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Classical and Distonic Radical Cations: A Valence Bond Approach

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Abstract: The conventional radical cations arising from the ionization of CH_3CH_2X (X = F, OH, NH_2, Cl, SH, PH_2), and their distonic isomers, $CH_2CH_2XH^{\bullet+}$, were studied by means of standard Møller–Plesset and G2 methods, and by an ab initio valence bond method. Among the conventional structures, two distinct states are considered. In the so-called **c**′ states, the unpaired electron is in an orbital that lies in the plane of the heavy atoms, while the **c**″ states have their unpaired electron in an orbital lying out of the plane. It is shown that **c**′ states are, as a rule, more stable than the **c**″ states, by up to approximately 20 kJ mol^{-1} depending on the nature of X, owing to a stabilizing interplay of resonating structures. While the geometries of the **c**″ states are rather similar to those of the neutral molecules, some of the **c**′ states display very different geometries, characterized by elongated C–C bonds, particularly when X = F or, to a lesser extent, when X = OH or Cl. These peculiar geometric features are rationalized by the valence bond analysis, which reveals that the C–C bond in these species is better viewed as a two-center, one-electron bond. The distonic radical cations are generally more stable than the conventional ones (by 20–100 kJ mol^{-1}), except for the less electronegative X groups of the series, namely X = SH and PH_2. In these two cases, together with X = NH_2, the radical cation displays a classical distonic structure, as regards the geometry and electronic state. On the other hand, considerable C–X elongation is found for X = F or Cl. In these last cases, the valence bond analysis shows that the radical cation is better viewed as an ion–molecule complex between an ionized ethylene and a neutral HX molecule. The electronic structure of the distonic radical cation with X = OH lies between the two previous limiting descriptions.

Keywords: ab initio calculations · electronic structure · radical cations · valence bond method

Introduction

The removal of an electron from a molecular substrate leads to a species bearing both a single unpaired electron and an electron hole responsible for a net positive charge. Due to their simultaneous cationic and radical characters, radical cations are able to undergo a large variety of reactions, and for this reason they are of great interest in various domains of condensed-phase chemistry,[1–5] in many biochemical processes,[6–8] and in gas-phase ion chemistry[9–11] Radical cations may possess a structure with the same atom connectivity as their parent neutral precursors, or they may rearrange to form new structures, which sometimes have no stable neutral counterpart. Of particular interest, in the first category of radical cations, are ionized enol[12] and ionized carbene,[13] which have demonstrated particularly high stability in the gas phase, at variance with that of the corresponding neutral species. In the second category are ion-neutral complexes[14] and cations best described by valence structures, in which the charge and radical centers are formally separated: so-called distonic radical cations.[15–18] Representative of this class are species bearing a carbon-centered radical and a positive charge located on a protonated heteroatom X, for example, $^{\bullet}CH_2\cdots XH^+$ (X = halogen, O, N, and so on). A number of studies have been devoted to the peculiarities of

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the structure and stability of distonic radical cations with respect to their conventional isomers (i.e. $^{\bullet}CH_2{\cdots}OH_2^+$ vs. $CH_3OH^{\bullet+}$).[19–31] As a rule, for the simplest series, $^{\bullet}CH_2XH^+$ distonic ions bearing heteroatoms X pertaining to the first-row elements are more stable than their conventional counterparts $CH_3X^{\bullet+}$, and the difference in stability increases with the electronegativity of X. By contrast, when X is a second-row element, the stability order is in favor of the conventional isomer radical cation. No such detailed information is presently available for the highest homologues even if several particular features concerning the geometrical parameters of some specific radical cations were observed from quantum chemical calculations. For example, an unusually long C–O bond was predicted theoretically for the distonic ion $^{\bullet}CH_2CH_2OH_2^+$[19,24] and, more surprisingly, a similar prediction has been made for the C–C bond of the conventional radical cations $CH_3CH_2OH^{\bullet+}$[19,24] and $CH_3CH_2Cl^{\bullet+}$.[30b]

The key for the understanding of the structural and thermochemical properties of radical cations, as well as their chemical reactivity, is evidently related to the radical and cationic characters of these peculiar reagents. From this point of view it is of interest to offer a description of the electronic structure of radical cations that complements the usual molecular orbital approach. To the best of our knowledge, no systematic study has been undertaken on radical cations by using the valence bond theory, which, by its use of resonance hybrid contributions, is able to offer a "localized" view of the radical and charge sites and thus a better understanding of its related reactivity and stability.

In the present work we examine the conventional, $CH_3CH_2X^{\bullet+}$ (**1c**–**6c**), and β- (or 1,2-) distonic, $CH_2CH_2XH^{\bullet+}$ (**1d**–**6d**), radical cations (X = F, OH, NH_2, Cl, SH, PH_2, Table 1) by using two different and complementary theoretical levels. A standard MP2/6–31G(d) level has been used for the geometry optimization, and the same basis set has been used for the valence bond treatment. Further, energy estimates were undertaken using the composite G2 method in order to provide accurate heat of formation values for both kinds of isomers.

Table 1. Investigated conventional (**c**) and distonic (**d**) radical cations.

CH_3CH_2F	**1c**	CH_2CH_2FH	**1d**
CH_3CH_2OH	**2c**	$CH_2CH_2OH_2$	**2d**
$CH_3CH_2NH_2$	**3c**	$CH_2CH_2NH_3$	**3d**
CH_3CH_2Cl	**4c**	CH_2CH_2ClH	**4d**
CH_3CH_2SH	**5c**	$CH_2CH_2SH_2$	**5d**
$CH_3CH_2PH_2$	**6c**	$CH_2CH_2PH_3$	**6d**

Results and Discussion

Conventional structures: Removing an electron from a lone pair of neutral CH_3CH_2X is expected to lead to a conventional structure, with the odd electron and the positive charge being formally located on the same atom. To better understand the electronic structure of these radical cations, it is important to distinguish between two typical situations according to the spatial location of the lone pair from which an electron has been removed: either 1) in the plane, or 2) out of the plane defined by the three heavy atoms. For $CH_3CH_2F^{\bullet+}$ and $CH_3CH_2Cl^{\bullet+}$ in their C_s geometries (see Figure 1), we are dealing with an A′ state in the first case (the singly occupied orbital is symmetrical with respect to the symmetry plane), and with an A″ state in the second case (the singly occupied orbital is mostly a p atomic orbital perpendicular to the symmetry plane). These lone pair molecular orbitals are represented schematically in Scheme 1, and labeled **a**′ (in the plane) and **a**″ (out of the plane), respectively.

Generalizing to the other members of the series of conventional structures, the label **c**′ will refer to the $CH_3CH_2X^{\bullet+}$ radical cations the singly occupied orbital of which lies in the plane of the heavy atoms, and **c**″ will refer to the conformers in which this orbital points out of the plane. For the four species **2c**, **3c**, **5c** and **6c**, the states **c**′ and **c**″ are connected by a rotation around the C–X bond. These conformers have been characterized as true minima on the corresponding potential-energy surfaces and are separated by small rotational barriers of less than 7 kJ mol^{-1} (MP2/6–31G(d) calculations). Thus, for X = OH or NH_2, the **c**′ state is the one that displays a CCOH or CCNH dihedral angle close to 90° (see **2c**′ and **3c**′ in Figure 1). Lastly, for X = SH or PH_2, the **c**′ state corresponds to a CCSH or CCPH dihedral angle much closer to 60° as displayed in Figure 1 for **5c**′ and **6c**′.

As a general rule, in **c**′ states, the unpaired electron may interact with the C–C bond, which lies in the same plane, while this is not the case for the **c**″ states. In valence bond terms, the electronic interaction occurring in the **c**′ states is characterized by the resonance between the six valence bond (VB) structures I–VI (Scheme 2), with two consequences: 1) as resonance is generally stabilizing, **c**′ states are expected to be more stable, or at least no less stable, than **c**″ states; 2) according to the respective weights of the various VB structures, the geometries of the **c**′ states may be quite different from those of the initial neutral species. On the other hand, no such interplay of VB structures can be envisaged for the **c**″ states, which are each described by a unique possible Lewis structure, in which the odd electron formally remains localized on the X site. It follows that the geometries of the **c**″ states, which are not subject to mesomeric interplay, are predicted to be close to those of the neutral molecules.

The total and relative energies for the **c**′ and **c**″ states of the conventional structures, as calculated at the MP2 and G2 levels, are displayed in Table S1 of the Supporting information. It is seen that, as predicted by the qualitative reasoning above, the **c**′ states are either equally stable or more stable than the **c**″ states for all species. However, the stability difference is significant (≈20 kJ mol^{-1} at the G2 level) only in two cases: fluoroethane and ethanol radical cations (X = F and X = OH). In the chloroethane case, the **c**′ state is more stable than the **c**″ state by only 4 kJ mol^{-1}. In the re-

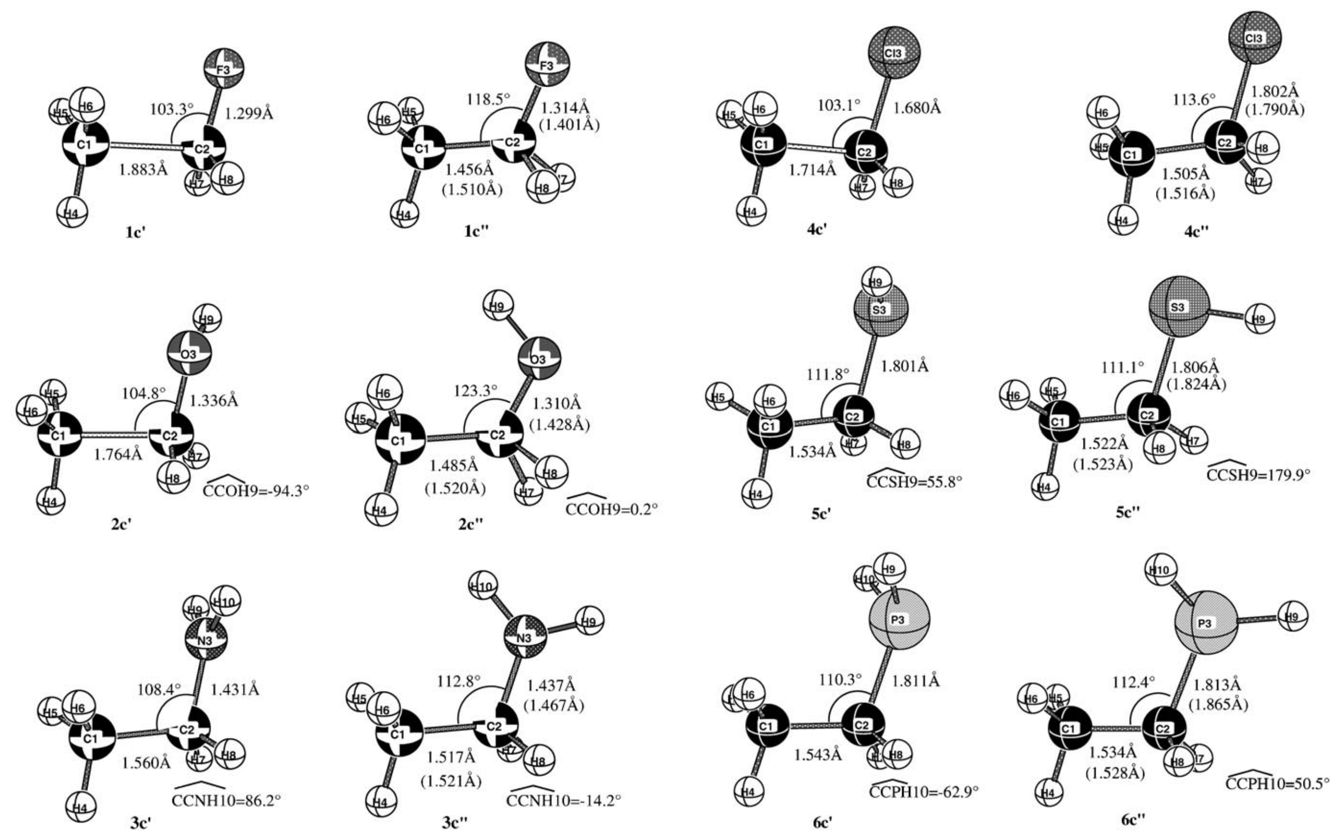


Figure 1. MP2/6–31G(d) optimized geometries of **1c′**–**6c′** and **1c″**–**6c″** radical cations (CC and CX bond lengths of the neutral are indicated in parentheses).

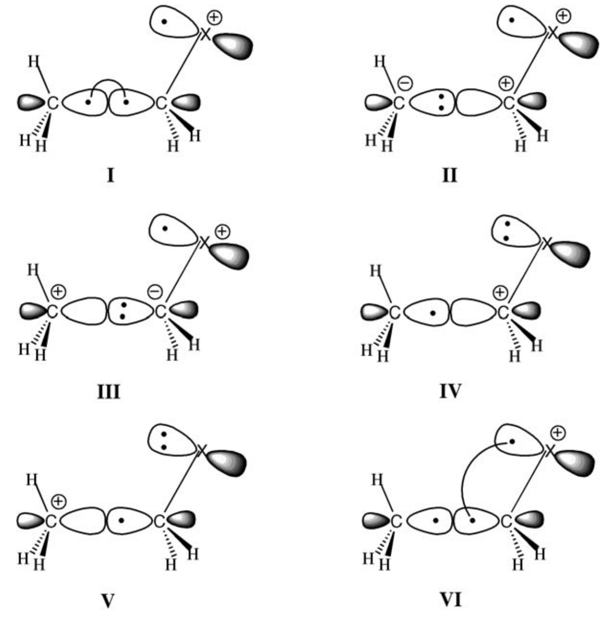

a' lone-pair MO

a" lone-pair MO

Scheme 1. The two possible orientations of the singly occupied molecular orbital.

maining cases ($X=NH_2$, SH, PH_2), the difference in stability does not exceed 2 $kJ\,mol^{-1}$.

Let us now consider the geometries, starting with the **c**″ states. As already noted, each **c**″ state is represented by a unique Lewis structure which closely resembles that of the corresponding neutral state, the only difference being the removal of a nonbonding electron. In accord, the main geometrical features (the C−C and C−X bond lengths) are found to be rather similar to those of the neutral states (Figure 1), especially when X belongs to the third row of the periodic table. For the others (X=F, OH, NH_2), the C−C and C−X bond lengths are shorter in the cations than in the neutral states. For the C−X bond, removing an electron from a π_X lone pair diminishes the Pauli repulsion between this lone pair and the neighboring π_{CH_2} orbital of the central carbon atom. In other words, a four-electron repulsion is



Scheme 2. Relevant VB structures for the description of the **c**′ states of the conventional ions.

transformed into a three-electron interaction, hence inducing the C−X bond shortening. Concomitantly, the three-electron bond delocalizes the charge and diminishes the average population of the central π_{CH_2} orbital. As a consequence, the Pauli repulsion between the two π_{CH_2} orbitals of the central and outer carbon atoms decreases, and the C–C bond length is shortened. Remarkably, the C–X and C–C shortenings are more and more significant as X is taken from left to right of the periodic table (X = NH_2, OH, F). This can be explained by the strength of the three-electron bond that exists between the π_X lone pair and the π_{CH_2} orbital of the neighboring carbon atom. This interaction increases as the orbitals that interact become closer in energy.[32] Since the π_{CH_2} orbital is bonding, it must be lower in energy than the X lone pairs which are non-bonding; however, the lone pairs get closer in energy to π_{CH_2} from X = NH_2 to X = F, owing to the increasing electronegativity of X. It follows that the three-electron interaction gets more and more significant in this series, and so too do the bond length shortenings.

The geometries of the **c**′ states are, in most cases, quite different from those of the neutral structures or **c**″ states. In structure **1c**′ of ionized fluoroethane the C–C bond is strongly elongated (1.883 Å) and the C–F bond further shortened (1.299 Å) relative to **1c**″. The situation is comparable, but to a considerably lesser extent, to replacing the fluorine by a chlorine atom. Indeed, in structure **4c**′, a significant lengthening (≈0.2 Å) of the C–C bond and a noticeable C–Cl shortening (≈0.1 Å) is noted relative to the neutral structure.

Like the fluoroethane cation **1c**′, ionized ethanol, **2c**′, displays a rather surprising geometry with respect to standard bond lengths, with unusually long C–C and short C–O bonds. This finding has proved to be independent of the computational method employed, since Møller–Plesset theory (MP2), quadratic configuration interaction (QCISD), and coupled cluster theory (CCSD) as well as DFT procedures using different basis sets give very similar results.[19] At the CCSD(T)/6–311G(d,p) level, Radom et al.[19] obtain C–C and C–O bond lengths of 1.745 and 1.338 Å, respectively. The MP2/6–31G(d) results obtained here (C–C = 1.765 and C–O = 1.336 Å, Figure 1) are in very close agreement with these various calculations.

Removal of one electron from ethylamine results in the disappearance of the pyramidal nature of the nitrogen atom. In structure **3c**′, which is close to C_s symmetry with a CCNH dihedral angle of 86.2°, the C–C bond is elongated while the C–N bond is shortened with respect to the neutral species. These changes in length are, however, very limited, since the C–C bond elongation and C–N bond shortening amount only to 0.039 and 0.036 Å, respectively. Changes in bond lengths relative to the neutral molecules are also found to be rather small in the **c**′ states of CH_3CH_2SH and $CH_3CH_2PH_2$.

The very unusual geometric features that are found in the **c**′ structures of some of the radical cations can be interpreted in terms of interacting VB structures. To provide some quantitative support to the reasoning, the weights of the relevant VB structures have been calculated by the VBSCF method, and are displayed in Table 2 for the conventional structures of the six species **1c**′–**6c**′. The electrons that are involved in the VB study are the two electrons of the C–C bond and the unpaired electron of X.

Table 2. Weights of valence bond structures **I**–**VI** for the **c**′ states of conventional radical cations $CH_3CH_2X^+$.

	1c′ (X = F)	**2c**′ (X = OH)	**3c**′ (X = NH_2)	**4c**′ (X = Cl)	**5c**′ (X = SH)	**6c**′ (X = PH_2)
I	0.044	0.394	0.638	0.550	0.658	0.672
II	0.003	0.044	0.105	0.063	0.096	0.093
III	0.040	0.166	0.194	0.204	0.219	0.228
IV	0.436	0.159	0.019	0.067	0.008	0.002
V	0.408	0.137	0.020	0.078	0.010	0.003
VI	0.067	0.101	0.024	0.038	0.009	0.002

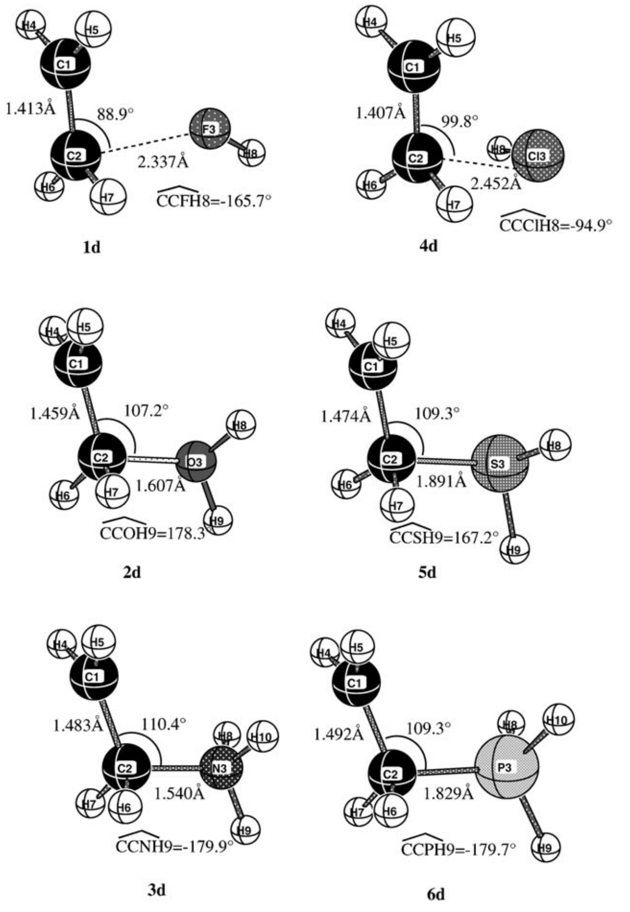
The six relevant VB structures are displayed in Scheme 2. Structures **I**, **II**, and **III** exhibit a σ C–C bond (involving one pure covalent component and two ionic components) and an unpaired electron on the X atom. Structure **VI** displays a C–X covalent π-type bond, with the unpaired electron on the outer carbon atom. Structure **IV** can be interpreted in two ways: it can be considered as involving an ionic C–X π bond, the ionic counterpart of the covalent π bond in **VI**, but it can also, together with structure **V**, be considered as a two-center, one-electron bond between the two carbon atoms. Such a bond is, of course, longer than a C–C two-electron bond.[33]

The calculated VB weights of ionized fluoroethane, **1c**′, point to a clear-cut bonding scheme for this radical cation. The cumulated weights for structures **I**–**III** amount to only 0.088, meaning that there is practically no two-electron bond contribution to the C–C link. On the other hand, structures **IV** and **V** are the major ones, with a weight much larger than that of the remaining structure **VI**. The predominance of **IV** and **V** means that the C–C link is made entirely of a two-center, one-electron C–C bond, in agreement with the large C–C bond length of 1.88 Å (Figure 1), which is close to the equilibrium bond length (1.96 Å) of a one-electron standard C–C bond in the $C_2H_6^{\cdot+}$ radical cation.[33]

Quite different is the bonding picture for the $CH_3CH_2NH_2^+$, $CH_3CH_2SH^+$, and $CH_3CH_2PH_2^+$ radical cations, **3c**′, **5c**′, and **6c**′. Here, contrary to the preceding case, structures **I**–**III** are clearly predominant, while the weights of **IV**–**VI** are small or negligible. This points to a "classical" bonding structure for these species, with a two-electron C–C bond, an unpaired electron located on the X atom, and practically no π-bonding contribution to the C–X bond. This picture is that of a neutral molecule from which a lone pair has been ionized, with little perturbation in the neighboring bonds. This is in accordance with the C–C and C–X bond lengths of **3c**′, **5c**′, and **6c**′ being, on the whole, close to those of the corresponding neutral molecules and, as a corollary, to the **c**″ states of the conventional radical cations.

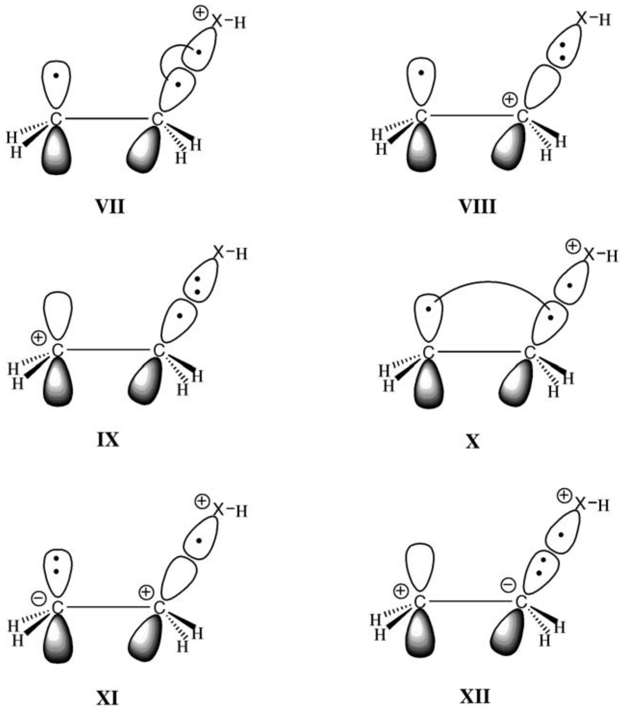
In between these two extremes, ionized ethanol and chloroethane, **2c**′ and **4c**′, exhibit intermediate bonding features with VB weights that are significant for practically all VB structures. Therefore, the C–C bond, in **2c**′ and **4c**′, is a mixture of two-electron and one-electron interactions, in agreement with the elongated C–C bond lengths (1.71–1.76 Å, Figure 1), which are intermediate between the standard two-electron and one-electron C–C bond lengths. It should be noted that structures **IV** and **V**, in which the X atom is neutral, are in principle favored by the electronegativity of the X atom, which tends to attract electrons and avoid positive charges. Remarkably, this tendency is reflected in the cumulated weights of **IV** and **V**, which increase in the series **4c′**, **2c′**, **1c′** (X = Cl, OH, F), in harmony with the increasing electronegativity of X. In summary, the C–C link displays a spectrum of bonding properties from a pure two-electron bond to a pure one-electron bond, in proportion with the electronegativity of the X atom. This accounts for the nonstandard geometries that arise from the MP2 calculations and from other previous computational results.[19]

Distonic structures: The radical cations **1d**–**6d** have been examined previously at a modest theoretical level.[27] Recently, density functional methods[24] were used to study **1d**–**3d**, and more specific studies have been devoted to the distonic ion **2d** by a variety of computational methods.[19,21,27] These data, together with our own results displayed in Figure 2, show that ions **1d**–**6d** may be divided roughly into two categories. In the first group, involving $CH_2CH_2FH^+$ and $CH_2CH_2ClH^+$ (**1d**, **4d**), the C–X bond is extremely elongated, while the C–C bond is very short (about 1.41 Å) relative to a standard two-electron C–C bond. According to these geometries, **1d** and **4d** can be viewed as weakly bonded complexes linking together an ethylene radical cation and an XH molecule. In the second group, the C–X bond lengths are much closer to the standard values and the C–C bond lengths are close to that of the standard C–C single bond (1.47–1.49 Å vs. 1.517 Å in the CH_3CH_2 radical). This category of radical cations, which involves **3d**, **5d** and **6d**, displays the geometries that one expects for standard distonic ions, with normal two-electron C–C and C–X bonds, and the positive charge being located on the X atom. Lastly, $CH_2CH_2OH_2^+$ (**2d**) could be considered as an intermediate case, with its slightly elongated C–X bond (1.61 Å); however, it is closer in nature to the second category.



1d 4d 2d 5d 3d 6d

Figure 2. MP2/6–31G(d) optimized geometries of distonic radical cations **1d**–**6d**.



VII VIII IX X XI XII

Scheme 3. Relevant VB structures for the description of the distonic ions **d**.

The valence bond approach of the distonic ions **1d**–**6d** is discussed using the six canonical forms **VII**–**XII** depicted in Scheme 3. Structure **VII** characterizes the classical distonic form, with a two-electron covalent bond between the central carbon atom and the XH cation, and an unpaired electron on the outer carbon atom. Structure **VIII** can belong to two types of bonding schemes: 1) it can be considered as the ionic counterpart of structure **VII**, necessary to account for the polar character of the C–X bond; 2) together with structure **IX**, it can be considered as contributing to the π-one-electron bond of an ionized ethylenic unit. Lastly, structures **X**–**XII** represent an XH radical cation with a neutral ethylene moiety displayed in its covalent and ionic π-bond representations.

The results of the VB computations, gathered in Table 3, clearly show that the participation of the canonical forms **X–XII** is negligible for the six distonic ions considered. Radical cations **1d** and **4d** ($CH_2CH_2FH^+$ and $CH_2CH_2ClH^+$) are almost entirely described in terms of structures **VIII** and **IX**, which characterize a one-electron π bond between the two carbons, and practically no C–X bond. These species are therefore best described as an ethylene radical cation that would be weakly interacting with an XH molecule. These results are in agreement with the short C–C bond lengths and the very long C-X distances calculated for these two species. On the other hand, **3d**, **5d** and **6d** (X=NH_2, SH and PH_2) have negligible weights for all VB structures except **VII** and **VIII**, and are therefore very well represented as classical distonic structures with a two-electron C–C bond and a two-electron polar C–X bond, in agreement with the bond lengths that are close to the standard lengths. The distonic radical cation **2d** ($CH_2CH_2OH_2^+$), belongs to the same category; however, its relatively reduced weight for structure **VII** explains the somewhat elongated C–O bond.

Table 3. Weights of valence bond structures **VII–XII** for the distonic radical cations **d** $CH_2CH_2XH^+$.

	1d (X=F)	**2d** (X=OH)	**3d** (X=NH_2)	**4d** (X=Cl)	**5d** (X=SH)	**6d** (X=PH_2)
VII	0.012	0.389	0.553	0.103	0.551	0.619
VIII	0.548	0.546	0.418	0.510	0.374	0.352
IX	0.431	0.034	0.010	0.299	0.027	0.006
X	0.004	0.019	0.012	0.055	0.030	0.012
XI	0.000	0.004	0.004	0.006	0.008	0.010
XII	0.004	0.008	0.003	0.026	0.010	0.001

Thermochemistry: Heats of formation of radical cations **1–6** of structures **c**′, **c**″, and **d** were calculated from the G2 atomization energies (see Computational Methods). Results obtained for $T=0$ and 298 K are presented in Table 4.

The 298 K heats of formation of conventional radical cations $CH_3CH_2X^{\cdot+}$ available in the literature are generally obtained by addition of the experimental ionization energy of the molecule to its 298 K heat of formation. The Δ_fH_{298} values obtained using the so-called "electron convention"[34] for X=F, Cl, OH, SH and NH_2 are equal to 862, 952, 781, 856 and 813 $kJ\,mol^{-1}$ respectively. Satisfactorily enough, these values match closely those calculated for the **c**″ conventional structures (Table 4). On the other hand, due to the difficulty in generating pure distonic ions in the gas phase as well as in solution, their thermochemical properties are mostly of theoretical origin. As a matter of fact, the heat of formation of only one of the examined species **1d–6d** has been determined experimentally. Thus, structure **2d**, $CH_2CH_2OH_2^{\cdot+}$, has been assigned to ions generated by the loss of CH_2O from ionized propane-1,3-diol[35] and ionized methoxy-2-ethanol.[36] A heat of formation of $\Delta H^\circ_{298}(\mathbf{2d})=732\pm5$ $kJ\,mol^{-1}$ was deduced from appearance energy measurements performed by using energy-selected electrons.[36] The G2-calculated value of 731 $kJ\,mol^{-1}$ (Table 4) is evidently in excellent agreement with experiment in this case.

Table 4. Heats of formation values and relative 298 K enthalpies ($kJ\,mol^{-1}$) calculated from G2 atomization energies.

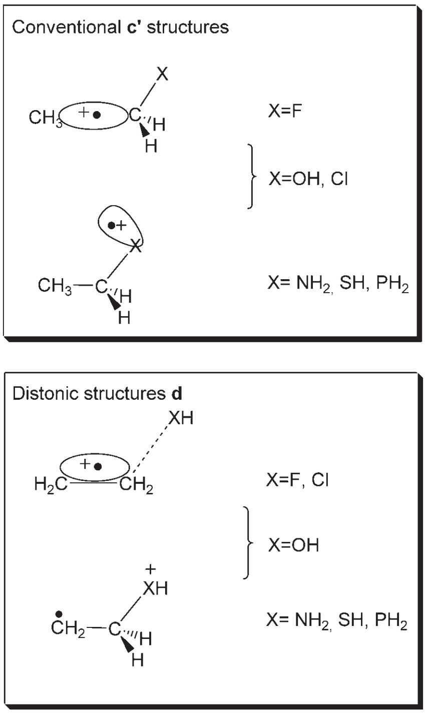
Species (X)	$\Delta_fH^\circ_0$ (G2)	$\Delta_fH^\circ_{298}$ (G2)	ΔH°_{298}(G2)
1c′ (F)	852	839	82
2c′ (OH)	783	767	36
3c′ (NH_2)	834	813	25
4c′ (Cl)	956	945	19
5c′ (SH)	868	851	0
6c′ (PH_2)	845	824	0
1c″ (F)	875	862	105
2c″ (OH)	806	788	57
3c″ (NH_2)	834	814	26
4c″ (Cl)	976	963	37
5c″ (SH)	868	852	1
6c″ (PH_2)	847	826	2
1d (F)	765	757	0
2d (OH)	746	731	0
3d (NH_2)	809	788	0
4d (Cl)	933	926	0
5d (SH)	924	908	57
6d (PH_2)	866	846	22

Examination of Table 4 reveals that the distonic radical cations are more stable than their conventional isomers when X=F, Cl, OH, NH_2. Incidentally, for these four species (**1d–4d**), the enthalpy difference $\Delta H^\circ_{298}=\Delta_fH^\circ_{298}$(**c**′ or **c**″)-$\Delta_fH^\circ_{298}$(**d**) increases along the series (X=NH_2, Cl, OH, F), thus following the order of increasing electronegativities for the X atom (see Table 4, last column). This nice correlation is readily explained by the fact that electronegative fragments tend to attract electrons and to let the positive charge delocalize in the remaining part of the molecule. This is particularly true for X=OH and Cl since, as discussed above, the corresponding distonic structures in fact consist of a neutral HX fragment interacting with ionized ethylene.

Conclusion

The present work demonstrates that removing an electron from a heterosubstituted molecule such as CH_3CH_2X may give rise to two different electronic states characterized by a singly occupied orbital lying either in the plane (**c**′ structure) or out of the plane (**c**″ structure) containing the heavy atoms. The **c**′ structure is generally the most stable, because it lends itself to an interplay between several resonance structures that give rise to some resonance energy. As a consequence of this mesomerism, the geometries of the **c**′ cationic states can be very different from those of the corresponding neutral states. In particular, significant C–C bond elongations are systematically observed in **c**′ states relative to neutral states, in proportion to the electronegativity of X. By contrast, the unpaired electron does not interact significantly with the C–C bond in structures **c**″, which are described by a unique Lewis structure. It follows that the geometries for these cationic states are close to the geometries of the corresponding neutral states, if one excepts a shortening of the C–X bond (when X belongs to the first row of the periodic table) that is due to a lowering of the Pauli electron repulsion between the electrons of X and those of the central carbon atom.

The valence bond analysis of the **c**′ structures reveals that the $CH_3CH_2X^{\bullet+}$ radical cation may be viewed as a classical X-ionized species only for X = NH_2, SH and PH_2. By contrast, for X = F, the **c**′ radical cation is more properly described as a CH_2X^+ carbocation linked to a $CH_3^{\bullet}$ radical by a two-center, one-electron C–C bond. An intermediate situation pertains to X = OH, Cl (Scheme 4).



Scheme 4. Summary of the electronic structures of conventional and distonic radical cations **1**–**6**.

As revealed by the valence bond calculations, the bonding picture of the distonic radical cations **d** $CH_2CH_2XH^{\bullet+}$, exhibits a spectrum that stretches between two extreme situations. For X = NH_2, SH and PH_2, the radical is well described by a pure distonic representation, that is, with the radical site on the terminal carbon atom, and the positive charge formally on X. By contrast, for X = F and Cl, the radical is better described as an ion–molecule complex between an ionized ethylene and a neutral HX molecule, leading to a considerable C–X bond elongation. Once again, the case X = OH is between these two extreme situations (Scheme 3).

The relative energies of the conventional and distonic radical cations have been evaluated at the G2 level. The major trends are that distonic structures are stabilized with respect to their conventional isomers by around 100 to 20 kJ mol^{-1} when X = F, OH, NH_2 and Cl, and destabilized in the two other cases, when X = SH and PH_2. All these trends are consistent with the electronegativity tendencies for the heteroatom of the X group.

Computational Methods

All calculations were performed in the standard 6–31G(d) basis set. The geometry optimizations were performed by means of the second-order Møller–Plesset perturbation method (MP2), in its spin-unrestricted form. Note that a problem that may occur in calculating open-shell systems is spin-contamination in the reference unrestricted Hartree-Fock wave function. For the species considered here, the spin contamination was negligible as attested by the $\langle S^2 \rangle$ values, which all lie in the range 0.754–0.776, very close to the value 0.75 expected for a pure doublet state.

The ab initio valence bond calculations were performed with the valence bond self consistent field (VBSCF) method.[37] With this method, the wave function is expressed as a linear combination of VB structures Ψ_I [Eq. (1)] that each represent a particular bonding picture (see VB structures **I**–**VI** and **VII**–**XII** in Schemes 2 and 3).

$$\Psi_{VBSCF} = \sum_i C_i \Psi i \tag{1}$$

While this method allows for the use of semidelocalized orbitals, here all the orbitals were kept strictly localized on a single atom or fragment, so as to keep the distinction between covalent and ionic bonds perfectly clear. At the VBSCF level, the orbitals and the coefficients of all the VB structures were optimized simultaneously. This computational level ensures left–right correlation in the description of the bonds.

The weights of the VB structures were determined by use of the Coulson–Chirgwin[38] formula, given in Equation (2), which is the equivalent of a Mulliken population analysis in VB theory.

$$W_i = C_i^2 + \sum_{j \neq i} C_i C_j \langle \Psi_i | \Psi_j \rangle \tag{2}$$

The Gaussian 98 series of programs[39] was employed for the Møller–Plesset and the G2[40] calculations. The ab initio valence bond calculations were performed with the XMVB program.[41] The enthalpies of formation of the various radical cations were calculated from the atomization energies at 0 K calculated by the standard G2 method and corrected to 298 K by the thermal corrections calculated at the HF/6–31G(d) level, scaled as usual following the method developed by Nicolaides et al.[42]

Total energies (MP2/6–31G(d) and G2) together with the full set of Cartesian coordinates of all optimized geometries are displayed in Tables S1 and S2 of the Supporting Information.

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