

Three-Electron Binding between Carbonyl-like Compounds and Ammonia Radical Cation. Comparison with the Hydrogen Bonded Complex

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Abstract: High-level ab initio calculations were performed on a two-center three-electron (2c–3e) bond between formaldehyde and the radical cation of ammonia. The stability of the resulting complex is found to be 21.8 kcal/mol, only 2.2 kcal/mol higher than the hydrogen bonded complex of the same species. Upon replacing the formaldehyde by thioformaldehyde (H₂C=S), the 2c–3e complex is found to be 20 kcal/mol more stable than the corresponding hydrogen bonded complex. The imine group is also studied via the H₂C=NH system. This compound exhibits a larger 2c–3e bond energy, 32.0 kcal/mol, but this is still 8.8 kcal/mol higher in energy than the hydrogen bonded complex. This is the first theoretical evidence of a possible 2c–3e complex involving organic unsaturated systems.

Introduction

Two-center three-electron (2c–3e) interaction can be stabilizing, leading to what is called in the following discussion a two-center three-electron (2c–3e) bonded complex. The 2c–3e bond is described as a “σ* bond”¹ due to the fact that the σ* orbital is singly occupied using molecular orbital (MO) theory (Scheme 1). Since an antibonding orbital is singly occupied, the bond order is reduced by a half. This type of chemical bond between two atoms, A and B, is traditionally noted A·:B.

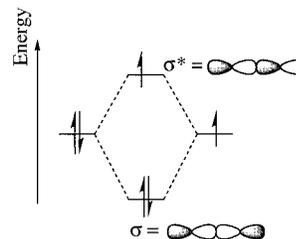
In the valence bond (VB) formalism, this interaction is depicted as a resonance between two VB structures. In a cationic system [A·:B]⁺ for instance, those are



The energy of the 2c–3e bond increases with the resonance energy. As analyzed in earlier studies,^{2,3,4} the 2c–3e bond strength strongly depends on the difference between the ionization potentials of the fragments. The VB picture⁵ evidences this fact: The resonance energy is large if the two VB structures are close in energy. In fact, the energy difference between the VB structures may be approximated as the difference between the ionization potentials of A and B. On the basis of this relationship, the strongest 2c–3e bonds are observed in homonuclear charged species. They are of the type [A·:A]⁺.

Indeed, most of the experimentally found 2c–3e bonds are homonuclear, as has been found for a number of [S·:S]⁺⁶

Scheme 1



complexes in small organic molecules. Homonuclear [N·:N]⁺⁷ and [Hal·:Hal]⁺⁸ (Hal: halogene) bonds have also been found experimentally. They have been detected and characterized by UV spectroscopy,^{6a,9} mass spectroscopy,^{6c,8} and electron spin resonance spectroscopy¹ as well as by chemically induced dynamic nuclear polarization (CIDNP) effects.¹⁰

Such (2c–3e) complexes are also possible intermediates in electron-transfer processes.¹¹ Consequently, these species can play a decisive role in radical chemistry. Despite the above statement on homonuclear binding, some intramolecular het-

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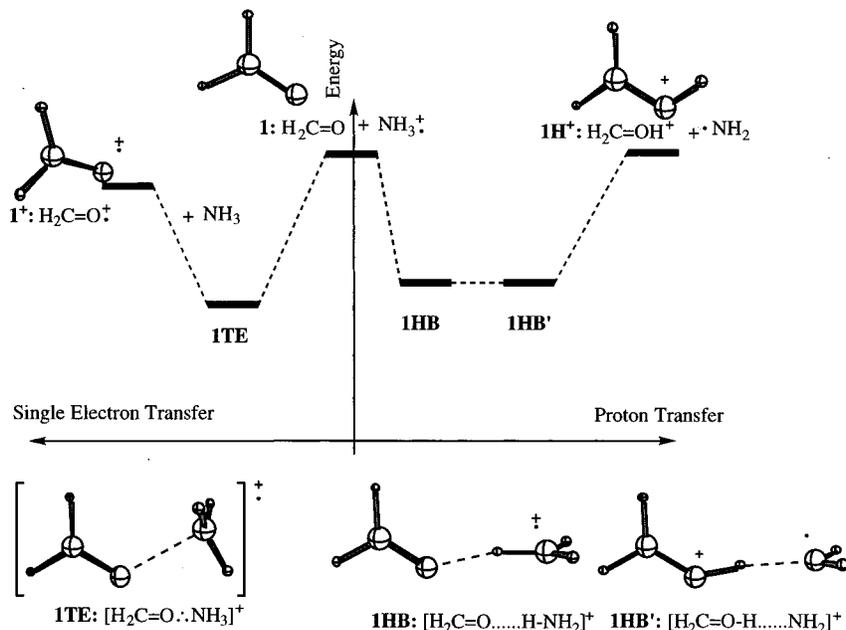


Figure 1. Qualitative reaction pathways of the formation of 2c–3e bonded complexes and hydrogen bonded complexes.

Table 1. Three-Electron Bonds in Saturated Systems as Calculated at the MP2/6-31G(d)//HF/6-31G(d) Level (from Ref 2)

compound	A : B	r_{AB} (Å)	D_{AB} (kcal mol ⁻¹)
[H ₂ O : NH ₃] ⁺	O : N	<i>a</i>	<i>a</i>
[H ₂ S : NH ₃] ⁺	S : N	2.441	33.3
[H ₃ N : NH ₃] ⁺	N : N	2.162	40.0

^a A proton transfer was reported.

eronuclear bonds ([I : C]¹ or [S : N]^{10,11}) have been described in recent publications.

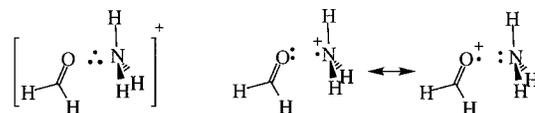
In a systematic theoretical study of 2c–3e bonded systems, Clark² predicted various stable homonuclear and heteronuclear 2c–3e bonded systems. His results which are relevant to the present study are summarized in Table 1. For the [H₂O : NH₃]⁺ system, the 2c–3e bond optimization was found to collapse to a hydrogen bonded system (vide infra). The other systems are stable despite a rather large bond length, characteristic for such odd electron binding.

For cationic homonuclear systems, Gill et al. focused on the competition between the formation of 2c–3e and hydrogen bonds.³ Their study especially introduced the transition state connecting a 2c–3e bond to the corresponding hydrogen bonded system. For the first-row elements, the 2c–3e bonds N : N, O : O, and F : F were found to be approximately 10 kcal/mol higher in energy than the corresponding hydrogen bonds. For the second-row elements, however, the 2c–3e bonds are more stable than the hydrogen bonded systems.

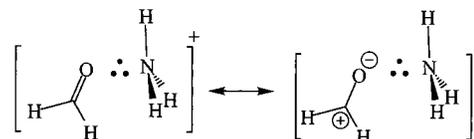
Hitherto, all studies of the 2c–3e binding “phenomena” only concern saturated systems. In this paper we intend to focus our theoretical study on a possible 2c–3e bond involving a lone electron pair of unsaturated organic functional groups, namely carbonyls, thionyls, and imines, in the neighborhood of an ammonia radical cation.

By starting from formaldehyde **1** (H₂C=O) and NH₃⁺, the radical cation of ammonia, two reaction pathways can be followed (Figure 1). On the left-hand side, the 2c–3e bonded complex (**1TE**) is considered as a intermediate in a single electron transfer (SET) process. One product of the SET is the radical cation H₂C=O⁺ (noted **1**⁺). Further on, NH₃ as a neutral closed shell species is also obtained. On the right-hand side, a

Scheme 2



Scheme 3



proton transfer via the intermediates **1HB** and **1HB'** is depicted. The proton transfer produces the cationic protonated carbonyl group (**1H**⁺) and the “π” radical of •NH₂. The structure **1HB** is the first hydrogen bonded complex which appears before the proton transfer occurs. In this structure, a lone pair of the carbonyl attracts a proton of the ammonia radical cation. The **1HB'** structure which follows represents the hydrogen bonded complex after the proton transfer. The lone pair of the deprotonated species •NH₂ and the hydrogen of the protonated formaldehyde **1H**⁺ are involved in this structure. Searches were only carried out on structures of type **HB**. However, in the imine case, the optimization collapsed to the proton-transfer structure **HB'**.

In accordance to Gill and Radom's study a transition state connecting **1TE** to the hydrogen bonded complexes **1HB** or **1HB'** could be found. This subject, however, requires a separate treatment¹² and is beyond the scope of this article. We rather use the hydrogen bond as a well-established interaction in order to compare it with the 2c–3e bond.

The study of the 2c–3e binding phenomena in unsaturated compounds is particularly interesting since the usual charge fluctuation in the 2c–3e bond (Scheme 2) may be strongly modified by an additional mesomeric effect (Scheme 3). Of course, if this mesomeric effect is increased in the 2c–3e bond due to a partial electron loss from the lone pair of the functional group, one may expect a modification of the reactivity of such

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Table 2. Ionization Potentials (eV) as Calculated Using the aug-cc-pVDZ Basis Set at Various Levels of Approximation on UMP2/6-31G(d) Optimized Geometries (without Zero-Point Vibrational Energy Correction)

	PMP3	CCSD(T)	exptl
NH ₃	9.90	9.98	10.16 ^a
H ₂ C=O	10.72	10.74	10.90 ^b
H ₂ C=S	9.12	9.20	9.38 ^b
H ₂ C=NH	9.77	9.82	9.88 ^c

^a See ref 16a. ^b See ref 16b. ^c See ref 16c.

compounds (modification of the electrophilicity of these species as well as the α -acidity of carbonyl and carbonyl-like compounds).

This modification may be comparable to the action of a proton on a carbonyl oxygen. Additionally, a chemical reactivity like that of electrophilic radicals¹³ should be observable. However, the study of the reactivity of such species is still far ahead and we will mainly focus here on the fact that such a complex might exist.

On the basis of quantum mechanical calculations, we will thus discuss in this paper the following issues:

(i) Could the 2c–3e complex be a stable intermediate in the single electron-transfer process between H₂C=X and NH₃⁺ (X being either an oxygen, a sulfur, or a NH group)?

(ii) How do the carbonyl-like functional groups compare with regard to their 2c–3e interaction?

(iii) How does the relative stability of the 2c–3e complex compared to that of a hydrogen bonded complex in the different unsaturated organic functional groups?

Computational Details

From the computational point of view, the hydrogen bond mainly involves electrostatic interactions and is already well-described at the Hartree–Fock (HF) level. However, previous studies have shown the importance of the electronic correlation for the correct description of the hemi-bonded systems. It is thus well-established that the Hartree–Fock level is not appropriate to describe quantitatively the bond energy. Density functional theory has been recently proven to be disappointing for the treatment of this kind of interaction and may strongly overestimate the 2c–3e bond energy.¹⁴ The calculation of the electronic correlation by means of Möller–Plesset perturbation at the second order (MP2 level) has been proven to be satisfactory.³ For this reason we used the frozen core unrestricted MP2/6-31G(d) level to optimize all the geometries in a balanced way. The nature of the stationary points was checked by calculating vibrational frequencies. This also provided the zero-point correction at this level for each structure. These values will be indicated in the following without scaling.

Since our study also deals with single electron-transfer processes, ionization potentials (IPs) of the dissociative fragments are involved. This requires both a large basis set and a high level of calculation. On the MP2/6-31G(d) optimized structures we thus performed single point calculations using the unrestricted coupled cluster formalism (CCSD-(T) level) with the augmented cc-pVDZ¹⁵ (aug-cc-pVDZ) basis set. Indeed, this level is able to predict quite accurately the ionization potentials of the investigated organic molecules (Table 2). This table also displays the results of the Möller–Plesset calculations at the third order, which also appear to be satisfactory when compared to the experimental values.¹⁶

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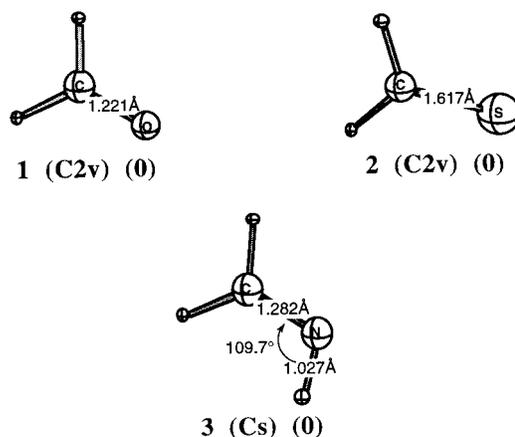


Figure 2. Geometrical parameters of the carbonyl-like starting materials as optimized at the UMP2/6-31G(d) level. The number in parentheses notes the number of imaginary frequencies.

For all of the calculations we used the Gaussian 94 package.¹⁷ Cartesian d orbitals (6D) were used in the 6-31G(d) basis, while 5D were used in the Dunning basis set aug-cc-pVDZ. In all the cases, the spin contamination was found to be well-corrected by the projection procedure. All of the computational information are provided in the Supporting Information (absolute energies, symmetry and states, spin contamination before $\langle S^2 \rangle$ and after the usual correction $\langle S^2 \rangle^A$, and xyz coordinates of each structures).

Results and Discussion

The starting materials are the carbonyl-like functional groups and the NH₃⁺ radical cation. Figure 2 displays the main geometrical parameters of the fragments as optimized at the UMP2/6-31G(d) level.

Three-Electron Bonds. The geometries obtained for the 2c–3e complexes of the carbonyl (**1TE**), the thiocarbonyl (**2TE**), and imine (**3TE**) systems are presented in Figure 3. The NH₃ fragment is σ bonded to the X atom (oxygen, sulfur, and nitrogen, respectively) of the unsaturated function group through the lone pair. The nitrogen atom is thus situated in the molecular plane. As the X...N bond is usually quite elongated compared to a “normal” two-center two-electron bond, a nearly free rotation of the ammonia around the X–N axis is found. In all of the cases two structures of C_s symmetry were found, approximately corresponding to the eclipsed and staggered forms of the equivalent saturated compounds.^{2,3} The “rotated” conformers are noted here as **TE'**. As discussed in the following, their energies are very close to the energies of the corresponding **TE** conformers (vide infra).

The 2c–3e bond length in the thionyl and in the imine compounds are similar to those of the saturated species. The $\angle NXC$ angles (120°, 95°, and 123° for X = O, S, and N, respectively) are consistent with the usual coordinations of these

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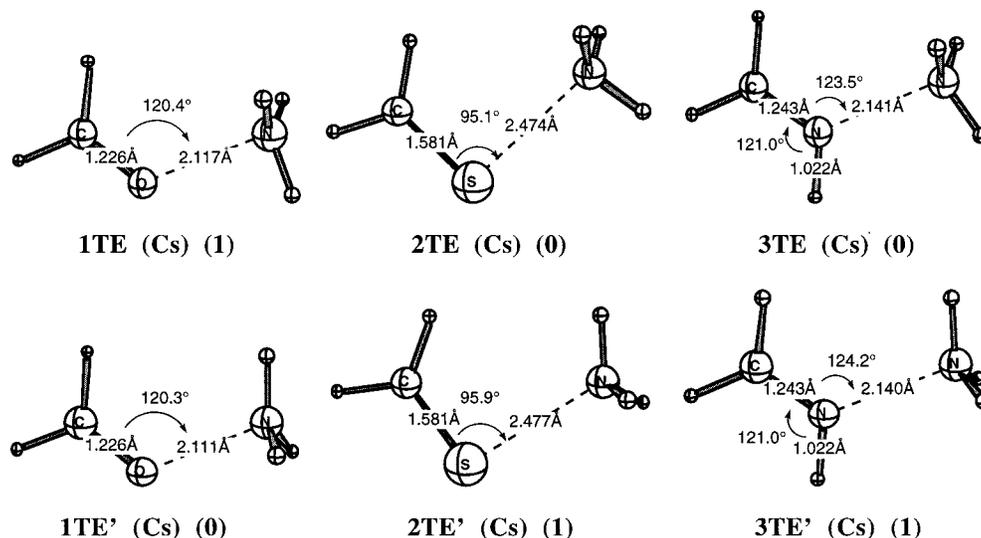


Figure 3. Geometrical parameters of the 2c–3e complexes as optimized at the UMP2/6-31G(d) level. The number in parentheses notes the number of imaginary frequencies.

Table 3. Relative Energies (kcal/mol) as Calculated at the Optimization Level UMP2/6-31G(d)

6-31G(D)	ZPC	HF	PUHF	MP2	PMP2
1 + NH ₃ ⁺	0.0	0.0	0.0	0.0	0.0
1 ⁺ + NH ₃	-0.2	19.9	18.2	30.3	28.7
1TE	3.6	-12.1	-13.8	-19.0	-20.6
1TE'	3.7	-11.8	-13.7	-19.0	-20.7
1HB	1.9	-23.2	-23.2	-23.9	-23.9
1H ⁺ + NH ₂	0.1	15.4	15.8	22.7	23.0
2 ⁺ + NH ₃ ⁺	0.0	0.0	0.0	0.0	0.0
2 ⁺ + NH ₃	0.9	-8.8	-13.5	-9.6	-14.4
2TE	3.8	-29.3	-35.9	-37.6	-44.1
2TE'	3.7	-29.1	-35.8	-37.4	-43.9
2HB	1.5	-14.8	-14.8	-17.1	-17.1
2H ⁺ + NH ₂	-1.9	9.2	9.6	13.3	13.7
3 ⁺ + NH ₃ ⁺	0.0	0.0	0.0	0.0	0.0
3 ⁺ + NH ₃	-0.5	-0.8	-4.4	5.0	1.5
3TE	4.4	-24.5	-30.3	-33.3	-38.5
3TE'	4.4	-24.5	-30.3	-33.3	-38.5
3HB'	2.7	-44.9	-44.6	-43.8	-43.6
3H ⁺ + NH ₂	0.4	-25.1	-24.7	-19.7	-19.3

atoms. The σ bonding and σ^* antibonding orbitals have indeed almost pure p character in the sulfur case, while they are sp^2 hybridized in the two other systems.

At the MP2/6-31G(d) level, the structure **1TE** has an imaginary frequency of only 12 cm^{-1} , denoting a very flat potential energy surface for this rotation. This can be seen in Table 3, where the relative energies of the investigated compounds at the level of the geometry optimization are displayed: structures **TE** and **TE'** are extremely close in energy. The results of the calculations using the larger basis set are displayed in Table 4. At the PMP3 level the difference in energy between these structures is again extremely small. In the following we will thus focus only on the structures **1TE**, **2TE**, and **3TE** rather than on the rotated conformers. At the CCSD(T) level the relative energies of the three-electron bonded systems, as compared to the starting materials are (in kcal/mol) -21.8 (**1TE**), -42.8 (**2TE**), and -35.7 (**3TE**). Furthermore, they are lower in energy than any of the investigated dissociative fragments. Such structures are therefore possible intermediates in SET processes.

However, the 2c–3e binding energy has to be calculated with respect to the dissociation fragments of lowest energy. As illustrated in Table 4, the starting materials are the energetically

Table 4. Relative Energies (kcal/mol) as Calculated Using Dunning's aug-cc-pVDZ Basis Set on UMP2/6-31G(d) Geometries

	HF	MP2	PMP2	PMP3	CCSD	CCSD(T)
1 + NH ₃ ⁺	0.0	0.0	0.0	0.0	0.0	0.0
1 ⁺ + NH ₃	17.5	25.2	23.4	19.1	17.7	17.5
1TE	-10.5	-18.5	-19.9	-18.4	-20.2	-21.8
1TE'	-10.2	-18.4	-19.9	-18.3		
1HB	-22.8	-23.9	-23.9	-23.9	-23.7	-24.0
1H ⁺ + NH ₂	12.3	18.0	18.3	15.1	15.1	15.6
2 + NH ₃ ⁺	0.0	0.0	0.0	0.0	0.0	0.0
2 ⁺ + NH ₃	-11.5	-14.4	-18.6	-17.9	-17.8	-17.9
2TE	-27.9	-38.6	-44.6	-42.4	-41.4	-42.8
2TE'	-27.7	-38.4	-44.4	-42.2		
2HB	-16.6	-12.1	-17.2	-18.0	-18.2	-18.7
2H ⁺ + NH ₂	5.5	8.3	8.5	6.0	4.9	4.9
3 + NH ₃ ⁺	0.0	0.0	0.0	0.0	0.0	0.0
3 ⁺ + NH ₃	-0.5	0.8	-2.8	-2.9	-3.4	-3.7
3TE	-20.1	-33.2	-38.2	-35.2	-34.0	-35.7
3TE'	-20.0	-33.2	-38.2	-35.2		
3HB'	-41.2	-43.6	-43.4	-44.1	-44.1	-44.5
3H ⁺ + NH ₂	-23.7	-21.7	-21.5	-23.0	-23.5	-23.3

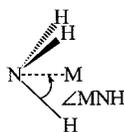
Table 5. Spin Densities as Calculated at the CCD/aug-cc-pVDZ Level on the Heavy Atoms of the 2c–3e Structures

	C	X	N
1TE	0.12	0.10	0.90
2TE	0.01	0.70	0.31
3TE	0.21	0.21	0.63

lowest dissociative fragments only in the case of the carbonyl compound **1**. For the thionyl **2** and imine **3** cases, the lowest dissociation fragments of the 2c–3e bond are those involving the cationic organic functional group **2⁺** and **3⁺**. In these cases a single electron transfer from **2** or **3** to NH₃⁺ occurs along the calculated reaction pathway. At the CCSD(T) level, the bond energy of the 2c–3e complexes are thus 21.8 kcal/mol for the compound **1TE**, 24.9 kcal/mol for **2TE**, and 32.0 kcal/mol for **3TE**. These values are of the same order of magnitude as in the saturated systems, but smaller by about 10 kcal/mol.

Spin density analyses on the non-hydrogen atoms as calculated at the CCD/aug-cc-pVDZ level are displayed in Table 5. This level of calculation is required for a reasonable accuracy. A strong, symmetrical, 2c–3e bond would display a spin density of 0.5 on each atom linked by this odd-electron bond. Indeed, in the most symmetrical 2c–3e bonded system of the investi-

Scheme 4



gated compounds (**3TE**), a spin density of 0.63 on the nitrogen atom of the NH₃ moiety is found. A spin density of 0.21 is found on the nitrogen as well as on the carbon atom of the imine moiety. Thus, the spin density distribution on both sides of the 2c–3e bond is close to 0.5. In unsaturated systems an electronic displacement (Scheme 3) is able to compensate for the loss of electron density on the X atom lone pair of the functional group.

The spin density on the imine moiety is therefore shared between the two atoms of the unsaturated functional group. In the complex **2TE**, the low spin density on the nitrogen atom reveals that the electron transfer from the sulfur lone pair to the nitrogen is almost complete in the 2c–3e complex. This is consistent with the VB analysis since the more stable dissociative fragments of the 2c–3e bond in this thiocarbonyl case are 2⁺ + NH₃. The 2c–3e bond must thus have a larger contribution from the corresponding VB structure. The same VB analysis also explains why in the carbonyl compound **1TE** a spin density close to 1.0 on the nitrogen atom is found. These results are also consistent with the pyramidalization angle of the NH₃ moiety. If we call M the midpoint of the three hydrogen atoms of NH₃ (Scheme 4), the values of the ∠MNH angles are 80°, 75°, and 70° in **1TE**, **3TE**, and **2TE**, respectively. Since the NH₃⁺ cation is planar (∠MNH = 90°) and the NH₃ neutral compound is pyramidalized (∠MNH = 67.5°), one can describe the degree of the electron transfer to the NH₃⁺ moiety using this ∠MNH coordinate.

Hydrogen Bonded Complexes. As mentioned in the Introduction, we will compare the 2c–3e bonded systems to the hydrogen bonded complexes (**HB**). The geometrical parameters of these systems are displayed in Figure 4. The hydrogen bonded complexes were found to be either planar, as in **1HB** (∠OHNH = 0°), or twisted, as in **2HB** (∠SHNH = 90°). As is observed for the case of the 2c–3e complexes, a nearly free rotation on the NH₃⁺ moiety is found. In the carbonyl complex, the energy difference between the planar and the twisted structures is only 0.05 kcal/mol, the planar structure being characterized as a minima. In the thionyl system, the structure **2HB** is 3.2 kcal/mol lower in energy than the corresponding planar structure.

Such a hydrogen bond can lead to a proton transfer from the NH₃⁺ moiety to the carbonyl-like system. A careful optimization of the hydrogen bonded structure **3HB** always collapsed to the **3HB'** structure where a proton has been transferred from the NH₃⁺ moiety to the imine. This fact is not surprising if one takes into account the strong stabilization of the iminium cation (3H⁺ + NH₂) compared to the other dissociative fragments (1H⁺ + NH₂ and 2H⁺ + NH₂).

Comparison of 2c–3e and the Corresponding Hydrogen Bond Stabilities. The hydrogen bonded complexes are used in this paper as a well-established interaction to which we can compare the unsaturated 2c–3e bonded complex. We find that in the first row (carbonyl and imine compounds) the hydrogen bonded complex is more stable than the corresponding 2c–3e bonded complex and is therefore the favored structure. Of course, in the case of tertiary amines, hydrogen bonded complexes cannot be formed. Therefore, the calculated structures of type 2c–3e are particularly relevant in these cases.

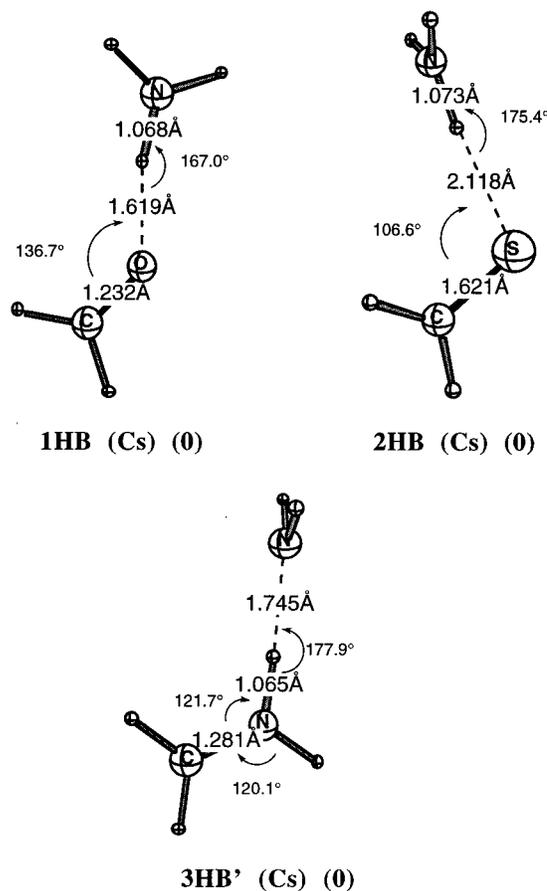


Figure 4. Geometrical parameters of the hydrogen bonded complexes as optimized at the UMP2/6-31G(d) level. The number in parentheses notes the number of imaginary frequencies.

For the thionyl compound, the 2c–3e complex is significantly more stable than the corresponding hydrogen bonded complex. The energy difference is greater than 20 kcal/mol. They should thus be stable intermediates in a SET process, even if an hydrogen bond can occur.

Charge Density Distribution in the Unsaturated 2c–3e Bonded Species. The reactivity of the carbonyl-like protonated species is very well established in organic chemistry. This reactivity is usually attributed to the positive charge density at the carbon atom. To estimate a possible reactivity of the investigated 2c–3e species, we have performed high-level charge density calculations on the neutral, the 2c–3e bonded complex, and the protonated species.

The results, as calculated at the CCD¹⁸ level, are displayed in Figure 6. In the carbonyl and in the imine cases, the charge density at the carbon atom in the 2c–3e complexes ranges between the one calculated for the corresponding neutral and protonated species. Therefore, a nucleophilic attack on this atom as is observed, for instance, for the addition of alcohols to the protonated carbonyl function in acetalization reactions should be possible. Concerning the α-acidity of more complex molecules of this type, one can anticipate a comparable α-acidity in both type of electrophiles. This α-acidity is involved in acid-catalyzed aldolization reactions.

Of course our 2c–3e complexes are open-shell species. Therefore, additionally to the electrophilic character, a reactivity like that of electrophilic radicals^{13,19} should be observed.

(18) CCD: Coupled Cluster calculations, using only Double substitution from the Hartree–Fock determinant. See: Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley J. S. *Int. J. Quantum Chem. XIV* 1978, 545–560.

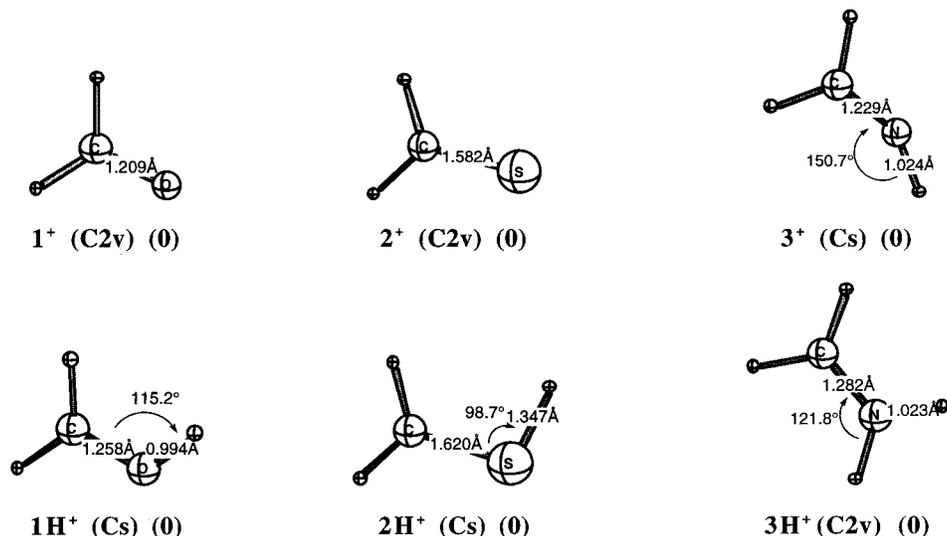


Figure 5. Single electron-transfer products (1^+ , 2^+ , and 3^+) and proton-transfer products ($1H^+$, $2H^+$, and $3H^+$) as optimized at the UMP2/6-31G(d) level. The number in parentheses notes the number of imaginary frequencies.

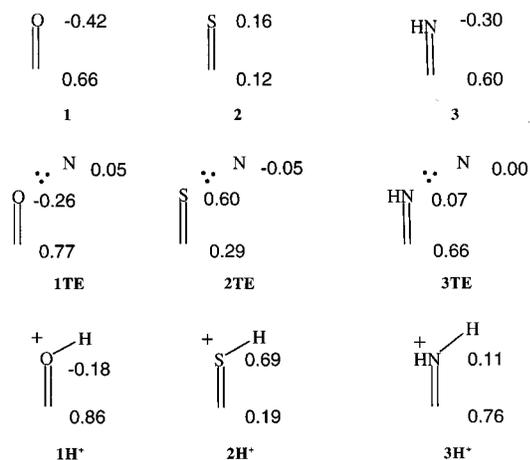


Figure 6. Charge density as calculated at the CCD/aug-cc-pvdz level for the neutral organic compounds (**1–3**), for the 2c–3e bonded systems (**1TE**, **2TE**, and **3TE**), and for the protonated species (**1H⁺**, **2H⁺**, and **3H⁺**).

In the case of the thiocarbonyl function, in the protonated species the charge is essentially located on the sulfur atom. In the corresponding 2c–3e species, the positive charge on the carbon atom is increased, but it remains rather low.

Conclusion

As in the case of the saturated species, the unsaturated compounds are able to form a 2c–3e bond between the lone pair of the unsaturated organic functional group and the odd electron of the NH_3^+ moiety. The stabilities of these complexes are comparable to the corresponding hydrogen bonded species.

(19) Schmittel, M.; Burghart, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2550–2589.

The extremely rich reactivity of these organic functions may be modified in such 2c–3e complexes with respect to the corresponding free groups because the 2c–3e bond modifies the usual mesomeric effect.

Radical cation species such as NH_3^+ are very reactive, but due to the fact that a 2c–3e bond might be generated in the complex, they are stabilized by 20–30 kcal/mol. We have shown that this NH_3^+ species should transfer its reactivity onto the functional groups. In the cases of the carbonyl and the imine function, charge density analysis of the 2c–3e species are in favor of this hypothesis.

For the thionyl group, we have shown that the formation of such a complex is much more favorable than the formation of a corresponding hydrogen bonded complex and the charge density analysis indicates a somewhat lower reactivity of these complexes. Finally, the N: \cdot N 2c–3e bond involving one imine function is not as strong as in the case of the corresponding saturated compounds, but it should be observed when hydrogen bond formation is impossible (in the case of tertiary amines). Further theoretical study of the substituent effects on these 2c–3e systems are in progress.

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Supporting Information Available: Tables of absolute energies, symmetry and states, spin contamination before $\langle S^2 \rangle$ and after the usual correction $\langle S^2 A \rangle$, and xyz coordinates for all the stationary points (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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