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DISTONIC RADICAL CATIONS

GUIDELINES FOR THE ASSESSMENT OF THEIR STABILITY†

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Abstract—*Ab initio* molecular orbital calculations on the distonic radical cations $\dot{C}H_2(CH_2)_n\overset{+}{N}H_3$ and their conventional isomers $CH_3(CH_2)_nNH_2^{+\cdot}$ (n = 0, 1, 2 and 3) indicate a preference in each case for the distonic isomer. The energy difference appears to converge with increasing n towards a limit which is close to the energy difference between the component systems $CH_3\dot{C}H_2+CH_3\overset{+}{N}H_3$ (representing the distonic isomer) and $CH_3CH_3+CH_3NH_2^{+\cdot}$ (representing the conventional isomer). The generality of this result is assessed by using results for the component systems $CH_3\dot{Y}+CH_3\overset{+}{X}H$ and $CH_3YH+CH_3X^{+\cdot}$ (or $CH_3YH^{+\cdot}+CH_3X$) to predict the relative energies of the distonic ions $\dot{Y}(CH_2)_n\overset{+}{X}H$ and their conventional isomers $HY(CH_2)_nX^{+\cdot}$ (X = NH_2, OH, F, PH_2, SH, Cl; Y = CH_2, NH, O) and testing the predictions through explicit calculations for systems with n = 0, 1 and 2. Although the predictions based on component systems are often close to the results of direct calculations, there are substantial discrepancies in a number of cases; the reasons for such discrepancies are discussed. Caution must be exercised in applying this and related predictive schemes. For the systems examined in the present study, the conventional radical cation is predicted in most cases to lie lower in energy than its distonic isomer. It is found that the more important factors contributing to a preference for distonic over conventional radical cations are the presence in the system of a group (X) with high proton affinity and the absence of a group (X, Y or perturbed C—C) with low ionization energy.

INTRODUCTION

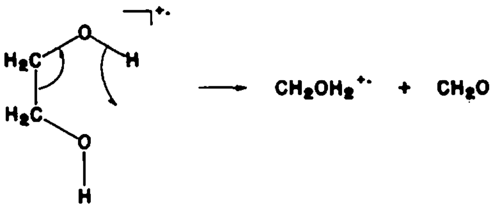
On the basis of extensive theoretical and experimental work, we[1] and others[2-11] have recently noted that gas-phase radical cations in which the charge and radical sites are formally separated often display a stability with respect to unimolecular decomposition which contrasts with that of the neutral molecules from which they are derived. For example, the methyleneoxonium radical cation ($\dot{C}H_2\overset{+}{O}H_2$) is found both theoretically[1g,j] and experimentally[1k,2b] to be more stable than its more conventional isomer, the methanol radical cation ($CH_3OH^{+\cdot}$). Again, the ethyleneoxonium radical cation ($\dot{C}H_2CH_2\overset{+}{O}H_2$) is more stable than the ethanol radical cation ($CH_3CH_2OH^{+\cdot}$).[1m,2a,12] Very recently, the trimethyleneoxonium radical cation ($\dot{C}H_2CH_2CH_2\overset{+}{O}H_2$) has also been observed.[2i]

We have introduced[1q] the term *distonic* (derived from the Greek *διεστώσ* (*diestos*) and the Latin *distans* meaning *separate*) radical cation to describe the general class of radical cations in which the charge and radical centres are separated. The term *ylidion* describes the subclass of distonic radical cations in which the charge and radical sites are on adjacent centres (e.g. $\dot{C}H_2\overset{+}{O}H_2$).

Many radical cations have several valence structures, one of which might have separated charge and radical sites. For example, formaldehyde radical cation can be written $\overset{+}{C}H_2\!-\!\dot{O}$. Should this ion be regarded as distonic? We would suggest that the term distonic be reserved for those radical cations which arise formally from ionization of neutral systems which are best written as zwitterions (ylides in the case of adjacent charges) or biradicals.[1p,4d] On this basis, $CH_2O^{+\cdot}$ (arising from $CH_2\!=\!O$) and $CH_2CH_2^{+\cdot}$ (arising from $CH_2\!=\!CH_2$) are not distonic radical cations whereas $\dot{C}H_2\overset{+}{O}H_2$ (arising from $\bar{C}H_2\!-\!\overset{+}{O}H_2$) and $\dot{C}H_2\overset{+}{O}CH_2$ (arising from $\dot{C}H_2O\dot{C}H_2$) are.

The stability of the (gas-phase) distonic radical cations is particularly striking given that the corresponding (zwitterionic or biradical) neutrals are generally not very stable at all. Thus, for example, the neutral systems $\bar{C}H_2\overset{+}{O}H_2$, $\bar{C}H_2CH_2\overset{+}{O}H_2$, . . . correspond to rather weak complexes of water with methylene, ethylene and so on.[13]

The absence of a stable neutral parent means that the distonic radical cations cannot be generated in the mass spectrometer by direct ionization. Typically, they are produced by means of an intramolecular rearrangement involving concomitant expulsion of a stable small neutral molecule. For example, the methyleneoxonium radical cation is produced[1k,2b] from ionized ethylene glycol by means of the rearrangement–fragmentation reaction:



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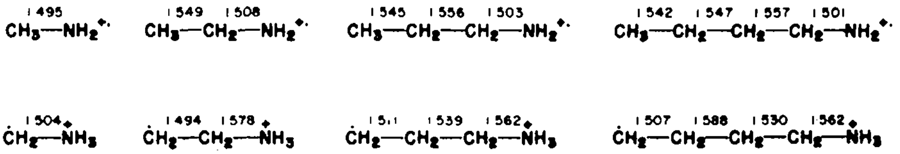

Fig. 1. Schematic representation of bond lengths between heavy atoms within fully-optimized all-*trans* structures (3-21G) of distonic radical cations $\dot{C}H_2(CH_2)_n\overset{+}{N}H_3$ and their conventional isomers $CH_3(CH_2)_nNH_2^{+\cdot}$.

It would be highly desirable to be able to predict *a priori* the circumstances under which distonic radical cations might be more stable than their conventional isomers. Guidelines to this effect and preliminary testing of these guidelines are reported in this paper.

We begin with an examination, using *ab initio* molecular orbital theory, of the effect of increasing the separation of the charge and radical sites in distonic radical cations. This is achieved through calculations on the distonic radical cations $\dot{C}H_2(CH_2)_n\overset{+}{N}H_3$ and their conventional isomers $CH_3(CH_2)_nNH_2^{+\cdot}$ for $n = 0$, 1, 2 and 3. In a second series of calculations, we examine whether the relative stabilities of distonic radical cations $\dot{Y}(CH_2)_n\overset{+}{X}H$ and their isomers $HY(CH_2)_nX^{+\cdot}$ ($X = NH_2$, OH, F, PH_2, SH, Cl; $Y = CH_2$, NH, O) can be predicted from the energies of the component systems $CH_3\dot{Y}$, $CH_3\overset{+}{X}H$, CH_3YH, $CH_3X^{+\cdot}$, $CH_3YH^{+\cdot}$ and CH_3X.

METHOD

Ab initio molecular orbital calculations were carried out with modified versions[14,15] of the Gaussian 80 and 82 programs.[16,17] Geometry optimizations were performed with the 3-21G$^{(*)}$ basis set[18] and improved relative energies obtained at the MP2/6-31G* level,[19,20] either directly or by assuming additivity of basis set enhancement and electron correlation effects:[21]

$$\Delta E(\text{MP2/6-31G*}) \approx \Delta E(\text{HF/6-31G*}) + \Delta E(\text{MP2/6-31G}) - \Delta E(\text{HF/6-31G}). \quad (1)$$

All-*trans* arrangements of the heavy-atom skeletons were assumed for the purpose of the analysis presented here. Deviations from such conformations need to be considered when making comparisons with experiment and will be discussed elsewhere.

We should stress that calculations at higher levels of theory would be possible for most of the systems examined in the present paper. Indeed, some of our previous work has included such higher level calculations.† However, our principal aim here is to examine the relationship between the directly calculated relative stabilities of distonic and conventional isomers of radical cations and the predictions which can be made from data on appropriate small molecules. We have tackled this task through calculations at modest levels of theory on a large set of radical cations. We believe that the levels of theory employed in this paper are probably sufficient in most (but perhaps not all) cases for the testing of such a relationship and help to obtain a broad-brush picture. On the other hand, absolute results for individual molecules may indeed be modified at higher levels of theory.

RESULTS AND DISCUSSION

Calculated total energies for optimized structures (Fig. 1) of the distonic radical cations $\dot{C}H_2(CH_2)_n\overset{+}{N}H_3$ and their conventional isomers $CH_3(CH_2)_nNH_2^{+\cdot}$ are presented in Table 1 and corresponding relative energies are shown in Table 2. It may be seen that the distonic radical cations are consistently lower in energy than their conventional isomers. The energy difference between the two forms appears to converge with increasing n towards a value of about 30 kJ mol^{-1}.

Is there a simple means of predetermining what this limiting energy difference between the distonic and conventional ions might be? Our approach to answering this question has been to examine energy differences between pairs of component systems which might serve as models for the distonic and conventional isomers. The simplest such pairs, $CH_4 + NH_3^{+\cdot}$ (for the conventional isomer) and $\dot{C}H_3 + \overset{+}{N}H_4$ (for the distonic isomer), only provide a very rough measure of the conventional–distonic energy difference, yielding 76 kJ mol^{-1} (ΔE for reaction (2), Table 3). Much better results are obtained for the larger model systems of reactions (3) and (4) of Table 3 for which the calculated energy changes are 42 and 39 kJ mol^{-1}, respectively. These energies are quite close to the limiting value of Table 2.

The correspondence between the limiting behaviour of Table 2 and results for the component systems of Table 3 suggests a possible means of assessment of the relative stabilities of distonic radical cations and their conventional isomers. These stabilities are related to the proton affinities (PAs) and ionization energies (IEs) of the appropriate model systems (e.g. CH_3NH_2 (cf. reaction 3) in the above case). The distonic isomer is favoured by a large proton affinity (which corresponds to a stabilization of the distonic form) or by a large ionization energy (which corresponds to a destabilization of the conventional isomer) of the relevant component molecules. More precisely, the energy change ΔE for reaction (3) is given in terms of PAs, IEs and C—H bond dissociation energies (BDEs) of component systems as

$$\Delta E = \text{PA}(CH_3NH_2) + \text{IE}(CH_3NH_2) - \text{BDE}(CH_3CH_3) - \text{IE}(H^{\cdot}). \quad (5)$$

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† See, in particular, Refs 1*l* and 1*r*.

Table 1. Calculated total energies (hartrees) for distonic radical cations $\dot{C}H_2(CH_2)_n\overset{+}{N}H_3$ and their conventional isomers $CH_3(CH_2)_nNH_2^{+\cdot}$, and appropriate component systems[a]

Species	Hf/6-31G	MP2/6-31G	HF/6-31G*
$CH_3NH_2^{+\cdot}$	−94.89776	−95.07169	−94.93148
$\dot{C}H_2\overset{+}{N}H_3$	−94.89765	−95.07809	−94.92994
$CH_3CH_2NH_2^{+\cdot}$	−133.92460	−134.18845	−133.97438
$\dot{C}H_2CH_2\overset{+}{N}H_3$	−133.93399	−134.20398	−133.98190
$CH_3CH_2CH_2NH_2^{+\cdot}$	−172.94574	−173.30088	−173.01180
$\dot{C}H_2CH_2CH_2\overset{+}{N}H_3$	−172.95492	−173.31495	−173.01903
$CH_3CH_2CH_2CH_2NH_2^{+\cdot}$	−211.96540	−212.41187	−212.04775
$\dot{C}H_2CH_2CH_2CH_2\overset{+}{N}H_3$	−211.97463	−212.42564	−212.05488
$\dot{C}H_3$	−39.54666	−39.62180	−39.55899
$\overset{+}{N}H_4$	−56.51622	−56.63348	−56.53056
CH_4	−40.18055	−40.27872	−40.19517
$NH_3^{+\cdot}$	−55.85916	−55.94555	−55.87311
$CH_3\dot{C}H_2$	−78.56867	−78.73208	−78.59706
$CH_3\overset{+}{N}H_3$	−95.53832	−95.74244	−95.57260
CH_3CH_3	−79.19747	−79.38477	−79.22861
$CH_3CH_2\dot{C}H_2$	−117.58639	−117.84025	−117.63117
$CH_3CH_2\overset{+}{N}H_3$	−134.56528	−134.85913	−134.61556
$CH_3CH_2CH_3$	−118.21601	−118.49403	−118.26339

[a] 3-21G optimized structures.

Table 2. Calculated relative energies ($\Delta E = E$(conventional) − E(distonic), kJ mol^{-1}) of distonic radical cations $\dot{C}H_2(CH_2)_n\overset{+}{N}H_3$ and their conventional isomers $CH_3(CH_2)_nNH_2^{+\cdot}$

Conventional	Distonic	ΔE[a]
$CH_3NH_2^{+\cdot}$	$\dot{C}H_2\overset{+}{N}H_3$	13
$CH_3CH_2NH_2^{+\cdot}$	$\dot{C}H_2CH_2\overset{+}{N}H_3$	36
$CH_3CH_2CH_2NH_2^{+\cdot}$	$\dot{C}H_2CH_2CH_2\overset{+}{N}H_3$	32
$CH_3CH_2CH_2CH_2NH_2^{+\cdot}$	$\dot{C}H_2CH_2CH_2CH_2\overset{+}{N}H_3$	31

[a] MP2/6-31G* values, evaluated via Eq. (1).

More generally, we might expect that a distonic radical cation $\dot{Y}(CH_2)_n\overset{+}{X}H$ will normally be more stable than its conventional isomer $HY(CH_2)_nX^{+\cdot}$ (e.g. $Y = CH_2$, $X = NH_2$) if the pair $CH_3\dot{Y} + CH_3\overset{+}{X}H$ lies lower in energy than the more stable of the pairs $CH_3YH + CH_3X^{+\cdot}$ or $CH_3YH^{+\cdot} + CH_3X$, corresponding respectively to

$$\Delta E = E(CH_3YH) + E(CH_3X^{+\cdot}) - E(CH_3\dot{Y}) - E(CH_3\overset{+}{X}H) \quad (6a)$$

or

$$\Delta E = E(CH_3YH^{+\cdot}) + E(CH_3X) - E(CH_3\dot{Y}) - E(CH_3\overset{+}{X}H) \quad (6b)$$

being positive. These conditions are equivalent respectively to the requirements that the energy change

$$\Delta E = \mathrm{PA}(CH_3X) + \mathrm{IE}(CH_3X) - \mathrm{BDE}(CH_3YH) - \mathrm{IE}(H^{\cdot}) \quad (7a)$$

Table 3. Calculated relative energies (ΔE, kJ mol^{-1}) for model components of distonic radical cations and their conventional isomers

Reaction	ΔE[a]
(2) $\dot{C}H_3 + \overset{+}{N}H_4 \rightarrow CH_4 + NH_3^{+\cdot}$	76
(3) $CH_3\dot{C}H_2 + CH_3\overset{+}{N}H_3 \rightarrow CH_3CH_3 + CH_3NH_2^{+\cdot}$	42
(4) $CH_3CH_2\dot{C}H_2 + CH_3CH_2\overset{+}{N}H_3 \rightarrow CH_3CH_2CH_3 + CH_3CH_2NH_2^{+\cdot}$	39

[a] MP2/6-31* values, evaluated via Eq. (1).

or

$$\Delta E = \mathrm{PA(CH_3X)} + \mathrm{IE(CH_3YH)} - \mathrm{BDE(CH_3YH)} - \mathrm{IE(H^{\cdot})} \quad \text{(7b)}$$

be positive.† We might expect the rule to hold most faithfully when *n* is large. Exceptions for "real" (as opposed to conformationally constrained) molecules may result from cyclic intramolecular interaction. There may also be exceptions for small *n* due to the superposition of specific short-range interactions.

The above guidelines potentially have powerful predictive value. Thus, on the basis of data, either experimental or theoretical, for a limited set of parent molecules ($CH_3\dot{Y}$, $CH_3\overset{+}{X}H$, CH_3YH, $CH_3X^{+\cdot}$, $CH_3YH^{+\cdot}$ and CH_3X), predictions which would otherwise not be straightforward may be made of the likely stability of a large set of distonic ions (e.g. $\dot{O}CH_2\overset{+}{P}H_3$) relative to their conventional isomers (e.g. $HOCH_2PH_2^{+\cdot}$). It is important to assess the generality and limitations of this and related predictive schemes and some initial steps in this direction are described below.

Calculated total energies for the set of component systems $CH_3\dot{Y}$, $CH_3\overset{+}{X}H$, CH_3YH, $CH_3X^{+\cdot}$, $CH_3YH^{+\cdot}$ and CH_3X with Y = CH_2, NH and O, and X = NH_2, OH, F, PH_2, SH and Cl are listed in Table 4. Theoretical relative energies, calculated according to Eq. (6a) or (6b), and experimental relative energies,[22] calculated according to Eq. (7a) or (7b), are presented in Table 5.

The theoretical and experimental values generally agree to about 40–50 kJ mol^{-1}. Further improvement is likely at higher levels of theory and such calculations are in progress.

According to the guidelines provided above, the results from Table 5 predict that, in most cases within the range of groups X and Y considered here, the

Table 4. Calculated total energies (hartrees) for distonic radical cations $\dot{Y}(CH_2)_n\overset{+}{X}H$ and their conventional isomers $HY(CH_2)_nX^{+\cdot}$ and appropriate component systems[a]

Species	MP2/6-31G*	Species	MP2/6-31G*
$CH_3NH_2^{+\cdot}$	−95.18927	$\dot{C}H_2\overset{+}{N}H_3$	−95.19670
$CH_3OH^{+\cdot}$	−114.94531	$\dot{C}H_2\overset{+}{O}H_2$	−114.97057
$CH_3F^{+\cdot}$	−138.88291[b]	$\dot{C}H_2\overset{+}{F}H$	−138.88992
$CH_3PH_2^{+\cdot}$	−381.41070	$\dot{C}H_2\overset{+}{P}H_3$	−381.38992
$CH_3SH^{+\cdot}$	−437.62160	$\dot{C}H_2\overset{+}{S}H_2$	−437.58235
$CH_3Cl^{+\cdot}$	−498.94253	$\dot{C}H_2\overset{+}{Cl}H$	−498.92025
$NH_2NH_2^{+\cdot}$	−111.22524	$\dot{N}H\overset{+}{N}H_3$	−111.17598
$NH_2OH^{+\cdot}$	−131.00046	$\dot{N}H\overset{+}{O}H_2$	−130.93856
$NH_2F^{+\cdot}$	−154.92092	$\dot{N}H\overset{+}{F}H$	−154.85257
$NH_2PH_2^{+\cdot}$	−397.45318	$\dot{N}H\overset{+}{P}H_3$	−397.39363
$NH_2SH^{+\cdot}$	−453.66171	$\dot{N}H\overset{+}{S}H_2$	−453.57881
$NH_2Cl^{+\cdot}$	−514.99398	$\dot{N}H\overset{+}{Cl}H$	−514.89248
$HONH_2^{+\cdot}$	−131.00046	$\dot{O}\overset{+}{N}H_3$	−130.96583
$HOOH^{+\cdot}$	−150.76379	$\dot{O}\overset{+}{O}H_2$	−150.70949
$HOF^{+\cdot}$	−175.08480[c]	$\dot{O}\overset{+}{F}H$	−174.97511[c]
$HOPH_2^{+\cdot}$	−417.27086	$\dot{O}\overset{+}{P}H_3$	−417.21910
$HOSH^{+\cdot}$	−473.46340	$\dot{O}\overset{+}{S}H_2$	−473.39239
$HOCl^{+\cdot}$	−534.76411[c]	$\dot{O}\overset{+}{Cl}H$	−534.63336[c]
$CH_3CH_2NH_2^{+\cdot}$	−134.36224	$\dot{C}H_2CH_2\overset{+}{N}H_3$	−134.37855
$CH_3CH_2OH^{+\cdot}$	−154.14534	$\dot{C}H_2CH_2\overset{+}{O}H_2$	−154.16019
$CH_3CH_2F^{+\cdot}$	−178.09144	$\dot{C}H_2CH_2\overset{+}{F}H$	−178.11961
$CH_3CH_2PH_2^{+\cdot}$	−420.58002	$\dot{C}H_2CH_2\overset{+}{P}H_3$	−420.56251
$CH_3CH_2SH^{+\cdot}$	−476.79435	$\dot{C}H_2CH_2\overset{+}{S}H_2$	−476.76285
$CH_3CH_2Cl^{+\cdot}$	−538.11741	$\dot{C}H_2CH_2\overset{+}{Cl}H$	−538.12306
$NH_2CH_2NH_2^{+\cdot}$	−150.38103	$\dot{N}HCH_2\overset{+}{N}H_3$	−150.39802
$NH_2CH_2OH^{+\cdot}$	−170.21064	$\dot{N}HCH_2\overset{+}{O}H_2$	−170.18050
$NH_2CH_2F^{+\cdot}$	−194.18628	$\dot{N}HCH_2\overset{+}{F}H$	−194.15771
$NH_2CH_2PH_2^{+\cdot}$	−436.59923	$\dot{N}HCH_2\overset{+}{P}H_3$	−436.57304
$NH_2CH_2SH^{+\cdot}$	−492.81540	$\dot{N}HCH_2\overset{+}{S}H_2$	−492.77661
$NH_2CH_2Cl^{+\cdot}$	−554.19770	$\dot{N}HCH_2\overset{+}{Cl}H$	−554.15747
$HOCH_2NH_2^{+\cdot}$	−170.21064	$\dot{O}CH_2\overset{+}{N}H_3$	−170.22169
$HOCH_2OH^{+\cdot}$	−190.00010	$\dot{O}CH_2\overset{+}{O}H_2$	−190.00986

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† Similar relationships have been employed by other authors. See, for example, Refs 4*d*, 5*b* and 8*c*.

Table 4—*continued*

Species	MP2/6-31G*	Species	MP2/6-31G*
$HOCH_2F^{+\cdot}$	−213.95071	$\dot{O}CH_2\overset{+}{F}H$	−213.97346
$HOCH_2PH_2^{+\cdot}$	−456.42072	$\dot{O}CH_2\overset{+}{P}H_3$	−456.38542
$HOCH_2SH^{+\cdot}$	−512.63865	$\dot{O}CH_2\overset{+}{S}H_2$	−512.58713
$HOCH_2Cl^{+\cdot}$	−573.95839	$\dot{O}CH_2\overset{+}{Cl}H$	−573.97385
$CH_3CH_2CH_2NH_2^{+\cdot}$	−173.53087	$\dot{C}H_2CH_2CH_2\overset{+}{N}H_3$	−173.54575
$CH_3CH_2CH_2OH^{+\cdot}$	−193.32557	$\dot{C}H_2CH_2CH_2\overset{+}{O}H_2$	−193.32503
$CH_3CH_2CH_2F^{+\cdot}$	−217.27789	$\dot{C}H_2CH_2CH_2\overset{+}{F}H$	−217.28893
$CH_3CH_2CH_2PH_2^{+\cdot}$	−459.74515	$\dot{C}H_2CH_2CH_2\overset{+}{P}H_3$	−459.72886
$CH_3CH_2CH_2SH^{+\cdot}$	−515.96206	$\dot{C}H_2CH_2CH_2\overset{+}{S}H_2$	−515.92641
$CH_3CH_2CH_2Cl^{+\cdot}$	−577.29774	$\dot{C}H_2CH_2CH_2\overset{+}{Cl}H$	−577.29532
$NH_2CH_2CH_2NH_2^{+\cdot}$	−189.57308	$\dot{N}HCH_2CH_2\overset{+}{N}H_3$	−189.56109
$NH_2CH_2CH_2F^{+\cdot}$	−233.35926	$\dot{N}HCH_2CH_2\overset{+}{F}H$	−233.27687
$HOCH_2CH_2OH^{+\cdot}$	−229.19659	$\dot{O}CH_2CH_2\overset{+}{O}H_2$	−229.15374
$HOCH_2CH_2F^{+\cdot}$	−253.15320	$\dot{O}CH_2CH_2\overset{+}{F}H$	−253.08425
$HOCH_2CH_2Cl^{+\cdot}$	−613.17001	$\dot{O}CH_2CH_2\overset{+}{Cl}H$	−613.10345
CH_3CH_3	−79.49429	$CH_3\dot{C}H_2$	−78.83518
CH_3NH_2	−95.50459	$CH_3\dot{N}H$	−94.85172
CH_3OH	−115.34538	$CH_3\dot{O}$	−114.68407
CH_3F	−139.33544	CH_3SH	−437.95233
CH_3Cl	−499.35399	$CH_3CH_3^{+\cdot}$	−79.07455
$CH_3\overset{+}{N}H_3$	−95.86714	$CH_3\overset{+}{P}H_3$	−382.05426
$CH_3\overset{+}{O}H_2$	−115.64102	$CH_3\overset{+}{S}H_2$	−438.25010
$CH_3\overset{+}{F}H$	−139.56883	$CH_3\overset{+}{Cl}H$	−499.59143

[a] 3-21G$^{(*)}$ optimized structures unless otherwise specified.
[b] MP2/6-31G* optimized structure, from Ref. 1*i*.
[c] 6-31G* optimized structure.

Table 5. Comparison of theoretical and experimental estimates of *E*(conventional − *E*(distonic), as calculated from component systems (kJ mol^{-1})

Component systems	ΔE	
	Theor.[a]	Exptl
$CH_3\dot{C}H_2 + CH_3\overset{+}{N}H_3 \rightarrow CH_3CH_3 + CH_3NH_2^{+\cdot}$	49	3
$CH_3\dot{C}H_2 + CH_3\overset{+}{O}H_2 \rightarrow CH_3CH_3 + CH_3OH^{+\cdot}$	96	55
$CH_3\dot{C}H_2 + CH_3\overset{+}{F}H \rightarrow CH_3CH_3^{+\cdot} + CH_3F$	−15	36
$CH_3\dot{C}H_2 + CH_3\overset{+}{P}H_3 \rightarrow CH_3CH_3 + CH_3PH_2^{+\cdot}$	−41	−18
$CH_3\dot{C}H_2 + CH_3\overset{+}{S}H_2 \rightarrow CH_3CH_3 + CH_3SH^{+\cdot}$	−80	−57
$CH_3\dot{C}H_2 + CH_3\overset{+}{Cl}H \rightarrow CH_3CH_3 + CH_3Cl^{+\cdot}$	−27	17
$CH_3\dot{N}H + CH_3\overset{+}{N}H_3 \rightarrow CH_3NH_2 + CH_3NH_2^{+\cdot}$	66	25
$CH_3\dot{N}H + CH_3\overset{+}{O}H_2 \rightarrow CH_3NH_2^{+\cdot} + CH_3OH$	−110	−110
$CH_3\dot{N}H + CH_3\overset{+}{F}H \rightarrow CH_3NH_2^{+\cdot} + CH_3F$	−273	−243
$CH_3\dot{N}H + CH_3\overset{+}{P}H_3 \rightarrow CH_3NH_2 + CH_3PH_2^{+\cdot}$	−24	4
$CH_3\dot{N}H + CH_3\overset{+}{S}H_2 \rightarrow CH_3NH_2^{+\cdot} + CH_3SH$	−104	−87
$CH_3\dot{N}H + CH_3\overset{+}{Cl}H \rightarrow CH_3NH_2^{+\cdot} + CH_3Cl$	−263	−189
$CH_3\dot{O} + CH_3\overset{+}{N}H_3 \rightarrow CH_3OH + CH_3NH_2^{+\cdot}$	43	6
$CH_3\dot{O} + CH_3\overset{+}{O}H_2 \rightarrow CH_3OH + CH_3OH^{+\cdot}$	90	58
$CH_3\dot{O} + CH_3\overset{+}{F}H \rightarrow CH_3OH^{+\cdot} + CH_3F$	−73	−75
$CH_3\dot{O} + CH_3\overset{+}{P}H_3 \rightarrow CH_3OH + CH_3PH_2^{+\cdot}$	−47	−15
$CH_3\dot{O} + CH_3\overset{+}{S}H_2 \rightarrow CH_3OH + CH_3SH^{+\cdot}$	−86	−54
$CH_3\dot{O} + CH_3\overset{+}{Cl}H \rightarrow CH_3OH^{+\cdot} + CH_3Cl$	−62	−21

[a] MP2/6-31G* values.

conventional isomer should be the more stable form. The distonic isomer should be preferred when $X = NH_2$ because of the high calculated proton affinity (952 kJ mol^{-1}) of CH_3NH_2 (stabilizing the distonic form). A preference for the distonic isomer is also predicted for several of the OH-containing systems (e.g. $Y = CH_3$, $X = OH$ and $Y = OH$, $X = OH$), largely due to the high IE (1050 kJ mol^{-1}) of CH_3OH (leading to a destabilization of the conventional isomer). However, this result is reversed if there is a more readily ionizable group (than OH) present in the molecule since under such circumstances Eqs (6b) and (7b) (rather than Eqs (6a) and (7a)) apply. Thus, for $Y = NH_2$, $X = OH$, the conventional isomer is predicted to be more stable due to the low IE (828 kJ mol^{-1}) of CH_3NH_2.

Likewise, there is a predicted strong preference for the conventional isomer in the case of the pairs with $X = F$, $Y = NH$ and $X = Cl$, $Y = NH$. This appears to be attributable to a combination of the relatively low proton affinities of CH_3F (613 kJ mol^{-1}) and CH_3Cl (623 kJ mol^{-1}) and the relatively low ionization energy of CH_3NH_2 already noted above.

Explicit calculations have been carried out for a selection of the distonic and conventional radical cations with $n = 0$, 1 and 2 in order to test the predictions of Table 5. Total energies are included in Table 4, a selection of optimized structures is displayed in Fig. 2, and relative energies are shown in Table 6.

Some of the optimized structures show interesting features including the long-bonded geometries noted previously for the radical cations of other saturated molecules.[1m,23-25] Details of the structural effects are tangential to the aim of this paper and will be discussed elsewhere together with results of higher-level calculations on these species. We note at this stage, however, that deviations from idealized geometries for both the conventional and distonic radical cations are likely to contribute to differences between the directly calculated and predicted relative energies for some of the systems under consideration.

We find that when $n = 0$, i.e. for comparisons of $HYX^{+\cdot}$ with $\dot{Y}\overset{+}{X}H$, the directly calculated relative energies differ substantially in several instances from the values based on the consideration of component systems. Errors of more than 200 kJ mol^{-1} can be seen. This result is not surprising and reflects the dominance in some of the systems of specific short-range interactions between the directly-bonded X and Y groups. The *direction* of the error in these worst cases corresponds to the conventional isomer being more stable than expected. This may be attributed to stabilizing π-type overlap in species such as $NH_2NH_2^{+\cdot}$.

When $n = 1$, i.e. in comparisons of $HYCH_2X^{+\cdot}$ with $\dot{Y}CH_2\underset{+}{X}H$, there is a significant improvement and, in most cases, calculated and predicted relative energies lie within about 50 kJ mol^{-1} of one another. Direct π-type overlap is no longer possible and, for example, the error for $NH_2CH_2NH_2^{+\cdot}$ vs $\dot{N}HCH_2\overset{+}{N}H_3$ is about 20 kJ mol^{-1} compared with a nearly 200 kJ mol^{-1} error noted above for the corresponding $n = 0$ systems. There are, however, a few cases where the agreement is very poor (e.g. $NH_2CH_2F^{+\cdot}$ vs $\dot{N}HCH_2\overset{+}{F}H$) suggesting that interaction between the X and Y groups is still significant. For example, the fluoro substituent in NH_2CH_2F makes the ionization energy considerably greater than that of the component system CH_3NH_2.† As a consequence, the conventional radical cation $NH_2CH_2F^{+\cdot}$ is less stable than expected. This additional relative

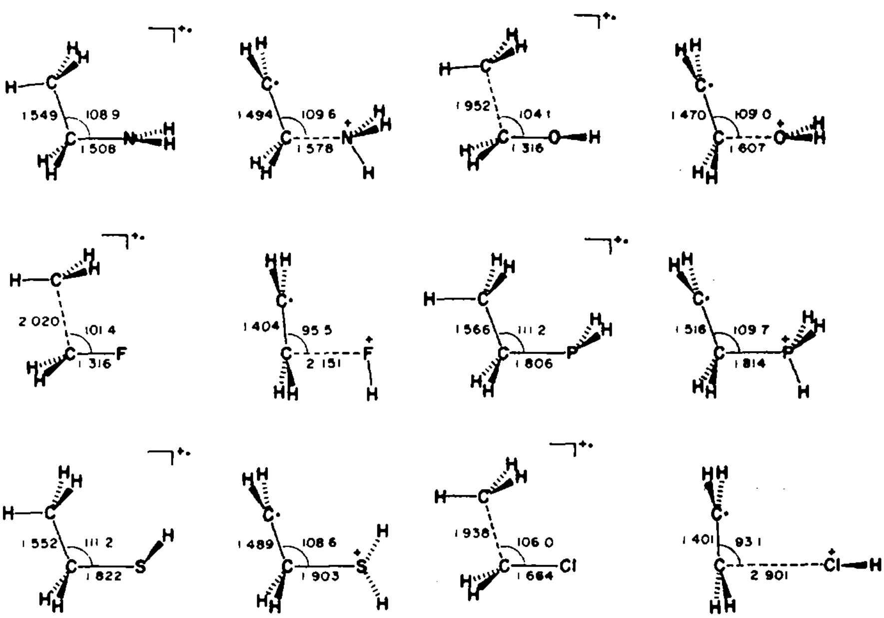

Fig. 2. Bond lengths between heavy atoms and skeletal bond angles within fully optimized structures (3-21G$^{(*)}$) of distonic radical cations $\dot{Y}(CH_2)_n\overset{+}{X}H$ and their conventional isomers $HY(CH_2)_nX^{+\cdot}$. Formal location of charge and radical sites shown for distonic ions.

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† Calculated values are $IE_a(NH_2CH_2F) = 913$ kJ mol^{-1} compared with $IE_a(CH_3NH_2) = 828$ kJ mol^{-1}.

destabilization of the conventional isomer is found for many of the systems with X = F or Cl. As can be seen from Fig. 2, some of the optimized geometries differ considerably from those of idealized models. The component molecules used in the prediction scheme are therefore less appropriate in some cases and this may also contribute to the deviations seen in Table 6.

We have only carried out a limited number of calculations at this stage for the $n = 2$ systems, i.e. comparisons of $HYCH_2CH_2X^{+\cdot}$ with $\dot{Y}CH_2CH_2\overset{+}{X}H$. It should be emphasized that these calculations have been performed with the heavy-atom skeleton in a constrained *trans* arrangement for the purpose of testing our predictive scheme. In practice, some of these species may well prefer alternative arrangements. Our results indicate substantially reduced errors for some of the $n = 1$ problem cases. For example, the error for $NH_2CH_2CH_2F^{+\cdot}$ vs $\dot{N}HCH_2CH_2\overset{+}{F}H$ is 57 kJ mol^{-1} compared with nearly 200 kJ mol^{-1} for the corresponding $n = 1$ systems. However, new problems arise for comparisons such as $NH_2CH_2CH_2NH_2^{+\cdot}$ vs $\dot{N}HCH_2CH_2\overset{+}{N}H_3$. It appears that the two NH_2 substituents in $NH_2CH_2CH_2NH_2^{+\cdot}$ stabilize the structure corresponding to ionization from the C_α—C_β bond to such an extent that it is more stable than the structure corresponding to ionization from the nitrogen lone

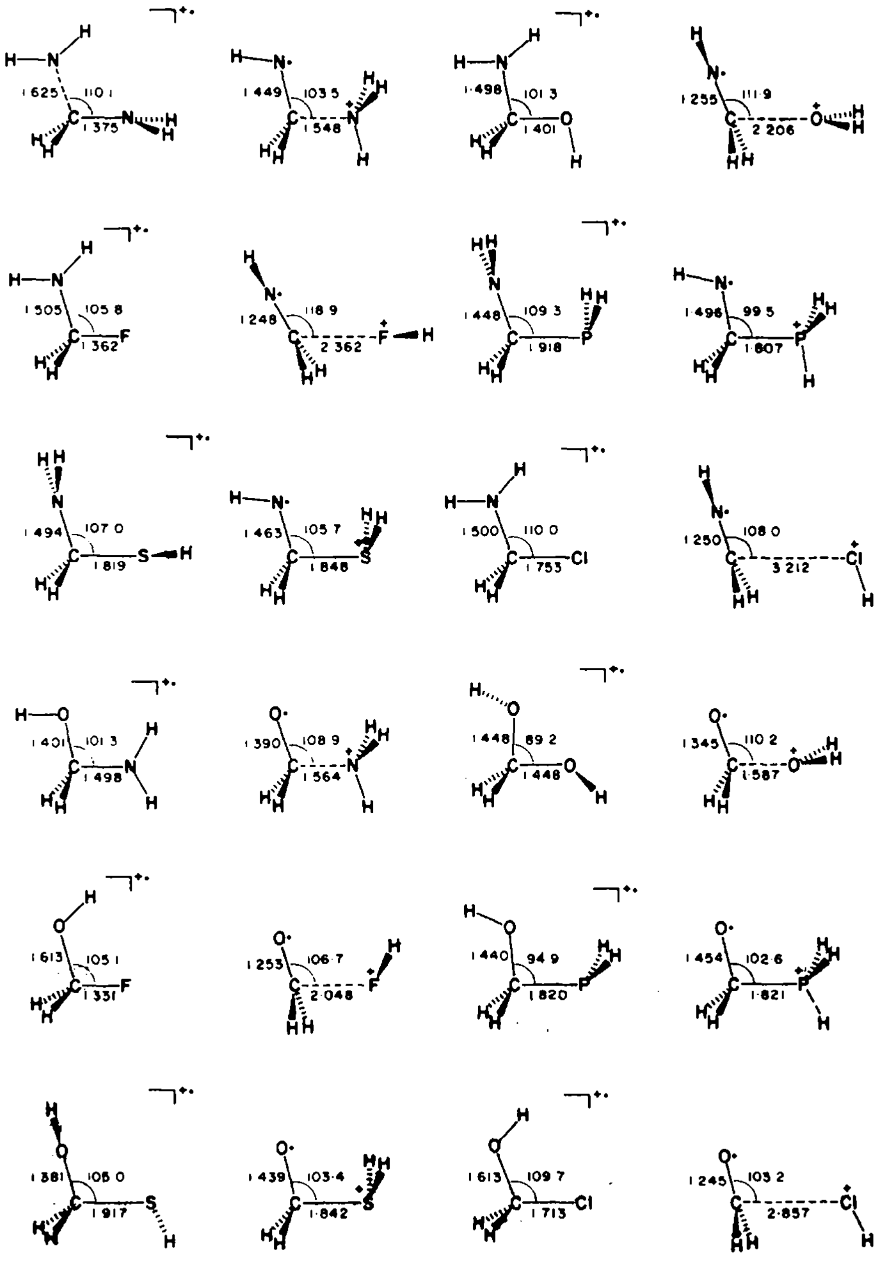

Fig. 2—*continued*.

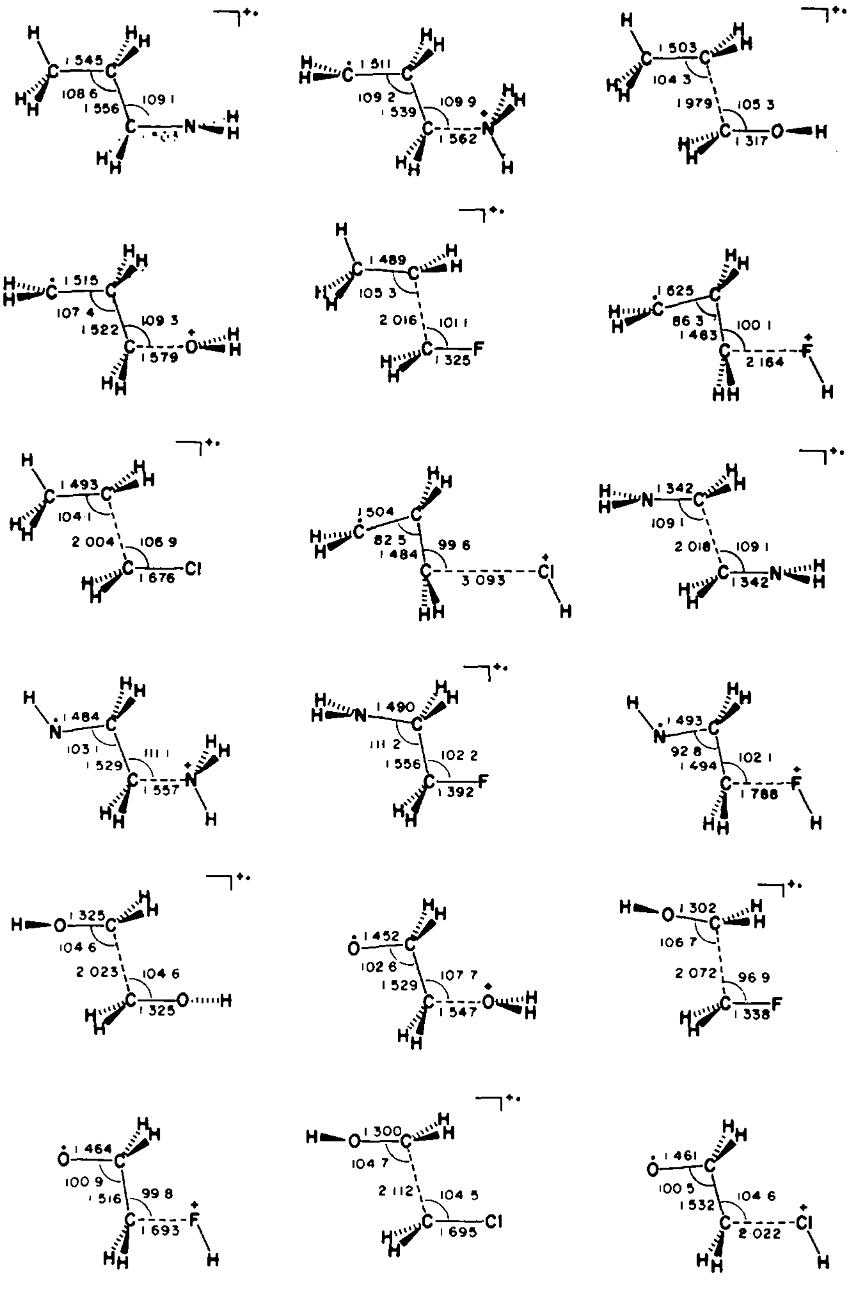

Fig. 2—*continued*.

pair.[23] The latter would have been expected to be more stable on the basis of ionization energy data for the component molecules (CH_3NH_2 and CH_3CH_3).† As a consequence, the conventional isomer (which displays a long C_α—C_β bond) is considerably more stable than predicted. Similar considerations apply to $CH_3CH_2CH_2OH^{+\cdot}$, $HOCH_2CH_2OH^{+\cdot}$, $HOCH_2CH_2F^{+\cdot}$ and $HOCH_2CH_2Cl^{+\cdot}$, the remaining poor cases in Table 6.

Calculations have not yet been completed on systems with $n = 3$. However, we anticipate that problems attributable to ionization from C—C bonds should be less severe since *reinforcing* effects of substituents on the C_α—C_β bond are no longer possible. The results for comparisons such as $NH_2CH_2CH_2CH_2NH_2^{+\cdot}$ vs $\dot{N}HCH_2CH_2CH_2\overset{+}{N}H_3$ may well be close to those predicted from a consideration of component systems.‡

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† Calculated values for the component molecules are $IE_a(CH_3NH_2) = 828$ kJ mol^{-1} and $IE_a(CH_3CH_3) = 1102$ kJ mol^{-1} whereas in fact $IE_a(NH_2CH_2CH_2NH_2) = 732$ kJ mol^{-1}.

‡ Note added in proof: calculations have now been completed for $NH_2CH_2CH_2CH_2NH_2^{+\cdot}$ and $\dot{N}HCH_2CH_2CH_2\overset{+}{N}H_3$. The calculated energy difference of 53 kJ mol^{-1} in favour of the distonic isomer compares well with the 66 kJ mol^{-1} predicted on the basis of component systems.

Table 6. Comparison of calculated and predicted relative energies (kJ mol^{-1}) of distonic radical cations $\dot{Y}(CH_2)_n\overset{+}{X}H$ and their conventional isomers $HY(CH_2)_nX^{+\cdot}$

		E(conventional) − E(distonic)[a]			
			Calc.		
Conventional	Distonic	$n = 0$	$n = 1$	$n = 2$	Pred.[b]
$CH_3(CH_2)_nNH_2^{+\cdot}$	$\dot{C}H_2(CH_2)_n\overset{+}{N}H_3$	20	43	39	49
$CH_3(CH_2)_nOH^{+\cdot}$	$\dot{C}H_2(CH_2)_n\overset{+}{O}H_2$	66	39	−1	96
$CH_3(CH_2)_nF^{+\cdot}$	$\dot{C}H_2(CH_2)_n\overset{+}{F}H$	18	74	29	−15
$CH_3(CH_2)_nPH_2^{+\cdot}$	$\dot{C}H_2(CH_2)_n\overset{+}{P}H_3$	−55	−46	−43	−41
$CH_3(CH_2)_nSH^{+\cdot}$	$\dot{C}H_2(CH_2)_n\overset{+}{S}H_2$	−103	−82	−94	−80
$CH_3(CH_2)_nCl^{+\cdot}$	$\dot{C}H_2(CH_2)_n\overset{+}{Cl}H$	−58	13	−6	−27
$NH_2(CH_2)_nNH_2^{+\cdot}$	$\dot{N}H(CH_2)_n\overset{+}{N}H_3$	−129	45	−31	66
$NH_2(CH_2)_nOH^{+\cdot}$	$\dot{N}H(CH_2)_n\overset{+}{O}H_2$	−163	−79		−110
$NH_2(CH_2)_nF^{+\cdot}$	$\dot{N}H(CH_2)_n\overset{+}{F}H$	−179	−75	−216	−273
$NH_2(CH_2)_nPH_2^{+\cdot}$	$\dot{N}H(CH_2)_n\overset{+}{P}H_3$	−156	−69		−24
$NH_2(CH_2)_nSH^{+\cdot}$	$\dot{N}H(CH_2)_n\overset{+}{S}H_2$	−218	−102		−104
$NH_2(CH_2)_nCl^{+\cdot}$	$\dot{N}H(CH_2)_n\overset{+}{Cl}H$	−266	−106		−263
$HO(CH_2)_nNH_2^{+\cdot}$	$\dot{O}(CH_2)_n\overset{+}{N}H_3$	−91	29		43
$HO(CH_2)_nOH^{+\cdot}$	$\dot{O}(CH_2)_n\overset{+}{O}H_2$	−143	26	−113	90
$HO(CH_2)_nF^{+\cdot}$	$\dot{O}(CH_2)_n\overset{+}{F}H$	−288	60	−181	−73
$HO(CH_2)_nPH_2^{+\cdot}$	$\dot{O}(CH_2)_n\overset{+}{P}H_3$	−136	−93		−47
$HO(CH_2)_nSH^{+\cdot}$	$\dot{O}(CH_2)_n\overset{+}{S}H_2$	−186	−135		−86
$HO(CH_2)_nCl^{+\cdot}$	$\dot{O}(CH_2)_n\overset{+}{Cl}H$	−343	41	−175	−62

[a] MP2/6-31G* values.

[b] From Table 5.

CONCLUDING REMARKS

The calculations in this paper indicate that the energy difference between the distonic radical cations $\dot{C}H_2(CH_2)_n\overset{+}{N}H_3$ and their conventional isomers $CH_3(CH_2)_nNH_2^{+\cdot}$ converges with increasing n towards a limit which may be approximated using energy data for appropriate small component systems. Generalization of this observation suggests that data for a limited number of small molecules ($CH_3\dot{Y}$, $CH_3\overset{+}{X}H$, CH_3YH, $CH_3X^{+\cdot}$, $CH_3YH^{+\cdot}$ and CH_3X) should permit the prediction of relative energies of a much larger set of distonic and conventional radical cations. However, explicit calculations on the larger systems reveal a sufficient number of exceptions that caution must be exercised in applying this and related predictive schemes. The predictions based on the small components are least useful for the species with $n = 0$ (i.e. $\dot{Y}\overset{+}{X}H$ vs $HYX^{+\cdot}$). For these systems, the conventional isomer is often *more* stable than expected due to favourable π-type interactions between the directly-bonded X and Y groups (e.g. $NH_2NH_2^{+\cdot}$). Such interactions are not important for the systems with $n = 1$ (i.e. $\dot{Y}CH_2\overset{+}{X}H$ vs $HYCH_2X^{+\cdot}$). The largest errors now occur for substituents (notably X = F) which have a large perturbing effect on the properties (notably the ionization energy) of the parent molecules. The conventional isomer is often *less* stable than expected in these cases. The preliminary calculations for systems with $n = 2$ (i.e. comparisons of $\dot{Y}CH_2CH_2\overset{+}{X}H$ with $HYCH_2CH_2X^{+\cdot}$) appear to indicate substantially reduced effects of this type. However, substantial deviations between predicted and calculated relative energies now occur for several systems (e.g. $NH_2CH_2CH_2NH_2^{+\cdot}$) for which the lowest-energy conventional isomer corresponds to ionization from the C_α—C_β bond rather than from a heteroatom lone pair. The conventional isomer is considerably *more* stable than expected in these cases. Finally, we note that the most favourable circumstances for a distonic radical cation to be preferred over its conventional isomer occur for systems which contain a group (X) with a high proton affinity but which do not contain a group (X, Y or perturbed C—C) with a low ionization energy. Further studies are in progress to determine the effect of higher-level calculations and of complete geometry relaxation ($n = 2$ systems) on the results presented here and to investigate the applicability of the predictive scheme to longer-chain-length radical cations.

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