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Short Strong Hydrogen Bonds: A Valence Bond Analysis

Stéphane Humbel*

Unité Mixte de Recherche 6519 "Réactions Sélectives et Applications", CNRS - Université de Reims Champagne-Ardennes, B.P. 1039, 51687 REIMS Cedex 2, France

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Short strong hydrogen bonds are modeled with two resonating bonding structures issued from a valence bond analysis. A formula giving the bond dissociation energy as a function of the difference in proton affinities (ΔPA) is demonstrated. This equation is expanded in Taylor series and compared to similar equations found in the literature. It is found that the correlations either from experimental data or derived from the Marcus equation can be justified by the same valence bond arguments.

Introduction

One might oversimplify the hydrogen bonding "puzzle"[1] by considering only two types of hydrogen bonding: the one occurring in neutral systems such as the water dimer [$HO{-}H\cdots OH_2$], and the one of charged systems such as the proton-bonded water dimer [$H_2O\cdots H^+\cdots OH_2$]. The present study is devoted to this second type of interaction, which involves somewhat larger bonding energies (25−50 kcal/mol vs 5−10 kcal/mol).

Different approaches have been, and are being, used to better understand and/or predict the hydrogen bonding strength. One might categorize them into two families. One based on the partitioning of the energy,[2] which usually provides a deep understanding of the different contributions to the hydrogen bond strength, and one based on fits of experimental or computed values,[3−6] which usually provides useful equations to predict the actual bond strength. The present contribution will focus on this second strategy, which has provided a rather large set of equations for the hydrogen bond strength. We shall find in the following a general theoretical basis to the experimental correlations and possibly unify these equations through a simple valence bond analysis.

We will consider hereafter the proton-bonded dimers as intermediates in a formal proton-transfer reaction between two bases. For instance in [AHB]$^+$, the transfer of an H$^+$ from A−H$^+$ to the B moieties, leads to A + $^+$H−B. One of the names of this type of hydrogen bonded complexes, "low barrier hydrogen bonds" (LBHB), comes from the shape of the potential energy surface for this type of reaction. The proton transfer in these systems involves indeed a low barrier, or is even barrierless (Figure 1). In this latter case, the potential energy surface is a single well and the proton can be considered as shared by the two bases A and B.

Among other contributions on the subject, those from Scheiner illustrate particularly well why some of these bonds are often named "short strong hydrogen bonds" (SSHB).[7] When the distance between the bases is large, the proton is localized on one of the bases because a significant barrier appears for the proton-transfer process.[8,9] The barrier is reduced, and even disappears, for a short distance between the two bases. A straightforward effect of a barrierless proton transfer is that symmetrical, or quasi-symmetrical, hydrogen bonded species are to be obtained. This disappearing/appearing barrier that depends on the distance between the bases can be driven by conformational restrictions that are likely to facilitate/impede the proton transfer, in biological systems for instance.[10] The geometrical parameters in these especially short bonds thus receive a large amount of attention, especially through crystal structure analysis.[11]

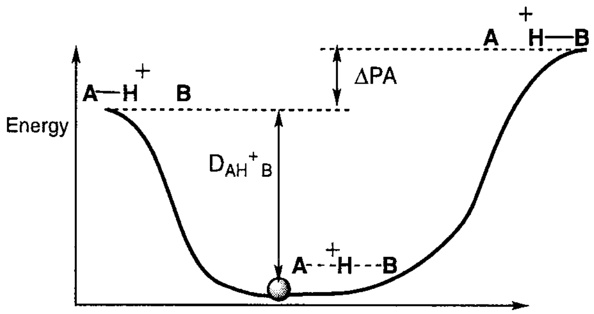

Figure 1. Shape of the potential energy surface as a function of the proton-transfer coordinate (barrierless process).

Among the short strong hydrogen bonded species, quasi-symmetrical proton-bonded dimers ($A\cdots H^+\cdots B$) are probably the most fascinating because the proton can be considered as shared between the two bases on a very flat potential energy surface. They have been the subject of numerous studies, some of them aiming to relate the bond dissociation energy (Figure 1, D_{AH^+B}) to the difference between the proton affinities of the bases (|ΔPA|). Various equations (eqs 1−4) have thus been proposed in the literature. Despite *nonlinear* correlations found in early works,[6] a number of fits of experimental or computed bond strengths were based on *linear* correlation.[3,4,12] This apparent disagreement is explained by the fact that within a reduced range of |ΔPA|, and when the atoms A and B are of the same type, the correlation seems to be very much linear. The set of molecules used for the fit and/or the starting hypothesis obviously predetermines the results, and the linear equations thereby obtained differ sometimes strongly one from the others. For instance, eqs 1 and 2 both propose a linear variation of the dissociation energy as a function of |ΔPA|, but the slope in eq 1 was found to be close to −0.5,[4] while for the same type of systems, $-OH^+O-$, the slope of eq 2 was −0.30.[3,12]

$$D_{AH^+B} = D_{AH^+A} - 0.5 \times |\Delta PA| \qquad (1)$$

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$$D_{\mathrm{AH^+B}} = a - b \times |\Delta\mathrm{PA}| \text{ with } b \sim 0.30 \tag{2}$$

$$\begin{cases} D_{\mathrm{AH^+B}} = D - |\Delta\mathrm{PA}|/2 + |\Delta\mathrm{PA}|^2/16D \\ D = (D_{\mathrm{AH^+A}} + D_{\mathrm{BH^+B}})/2 \end{cases} \tag{3}$$

$$D_{\mathrm{AH^+B}} = A \times \exp(-B \times |\Delta\mathrm{PA}|) \tag{4}$$

Marcus theory[13] can be used to find a common ground for these two first eqs 1 and 2. When applied to two parabolas with negative curvatures (inverted barrier),[14] Marcus theory leads to eq 3, where D is the average of the dissociation energies of the symmetrical proton-bonded dimers $D_{\mathrm{AH^+A}}$ and $D_{\mathrm{BH^+B}}$. This third proposal can easily be related to the two first equations: as far as the slope is concerned, eq 3 would be equivalent to eq 1 if the positive second order term in $|\Delta\mathrm{PA}|$ is simply neglected. Similarly for eq 2, one can consider that the slope of −0.30 accounts for the positive second-order term of eq 3. The equations (1−3) can thus be understood from the same "cornerstone", Marcus theory. This being said, the nature of the bonding remains in fact very much unclear.

The fourth description (eq 4), with an exponential variation of the dissociation energy with $|\Delta\mathrm{PA}|$, has been more recently proposed on the basis of an even larger scale of $|\Delta\mathrm{PA}|$.[5b] This latter proposal apparently does not fit with the other descriptions, although all four equations were properly gauged on experimental facts. A rational, physically grounded formulation appears to be needed to understand, and possibly unify, these different equations.

In a recent work on the subject,[15] we adapted a formula derived from the resonant description of odd electron bonds[16] to the case of these short strong hydrogen bonds:

$$D_{\mathrm{AH^+B}} = \left(\sqrt{|\Delta\mathrm{PA}|^2 + (2D)^2} - |\Delta\mathrm{PA}|\right)/2 \tag{5}$$

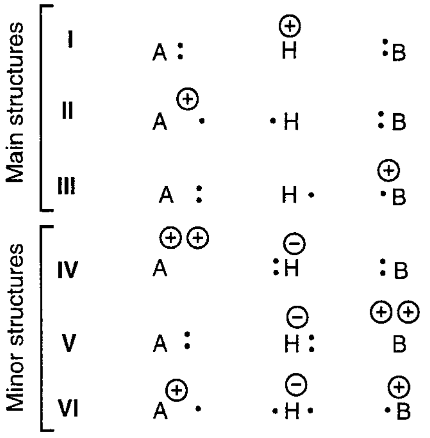
We shall see in the present contribution the proper demonstration of this equation, based on the resonance between two hydrogen-bonded structures. Although the resulting eq 5 does not, at a first glance, resemble the previously published equations, simple Taylor series will make the necessary link between eq 5 and the other equations (1−4).

Valence Bond Description of the Hydrogen Bonds

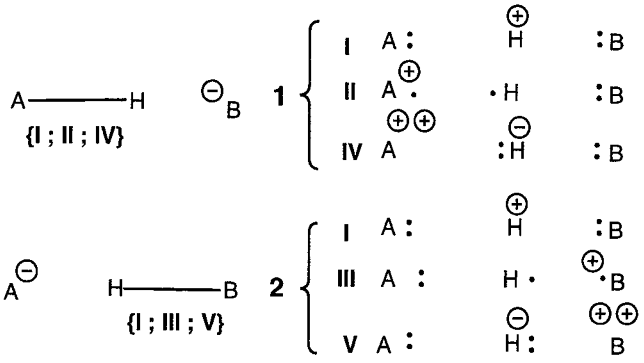
The valence bond (VB) description of the hydrogen bonding involves the distribution of the electrons among the orbitals that are believed to be active in the hydrogen bonding, i.e., in the corresponding proton-transfer reaction. Considering the reaction $\mathrm{A{-}H^+ \cdots :B \rightarrow A: \cdots {}^+H{-}B}$, a total of only four electrons are to be considered as active. Six VB structures are thus obtained, as depicted in Scheme 1.[17] The structures **IV−VI** are expected to have a small contribution to the total wave function: they bear a large charge separation, and/or the hydrogen is negatively charged.

To simplify our understanding, and to obtain an analytical straightforward resolution, one can reduce the 6 × 6 valence bond description to an interaction between only two structures. Such a reduction is grounded on the small contribution of structure **VI** to the wave functions. Scheme 2 shows how the different VB structures **I−V** could be grouped in such a way that only two chemically meaningful structures (**1−2**) remain to consider. The structure **II** describes indeed the covalent contribution to the A−H bond, while **I** and **IV** are the corresponding ionic structures. Similarly, **III** is the covalent structure of the B−H bond while **I** and **V** are the corresponding ionic valence bond structures.

SCHEME 1



SCHEME 2



SCHEME 3

$$\begin{array}{cc} \mathbf{H} & \begin{array}{cc} \mathbf{1} & \mathbf{2} \end{array} \\ \begin{array}{c} \mathbf{1} \\ \mathbf{2} \end{array} & \begin{pmatrix} 0 & -D \\ -D & |\Delta\mathrm{PA}| \end{pmatrix} \end{array} \Longrightarrow \begin{array}{cc} & \begin{array}{cc} \mathbf{1} & \mathbf{2} \end{array} \\ \begin{array}{c} \mathbf{1} \\ \mathbf{2} \end{array} & \begin{vmatrix} 0-\varepsilon & -D \\ -D & |\Delta\mathrm{PA}|-\varepsilon \end{vmatrix} \end{array} = 0$$

$$\Longrightarrow \varepsilon^2 - \varepsilon|\Delta\mathrm{PA}| - D^2 = 0$$

These structures **1** and **2** can no longer be called "valence bond" structures as they rather represent *groups* of valence bond structures. Because they correspond to two different bonding schemes, we shall simply call them in the following "bonding structures". The interaction between these two bonding structures (**1−2**) is easily described with a 2 × 2 reduced Hamiltonian (Scheme 3). One can consider that structure **1** (for instance) is lower in energy than **2** and defines the origin of the energies in the reduced Hamiltonian. The energy of the second structure (**2**) can easily be related to this origin: in a nonsymmetrical system such as $[\mathrm{AH^+B}]$, going from **1** to **2** requires to remove the proton from $\mathrm{A{-}H^+}$ (which involves −PA(A)) and pass it to B (which involves PA(B)). Structure **2** is thus $|\Delta\mathrm{PA}|$ higher in energy than **1**. The second diagonal term of the matrix is thus set to the difference between the proton affinities of the bases A and B: $|\Delta\mathrm{PA}|$. The off-diagonal term can be set to the yet undefined (negative) value $-D$, without further consideration in a first step. Neglecting the overlap, the lowest root resulting from the Hamiltonian diagonalization leads us directly to eq 5 as a definition of the dissociation energy of an unsymmetrical $[\mathrm{AH^+B}]$ system.

Before going further in the analysis of the equation, we shall first discuss our choice for the reduced Hamiltonian matrix

SCHEME 4

$$\begin{array}{c@{}c} \mathbf{H} & \begin{array}{cc}\mathbf{1} & \mathbf{2}\end{array} \\ \begin{array}{c}\mathbf{1}\\ \mathbf{2}\end{array} & \begin{pmatrix} 0 & -D \\ -D & 0 \end{pmatrix} \end{array} \Longrightarrow \begin{array}{c@{}c} & \begin{array}{cc}\mathbf{1} & \mathbf{2}\end{array} \\ \begin{array}{c}\mathbf{1}\\ \mathbf{2}\end{array} & \begin{vmatrix} 0-\varepsilon & -D \\ -D & 0-\varepsilon \end{vmatrix} \end{array} = 0$$

$$\Longrightarrow \varepsilon^2 - D^2 = 0 \Leftrightarrow \varepsilon = \pm D$$

elements. The difference in energy between the two bonding structures **1** and **2** has been set to $|\Delta PA|$. This value accurately describes the energy difference between the two bonding structures at *infinite* distance between the bases. In our case of short strong hydrogen bonds, the distance between the bases is obviously small and our value $|\Delta PA|$ neglects many terms that describe the interaction between the bases and the proton. These terms are introduced in our description via the off diagonal term, $-D$. A definition for D is obtained when eq 5 is compared to eq 3. If the two bases are assumed to share a similar proton affinity (i.e., if $|\Delta PA|$ is smaller than $2D$), which is usually the case in SSHB, eq 5 can be expanded in Taylor series as shown in eqs 6 and 7.[15]

When this is held to the zeroth order in x, the resulting linear eq 8 corresponds to the Marcus eq 3 truncated to the first order in $|\Delta PA|$.

$$D_{AH^+B} = \left((2D)^2\left(\frac{|\Delta PA|^2}{(2D)^2} + \frac{(2D)^2}{(2D)^2}\right) - \left|\Delta PA\right|\right)/2$$

$$= D(\sqrt{x+1}) - |\Delta PA|/2, \text{ with } x = \frac{|\Delta PA|^2}{(2D)^2} \quad (6)$$

$$\sqrt{x+1} = 1 + \frac{x}{2} - \left(\frac{x^2}{8}\right) + \cdots \quad (7)$$

$$D_{AH^+B} = D - |\Delta PA|/2 \quad (8)$$

$$D_{AH^+B} = D - |\Delta PA|/2 + |\Delta PA|^2/8D \quad (9)$$

Held to the first order in x, we obtained eq 9 that can be compared to 3. The terms at the second order in $|\Delta PA|$ differ in the two equations, Marcus equation having a 2-fold smaller second order correction. It should be noted that if this expansion in Taylor series were to be held one step further, to the second order in x, it would add a negative corrective term to (9), $\{-x^2/8 = -|\Delta PA|^4/128D^3\}$. Marcus derived eq 3, which is truncated to the second order in ΔPA, already includes this correction in its smaller second-order term in ΔPA. It is thus understandable as a corrected Taylor series expansion of eq 5. This analysis prompted us to use the same definition for D: the average of the dissociation energies of the symmetrical proton-bonded dimers $[AH^+A]$ and $[BH^+B]$.

It is interesting to note that this definition for D also holds for symmetrical systems such as $[AH^+A]$. For such symmetrical systems where $A = B$ and $|\Delta PA| = 0$, the Hamiltonian diagonalization leads to $\epsilon = -D_{AH^+A} = -D$, Scheme 4, which gives a definition for D that is consistent with our previous formulation: $D = (D_{AH^+A} + D_{BH^+B})/2$, with $A = B$.

Having at hand a new formula for the dissociation energy, it is interesting to reach the exponential definition as presented in eq 4. When D is factorized in eq 9, the Taylor series of $\exp(x)$ for $x = (-\Delta PA/2D)$ is evidenced (10). The resulting eq 11 can enlighten some interesting features of the original exponential eq 4.

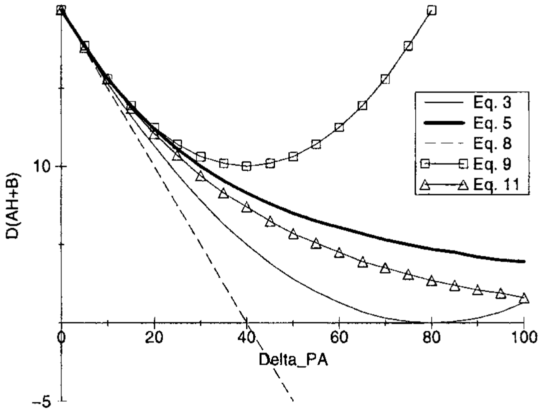


Figure 2. Shape of the D_{AH^+B} variations as a function of ΔPA when D is set to 20.

$$D_{AH^+B} = D\left(1 + (-|\Delta PA/2D) + \frac{1}{2}(-|\Delta PA|/2D)^2\right) \quad (10)$$

$$D_{AH^+B} = D\exp(-|\Delta PA|/2D) \quad (11)$$

The comparison of the two equations (eqs 4 and 11) prompts us to set $A = D$ and $B = 1/(2D)$, an assignment which is valid for fully resonating hydrogen-bonded systems. This result is in agreement with the relation between the symmetry of the proton bonded complexes and the value of the product $A \times B$.[5b] It has been indeed proposed that a symmetrical proton bonded systems (fully resonant) should have a $A \times B$ product of 0.50, a value that is encountered in many cases.[18]

The curves in Figure 2 show how all the descriptions discussed here are similar when ΔPA is small before D. For larger ΔPA, the role of the second order correction in Marcus, eq 3, is particularly well shown when the corresponding curve is compared to the one obtained for eq 9. Among the approximations of eq 5, the exponential approximation is clearly the closest to the original curve. It is thus not surprising that, using a set of short strong hydrogen bonded systems with a large scale of ΔPA between the bases, Zeegers-Huyskens obtained a good *exponential* fit. As mentioned by this author, the product $A \times B$ must be close to 0.5 for strongly resonating systems (single-well potentials), and any deviation from this value should originate from the nature of the bonding (localized proton for instance). From our analysis, A and B could also be calculated using experimental or computed values for D. This would involve only the dissociation energies of symmetrical systems.

Applied to the dissociation energy of the slightly nonsymmetrical proton bonded system $CH_3OH\cdots OH_2$, for instance, one would need the dissociation energies of the corresponding symmetrical proton-bonded dimers $H_2O\cdots H^+\cdots OH_2$ and $CH_3OH\cdots H^+\cdots HOCH_3$ (Table 1). With D being calculated as the average of these two dissociation energies, 31.5, one would obtain A=31.5 and B=0.0159, in good agreement with the fitted values obtained by Zeegers-Huyskens,[5b] $A = 31$; $B = 0.0155$. Using eq5 for this case, the dissociation energy is underestimated by 2.6 kcal/mol.

Of course, as the bonding deviates from a resonant situation, i.e., when ΔPA gets large, the accuracy of the resonating equation (eq 5) should get poorer, underestimating the dissociation energy. An example is given in Table 1 with $H_3N\cdots H^+\cdots OH_2$ ($\Delta PA = 37.5$ kcal/mol). For such a system,

TABLE 1: Dissociation Energies of Selected Proton Bonded Systems

	ΔPA	D	eq 5	D_{exp}
$H_2O\ H^+\ OH_2$	0	31.6	31.6	31.6[a]
$MeOH\ H^+\ OHMe$	0	31.4	31.4	31.4[e]
$MeOH\ H^+\ OH_2$	15.4[c]	31.5	24.7	27.3[d]
$H_3N\ H^+\ NH_3$	0	24.8	24.8	24.8[b]
$H_3N\ H^+\ OH_2$	37.5[d]	28.2	15.1	20.6[d]
$MeH_2N\ H^+\ NH_2Me$	0	21.4	21.4	21.4[b]
$MeH_2N\ H^+\ OH_2$	47.6[d]	26.5	11.8	18.4[d]

[a] From ref 19. [b] From ref 20. [c] From ref 5b. [d] From ref 3. [e] From ref 4.

D is set to (31.6+24.8)/2 = 28.2 and eq 5 underestimates the experimental binding energy by 5.5 kcal/mol (Table 1). The situation gets even worse as ΔPA increases as it is the case in $MeH_2N\cdots H^+\cdots OH_2$ (ΔPA = 47.6 kcal/mol). Following the same guideline for the calculation of D, a deviation of about 6.6 kcal/mol from the experimental value is obtained.

These selected examples finally give us the opportunity to discuss why the ΔPA match is not the only criterion to predict the hydrogen bond strength. There are indeed numerous examples where bases with a large ΔPA are more strongly bonded together than bases with a smaller ΔPA. In Table 1 for instance, D_{exp} is smaller in $H_3N\cdots H^+\cdots NH_3$ (24.8 kcal/mol) than in $MeOH\cdots H^+\cdots OH_2$ (27.3 kcal/mol) although ΔPA is smaller in the former case (0.0 vs 15.4). Our analysis shows that an other parameter, D must be also considered. In this context, we shall just recall that one can define D as the average value of the hydrogen bond strengths in the "parent" *symmetrical* systems, and that the hydrogen bond strength is an increasing function of D. Applied to the example mentioned in Table 1, D is simply larger in $MeOH\cdots H^+\cdots OH_2$ (31.5 kcal/mol) than in $H_3N\cdots H^+\cdots NH_3$ (24.8 kcal/mol), and compensates the ΔPA difference.

This D factor also enlightens as to why the hydrogen bonding energies are often particularly large in anionic species such as $[B\cdots H\cdots F]^-$, i.e., involving F^- as one of the two bases.[5a] One of the "parent" *symmetrical* proton bonded dimers, $[F\cdots H\cdots F]^-$, simply bears one of the largest hydrogen bond strength known to date (up to 44 kcal/mol).[21] In such $[B\cdots H\cdots F]^-$ species the D factor gets thus particularly large and, again, is likely to balance the ΔPA difference between the bases. It results from this a large hydrogen bond strength.

Conclusion

Our eq 5 is a rational formulation of eqs 1−4, which were gauged on experimental data. The formula is ground on the resonance between two chemical structures and should apply to the cases where the hydrogen bonding is indeed resonant in nature (single-well potential, small ΔPA). In these cases it is expected to bear a reasonable accuracy (2−3 kcal/mol). In other cases it can only be used to measure the resonance contribution to the hydrogen bonding. As ΔPA gets large, the resonance contribution gets small, and other effects are likely to dominate in the bonding. In these cases our equation is likely to underestimate the dissociation energy.

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