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# Distonoid Ions

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By Yates, Bouma, and Radom's definition, distonic radical ions are those formally arising by ionization of diradicals or zwitterionic molecules (including ylides). These ions differ, therefore, from conventional radical ions by displaying the charge site and unpaired electron site (spin) localized mandatorily on separate atoms or group of atoms; that is, these sites are separated in all of their major resonance forms. Many conventional radical ions with a major resonance form in which charge and spin sites reside formally on the same atom or group of atoms display, however, high degree of *discretionary* (non-mandatory) charge-spin separation. By analogy with the metal/metalloid terminology, we propose that these distonic-like radical ions be classified as *distonoid ions*. Radical ions would, therefore, be divided into three sub-classes: conventional, distonic, and distonoid ions. B3LYP/6-311 + G(d,p) calculations for a proof-of-principle set of radical cations are used to demonstrate the existence of many types of distonoid ions with a high degree of discretionary charge-spin separation. Reliable calculations are indispensable for probing distonoid ions, since an ion that was expected to be distonoid (by the analysis of its resonance forms) is shown by the calculations to display a characteristic conventional-ion electronic distribution. Similarly to many distonic radical ions, and in sharp contrast to a conventional radical ion (ionized 1,4-dioxane), the gas-phase intrinsic bimolecular reactivity with selective neutrals of a representative distonoid ion, ionized 2-methylene 1,3-dioxolane, is found to include dual ion-radical type reactions. (J Am Soc Mass Spectrom 2006, 17, 1014–1022) © 2006 American Society for Mass Spectrometry

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**D**istonic ions [1], although at first considered unusual and surprisingly stable, have become a thoughtfully studied, fully-recognized, and useful [2] class of common gas and condensed-phase ions. In the gas phase, most distonic radical ions are formed by isomerization or rearrangements of conventional radical ions, or from bimolecular reactions. The existence of distonic radical ions as rather stable species is striking because many of them arise formally from ionization of unstable neutral molecules. Calculations have shown, however, that they are often (not always) [3] more stable than their conventional radical ion counterparts.

From the Greek (*diestos*) and the Latin *distans* meaning separate, Yates, Bouma and Radom introduced in 1984 the term distonic for radical ions (cations and anions) in which the charge and radical sites are separated [4]. They later added the need for mandatory separation of charge and spin sites by suggesting that “. . .the term distonic be reserved for those radical ions that arise formally from ionization of neutral systems, which are best written as zwitterions (ylides in the case of adjacent charges) or

biradicals” [3]. By necessity, therefore, distonic ions always display in a formal, conventional valence bond description, spatially separated radical and charge sites regardless of the resonance form used. The charge and radical sites may reside on adjacent centers such as in  $\cdot\text{CH}_2\text{OH}_2^+$  (an  $\alpha$ -distonic radical ion), or be separated by a spacing atom or group of atoms such as in  $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$  (a  $\beta$ -distonic radical ion). Distonic radical ions are sometimes found to react as bidentate species, that is, either as radicals with an inert charge site, or as ions with an inert radical site, or even more fascinating, as both [5]. Although conventional radical cations may also display dual ion-radical reactivity, these characteristics are more likely to be observed for distonic ions (within a set of isomers for instance) if selective neutral reactants are properly chosen [1].

The definition of distonic radical ions proposed by Yates et al. is convenient, since it can be applied with confidence by inspection of the neutral counterpart (as long as zwitterions and diradicals can be unambiguously recognized). In addition, it is apparently unambiguous since ions arising from zwitterions or diradicals necessarily display separate charge and spin sites in all of their resonance forms. There are, however, many conventional radical ions with distonic-like attributes, that is, with a high degree of discretionary (non-man-

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Published online May 19, 2006

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datory) charge-spin separation, which are overlooked due to the strictness of the distonic ion definition.

In this work, we discuss examples of such ions and propose, by analogy with the metal/metalloid terminology, their general classification as distonoid ions. To exemplify our proposal, we performed B3LYP/6-311+G(d,p) calculations of charge and spin densities for a set of proof-of-principle radical ions that we expected to display distonoid character. The gas-phase intrinsic bimolecular reactivity of ionized 2-methylene-1,3-dioxolane, an ion with strong distonoid ion character according to the calculations, has also been investigated.

## Experimental

The MS<sup>2</sup> and MS<sup>3</sup> experiments [6] were performed using an Extrel [Pittsburgh, PA] pentaquadrupole (QqQqQ) mass spectrometer [7]. The QqQqQ consists of three mass-analyzing quadrupoles (Q1, Q3, Q5) in which ion mass-selection and mass-analysis are performed, and two radio-frequency-only reaction quadrupoles (q2, q4). Reactions were then performed in q2 with selected neutral reactants. For the MS<sup>2</sup> experiments, 5 of *m/z* 86 was generated by dissociative 70 eV electron ionization (EI) of 2,2-pentamethylene-1,3-dioxolane and mass-selected by Q1. After its ion-molecule reactions in q2 with the neutral reagents, Q5 was used to record the product ion mass spectrum, while operating Q3 and q4 in the “full” ion-transmission rf-only mode.

For the MS<sup>3</sup> experiments, a product ion of interest was mass-selected in Q3 and dissociated in q4 by collisions with argon, while Q5 was scanned across the desired *m/z* range to record the sequential product triple stage (MS<sup>3</sup>) mass spectra. Nominal sample and neutral gas pressures were typically  $5 \times 10^{-6}$  and  $5 \times 10^{-5}$  torr, respectively, as monitored by a single ionization gauge located centrally in the vacuum chamber. The target gas pressure corresponds to a typical beam attenuation of 50 to 70%, viz., to multiple collision conditions. However, lower reaction yields but similar sets of products were always observed at lower pressure, mainly single collision conditions in q2 [8]. Instrumental parameters such as quadrupole offset potentials and lens voltages were adjusted to maximize the abundance of the ion/molecule reaction products. The collision energies, calculated as the voltage differences between the ion source and the collision quadrupole, were typically near 1 eV for ion-molecule reactions and 15 eV for CID.

Molecular orbital calculations were performed using GAUSSIAN98, and electronic energies after full structure optimization were obtained using B3LYP/6-311+G(d,p) calculations [9]. The geometries and energies of the investigated species are available from the authors upon request. All species have been characterized as energy minima by displaying only real vibrational frequencies.

## Results and Discussions

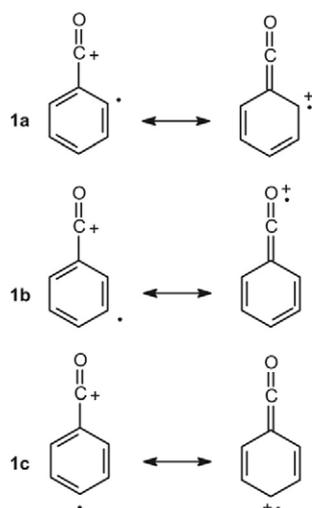
### General Examples of Distonoid Ions

Ionized vinyl alcohol, the enol form of acetaldehyde, displays three major resonance forms: one conventional-ion form and two distonic-ion forms, that is,  $\text{CH}_2=\text{CH}-\text{O}^+-\text{H} \leftrightarrow \cdot\text{CH}_2-\text{CH}=\text{O}^+-\text{H} \leftrightarrow \cdot\text{CH}_2-\text{CH}^+-\text{OH}$ . Despite the two major distonic forms, this ion cannot be classified as distonic since the best representation of its neutral counterpart is  $\text{CH}_2=\text{CH}-\text{OH}$ , not the zwitterionic form  $^-\text{CH}_2-\text{CH}=\text{O}^+\text{H}$  [1]. But ionized enols (as well as other alkenes with charge or spin stabilizing substituents, or both; see ions **5**, **6**, **10**, and **13** below) have been demonstrated to display, owing to the  $\pi$  C=C nature of their HOMO, a high degree of distonic-like discretionary charge and spin separation [10]. This configuration suggests that ionized vinyl alcohol is best represented by the distonic resonance forms  $\cdot\text{CH}_2-\text{CH}=\text{O}^+-\text{H} \leftrightarrow \cdot\text{CH}_2-\text{CH}^+-\text{OH}$ . Gerbaux et al. [11] also found that ionized enols display characteristic reactivity as compared to their keto counterparts, that is, that ionized enols undergo a unique H-by-NO substitution reaction with *t*-butyl nitrate. We, therefore, propose that ionized vinyl alcohol be classified as a distonoid ion.

As for distonic radical ions, charge and spin separation of distonoid ions is a stabilizing factor that may account for the interesting inversion of stability order observed for neutral and ionized keto/enol pairs [11]. Ionized acetaldehyde and carbonyl compounds in general have, in contrast, an electronic configuration (owing to the nonbonding HOMO of carbonyl compounds localized on the oxygen atom) and reactivity [11] typical of conventional radical cations. Theoretical calculations on carbonyl compounds place the unpaired electron mainly on oxygen, whereas the charge resides mainly on the carbonyl carbon and adjacent atoms or group of atoms. However, this apparent distonic distribution results from the high electronegativity of the oxygen and charge dispersion via inductive effects, the C=O bond length being as short as that of neutral carbonyl groups, see [12].

The isomeric series of ortho, meta, and para-dehydrobenzoyl cations (**1a–c**) constitutes another challenging case for radical ion classification [6]. Although they all display a distonic-ion resonance form, they can also be represented by a conventional-ion form. The meta isomer **1b** can be represented by an allenic resonance form whereas the ortho (**1a**) and para (**1b**) isomers can be viewed as ionized carbenes with the charge and spin sites residing on the same carbon atom. Should we therefore classify **1a–c** as conventional or distonic radical ions?

We have shown, however, by theoretical calculations that **1a–c** display similar electronic structures with high degrees of discretionary charge-spin separation. The ions also display strong duality of chemical behavior,

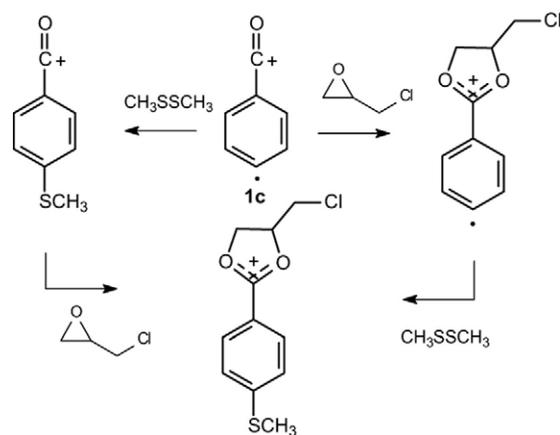
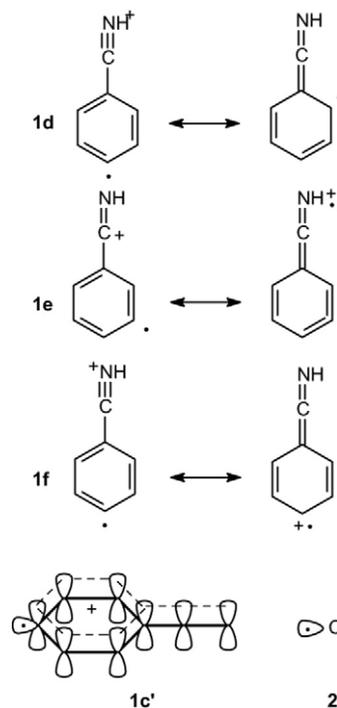


reacting selectively (when selective neutral reactant partners are properly chosen) either as free radicals with inert charge sites, or as acylium ions with inert radical sites (Scheme 1), or even as both [5].

From *ab initio* calculations, we learned that the charge and spin densities of **1a–c** parallel those of the benzoyl cation and the phenyl radical, respectively; hence that all three **1a–c** display electronic structures characteristic of  $\sigma$ -localized phenyl radicals and  $\pi$ -delocalized aromatic benzoyl cations (**1c'**). Infringing on the definition of Yates et al., we applied molecular orbital formalism to create a new class of distonic radical ions with molecular orbital-separated charge and spin sites with **1a–c** being the first members [6]. Later, Flammang et al. [13] also found for **1d–f** (isomers of ionized benzonitrile) electronic distributions similar to that of **1a–c**, whereas Schwarz et al. [14] also used the same formalism to classify the radical anion of carbon dioxide (**2**) as the first distonic anion of this class. As theoretical calculations predict, the negative charge (the extra electron) and the spin site (the unpaired electron) of **2** are located in different symmetry planes, that is, in orthogonal  $\sigma$  and  $\pi$ -orbitals, hence the unpaired elec-

tron is delocalized mainly on the central carbon whereas the negative charge is delocalized mainly on the two oxygens.

We herein rectify our classification of **1a–c** as distonic radical ions, noting that these interesting ions as well as **1d–f** are typical examples of  $\pi/\sigma$ -distonoid ions. We also propose that the radical anion of carbon dioxide (**2**) be classified as a  $\pi/\sigma$ -distonoid anion.

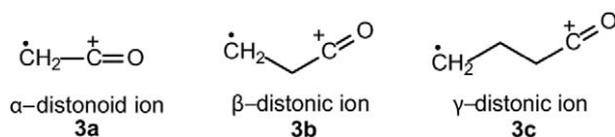


Scheme 1

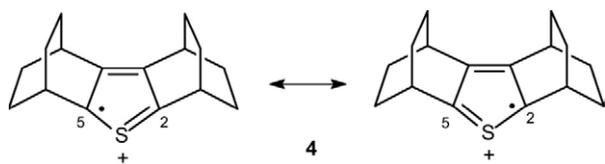
Yet for **1a** and **1c**, one could argue that the definition of Yates et al. already classifies the ions as distonic since ionized carbenes could be viewed as ionized diradicals. But this adjustment is rather ambiguous. In a strict sense, carbenes are not diradicals. The IUPAC definition [15] states, for instance, that diradicals are even-electron molecular entities with two radical centers located on different (separate) atoms acting nearly independently of each other, whereas carbenes have the two radical centers located on the same atom. In addition to this ambiguity of carbene-diradical classification, adding carbenes to the set of neutral counterparts of distonic radical ions would create other sources of doubt. For instance, would we then consider the simplest ionized carbene  $\text{H}_2\text{C}^{+\cdot}$  as well as other nondelocalized carbenes as distonic radical ions? Certainly not, since the assignment would corrupt the meaning of the term distonic! The spin and charge sites of  $\text{H}_2\text{C}^{+\cdot}$  do reside on orthogonal orbitals but these atomic orbitals belong to the same (group of) atom(s). Not all ionized carbenes display the properties expected for distonic radical ions.

Ambiguity for conventional versus distonic radical ion classification is also encountered for the series of acyclic distonic acylium ions **3a–c** [16]. The  $\gamma$ -(**3c**) [17]

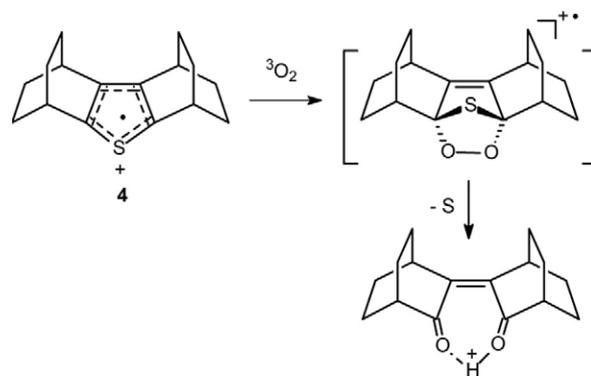
and  $\beta$ -distonic (**3b**) [18] ions are well-known and easily accessible gaseous ions. Since these ions arise formally from ionization of diradicals, charge-spin separation is formally mandatory and they are unequivocally classified as distonic radical ions. However, the lowest member of this homologous series, **3a**, arising formally from ionization of ketene (best represented as  $\text{CH}_2=\text{C}=\text{O}$  when a conventional valence bond description is used) cannot be classified as an  $\alpha$ -distonic radical ion. But **3a** has been found to display high degree of discretionary charge-spin separation and a pronounced charged-radical bimolecular reactivity[1, 19]. Therefore, we propose that **3a** be classified as an  $\alpha$ -distonoid ion [20].



Ionized thiophenes offer another ambiguous case of conventional versus distonic radical ion classification. Recently, Wakamiya et al. [21] reported the first isolation of a salt of a thiophene radical cation highly stabilized by annelation with bicyclo[2.2.2]octane:  $4/\text{SbCl}_6^-$ . Their theoretical calculations predicted a pronounced distonic-like electronic distribution for **4**<sup>+</sup>; the odd-spin density is mostly on the 2,5-methylene groups whereas the charge is mainly on the sulfur atom. They also found this configuration to be in good agreement with the hyperfine coupling constant  $a_{\text{H}}$  of the five-line signal obtained by ESR spectroscopy.



In solution, triplet oxygen was found to add to the 2,5-positions of **4** in an interesting radical annelation reaction (Scheme 2) [22]. Reactions with triplet oxygen are particularly informative since this biradical molecule has been shown to add selectively to some distonic ions; for instance, Gross et al. [22] found that the  $\beta$ -distonic ion  $\text{Py}^+-\text{CH}_2\text{CH}_2^\cdot$  forms an abundant adduct with  $\text{O}_2$  whereas isomeric ethyl pyridine conventional radical cations fail to form such adducts. This strong *radical* reactivity therefore supports the distonic-like description for **4**; hence we propose that **4** is best classified as a distonoid ion. We have recently observed that the simplest ionized thiophene also displays a high degree of discretionary charge-spin separation and ion/molecule reactivity that support its classification as a distonoid ion [14].



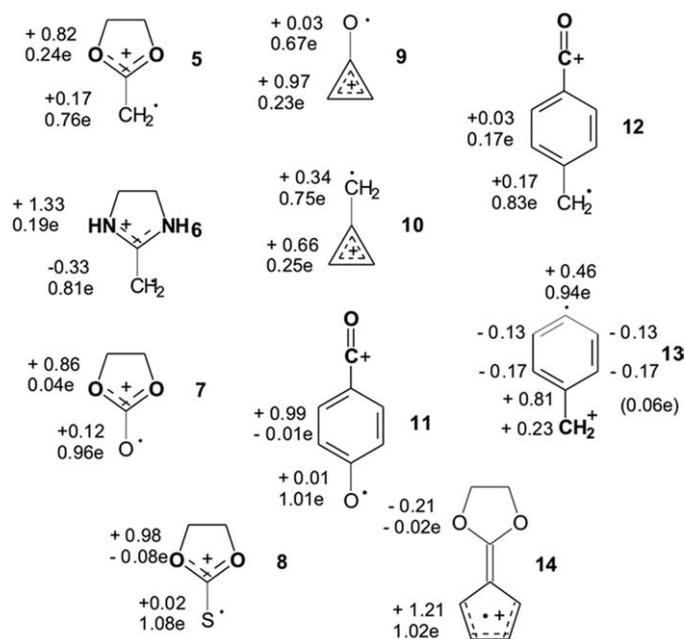
Scheme 2

### A Proof-of-Principle Set of Potentially Distonoid Ions

Numerous other radical ions are predicted by the inspection of their major resonance forms to display distonoid ion character, as we illustrate herein for ions **5–14**. We therefore performed B3LYP/6-311+G(d,p) calculations to verify whether **5–14** can in fact be classified as distonoid ions (Figure 1).

The calculations show that **5–13** display, as expected, high degree of discretionary charge-spin separation (predominance of the distonic-ion resonance form, see Figure 1), and that they can be therefore classified as distonoid ions. The charge on **5** is mainly (de)localized across the 1,3-dioxolane ring (+0.82), whereas the unpaired electron is localized mainly on the 2-methylene group (0.76 e). This highly localized spin site is also evident when examining the SOMO of **5** (Figure 2). Electronic distributions even more *distonoid* than **5** are observed for **6**, **7**, and **8**. For **8**, for instance, charge is nearly fully (de)localized across the 1,3-dioxolane ring (+0.98), whereas spin density is highly concentrated on the sulfur atom (1.08 e). Ions **9** and **10** have their charge sites highly stabilized in an aromatic cyclopropenyl cation-like electronic distribution (+0.97 and +0.66 respectively), whereas spin density is concentrated mostly on the exocyclic oxygen (0.67 e) and ethylene group (0.75 e), respectively. Ion **13** is easily recognized as displaying *molecular orbital*-separated radical and spin sites; that is, as a  $\pi/\sigma$ -distonoid ion, but such a concept of charge-spin orbital separation is not so easily applied to **11** and **12**. The charge and spin densities calculated for **11**, **12**, and **13** fully corroborate their general description as distonoid ions.

The results for **14** are interesting since our intuition based on the prevalence of a given resonance form failed for this ion. We predicted for **14** a pronounced distonoid character with the positive charge delocalized across the 1,3-dioxolane ring (dioxolanylium ion-like structure) [23] and the odd spin mainly placed on, and hence delocalized across, the cyclopentadiene ring. The electronic distribution calculated for **14** (Figure 1) is, however, not distonoid at all. The unpaired electron

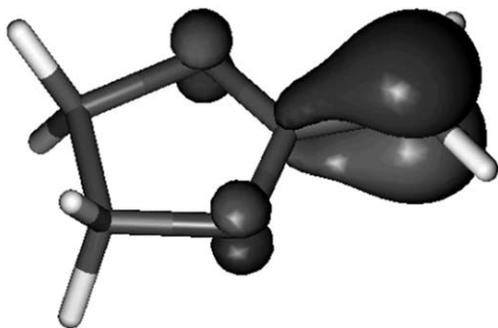


**Figure 1.** Mulliken charge and spin densities for **5–14** as predicted by B3LYP/6-311+G(d,p) calculations. For clarity, the ions are represented in resonance forms that most closely reflect either their distonic-like (distonoid) or conventional radical ion electronic distributions. Their structures are also split into two subunits (one of those is shown in bold) for which summation values of charge and spin densities are given, except for **13**, for which charge density is given for each carbon center.

and the positive charge are not placed on different rings, but are highly (de)localized across the cyclopentadiene ring. Predictions based on the prevalence of a resonance form are, therefore, not always a reliable approach for distonoid versus conventional radical ion classifications.

### Intermediate Cases

Although we have not encountered such cases, certainly there are many halfway cases, that is, ions that display intermediate degrees of charge-spin separation. The extent of charge-spin separation should also vary according to the method and level of theoretical calculation used, particularly with regard to charge distribution, that is known to vary considerably according to the method used [24]. Such ions with mixed conventional and distonoid ion nature should, therefore, be-



**Figure 2.** Graphical representation of the SOMO of **5**.

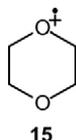
have accordingly, with properties resembling their distonic-distonoid intermediate nature.

### Ion/Molecule Chemistry of Distonoid Ions

Distonic radical ions have been shown to display a number of radical-type reactions, often in sharp contrast to their conventional radical isomers, particularly when selective neutral reactant partners are properly chosen [1]. For instance, Kenttämä et al. [25] have shown that several distonic radical ions abstract  $\text{CH}_3\text{S}^\cdot$  from dimethyl disulfide and  $\text{CH}_3\text{Se}^\cdot$  from dimethyl diselenide [26] (the recombination energies of the distonic radical ion should be lower than the IE of dimethyl disulfide or dimethyl diselenide, respectively). Distonic radical ions have been also shown to transfer ionized methylene ( $\text{CH}_2^+$ ) to neutrals such as ammonia and pyridine [1, 27] and to abstract either the allyl radical or the halide, or both, from allyl halides [28]. As for distonic radical ions and due to similar electronic distributions, distonoid ions are likely to display similar higher proclivity to undergo ion-radical reactions. That is, as long as a selective neutral reactant partner is properly chosen, distonoid ions should react either as a radical with an inert charge site or as an ion with an inert radical site, or as both [29]. Distonoid ions with coordinatively saturated charge sites should react predominantly as radicals with inert charge sites [30].

Using **5** (an ionized alkene with charge stabilizing alkoxy substituents) and ionized 1,4-dioxane **15** (a “classical” conventional radical cation) as a pair of dis-

tonoid/conventional ions, we tried to find selective neutral reactants able to access the dual ion-radical reactivity of distonoid ions. We reacted **5** and **15** with dimethyl disulfide, pyridine, allyl bromide, and butadiene. Based on similar characteristic reactions of distonic radical ions with ethene [31], butadiene was chosen as we expected this diene to promote selective allylic homologation of the radical site of **5**.



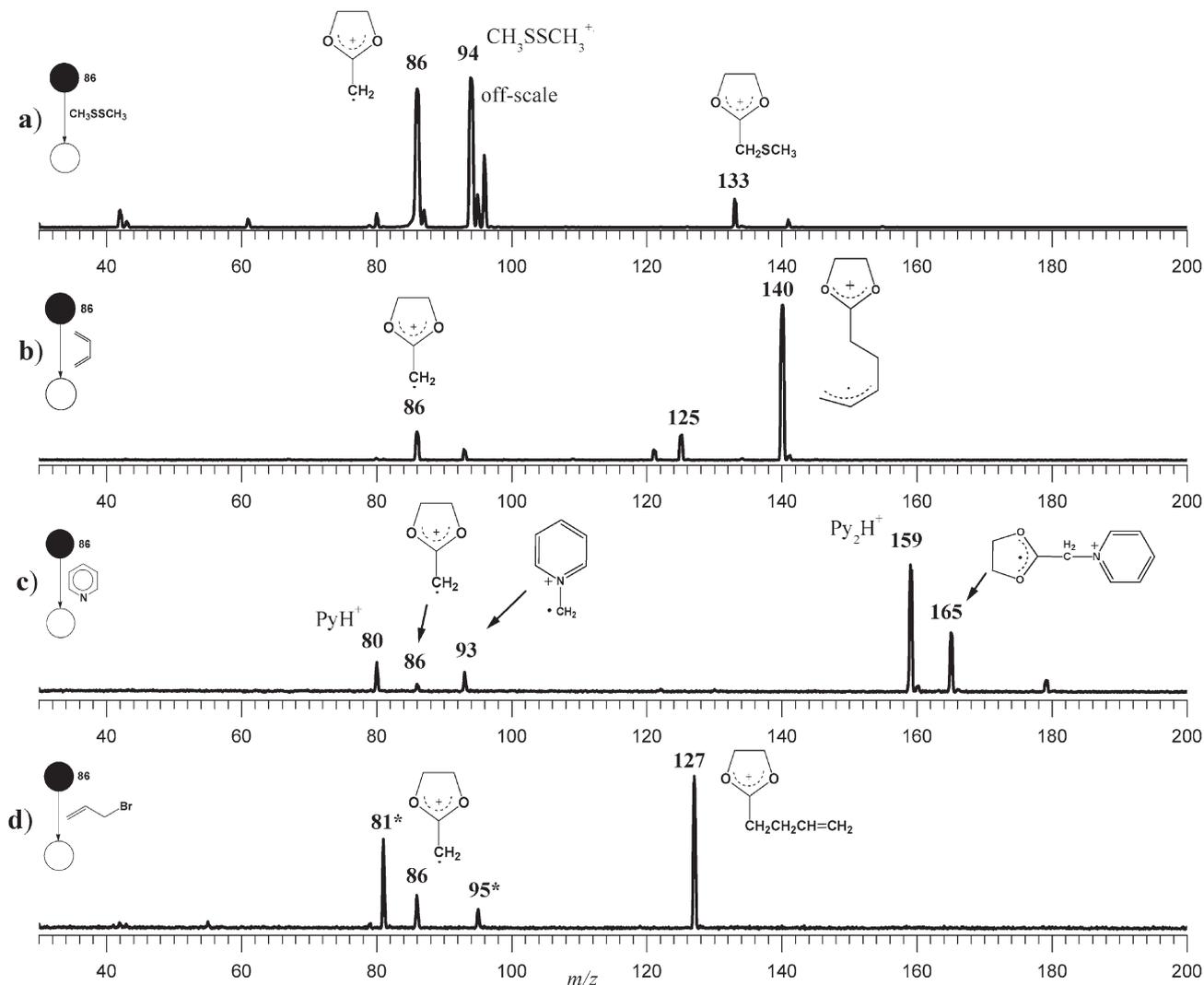
### Dimethyl Disulfide

Figure 3a shows the product ion mass spectrum for the low-energy (near 1 eV) reaction of **5** with dimethyl disulfide. Electron-transfer dominates, yielding  $\text{CH}_3^{32}\text{S}^{32}\text{SCH}_3^+$ .

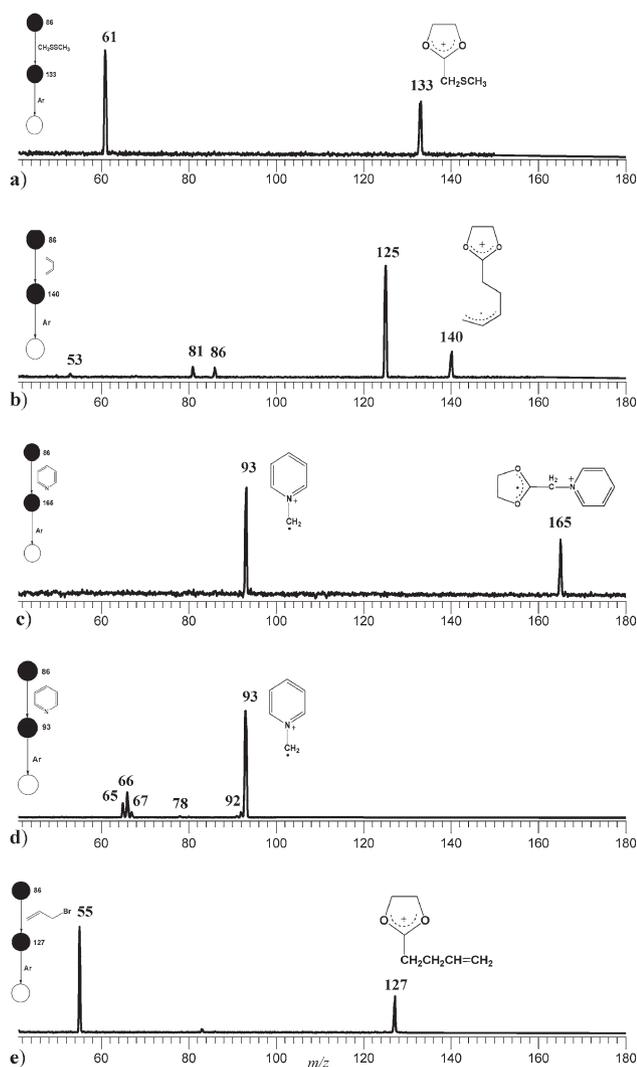
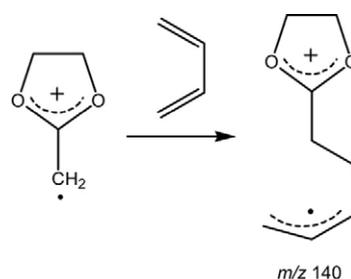
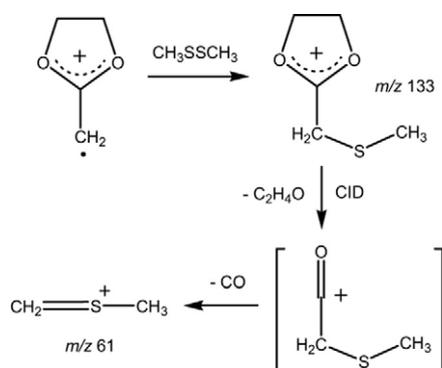
of  $m/z$  94 as the major product (off-scale) as well as the corresponding  $^{33}\text{S}$  and  $^{34}\text{S}$  isotopologue ions of  $m/z$  95 and 96, but **5** also abstracts  $\text{CH}_3\text{S}^\bullet$  from dimethyl disulfide to form the ion of  $m/z$  133 and its corresponding sulfur isotopologues of  $m/z$  134 and 135 (Scheme 3). CID of the product ion of  $m/z$  133 (Figure 4a) yields a single ion of  $m/z$  61 likely via consecutive losses of ethylene oxide and CO from the dioxolane ring (Scheme 3). Such dissociation chemistry matches that displayed by many dioxolanylium ions [32], thus corroborating the proposed structure (Scheme 3). Ion **15** reacts exclusively by electron-transfer (spectrum not shown). But the quite limited extent by which  $\text{CH}_3\text{S}^\bullet$  abstraction occurs for **5** shows that dimethyl disulfide is poorly selective in distinguishing the distonoid **5** from its conventional isomer **15** via radical reactivity.

### Butadiene

Reaction of **5** with butadiene (Figure 3b) occurs promptly and nearly exclusively by a single pathway



**Figure 3.** Double-stage (MS<sup>2</sup>) product ion mass spectra for ion/molecule reactions of **5** of  $m/z$  86 with (a) dimethyl disulfide, (b) 1,3-butadiene, (c) pyridine, and (d) allyl bromide. Note that the major product ion of  $m/z$  94 in (a) is off-scale.



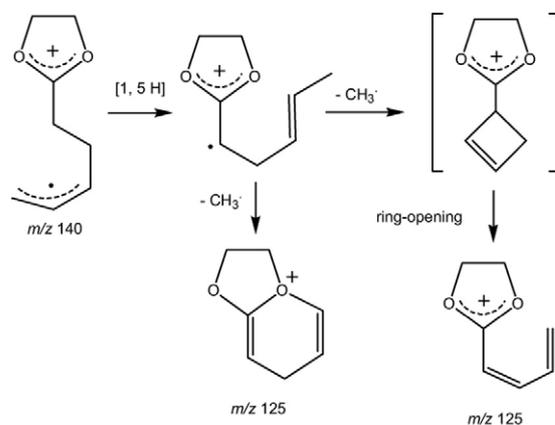
**Figure 4.** Triple-stage ( $MS^3$ ) sequential mass spectra for product ions formed in reactions of **5** with (a) dimethyl disulfide ( $m/z$  133), (b) 1,3-butadiene ( $m/z$  140), (c) pyridine ( $m/z$  165), (d) pyridine ( $m/z$  93), and (e) allyl bromide ( $m/z$  127).

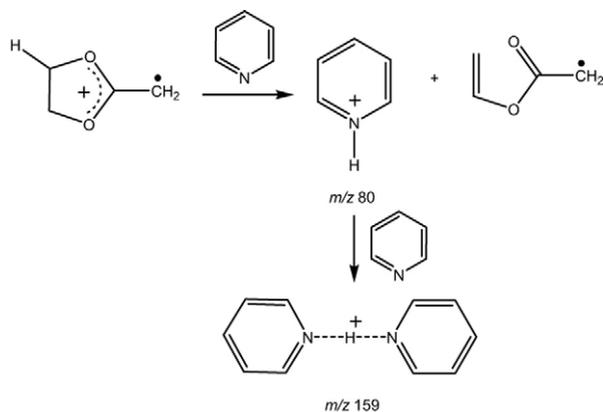
that yields the product ion of  $m/z$  140 and its fragment of  $m/z$  125. The exceptional impetus of such a reaction, which promotes the expected allylic homologation of the radical site of **5**, is likely provided by the high stability of the “allylic”-distic ion formed. With butadiene, therefore, the distonoid ion **5** acts predominantly as expected, that is, as a radical with an inert charge site (Scheme 4). Again **15** reacts, now in sharp contrast to **5**, predominantly by electron and proton transfer (spectrum not shown). B3LYP/6-311+G(d,p) calculations on several possible structures for the product ion of  $m/z$  140, including those arising from cycloaddition across a putative C2-methylene double bond and nucleophilic addition on C2, show that the most stable product is formed indeed by radical-site homologation of **5** (Scheme 4).

CID of the product ion of  $m/z$  140 (Figure 4b) yields nearly exclusively a single fragment ion of  $m/z$  125. Scheme 5 provides two rationalizations for this favored dissociation, which requires methyl radical loss and must therefore be preceded by H-shift. One such process yields a highly resonance stabilized  $\alpha,\beta$ -unsaturated 1,3-dioxolanylium ion [33]. Note that dissociation of  $m/z$  140 to an ion of  $m/z$  125 also occurs to some extent even with the low-energy collision conditions (near 1 eV) used for ion/molecule reactions (Figure 2b).

### Pyridine

In reactions with pyridine (Figure 3c), **5** displays dual ion-radical reactivity. Proton transfer yields protonated

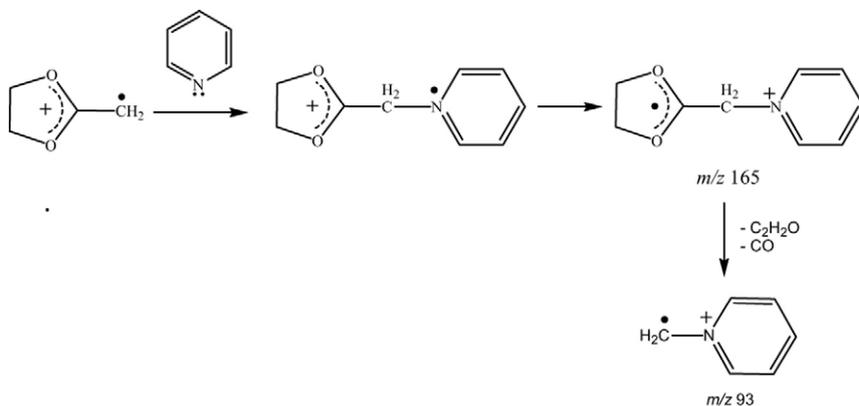




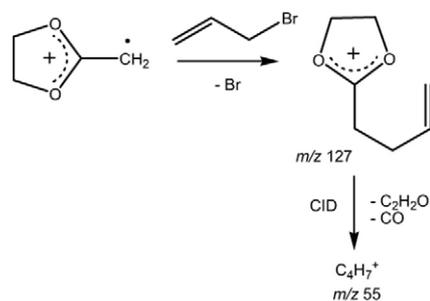
Scheme 6

pyridine of  $m/z$  80 and subsequently the pyridine proton dimer of  $m/z$  159, whereas ionized methylene transfer yields the distonic ion of  $m/z$  93 via the adduct of  $m/z$  165. Again, **15** reacts with pyridine probably by electron-transfer followed by a secondary reaction that forms protonated pyridine (spectrum not shown). In proton transfer reactions to pyridine, the distonoid ion **5** acts as a cation (a protonated molecule) with an inert radical site transferring its most acidic C4-H proton (Scheme 6). In ionized methylene transfer to pyridine via the intact adduct, **5** acts distinctively as a radical with an inert charge site since pyridine must bind to the methylene carbon to allow for  $\text{CH}_2^+$  transfer (Scheme 7). A similar radical-type mechanism has been proposed for ionized methylene transfer of the “cousin” distonic ion  $(\text{CH}_3\text{O})_3\text{P}^+\text{OCH}_2\text{CH}_2^\cdot$  to  $(\text{CH}_3\text{O})_3\text{P}=\text{O}$  [34].

CID of the intact distonic radical ion of  $m/z$  165 (Figure 4c) shows that it readily loses ethylene oxide and CO to form the fragment ion of  $m/z$  93 (Scheme 7). The ionized methylene transfer product of  $m/z$  93 (Figure 4d) dissociates not so promptly to a series of fragment ions of  $m/z$  92, 78, 67, 66, and 65. This dissociation chemistry is the same as that displayed by the distonic radical ion formed upon  $\text{CH}_2^+$  transfer from the  $\alpha$ -distonic radical ion  $\cdot\text{CH}_2\text{-O-CH}_2^+$  to pyridine [35].



Scheme 7



Scheme 8

### Allyl Bromide

In reactions with allyl bromide (Figure 3d), the distonoid ion **5** reacts again as anticipated, that is, as a charged radical efficiently abstracting allyl radical to form the major product ion of  $m/z$  127 (Scheme 8). Either allyl radical or bromine abstraction, or both, have been observed in reactions of distonic radical ions with allyl bromide; [28, 36]. Ions of  $m/z$  81 and 95 are likely secondary products arising from electron-transfer ionization of allyl bromide [22]. In sharp contrast, **15** reacts predominantly by electron-transfer (spectrum not shown). CID of  $m/z$  127 (Figure 4e) yields promptly and nearly exclusively a fragment ion of  $m/z$  55 (Scheme 8) in a route that can be rationalized as involving sequential losses of ethylene oxide and CO—again the characteristic dissociation of 1,3-dioxolanylium ions [33].

### Conclusions

A new class of radical ions, the *distonoid ions*, has been proposed and the basis of a new scheme for radical ion classification has been introduced. Radical ions are ideally divided in three sub-classes: (1) conventional radical ions with charge and spin sites concentrated on the same atom or group of atoms; (2) distonic radical ions with mandatory separation of their charge and spin sites; and (3) distonoid ions with a high degree of *discretionary* (non-mandatory) charge-spin separation.

As evidenced by **5** and as expected owing to similar electronic distributions, distonoid ions share with their “cousins” the distonic radical ions, dual ion-radical reactivity as long as the neutral reactant counterpart is properly selected.

## Acknowledgments

The authors are greatly indebted to a reviewer for fruitful discussions and for the suggestion of the term distonoid. They also thank the São Paulo State (FAPESP) and the Brazilian National Research Foundation (CNPq) for financial support.

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