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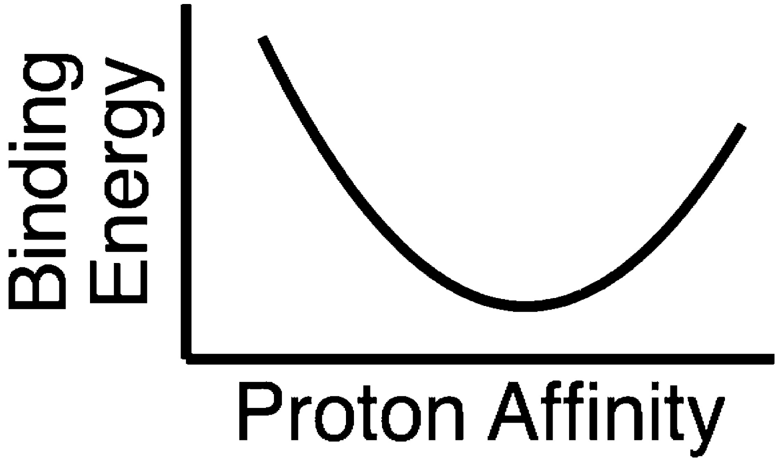

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Proton-Bound Homodimers: How Are the Binding Energies Related to Proton Affinities?

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Abstract: High-level quantum chemical calculations [G3(MP2)-RAD//MP2/6-31+G(d,p)] have been employed to investigate the relationship between the binding energy (BE) of a substrate (X) and its protonated form $[H-X]^+$ with the proton affinity (PA) of the substrate (X) in several series of protonated homodimers ($[X\cdots H-X]^+$). We find that for each series of closely related substrates, the binding energy (BE) is correlated with the proton affinity (PA) in an approximately quadratic manner. Thus, for a given series, the BE initially increases in magnitude with increasing PA, reaches a point of maximum binding, and then becomes smaller as the PA increases further. This behavior can be attributed to the competing effects of the exothermic partial protonation of the substrate and the endothermic partial deprotonation of the protonated substrate. As the PA increases, protonation of X contributes to increased binding but the penalty for partial deprotonation of $[H-X]^+$ also increases. Once the PA becomes sufficiently high, the penalty for the partial deprotonation of $[H-X]^+$ dominates, leading to maximum binding occurring at intermediate PA.

Introduction

Hydrogen bonding and protonation play a vital role in many chemical and biological systems. As a result, these interactions have been extensively investigated both experimentally and theoretically.[1] They are related phenomena that can both be viewed as acid−base interactions, with hydrogen bonding being a relatively weak interaction, while protonation is very strong. It has been observed, for a set of closely related bases, that there exist linear correlations between proton affinities and hydrogen-bond enthalpies.[2] In addition, on the basis of structure correlations from X-ray crystallographic data, it has been proposed that hydrogen-bond formation in general could be regarded as the incipient stage of the proton-transfer process.[3] These observations suggest that protonation data should be useful for predicting features of hydrogen bonding, such as the conditions under which hydrogen-bond formation leads to proton transfer. On the other hand, it has been demonstrated by quantum chemical calculations that protonation and hydrogen bonding may occur at different sites of a given substrate.[4] This has been attributed to hydrogen bonding preferring a site with a localized lone pair, whereas protonation prefers a site that leads to a product in which the charge can be delocalized.

It has been found that, for closely related hydrogen-bonded systems that exhibit a single minimum along the proton-transfer coordinate, the binding energy between the proton donor (H−D) and the acceptor (A) shows an inverse relationship with the difference in the proton affinities (ΔPA) of D and A.[5] Thus, the closer the proton affinities of D and A, the stronger the binding, with the strongest binding occurring when ΔPA is zero, that is, when D and A are the same. However, within this class of protonated homodimers ($\Delta PA = 0$) the bond energies are not all equal. For instance, the bond energies in $[H_2O\cdots H-OH_2]^+$ and $[H_3N\cdots H-NH_3]^+$ are 150.7 and 103.8 kJ mol^{-1}, respectively.[6,7] What determines the binding energies in such systems? Do the binding energies increase or decrease with increasing proton affinity? In this article, we examine the relationship between hydrogen-bond energies and proton affinities for the proton-bound homodimers $[X\cdots H-X]^+$ for the variety of components (X) shown in Figure 1. These substrates are chosen for their simplicity (sp^3 first-row bases) and for their varying electronic effects, induced by strongly electron-withdrawing (multiple F) or electron-donating (multiple Me and *t*-Bu) groups.

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NF_3
NHF_2
NH_2F
NH_3
NH_2Me
$NH_2(t\text{-Bu})$
NMe_3
$NMe_2(t\text{-Bu})$

OF_2
OHF
OH_2
$OH(Me)$
OMe_2
$OH(t\text{-Bu})$
$OMe(t\text{-Bu})$

F_2
FH
FMe
$F(t\text{-Bu})$

Ne

Figure 1. Components (X) of the proton-bound homodimers $[X\cdots H-X]^+$ examined in the present study.

Computational Methods

Standard ab initio molecular orbital calculations[8] were carried out with the Gaussian 03 program.[9] Geometries were optimized at the MP2/6-31+G(d,p) level of theory. Vibrational frequencies were computed to establish that all structures correspond to local minima on their potential-energy surfaces. Improved energies were obtained with a modified version of the high-level G3(MP2)-RAD[10] composite method. While the standard G3(MP2)-RAD energy is obtained with the formula, CCSD(T)/6-31G(d) + MP2/G3MP2Large − MP2/6-31G(d), the modified procedure employed here replaces the 6-31G(d) basis set with 6-31+G(d,p), to obtain a better description of H-bonded systems. Zero-point vibrational energies (ZPVEs) and thermal corrections to enthalpies, derived from MP2/6-31+G(d,p) frequencies, were incorporated into total energies.

It has been previously found that H−X stretching vibrations in some H-bonded systems become highly anharmonic as the hydrogen bond acquires increased proton-shared character (e.g., the H−F stretch in $H_3N\cdots H-F$ as a function of field strength, the H−Br stretch in $H_3N\cdots H-Br$, or the X−H stretch in $X-H-X^-$ bihalide anions), leading to large differences between computed harmonic and (unscaled) anharmonic frequencies.[11] Our preliminary calculations (Table S4 of Supporting Information) indicate that ZPVEs derived from scaled (by 0.9608) harmonic frequencies differ from those obtained from one-dimensional anharmonic frequencies[12] by up to 11 kJ mol^{-1}. However, the differences in binding energies obtained using scaled harmonic ZPVEs on the one hand and those obtained incorporating anharmonic ZPVEs on the other are much smaller (±3 kJ mol^{-1}), owing to a partial cancellation of anharmonicity effects in the H-bonded complexes and their components. As a result, we have used scaled MP2/6-31+G(d,p) harmonic frequencies in the evaluation of ZPVEs (0.9608) and thermal corrections to enthalpies (1.0084), employing standard literature scale factors.[13,14]

Results and Discussion

The optimized geometries for $[H_2O\cdots H-OH_2]^+$ (**1**) and $[H_3N\cdots H-NH_3]^+$ (**2**) are shown in Figure 2 as representative examples of the protonated homodimers. Among the systems examined in the present study, the proton is shared equally between the two component moieties for Y = Ne, F, and O,[15] as exemplified by $[H_2O\cdots H-OH_2]^+$ (**1**). However, this is generally not the case for Y = N (e.g., **2**). For F(*t*-Bu), both protonation (**3**) and hydrogen bonding with $[H-F(t\text{-Bu})]^+$ (**4**) lead to substantial lengthening of the F−C bond. Thus, for example, for $[H-F(t\text{-Bu})]^+$, the structure resembles that of a complex between HF and a *tert*-butyl cation (**3**). The situation is less dramatic for the proton-bound dimer, which has a symmetrical C_{2h} structure (**4**). It has been previously found, by Fourier-transform mass spectrometry and computational quantum chemistry, that protonation of 1-fluoroadamantane leads to cleavage of the C−F bond.[16] Furthermore, density functional theory calculations indicate that C−F bond cleavage in 1-fluoroadamantane can also be induced by hydrogen bonding with a relatively strong proton donor.[17] Our optimized structures for **3** and **4** are in accord with the results from these studies.

Figure 3 shows a plot of the binding energy between X and its protonated form, $[H-X]^+$, that is, the enthalpy for the reaction $X + [H-X]^+ \rightarrow [X\cdots H-X]^+$, versus the proton affinity of X. There is no trivial correlation between the proton affinity and the binding energy that could account for all the substrates. However, certain “subgroups” of substrates appear to exhibit striking quadratic relationships.

Examining first the series Ne, FH, OH_2, and NH_3, we can see that the binding energy initially increases in magnitude as the proton affinity increases, reaches a maximum at OH_2, and becomes smaller for NH_3. The correlation between the binding energies (BE) and the proton affinities (PA) can be approximately described by the following equation:

$$\mathrm{BE} = 5.17 \times 10^{-4}\,\mathrm{PA}^2 - 0.616\,\mathrm{PA} + 40.0 \quad (R^2 = 0.993) \quad (1)$$

In a similar manner, a quadratic correlation is observed for the series F_2, FH, FMe and F(*t*-Bu), in which the binding initially increases as the PA increases but eventually decreases, according to the equation

$$\mathrm{BE} = 1.57 \times 10^{-3}\,\mathrm{PA}^2 - 1.74\,\mathrm{PA} + 344 \quad (R^2 = 0.997) \quad (2)$$

Similar correlations are also observed for the substituted OH_2 series:

$$\mathrm{BE} = 7.61 \times 10^{-4}\,\mathrm{PA}^2 - 1.14\,\mathrm{PA} + 287 \quad (R^2 = 0.980) \quad (3)$$

and for the substituted NH_3 series:

$$\mathrm{BE} = 5.69 \times 10^{-4}\,\mathrm{PA}^2 - 0.981\,\mathrm{PA} + 317 \quad (R^2 = 0.979) \quad (4)$$

To try to understand these results, we note initially that, in qualitative terms, the PA of a given substrate (X) depends largely

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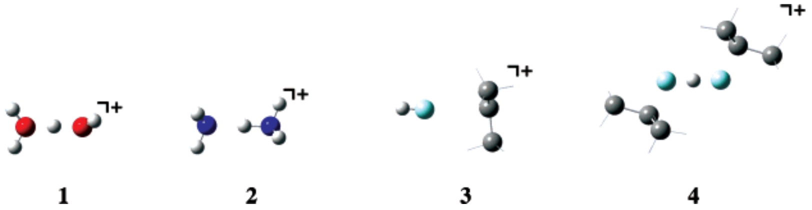

Figure 2. MP2/6-31+G(d,p) optimized geometries for $[H_2O\cdots H{-}OH_2]^+$ (**1**), $[H_3N\cdots H{-}NH_3]^+$ (**2**), [H−F(*t*-Bu)]$^+$ (**3**), and [(*t*-Bu)F···H−F(t-Bu)]$^+$ (**4**).

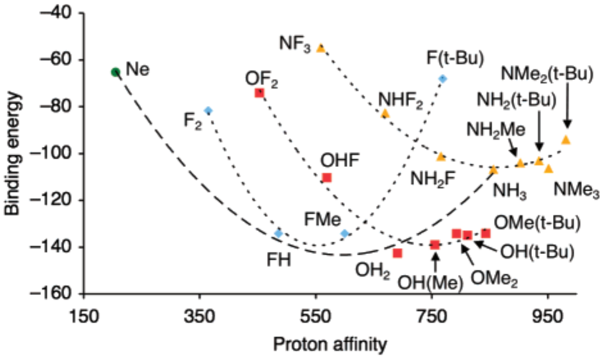

Figure 3. Binding energies (kJ mol^{-1}) between X and [H−X]$^+$ in the proton-bound homodimers [X···H−X]$^+$ versus the proton affinities (kJ mol^{-1}) of X.

on the capacity of the protonated form ([H−X]$^+$) to disperse the acquired positive charge. A less electronegative substrate better accommodates the positive charge and hence would generally have a higher PA. Thus, the PA increases along the sequence Ne < FH < OH_2 < NH_3, and also increases as the substituents become more electron-donating, F < H < Me < *t*-Bu.

Formation of a proton-bound homodimer between X and [H−X]$^+$ involves partial protonation of X and partial deprotonation of H−X$^+$. In a given series of protonated homodimers, at low PA, partial protonation of the acceptor and partial deprotonation of the donor can be expected to contribute only modestly to the overall binding energy. At high PA, while partial protonation of the acceptor contributes to a stronger binding, the penalty for partial deprotonation of the donor becomes large and dominant. Maximum binding occurs when the proton affinity has an intermediate magnitude. It has been demonstrated for a wide range of hydrogen-bonded heterodimers that the proton donor influences the binding more than the proton acceptor.[18] In the case of the proton-bound homodimers, this is reflected in the dominant penalty for deprotonation of the proton donor as the PA increases. Indeed, for substrates of high PA, such as most of the substituted NH_3 series, this high penalty for the partial deprotonation of the donor undoubtedly contributes to the nonsymmetrical structures in the proton-bound dimers.

Figure 3 and eqs 2−4 show that the sensitivities of the binding energies to the value of the proton affinity decrease in going from the substituted FH series to the OH_2 and NH_3 series. The fact that there are different BE−PA correlations for different series of substrates is indicative of factors other than PA at play, and this is the subject of our ongoing investigations.

Concluding Remarks

In this study, we have examined the binding energies in a series of related proton-bound homodimers [X···H−X]$^+$ and find that they neither increase nor decrease monotonically with increasing proton affinity of X. Instead, we observe quadratic behavior for the various series of proton-bound homodimers. The binding energies initially increase as the PA increases. However, once the PA becomes sufficiently high, the penalty for the partial deprotonation of [H−X]$^+$ dominates the benefit of partial protonation of X. As a result, the binding energy starts to decrease, giving rise to the quadratic correlations.

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Supporting Information Available: Complete ref 9, Gaussian 03 archive entries for MP2/6-31+G(d,p)-optimized geometries of relevant equilibrium structures, calculated G3(MP2)-RAD total energies, calculated [G3(MP2)-RAD] proton affinities and hydrogen-bonding energies, and a comparison of (scaled) harmonic and anharmonic estimates of the ZPVE contributions to the binding energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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