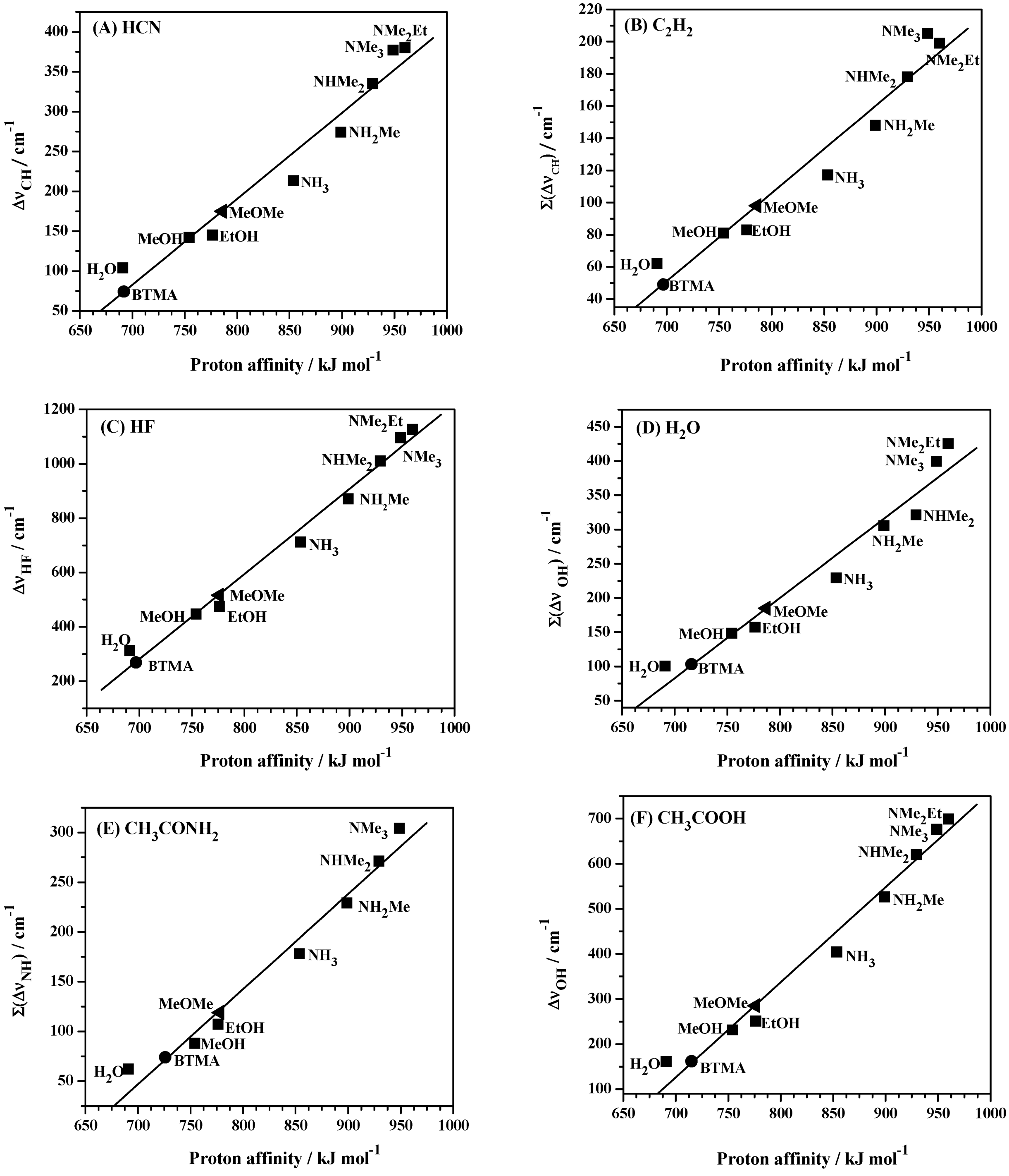

Figure 2. Plots of total lowering of X−H stretching frequencies of (A) HCN, (B) C_2H_2, (C) HF, (D) H_2O, (E) CH_3CONH_2, and (F) CH_3COOH moieties in various hydrogen-bonded complexes vs proton affinities of the acceptors. The straight line is a linear-least-squares fit to the data points, excluding the MeOMe (left-pointing solid triangle) and BTMA (●).

TABLE 4: Estimated Proton Affinities from the Correlation Plots

	HCN	C_2H_2	HF	H_2O	CH_3CONH_2	CH_3COOH	estd PA	exptl PA[a]	ratio
MeOMe	786	786	776	787	778	776	781.5	792.3	1.014
BTMA[b]	692	697	697				695.3	836.8	1.204
BTMA[c]				717	726	718	720.3	836.8	1.162

[a] Proton affinity of BTMA was calculated using G2 theory. [b] Linear donors. [c] Nonlinear donors.

ing observation can be made from Table 4: the proton affinity (PA) of BTMA estimated from the correlation for the linear donors, viz., HCN, C_2H_2, and HF (average PA 695.3 kJ mol^{-1}) was always lower in comparison with that estimated from nonlinear donors, viz., H_2O, CH_3CONH_2, and CH_3COOH (average PA 720.3 kJ mol^{-1}). However, the estimated proton affinity of BTMA is much less than its G2 proton affinity value of 836.2 kJ mol^{-1}.[12a] Another interesting observation is that, even though linear HF forms an asymmetrically bifurcated dihydrogen-bonded complex with BTMA, similar to other

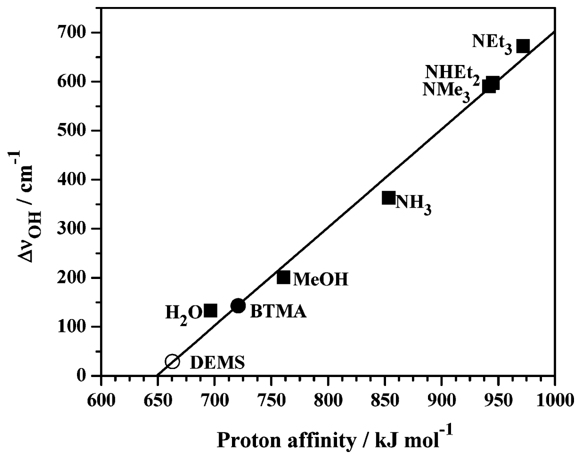

Figure 3. Plot of lowering of O−H stretching frequency of phenol moiety in various hydrogen-bonded complexes vs proton affinities of the acceptors. The straight line is a linear-least-squares fit to the data points, excluding the BTMA (●) and DEMS (○). From the fit the proton affinities of BTMA and DEMS can be estimated as 721 and 663 kJ mol^{-1}, respectively.

nonlinear molecules, the estimated proton affinity is in accord with that of two other linear molecules, HCN and C_2H_2. The most important inference is that the proton affinity correlation for the hydrogen-bonded systems underestimates the proton affinity of dihydrogen bond acceptor. This implies that the estimated proton affinity of a dihydrogen bond acceptor has to be scaled to match the experimental value. The scaling factors are 1.204 for the linear donors and 1.162 for the nonlinear donors (see Table 4).

At this stage, it is important to verify the reliability of the scaling factors. Mikami and co-workers have investigated several hydrogen- and dihydrogen-bonded complexes of phenol in the gas phase, using the fluorescence dip infrared (FDIR) spectroscopic technique.[5,11,18] Figure 3 shows the plot of the shift in the O−H stretching frequency of the phenol moiety in various hydrogen-bonded complexes vs proton affinities of the acceptors.[19] It is evident from Figure 3 that, once again, the lowering of the O−H stretching frequency of the phenol moiety is linearly correlated with proton affinities of the bases. Using the observed lowering of the O−H stretching frequency of 143 cm^{-1} in phenol−borane−trimethylamine (phenol−BTMA) and 29 cm^{-1} in phenol−diethylmethylsilane (phenol−DEMS), the proton affinities of BTMA and DEMS can be estimated as 721 and 663 kJ mol^{-1}, respectively. The proton affinities of both BTMA and DEMS from the linear correlation are grossly underestimated from the corresponding G2 values of 836.8 and 768 kJ mol^{-1}, respectively. This once again points to the fact that dihydrogen bonding is not a simple variation of hydrogen bonding.[12]

Since both BTMA and DEMS are nonlinear molecules, the estimated proton affinities should be scaled with the factor of 1.162 before comparison with the experimental values. Scaled proton affinity values of BTMA and DEMS are 837.8 and 770.4 kJ mol^{-1}, respectively, which are in excellent agreement with the corresponding G2 proton affinity values of 836.8 and 768 kJ mol^{-1}.[20] This excellent agreement between the scaled estimated and G2 values of proton affinities verifies the credibility of our scaling factors for dihydrogen-bonded complexes. Furthermore, since it is well-known that the shift in X−H is a quantitative measure of the stabilization of a hydrogen-bonded complex,[9,15] the linear correlation (Figures 2 and 3) implies that the stabilization of the hydrogen-bonded complex is proportional to the proton affinity of the accepting base. Hence, from the data presented above it can be inferred that given the same values of proton affinities the hydrogen-bonded complex will be 16−20% stronger than the corresponding dihydrogen-bonded complex.

Conclusions

In summary, several hydrogen-bonded complexes of six different donor molecules, viz., HCN, C_2H_2, HF, H_2O, CH_3CONH_2, and CH_3COOH were calculated at the MP2/6-311++G(d,p) level of theory along with dihydrogen-bonded complexes of borane−trimethylamine. The shifts in the X−H stretching frequencies of the donors were examined and were correlated with the proton affinities of the acceptors. The proton affinity of borane−trimethylamine, a dihydrogen bond acceptor, was grossly underestimated using the linear correlation of hydrogen-bonded systems. The estimated proton affinity of a dihydrogen bond acceptor should be scaled by a factor of 1.204 in the case of linear donors and 1.162 for nonlinear donors in order to compare with the experimental value. Finally, it can be said that under identical conditions the dihydrogen-bonded complex is about 16−20% weaker than the corresponding hydrogen-bonded complex.

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(19) 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 of hydrogen bonding (σ vs π). However, we now believe that this might not be entirely correct. Hence, in the present paper we have chosen only the σ hydrogen-bonded complexes.

(20) The experimental proton affinities of both BTMA and DEMS are not available in the literature; hence we compare with the G2 proton affinities. It is well-known that G2 theory is a reliable method for calculating the molecular energies,[13] and it has been successfully applied in calculating the absolute proton affinities of several bases, with an accuracy of ±10 kJ mol^{-1}. For example, see: (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**, *119*, 9014.