Substituent Effects on Two-Center Three-Electron Bonds and Hydrogen Bonds Involving Unsaturated Organic Functional Groups and an Ammonia Radical Cation—The Resonance Contribution

Stéphane Humbel,*[a] Norbert Hoffmann,[b] Isabelle Côte,[a] and James Bouquant[a]

Dedicated to the memory of Professor Josselin Chuche

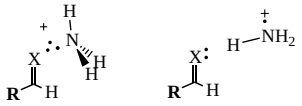
Abstract: A theoretical investigation of the substituent effects on the two-center, three-electron (2c–3e) bond involved between unsaturated functional groups and an amine nitrogen is presented. The competitive hydrogen-bonded complexes are also studied. In both cases, the bond energies are found to be in the range of 20–30 kcal mol^{-1}. The variation of these energies is discussed with respect to the electron-donating effect of the substitutents, as well as with respect to the π-bonded atom of the organic functional group (O, S, NH). For the 2c–3e bonds, the results are discussed on the basis of the differences of the ionization potential (ΔIP) of the separated fragments and can be rationalized through the valence bond theory. For the hydrogen bonds, the substituent influence is discussed by using the differences of the proton affinities (ΔPA) of the substrates. The resonating nature of the hydrogen bond in these cationic systems is investigated and is found to account for most of the binding energy. Marcus theory is compared with the proposed resonating model.

Keywords: ab initio calculations · hydrogen bonds · ion-molecule complex · resonance model

Introduction

When they involve saturated organic functional groups, two-center, three-electron (2c–3e) bond complexes are frequent in both experimental and theoretical studies.[1–4] These bonds are mainly involved in charged symmetrical systems, when both hemibonded partners possess a similar ionization potential (IP). This point is well explained by the resonating nature of the hemibonded species[5] and has been demonstrated elsewhere.[6] Let us just remind here that the bond strengths are shown to be larger for a small difference in the ionization potentials of the partners.[1b] They are thus favored in symmetrical systems, but one may consider the cases of unsymmetrical systems in which both partners possess similar, but not equal, IPs. Those are expected to form a 2c–3e bond. Curiously a relatively small number of unsymmetrical 2c–3e bonded systems are discussed in the literature.[7]

In the class of unsymmetrical 2c–3e bonded systems, we have recently studied the case of complexes that contain unsubstituted unsaturated functions (like carbonyl, thiocarbonyl, or imine) and the radical cation of ammonia ($NH_3^{\bullet+}$).[8] We showed that these unsaturated compounds might form stable 2c–3e bonded complexes with the radical cation of ammonia despite the fact that the 2c–3e bonds were unsymmetrical. These unsaturated functional groups are expected to possess a great sensitivity to the electronic effects of the substituents, especially when π donors are involved. Here we aim to study the substituent effects on the 2c–3e bonded species that might be formed between substituted, unsaturated organic functional groups and the radical cation of ammonia (**TE**).[9]



TE **HB**

Our compounds might also form a hydrogen-bonded complex (**HB**). The hydrogen bonds in these radical cations can be classified as "short–strong" (SSHB) or "low-barrier" hydrogen bonds (LBHB).[10] The later term indicates the fact that the barrier of the proton transfer from the nitrogen atom onto the X atom is low in energy. Whether or not a system possesses such a barrier has been the subject of many publications in the past years and is still an important problem. Scheiner, for instance, performed detailed studies on this problem by calculating the appearance of a barrier

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when varying the distance between the heavy atoms involved in the bond.[11] In this paper we will not focus on the barrier height, which is small and can appear or disappear depending on the level of calculation.[12] Rather we wish to concentrate on the resonating nature of the bonds.

In the following we shall thus answer these questions:

1) What is the range of energies of both the 2c–3e and the hydrogen bonds?
2) How do the substituents modify the 2c–3e bond strength?
3) How do they modify the hydrogen bond strength?
4) How does the resonance contribute to the hydrogen bond in those cationic systems?

Computational Details

The calculations were carried out by using the Gaussian 94 package.[13] The optimizations were all done at the unrestricted MP2/6-31G(d) level (frozen core) and the stationary points were characterized by mean of analytical second derivatives. Cartesian d orbitals were used (6D) at this stage. This level of calculation usually gives satisfactory results for both hydrogen bonds and 2c–3e bonded complexes. However, we intend to use calculated ionization potentials and proton affinities of each fragment involved. These quantities usually require large basis sets and a high level of calculation to take into account the modification of the electronic correlation. The energy calculations were thus performed by using the substantially larger basis set from Dunning[14] (aug-cc-pvdz)[15] and at a significantly higher level of calculation (MP4). However, owing to a substantial spin contamination in some cases ($\langle S^2 \rangle$ up to 0.89), we shall only use in the following the projected MP3 values (noted PMP3). The spin contamination after projection was always found to be very small ($\langle S^2 A \rangle$ up to 0.76). This calculation level, PMP3/aug-cc-pvdz, was found to predict correctly the coupled cluster results (CCSD(T)) in our previous study.[8] Similar results about the PMP3 quality relative to the CCSD(T) level have also been obtained by using the IMOMO-ONIOM[16] method is the case of carbonyl derivatives (X = O).[17]

Results

The potential energy surface (PES) of interest is depicted in Figure 1. The label **x** stands for carbonyls (**x** = **1**), thiocarbonyls (**x** = **2**), and imines (**x** = **3**), while **R** stands for the substituent (H, CH_3, NH_2). Starting from $\mathbf{x} + NH_3^{\cdot+}$, in the middle, we will first study the single electron transfer (SET) reaction (right-hand side). This path leads to the radical cation of the unsaturated species ($\mathbf{x}^+$) and the closed-shell ammonia. It goes through the local minimum of the 2c–3e bonded intermediate **xTE**.

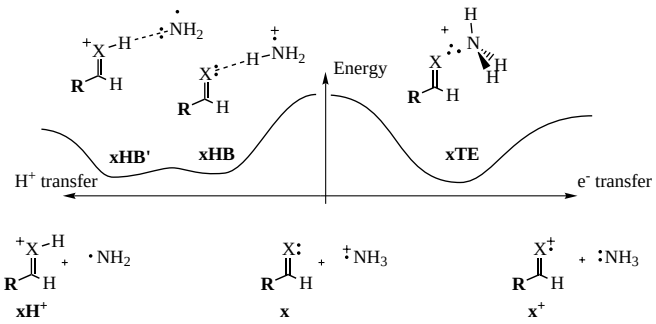
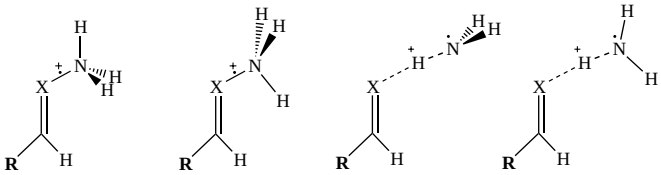


Figure 1. Qualitative potential energy surface of interest, X = O, S, NH and **R** = H, CH_3 NH_2.

As mentioned in the introduction, the investigated species might also form a hydrogen bonded complex, which is on the way of the proton transfer reaction depicted on the left-hand side of Figure 1. This path might go through a hydrogen bonded species **xHB** (involving **x** and NH_3^+), then through a second type of hydrogen bond denoted **xHB′** (involving $\mathbf{xH}^+$ and $^{\cdot}NH_2$), and finally leads to the separated protonated species ($\mathbf{xH}^+$) and the $^{\cdot}NH_2$ π radical. The barrier between **xHB** and **xHB′** was found to be extremely low in energy and most frequently, we obtained only one type of hydrogen bond complex, **xHB** or **xHB′**, on a very shallow potential energy surface (PES). The barrier for the proton transfer inside radical-cation complexes is indeed frequently found to be either extremely low or non existent.[11, 18]

Both σ (**R** = CH_3) and π (**R** = NH_2) electron-donating effects were studied and compared with the corresponding unsubstituted systems (**R** = H). It is noteworthy that the π-donating effect of the NH_2 substituent contributes only moderately to the stabilization of the 2c–3e bond as well as to the hydrogen bond, since these bonds are of σ type (located at the lone pair of the organic functional groups).

Geometry optimizations: The geometry optimizations of the complexes **xTE** and **xHB** (or **xHB′**) were carried out in C_s symmetry and checked as minima by means of frequency analysis.[19] All our calculations deal with an approach of the ammonia from the *trans* side of the substituent. The other approach (*cis* side) was indeed found to lead to species slightly higher in energy. For the 2c–3e bonded complexes we always



Abstract in French: *Nous présentons ici une étude théorique des effets de substituants sur des liaisons à deux centres et trois électrons (2c–3e) mises en jeu entre une fonction organique insaturée et l'atome d'azote d'amines. La liaison hydrogène qui est compétitive avec cette interaction est aussi étudiée. Les énergies de liaisons sont trouvées comparables (20–30 kcal mol⁻¹). Les variations de ces énergies de liaisons sont analysées en fonction de l'effet donneur des substituants et de l'hétéro-atome des différentes fonctions insaturées (O, S, NH). Pour les liaisons de type 2c–3e, cette discussion s'appuie sur la différence de potentiels d'ionisation et trouve sa base dans la théorie de la liaison de valence (Valence Bond). Les liaisons hydrogène sont commentées en fonction de la variation de l'affinité protonique des partenaires. La nature résonante de ces liaisons hydrogènes dans des cations est étudiée et trouvée comme étant la cause majoritaire de la stabilisation par liaison hydrogène. La théorie de Marcus est comparée au modèle résonant que nous proposons.*

present here the compound of type **xTE** rather than the rotated compound **xTEa**. In fact, a nearly free rotation around the X–N axis was observed. For the hydrogen bonded complexes, two kinds of structures were investigated, the twisted **xHB** and the planar **xHBa**. Only in the $H_2C{=}O$ case was the **xHBa** structure found to be energetically favored. All the other cases were twisted (**xHB**). However, the energy difference is extremely small.

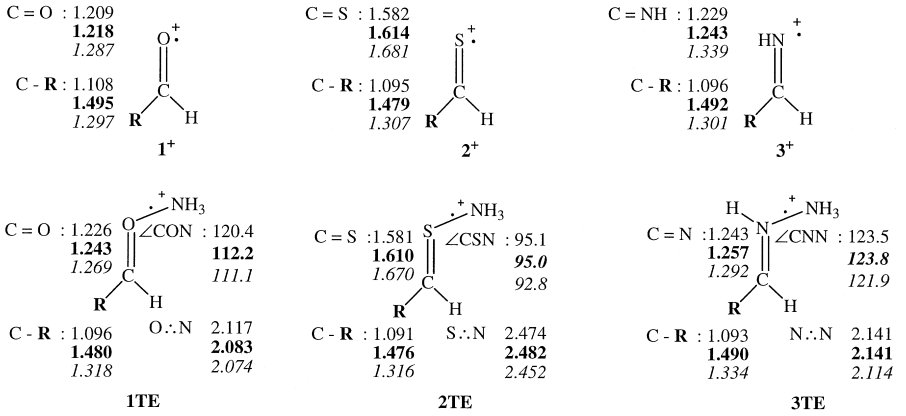


Figure 3. Main geometrical parameters (bond lengths in Å, bond angles in °) of $\mathbf{x}^+$ and **xTE** as optimized at the MP2/6–31G(d) level. **R** = H (plain), CH_3 (bold), and NH_2 (italic).

Whether the hydrogen bonded complexes should be expected as **HB**-like or as **HB′**-like (Figure 1 left-hand side) is indicated by the sign of the difference of proton affinity (vide infra).

Fragments: The fragments of the PES are of a special interest as they provide the starting point for both ionization potentials (IP) and proton affinities (PA) of the substrates. The important geometrical parameters of the MP2/6-31G(d) optimized unsaturated neutral fragments are displayed in Figure 2. Except for the formamide (X = O, **R** = NH_2) and the formamidine (X = NH, **R** = NH_2) whose nitrogen is found to be pyramidalized at this level of calculation and thus adopt a C_1 symmetry, all these fragments bear a C_s symmetry.

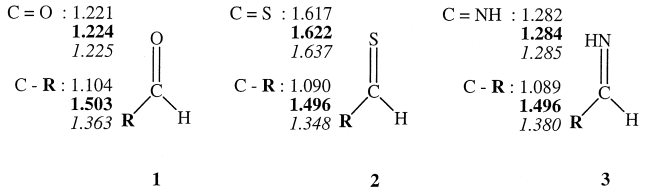


Figure 2. Main geometrical parameters (bond lengths in Å) of the neutral unsaturated fragments as optimized at the MP2/6–31G(d) level. **R** = H (plain), CH_3 (bold), and NH_2 (italic).

2c–3e: The dissociation fragments of the 2c–3e bonded species **xTE** might be either the starting materials ($\mathbf{x} + NH_3^+$) or the SET products ($\mathbf{x}^+ + NH_3$). Figure 3 displays the main geometrical parameters of the $\mathbf{x}^+$ fragments and of the 2c–3e bonded complexes **xTE**. Except for the radical cation of the formamidine fragment, which has an out of plane hydrogen and thus adopts a C_1 symmetry, all these species bear a C_s symmetry. The bond lengths for these complexes are rather large, since such 2c–3e bonds are most stabilized for a low overlap (S = 1/3) between the fragments.[1a, 5]

Hydrogen bonds: The dissociation fragments of the hydrogen bonds might be either the starting materials ($\mathbf{x} + NH_3^+$) or the proton transfer products ($\mathbf{xH}^+ + {}^{\bullet}NH_2$) (see Figure 1 left-hand side). Figure 4 displays the main geometrical parameters of the $\mathbf{xH}^+$ fragments and of the hydrogen bonded complexes **xHB** or **xHB′**. All the species possess a C_s symmetry. The nature of the preferred hydrogen bond is indicated by the sign of ΔPA, that is, the difference in proton affinities as obtained

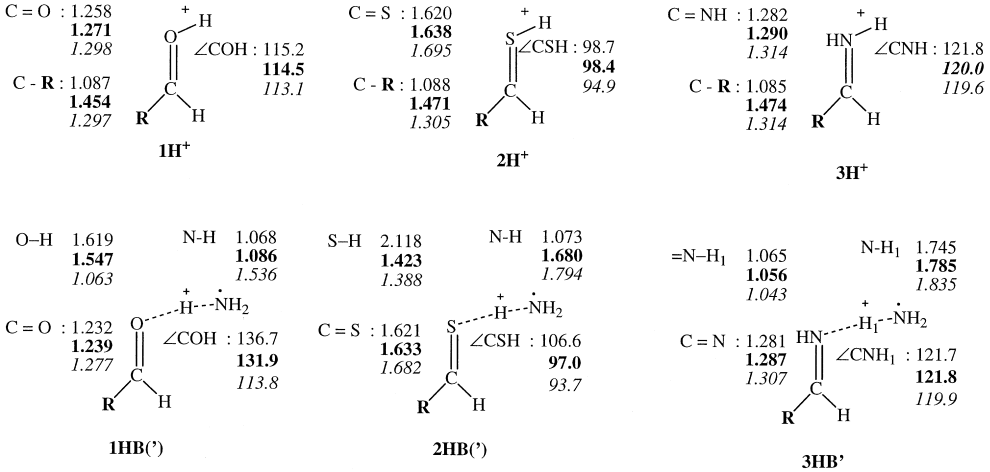


Figure 4. Main geometrical parameters (bond lengths in Å, bond angles in °) of the proton transfer fragments ($\mathbf{xH}^+$) and of the hydrogen bonded species as optimized at the MP2/6–31G(d) level. These might be either **HB**- or **HB′**-like, depending on the sign of ΔPA (see text). **R** = H (plain), CH_3 (bold), and NH_2 (italic).

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from Equation (1): **HB**-like structures for $\Delta PA > 0$ and **HB′** when $\Delta PA < 0$. The proton affinities are displayed and discussed later.

$$\Delta PA = PA(\mathbf{x}) - PA(^{\cdot}NH2) \quad (1)$$

Positive ΔPA are encountered in three systems that are carbonyls with $\mathbf{R} = H$ or CH_3 and thiocarbonyl when $\mathbf{R} = H$. For the other systems **HB′**-like hydrogen bonds are expected to be lower in energy than **HB**-like hydrogen bonds ($\Delta PA < 0$). In some rare cases (for the smallest ΔPAs) we found both **HB**- and **HB′**-like structures. Only the preferred structures (according to the sign of ΔPA) are presented in Figure 4.

Calculated potential energy surfaces: Figure 5 displays the potential energy surfaces calculated in this work. Here, we would like to comment on the main trends when comparing 2c – 3e and hydrogen binding for these systems.

It is shown that in carbonyl cases (**1**), the hydrogen bonded species are about 7 kcal mol^{-1} more stable than the corresponding 2c – 3e bonded species. For the thiocarbonyl species (**2**) the order of stability is reversed and the hydrogen bonded complexes are more than 20 kcal mol^{-1} higher in energy than the corresponding 2c – 3e bonded species. This is not very surprising taking into account the usual reluctance of sulfurs to form an hydrogen bond. Finally, in the case of the imines (**3**), the hydrogen bonded species are about 10 kcal mol^{-1} more stable than the 2c – 3c bonded species. This result is more surprising because the homonuclear N–N bond was expected to be among the strongest 2c – 3e interactions. However, the hydrogen bonded species are of the type **HB′**, which means that a proton has already transferred onto the nitrogen of the imine. The hydrogen bonded complex therefore involves an iminium ion and the $^{\cdot}NH_2$ radical moiety. Those iminiums are known to be very stable. Note that the dissociative fragments of the NH_2 substituted imine case (amidinium) are especially stable (-41.2 kcal mol^{-1}), nearly as stable as the 2c – 3e bonded complex. This stability is well explained through the symmetrical charge delocalization which can occur in the amidinium and drives down the PES toward stable hydrogen bonded complexes.

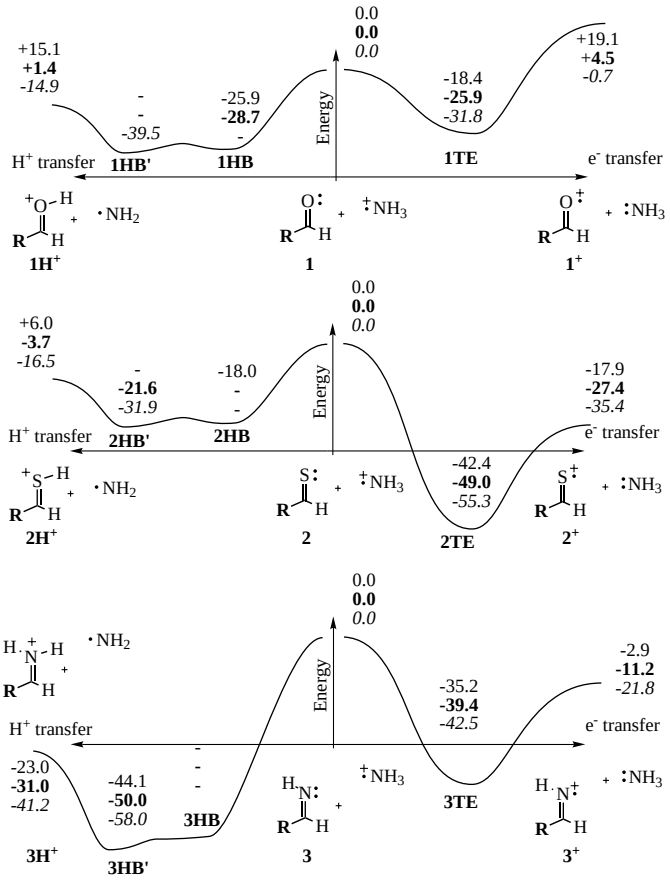

Figure 5. The potential energy surfaces (kcal mol^{-1}) as calculated at the PMP3/aug-cc-pvdz//MP2/6 – 31G(d) level. The substituent on the organic function is noted as follow : $\mathbf{R} = H$ (plain), CH_3 (bold), and NH_2 (italic). The different functions are presented in the different parts : **1** for carbonyl (top), **2** for thiocarbonyls (middle), and **3** for imines (bottom).

Discussion

It is noteworthy that in the carbonyl cases the substituent effect *increases* the 2c – 3e binding energy (as calculated with respect to the lowest dissociative fragments) from 18.4 ($\mathbf{R} = H$) up to 31.1 kcal mol^{-1} ($\mathbf{R} = NH_2$), while this effect *decreases* it in the imine cases (from 32.2 down to 20.7 kcal mol^{-1}).[20] The same electron-donating effect leads to an opposite behavior depending on the nature of the X atom. The substituent effects can be analyzed in detail by using the resonating nature of the bonds. The 2c – 3e binding is well known to be a purely resonance phenomena, and we will see how this aspect can be used to understand the substituent effects on the binding energies.

Resonance: In a dissymetric 2c – 3e bonded system, say $[A\cdot\cdot B]^+$ for instance, the 2c – 3e bond is depicted as a resonance between the valence bond structures $\mathbf{AB}^+$ and $^+\mathbf{AB}$. As usual, the resonance would be larger if the difference in energy between the resonating structures is small.

In a previous publication we detailed how the resonance can be depicted in 2c – 3e bonds using these two resonating structures:[6] The difference in energy between the structures $\mathbf{AB}^+$ and $^+\mathbf{AB}$ is an important factor and we approximated it as the energy difference between the ionization potentials of A and B ($|\Delta IP|$). Going from $\mathbf{AB}^+$ to $^+\mathbf{AB}$ requires the removal of one electron from the lone pair of the fragment A in $\mathbf{AB}^+$ and to pass it to the B^+ fragment.

Another important factor is the coupling constant between the resonating structures; this was approximated to $-(D_{AA} + D_{BB})/2$ when both partners are close in energy, where D_{AA} and D_{BB} are the binding energies of the symmetrical systems $A\cdot\cdot A$ and $B\cdot\cdot B$, respectively. This simply means that if $|\Delta IP| = 0$, the binding energy of the $A\cdot\cdot B$ system would be in between those of $A\cdot\cdot A$ and $B\cdot\cdot B$.

Solving the resonating system for $|\Delta IP| \neq 0$ led to Equation (2) below, which was transformed in Equation (3) when ΔIP is small before $(D_{AA} + D_{BB})/2$. Equation (3) shows the exponential dependency of D_{AB} toward $|\Delta IP|$ formerly mentioned by Clark.[1b]

$$D_{AB} = -(|\Delta IP| - \sqrt{|\Delta IP|^2 + (D_{AA} + D_{BB})^2})/2 \quad (2)$$

$$D_{AB} \approx [(D_{AA} + D_{BB})/2]\exp(-|\Delta IP|/2\sqrt{D_{AA} D_{BB}}) \quad (3)$$

In the following discussion we will keep in mind the $|\Delta IP|$ dependency to discuss the substituent effects on the 2c–3e bond strength. Equation (2) will also be adapted to the hydrogen binding for numerical tests on the resonating nature of the cationic hydrogen bond.

2c–3e bond strength analysis: The relevant calculated IPs are displayed in Table 1. As expected, they all decrease as the substituent-donating effect increases (H, CH_3, NH_2), stabilizing the cationic species more than the neutral one. Moreover, we are concerned with the *difference* between the ionization potentials. It is found here that when $\mathbf{R} = H$ or CH_3, the carbonyl compound has a higher IP than the one of the NH_3 moiety. The aforementioned single electron transfer (SET) path shall thus be endothermic in these two cases. In contrast, all the other species (amide, thicarbonyls, and imines) possess lower IPs than that of ammonia, and the SET path is thus found to be exothermic in these cases.

Table 1. Ionization potentials [kcal mol^{-1}] of the fragments as calculated at the PMP3/aug-cc-pvdz level.[a,b]

Systems	H[c]	R: CH_3	R: NH_2
IP(**1**)	247.3	232.7	227.5
IP(**2**)	210.3	200.9	192.9
IP(**3**)	225.4	217.0	206.5

[a] As calculated at the same level, the IP of NH_3 accounts for 228.2 kcal mol^{-1}. [b] **1** stands for the carbonyls, **2** for the thiocarbonyls, and **3** for the imines. [c] From ref. [8].

It is also noteworthy that in some cases the IPs of the organic substrates are very close to the IP of NH_3, particularly for the formamide ($X = O$, $\mathbf{R} = NH_2$) and for the unsubstituted imine ($X = NH$, $\mathbf{R} = H$). According to the resonance model, these are the cases we expect to form the strongest 2c–3e bonds.

As mentioned earlier, the bond strength has to be calculated with respect to the lower dissociative fragments, which are indicated by the sign of ΔIP when calculated with Equation (4).

$$\Delta IP = IP(\mathbf{x}) - IP(NH_3) \quad (4)$$

A positive ΔIP reveals that the starting materials (Figure 1) are the lower dissociative fragments, while a negative ΔIP points out that the SET products ($\mathbf{x}^+ + NH_3$) are the lower dissociative fragments. Table 2 indicates the relative energies that are relevant for the following discussion.

Table 2. ΔIP values[a] relative to the $\mathbf{x} + NH_3^+$ starting materials (plain) [Eq. (4)], and 2c–3e bond strength (italic) as calculated using the lowest dissociative fragments of the 2c–3e bond.

Species		R: H[b]	R: CH_3	R: NH_2
$\mathbf{1} + NH_3^+$		0.0	0.0	0.0
$\mathbf{1}^+ + NH_3$	(ΔIP)	19.1	4.5	−0.7
1TE	(D_0)	*18.4*	*25.9*	*31.1*
$\mathbf{2} + NH_3^+$		0.0	0.0	0.0
$\mathbf{2}^+ + NH_3$	(ΔIP)	−17.9	−27.4	−35.4
2TE	(D_0)	*24.5*	*21.6*	*19.9*
$\mathbf{3} + NH_3^+$		0.0	0.0	0.0
$\mathbf{3}^+ + NH_3$	(ΔIP)	−2.9	−11.2	−21.8
3TE	(D_0)	*32.2*	*28.2*	*20.7*

[a] In kcal mol^{-1} at the PMP3/aug-cc-pvdz//MP2/6–31G(d) level of calculation. [b] From ref. [8].

In the carbonyl cases in which fragments $\mathbf{1}^+$ and NH_3 are higher in energy than $\mathbf{1} + NH_3^+$ ($\mathbf{R} = H$ or CH_3), the electron-donating effect, by lowering $\mathbf{1}^+ + NH_3$ energy, diminishes the ΔIP value, and thus increases the 2c–3e bond strength. The largest 2c–3e bond strength in this series is encountered in the formamide case ($X = O$, $\mathbf{R} = NH_2$) with a small negative ΔIP (−0.7 kcal mol^{-1}). As the *absolute value* of ΔIP is continuously decreasing in this series, we find a continuous increase of the 2c – 3e bond strength.

As we shall see in the following, one should certainly not consider as a rule that a stronger electron-donating effect should lead to a stronger 2c–3e bond as is the case above. The thiocarbonyl and imine series illustrate this point. As indicated by the negative values of ΔIP, the lower dissociative fragments of the unsubstituted 2c–3e complex are the cationic species $\mathbf{x}^+$ and the neutral ammonia NH_3. Increasing the electron-donating ability of the substituent leads to a further stabilization of the fragments $\mathbf{x}^+ + NH_3$ with respect to $\mathbf{x} + NH_3^+$. As a consequence, the ΔIP *absolute value* increases and thus the 2c–3e binding energy diminishes.

This simple analysis not only explains an opposite behavior of the 2c–3e bond strength toward substituent-donating effect, that is, an *increase* of the 2c–3e bond strength in the carbonyl case, while a *decrease* is found in the other cases. It also permits us to predict how the 2c–3e bond strength would vary beyond our examples: The complex between the carbonyl species and the radical cation of ammonia was found to exhibit a larger 2c–3e bond energy as the substituent-donating effect increases. Lets consider now, for instance, a further increase in the electron-donating effect of $\mathbf{R} = NH_2$ in the formamide (as it would be the case in *N*,*N*-dimethylformamide, $\mathbf{R} = N(CH_3)_2$). One should expect ΔIP to decrease significantly in value (more negative), but, and more importantly for our matter, to *increase in absolute value*. It is noteworthy to mention how the same electron-donating effect, which was contributing to increase the 2c–3e bond strength up to this point, would now contribute to decrease it. Figure 6 qualitatively illustrates the relationship between the electron-donating effect and the bond energy.

Moreover, this whole study not only provides an efficient tuning strategy to strengthen or circumvent the 2c–3e interaction by the use of electron-donating or -withdrawing substituents on both reaction partners. Its spirit might also be

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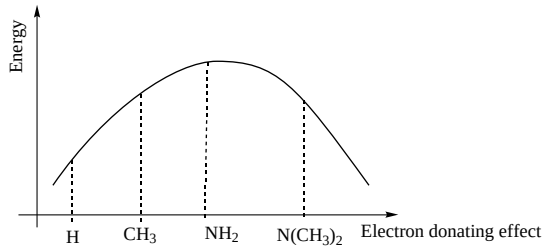

Figure 6. Qualitative modification of the 2c – 3e binding energy when increasing the electron-donating effect of the substituent on the carbonyl.

applied to the hydrogen bond strength as we shall see in the following.

While the ionization potential (IP) of the unsaturated moiety decreased as the electron-donating effect of **R** increased, the proton affinities (PA) increase as the electron-donating effect of **R** increased.

Hydrogen bond strength: The hydrogen bond strength can easily be related to the basicity (proton affinity, Table 3) of the organic species. For **HB**-like systems (Figure 4 and 5), electron-donating substitutents increase the basicity on the heteroatom of the unsaturated organic functional group. It is thus well understood why the hydrogen bond strength increases (Table 4) when increasing the electron-donating effect of the substituent. For **HB′**-like hydrogen bonds ($\Delta PA < 0$), the bond strength should be related to the acidity of the hydrogen on the **X** atom of the protonated organic function **xH**$^+$. Now, the larger electron-donating effect of the **R** substituent diminishes the acidity of this hydrogen, and leads to weaker hydrogen bond (imine series).

Table 3. Proton affinities of the fragments as calculated at the PMP3/aug-cc-pvdz level [kcal mol^{-1}].[a,b]

		R	
Systems	H[c]	CH_3	NH_2
PA(**1**)	178.1	191.8	208.1
PA(**2**)	187.2	196.9	209.7
PA(**3**)	216.2	224.2	234.4

[a] As calculated at the same level the proton affinity of $^{\bullet}NH_2$ accounts for 193.2 kcal mol^{-1}. [b] **1** stands for the carbonyls, **2** for thiocarbonyls, and **3** for imines. [c] From ref. [8].

Table 4. Hydrogen bonded species and corresponding fragments energies.[a] The ΔPA values are calculated by use of Equation (1), the $\mathbf{x} + NH_3^+$ starting materials being the energy reference. The hydrogen bond strength (italic) are calculated using the lowest dissociative fragments of the bond.

			R	
Species		H[b]	CH_3	NH_2
1 + NH_3^+		0.0	0.0	0.0
1H$^+$ + NH_2	(ΔPA)	15.1	1.4	− 14.9
1HB(′)[c]	(D_0)	*23.9*	*28.7*	*25.6*
2 + NH_3^+		0.0	0.0	0.0
2H$^+$ + NH_2	(ΔPA)	6.0	− 3.7	− 16.5
2HB(′)[c]	(D_0)	*18.0*	*17.9*	*15.3*
3 + NH_3^+		0.0	0.0	0.0
3H$^+$ + NH_2	(ΔPA)	− 23.0	− 31.0	− 41.2
3HB′	(D_0)	*21.1*	*19.0*	*16.8*

[a] In kcal mol^{-1}, PMP3/aug-cc-pvdz//MP2/6 – 31G(d) level of calculation. [b] From ref. [8]. [c] **HB**- or **HB′**-like hydrogen bond, see Figure 5.

Unfortunately, this acid/base analysis does not allow for a systematic discussion of the hydrogen bond strength, especially when the nature of the hydrogen bond changes within a series (e.g., for carbonyl systems, in which the **HB**-like bond becomes an **HB′**-like one on going from **R** = CH_3 to **R** = NH_2).

However, the binding-energy modification can be discussed in a more straitforward way by using the ΔPA of the reaction partners. Several parametrized formulas have been published previously. Up to now, they mainly agree on the fact that the bond energy is linearly correlated to the difference in the proton affinities.

Meot-Ner proposed[21] that the variation of the hydrogen bond strength in an heteronuclear cationic systems AH$^+$B (D_{AH^+B}) follows Equation (5), where a and b are fitted parameters; these are given in Table 5 for the different cases of our study.

$$D_{AH^+B} = a - b\,|\,\Delta PA\,| \quad (5)$$

Table 5. Meot-Ner[21] parameters relevant for our study.[a]

Bond	a	b
$-NH^+\cdots O$	28.3	0.23
$-NH^+\cdots S$	22.3	0.26
$-NH^+\cdots N$	23.2	0.25

[a] These parameters were optimized for saturated systems.

Larson and McMahon[22] suggested another linear dependency of the binding energy on ΔPA in unsymmetrical hydrogen bonded cationic dimers [Eq. (6)].

$$D_{AH^+B} = D_{AH^+A} - 0.5\,|\,\Delta PA\,| \quad (6)$$

This second equation is a little more general than Equation (5) in the sense that the a parameter of Equation (5) is replaced in Equation (6) by the binding energy of one of the symmetrical system D_{AH^+A}, which can be calculated. However, both are empirically optimized formulas and are expected to fail in unexpected cases. Moreover, they do not possess a clear physical meaning.

Marcus theory[23] gives a common basis to Equations (5) and (6) as we will see in the following. When applied to two parabolas with negative curvatures (inverted barrier), [24] Marcus theory leads to Equation (7), in which D, as indicated in Equation (8), is the average of the dissociation energies of the symmetrical proton bonded dimers D_{AH^+A} and D_{BH^+B}. The values of D_{AH^+A} and D_{BH^+B} can be calculated by using the dissociation reactions given in Equations (9) and (10), respectively.

$$D_{AH^+B} = D - |\,\Delta PA\,|/2 + |\,\Delta PA\,|^2/16D \quad (7)$$

$$D = (D_{AH^+A} + D_{BH^+B})/2 \quad (8)$$

$$H_2C{=}X\cdots H^+\cdots X{=}CH_2 \longrightarrow H_2C{=}XH^+ + X{=}CH_2 \quad X = O, S, NH \quad (9)$$

$$H_2{}^{\bullet}N\cdots H^+\cdots N^{\bullet}H_2 \ \text{(triplet)} \longrightarrow H_2{}^{\bullet}NH^+ + N^{\bullet}H_2 \ \text{(doublets)} \quad (10)$$

It is noteworthy that Equation (7) resembles Equation (5), if the a parameter is read as D, and if one considers the b

parameter ($b \approx 1/4$) to be and approximation of $1/2 - |\Delta PA|/16D$. Equation (7) resembles also Equation (6) in a similar manner.

Another way of describing the hydrogen binding in cationic species is to consider its resonating nature as suggested when the barrier of the proton transfer is small or non-existent.[10, 11, 18, 24, 25] This resonating nature possesses similarities with the three electron bond. When adapted from the 2c–3e bond to our hydrogen bond problem, Equation (2) leads to Equation (11).[26] It is interesting to note that when ΔPA is small before $2D$, Equation (11) can be expanded into a Taylor series and leads to Equation (12), which resembles the Marcus Equation (7).[27]

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

$$D_{AH^+B} = D - |\Delta PA|/2 + |\Delta PA|^2/8D \quad (12)$$

We also note that only the last term differs in the Marcus Equation (7). For small ΔPA, both descriptions are equivalent. However, the Equations (11) and (12) are derived from the resonating nature of the bond. Therefore, it will be in the following of special interest to compare the different descriptions, and show what part the resonance plays in the binding energy.

The MP2/6-31G(d) optimized geometries[28] of the symmetrical proton-bonded dimers AH^+A and BH^+B are displayed in Figure 7. For the sake of simplicity we calculated the

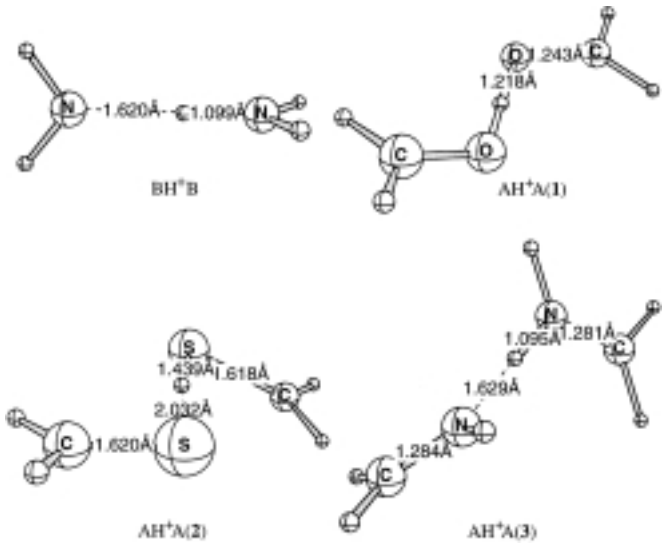

Figure 7. Homonuclear hydrogen bonded species. BH^+B is the biradical triplet, which most resembles the proton-bonded dimer of the $^{\bullet}NH_2$ moiety. The AH^+A systems are closed shell singlets. Following the previous notation we name them AH^+A(**1**) for the carbonyl, AH^+A(**2**) thionyl, and AH^+A(**3**) imine cases.

values of D [Eqs. (7)–(11)] only for the unsubstituted cases (**R** = H), and used them for all the cases (**R** = H, CH_3, NH_2). The binding energy D_{AH^+A} is indeed not expected to vary much in such symmetrical systems.[24]

The numerical results of Equation (11) as well as the values of D_{AH^+A}, D_{BH^+B} are shown in Table 6. In order to present an homogeneous treatment, we also included the results obtained when using Equations (5), (6) and (7).

Table 6. Hydrogen bond strength[a] as estimated by using various approximations, compared with the calculated values D_0 and ΔPA.[a]

Species		R = H	R = CH_3	R = NH_2
	(ΔPA)	*15.1*	*1.4*	*– 14.9*
1HB(′)[e]	Eq. (5)[c]	24.8	28.0	24.9
	Eq. (6)[d]	23.2	30.0	23.3
	Eq. (7)	21.3	27.7	21.4
D_{AH^+A}(**1**) = 30.7	Eq. (11)	21.8	27.7	21.9
	(**D_0**)[a]	**23.9**[b]	**28.7**	**25.6**
	(ΔPA)	*6.0*	*– 3.7*	*– 16.5*
2HB(′)[e]	Eq. (5)[c]	21.3	20.7	18.0
	Eq. (6)[d]	23.0	24.2	17.8
	Eq. (7)	18.2	19.2	13.6
D_{AH^+A}(**2**) = 16.1	Eq. (11)	18.3	19.3	14.4
	(**D_0**)[a]	**18.0**[b]	**17.9**	**15.3**
	(ΔPA)	*– 23.0*	*– 31.0*	*– 41.2*
3HB′	Eq. (5)[c]	17.5	15.5	12.9
	Eq. (6)[d]	15.9	11.9	6.8
	Eq. (7)	16.4	13.4	10.1
D_{AH^+A}(**3**) = 27.4	Eq. (11)	17.6	15.4	13.1
	(**D_0**)[a]	**21.1**[b]	**19.0**	**16.8**

[a] In kcal mol^{-1} from PMP3/aug-cc-pvdz//MP2/6–31G(d) level of calculation. D_{BH^+B} = 26.0 kcal mol^{-1} at this level. [b] From ref. [8]. [c] By using Equation (5) and the appropriate parameters from Table 5. [d] By using Equation (6) with the largest of D_{AH^+A} and D_{BH^+B} for D_{AH^+A}. [e] **HB**- or **HB′**-like hydrogen bond, see Figure 5.

Equation (11) agrees reasonably well with the fully calculated values (D_0). In some cases, an underestimation of about 3–4 kcal mol^{-1} on the binding energy is obtained. On the other hand, the empirical linear Equations (5) and (6) do not perform much better. Equation (6) was optimized only for oxygen atoms, and it is not surprising that it fails for the other cases. Equation (5), however, uses a specific set of parameters for each kind of system, and also displays a small error (about ±3–4 kcal mol^{-1}) when compared with the fully calculated values.

The small underestimation of the binding energy by using Equation (11) is found to correlated with ΔPA. It is particularly manifest for imine cases. As ΔPA gets large, the resonance gets low and Equation (11) underestimates the binding energy, indicating that as the resonance diminishes, another interaction (electrostatic for instance) increases. As this modification is not taken into account in our equation, we expect the underestimation of the binding energy to be more important for larger ΔPA. A correction could be done by adding an electrostatic term of minor contribution, for instance: Most of the electrostatic interactions are already taken into account by using $(D_{AH^+A} + D_{BH^+B})/2$ in Equation (11). The error might thus correspond to a modification of this term when the proton gets more strongly bonded to the X atom as in the imine cases (large ΔPA). This correction is, however, not trivial, and should be tested on a large variety of examples, which is beyond the interest of this paper.

The results of both the Marcus theory [Eq. (7)] and Equation (11), based on the resonance model, are shown in Figure 8 for the imine cases. As mentioned earlier, both descriptions are similar, especially when ΔPA is small.

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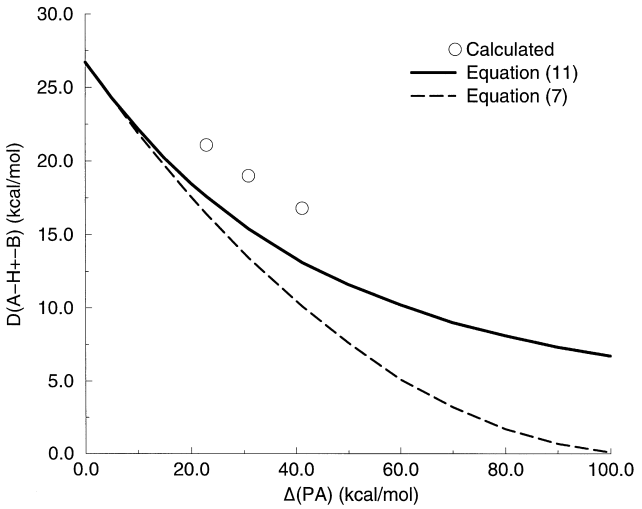

Figure 8. Hydrogen bond energy as a function of ΔPA for large ΔPA in the case of the imines. The calculated points (circles) are the results from the MP3/aug-cc-pvdz//MP2/6 – 31G(d) level.

Conclusion

We have determined the substituents effects on the bond strengths of the 2c – 3e bonds between a variety of unsaturated organic functional groups and the ammonia radical cation ($NH_3^{\bullet+}$). Using the valence bond theory, we related the 2c – 3e bond strength variation to the IPs of fragments. In the case of endothermic SET ($\Delta IP > 0$, $\mathbf{X} = O$), electron-donating substituents increase the strength of the 2c – 3e bond, while in the case of exothermic SET, these substituents diminish the bond strength.

We also calculated the corresponding hydrogen bonded complexes which compete with the 2c – 3e interaction. In both cases, bond energies were found to be in the same range of 20 – 30 kcal mol^{-1}. The resonating model of 2c – 3e bonds can be applied to the description of the hydrogen binding in those cationic systems. Equation (11) accounts for most of the binding energy, even for quite large ΔPA. More data are, however, required to confirm this finding. Nevertheless, we have also shown that Marcus theory and the resonance model of the hydrogen bond are very similar, especially in the case of low ΔPA.

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Equation (3). Similarly, our proposal could be formulated to show an exponential variation of the proton binding energy toward ΔPA for small ΔPA. Such an expression could be compared with the empirical expression proposed by T. Zeegers-Huyskens, *J. Mol. Struct.* **1988**, *177*, 125: $D_{AH^+B} = x\exp(-x' \mid \Delta PA \mid)$. One would therefore find $x \approx D$ and $x' \approx 1/(2\sqrt{D_{AH^+A}\, D_{BH^+B}})$.

[28] It is found that the geometry optimization of the AH^+A systems collapsed to unsymmetrical hydrogen bonded complexes in all cases but the carbonyl one (which bear a symmetrical minimum). In all the other cases the symmetrical structure was found to be a transition state to the proton transfer, and we prefered to use the unsymmetrical D_{AH^+A} in these cases.

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