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Ionized Benzonitrile and Its Distonic Isomers in the Gas Phase

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The dehydrobenzonitrilium distonic radical cations **a**−**c**, isomers of benzonitrile radical cation **d**, were prepared by collisional dehalogenation of protonated halogenobenzonitriles and characterized by tandem mass spectrometry (MS/MS/MS experiments and ion−molecule reactions) making use of a hybrid mass spectrometer of sector−quadrupole−sector configuration. These experimental results were further supported by density functional theory calculations at the B3LYP/6-311++G(3df,2p) level, indicating that although the distonic ions are less stable than ion **d** by ca. 45−50 kJ mol^{-1}, they are protected against isomerization by relatively large energy barriers. Relative energies of benzonitrile and its isomers as well as their proton affinities and ionization energies were also evaluated. N-protonation in benzonitrile is about 120 kJ mol^{-1} more exothermic than ring protonation.

Introduction

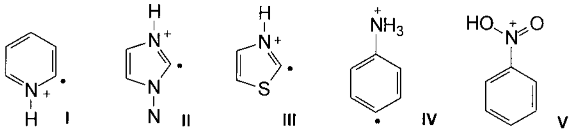
Distonic ions are species in which the charge and radical sites are centered at different atoms.[1] In the past decades, such radical cations have gained considerable experimental and theoretical interest,[2−4] and their formation and high stability have allowed a number of gas-phase ion processes to be understood.

The gas-phase stability of an extensive series of α-distonic radical cations derived from heterocyclic compounds was also clearly demonstrated in recent years by using tandem mass spectrometric methods. Typical examples such as **I**−**III** are shown in Scheme 1,[5−8] but other examples have been reported as well in the series of five- and six-membered rings including pyrazine, s-triazole, etc.[9−10]

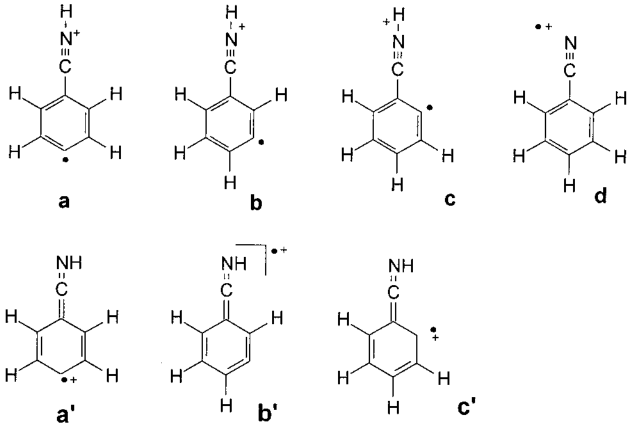
Examples of distonic ions derived from carbocyclic aromatic ions have been relatively less described in the literature. Using Fourier transform ion cyclotron resonance (FT-ICR) experiments, Kenttamaa et al.[11] have convincingly supported the formation of dehydroanilinium ion **IV**, a distonic isomer of the conventional aniline radical cation. Structure identification of **IV** was based on ion−molecule reactions with dimethyl disulfide, which resulted in the abstraction of a methylthio radical by **IV** but not by the molecular ion of aniline.[11]

More recently, several isomers of nitrobenzene radical cation were identified as stable structures in the gas phase.[12] Among these, the ylide-ion **V** was prepared from protonated 1,4-dinitrobenzene upon collisional loss of NO_2, unambiguously characterized by MS/MS/MS and calculated to be less stable than the conventional nitrobenzene ions by ca. 40 kJ mol^{-1}.

SCHEME 1



SCHEME 2



In this paper we report on the preparation of the distonic isomers **a**−**c** of ionized benzonitrile **d** (Scheme 2). These ions, which can also be represented by carbenic (**a'**, **c'**) or allenic (**b'**) resonance structures, were generated by either collisional deiodination of protonated iodobenzonitriles or dissociative ionization of ortho-substituted benzonitriles (for ions **c**) and characterized by high energy collisional activation, neutralization−reionization experiments, and ion−molecule reactions. The

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experimental findings were further supported by density functional theory computations.

Experimental Section

The spectra were recorded on a large-scale tandem mass spectrometer (Micromass AutoSpec 6F, Manchester) combining six sectors of $c_1E_1B_1c_2E_2c_3c_4E_3B_2c_5E_4$ geometry (E stands for electric sector, B for magnetic sector, and c for collision cell).[13] General conditions were 8-kV accelerating voltage, 200-μA trap current (in the electron ionization mode, EI), 1-mA current (in the chemical ionization mode, CI), 70-eV ionizing electron energy, and 200 °C ion source temperature. Solid samples were introduced with a direct insertion probe, while liquid samples were injected in the ion source via a heated (180 °C) septum inlet.

Collisional activation (O_2) of fast (8 keV kinetic energy) mass selected ions was performed in c_4, and the CA spectra were recorded by scanning the field of E_3, collecting the ions in the fifth field-free region with an off-axis photomultiplier detector. The NR (NH_3/O_2) unit is situated in the fourth field-free region, c_3 and c_4 being the neutralization and the reionization cells, respectively. The NR spectra were recorded in a similar way, the collisional reionization with oxygen in c_4 being preceded by collisional reduction of the ions with ammonia in c_3.

The installation of an rf-only quadrupole collision cell (Q_{cell}) inside the instrument between E_2 and E_3 has also been reported elsewhere.[14] This modification allows the study of associative ion−molecule reactions and the study of collisional activation of decelerated ions. Briefly, the experiments utilizing the Q_{cell} consist of the selection of a beam of fast ions (8 keV) with the first three sectors ($E_1B_1E_2$) and the deceleration of these ions to approximately 5 eV (to maximize ion−molecule reactions) or 20−30 eV (to maximize collision-induced dissociations). The interaction between the ions and the reagent gas (the pressure of the gas is estimated to be about 10^{-3} Torr) is thereafter realized in the Q_{cell}, and, after reacceleration at 8 keV, all the ions generated in the quadrupole are separated and the mass is measured by scanning the field of the second magnet. The high-energy CA spectra of mass-selected (with B_2) ions generated in the Q_{cell} can be recorded by scanning the field of E_4 after collisional excitation in c_5.

The NR mass spectra of ions **c** and **d** were also measured on the tandem quadrupole acceleration−deceleration mass spectrometer described previously.[15] Dimethyl disulfide was used for collisional neutralization of 8200-eV precursor ions at 70% transmittance of the ion beam. O_2 at 70% ion transmittance was used for collisional reionization of neutral intermediates. The neutral lifetime was 4.8 μs.

The iodobenzonitriles **1**−**3** were prepared according to literature procedures,[16] while benzonitrile **4** and 2-cyanobenzaldehyde **5** were commercially available (Aldrich) and were used without any further purification.

Results and Discussion

1. Preparation of the $[C_7H_5N]^{\bullet+}$ Radical Cations. Chemical ionization of iodobenzonitriles **1**−**3** using either methane or methanol as a reagent gas produces abundant protonated molecules. Given the fact that the proton affinity of benzonitrile, which varies from 820[17a] to 812 kJ mol^{-1},[17b] is larger than the proton affinity of benzene (759 kJ mol^{-1})[17] and also higher than the proton affinity predicted from a correlation between benzenic PA's and the σ^+ constants,[18] the regiospecific protonation at nitrogen in 4-iodobenzonitrile is expected to occur during the chemical ionization process, as shown in Scheme 3 for **1H**$^+$.

SCHEME 3

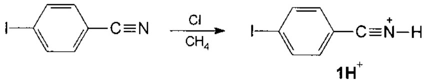
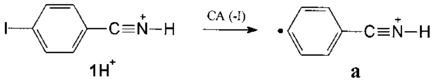


TABLE 1: Major Ions in the CA Spectra of Protonated Iodobenzonitriles 1−3H$^+$ (methane chemical ionization, *m/z* 230 Ions, 8 keV) with Helium or Oxygen as the Target Gas

MH$^+$	Gas	M/z	203	127	115	103	102	76	75	74
2-iodo	He		10	5		100	34	28	14	7
3	O_2		9	**24**	**36**	100	32	26	16	8
3-iodo	He		14	5	<1	100	35	30	13	7
2	O_2		13	**22**	**56**	100	31	31	14	6
4-iodo	He		6	5	<1	100	35	27	10	6
1	O_2		10	**27**	**59**	100	32	31	12	9

N-protonated structures **1**−**3H**$^+$ are readily dehalogenated by collisional activation. For instance, in the high kinetic energy regime (8 keV, Table 1), the ions at *m/z* 103 represent the base peak of the CA spectra. We have observed on several occasions that the loss of a halogen atom from protonated halogenated heterocycles can be significantly enhanced by using oxygen as the target.[19] The CA spectra have therefore been recorded under these particular conditions. However, in this case molecular oxygen increased the yield of doubly charged ions (charge stripping) and the yield of I$^+$ ions, but not the yield of [MH−I]$^+$ ions. Such an unexpected behavior, in view of the fact that the ionization energy of iodine is relatively high (10.45 eV),[17] is found to be a quite general trend for a series of iodinated protonated (hetero)aromatic compounds, even though the effect of the collision gas appears to be mainly related to its mass.[20]

SCHEME 4



In the low kinetic energy regime (within the quadrupole collision cell, see experimental), deiodination of **1**−**3H**$^+$ is also a very efficient reaction and, for instance with **1H**$^+$, this reaction yields abundant [MH−I]$^+$ (ca. 7% of the unreacted *m/z* 230 species), while the other ion products (*m/z* 203 and 76) represent less than 0.07%. That the deiodination reaction can be performed in the Q_{cell} is of particular interest as it allows one to prepare [MH−I]$^+$ ions that can be investigated by high energy CA spectra. This avoids the drawbacks of the MS/MS/MS methodology, that is low mass resolution and sensitivity, especially when the mass of the neutral lost is high (iodine in the present case).

2. High Energy Collisional Activation of the $[C_7H_5N]^{\bullet+}$ Radical Cations. "Conventional" MS/MS/MS experiments were conducted on protonated iodobenzonitriles **1**−**3H**$^+$. The CA spectra of the *m/z* 103 ions formed by collisional deiodination were found to be somewhat different from the CA spectrum of ionized benzonitrile. However, because of the substantial reduction of product ion translational energy after diodination and the poor mass resolution in the MIKE spectra (Figure 2), more accurate CA data were needed to allow unambiguous differentiation of the isomeric species.

In contrast, mass selection of the *m/z* 103 ions generated from **1H**$^+$ by collisional activation *in the Q_{cell}* gives, after reacceleration to 8 keV, the CA spectrum depicted in Figure 3b. This spectrum is distinctively different from the CA spectrum of benzonitrile molecular ions (Figure 3a), pointing toward the formation of an isomeric species by protonation/deiodination

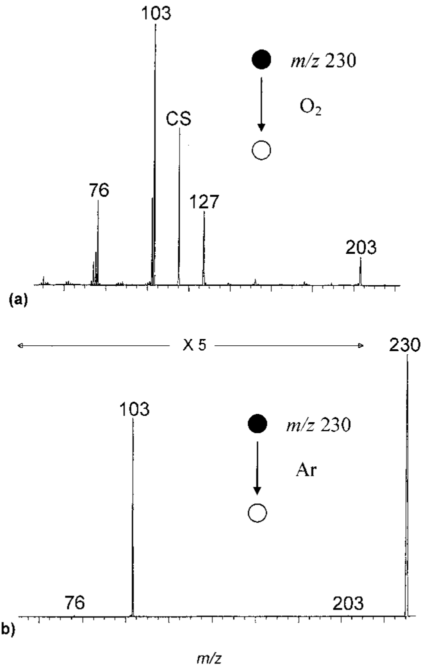


Figure 1. High-energy CA spectrum (oxygen) of protonated 4-iodobenzonitrile **1H**$^+$ (a) and low-energy CA spectrum (argon) of the same ions (b). CS refers to charge stripping. The terminology, introduced by Schwartz et al.,[36] is used to schematize the sequence of reactions: a filled circle represents a fixed (or selected) mass, an open circle, a variable (or scanned) mass, whereas the neutral reagent or collision gas that causes the mass transitions is shown between the circles.

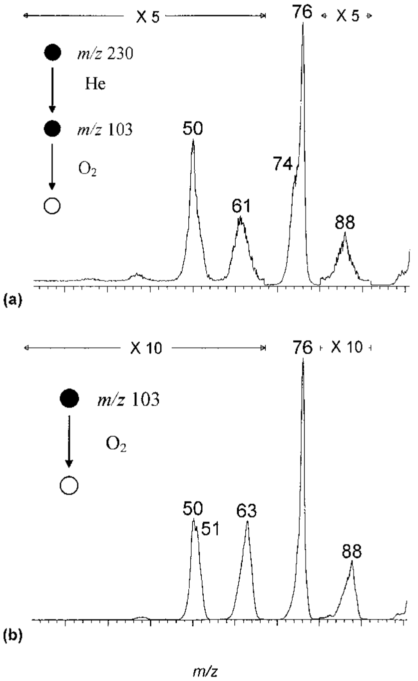


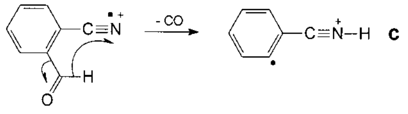
Figure 2. CA spectra (oxygen) of *m/z* 103 ions produced by collisional deiodination (helium) of **1H**$^+$ ions (a) and ionization of benzonitrile (b). Kinetic energy of the ions: 3582 eV.

of **1**. Major differences are seen at *m/z* 77, 63, 51, 39, and 26; these peaks are found significantly higher in intensity in the case of the "conventional" ion **d** and, in fact, a close inspection of relative intensities (e.g., in the *m/z* 41−33 region) reveals that *m/z* 39 ions are nearly absent in Figure 1b, strong evidence for the production of a *pure* beam of distonic (carbenic) $[C_7H_5N]^{\bullet+}$ radical cations. The ion we assign structure **a** showed somewhat more abundant *m/z* 74 ions and also doubly charged *m/z* 51.5 ions (Scheme 4). The increased efficiency of charge stripping is usually observed for distonic ions when compared to their conventional isomers.[21]

All these results indicate that the distonic species **a** is a stable and distinct isomer of ionized benzonitrile **d** in the gas phase.

Similarly, the CA spectra of the $[MH-I]^+$ ions prepared starting from both 2- and 3-iodobenzonitriles **2** and **3** afford strong evidence for the production of new distonic ions. It is, however, worth noting that the spectra of the isomeric **a**−**c** species are virtually indistinguishable.

SCHEME 5



Strong ortho-effects have been frequently reported to occur in the mass spectra of aromatic compounds.[22] If the CN group in benzonitrile derivatives can act as a hydrogen acceptor, several disubstituted derivatives can be considered for the production of distonic ions **c**. The EI mass spectra of 2-cyanobenzaldehyde,[23] 2-cyanobenzoic acid, and 2-cyanoacetophenone suggest that this is indeed the case. Abundant loss of carbon monoxide (carbon dioxide or ketene) from the molecular ions differentiate readily these *o*-disubstituted compounds from their isomeric *m*- or *p*-isomers. The CA spectrum of the $[M-CO]^{\bullet+}$ ions (see Scheme 5) is identical with the spectrum of the $[MH-I]^+$ ions from **3H**$^+$. Clearly, the loss of CO (CO_2 or CH_2CO) is preceded by hydrogen migration on the nitrogen atom to form distonic ion **c**.

3. Ion−Molecule Reactions of $[C_7H_5N]^{\bullet+}$ Radical Cations. Nitric oxide has been described in several instances as an efficient trapping reagent of distonic radical cations. Because of its relatively high ionization energy (IE = 9.26 eV),[17] charge exchange is usually less competitive than in reactions with disulfides or diselenides and other structurally significant reactions are often operative. Representative examples of ion−molecule reactions are attachment of $NO^\bullet$, trapping of small radical cations by $NO^\bullet$, or displacement of neutral molecules by $NO^\bullet$.[24]

The benzonitrile radical-cation reacts with nitric oxide by charge exchange to form NO^+ (*m/z* 30), in agreement with the relative ionization energies (9.62 eV for benzonitrile). $NO^\bullet$ attachment is also observed, but in a poor yield (<5%). The ionization energies of the neutral molecules corresponding to the distonic ions are predicted to be lower than that of benzonitrile and, consequently, one may expect different yields of charge exchange and $NO^\bullet$ attachment reactions. That was indeed observed for the $[MH-I]^+$ ions, but because of very low signal-to-noise ratios it was not possible to quantify accurately this effect. This loss of sensitivity may be caused by the dramatic reduction of translational energy in the collisional deiodination reaction, resulting in a substantial loss of ions in the Q_{cell} device.

As indicated previously (see Figure 1b), collisional activation of **1H**$^+$ at low collisional energies generates quasi exclusively $[MH-I]^+$ fragment ions. We therefore attempted ion−molecule reactions with $NO^\bullet$ of a mixture of stable **1H**$^+$ ions and their $[MH-I]^+$ fragments produced in the Q_{cell}. Ions at *m/z* 133 (Figure 4) are indeed generated under these conditions, but the high-energy CA spectrum of these ions indicates that they correspond to C-protonated nitrosobenzonitrile and do not therefore result from an $NO^\bullet$ attachment to distonic ions **a**, which

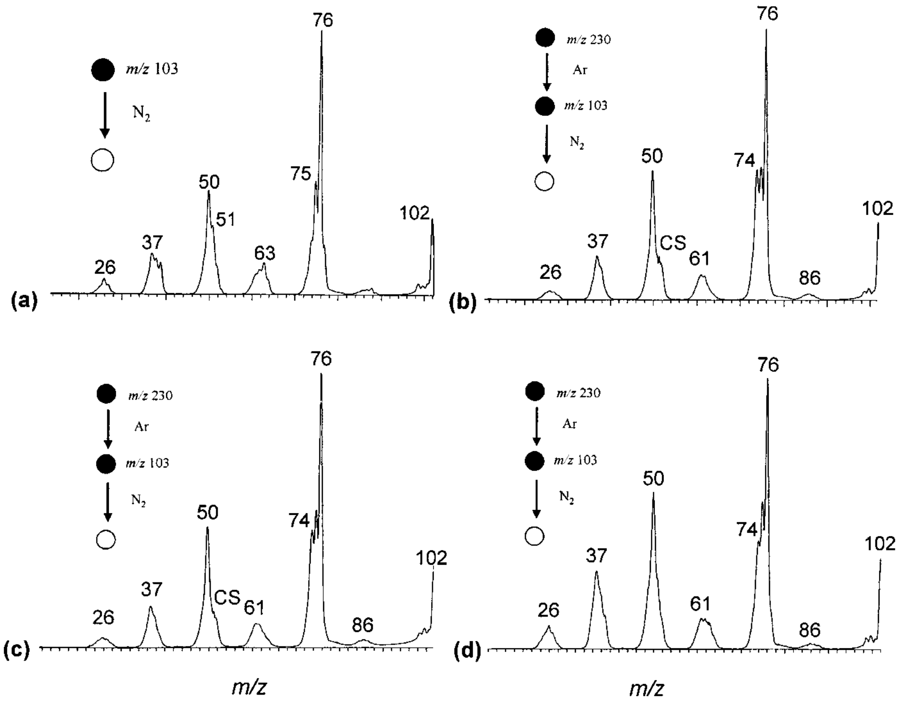


Figure 3. CA spectra (nitrogen collision gas) of benzonitrile radical cations (a) and of *m*/*z* 103 ions produced by collisional deiodination (argon collision gas) of protonated 4-iodobenzonitrile **1H**$^+$ (b), protonated 3-iodobenzonitrile **2H**$^+$ (c), and protonated 2-iodobenzonitrile **3H**$^+$ (d). Kinetic energy of the ions: 8 keV.

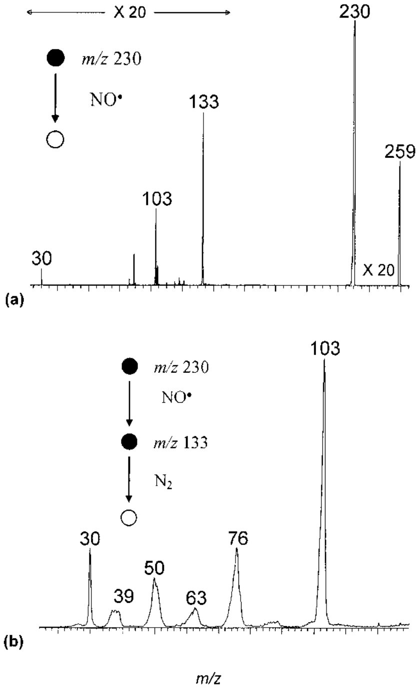


Figure 4. (a) Interaction in the Q_{cell} of the mixture of protonated 4-iodobenzonitrile **1H**$^+$ and *m*/*z* 133 ions with nitric oxide (B scan, the peak at *m*/*z* 230 is off-scale) and (b) CA spectrum (nitrogen) of the *m*/*z* 133 ions.

should produce an isomeric, N(nitrile)-protonated, nitrosobenzonitrile. The reason for this peculiar behavior is not clear at the moment. It is worthy of note that, in the ion−molecule reactions shown in Figure 4, an intense peak appears at *m*/*z* 259, corresponding formally to the replacement of an hydrogen atom by NO$^•$. This unexpected process appears to be quite general for protonated benzonitriles[25] but cannot explain the formation of the *m*/*z* 133 ions.

An NO-catalyzed isomerization of ion **a** into ion **d** is also probably excluded as an isomeric distonic species (ion **c**, vide infra) reacts with nitric oxide to produce *m*/*z* 133 ions, presumably N(nitrile)-protonated 2-nitrosobenzonitrile.

4. Ion−Molecule Reactions of [C_7H_5N]$^{•+}$ Radical Cations c. As explained before, the ortho-distonic (carbenic) species **c** can be produced by dissociative ionization in the ion source, making thus the study of ion−molecule reactions more easy to perform. The following discussion will concern the reactivity of ion **c** toward nitric oxide, acetone, dimethyl disulfide, and *tert*-butyl nitrite.

The reaction of ion **c** with NO$^•$ was found to be very efficient in that the charge exchange reaction occurring with ionized benzonitrile is now cleanly replaced by NO$^•$ attachment forming *m*/*z* 133 ions (Figure 5a). The CA spectrum of these ions features a base peak for the loss of NO$^•$ (*m*/*z* 103) and all the peaks observed at lower masses indicate that the ion−molecule reaction product is N(nitrile)-protonated nitrosobenzonitrile (Figure 5b).

Recently, we have observed that *tert*-butyl nitrite was a valuable reagent for the characterization of various isomeric ionized species in the gas phase. For instance, enolic radical cations readily react with the formation of vinyl nitrite ions, a reaction not observed for the ketonic ions.[26] Ionized benzonitrile reacts with neutral *tert*-butyl nitrite mainly by charge exchange (11%, identified by a peak at *m*/*z* 88 for a methyl loss) and protonation (89%, identified by peaks at *m*/*z* 104, 86, and 57). Protonation is also a prominent reaction for ions c generated from 2-cyanobenzaldehyde (78%), but the second reaction of importance is the attachment of NO$^•$ followed by loss of *tert*-butyl alcohol to form an ion at *m*/*z* 132. 2-Nitrosobenzonitrile ions are produced by the latter reaction, as evidenced by the CA spectrum shown in Figure 6.

The reaction with neutral acetone of ionized benzonitrile and its ortho-carbenic isomers was also attempted by analogy with the oxygen radical anion transfer to some ionized carbenes that was reported recently.[27] Such a reaction was not observed for

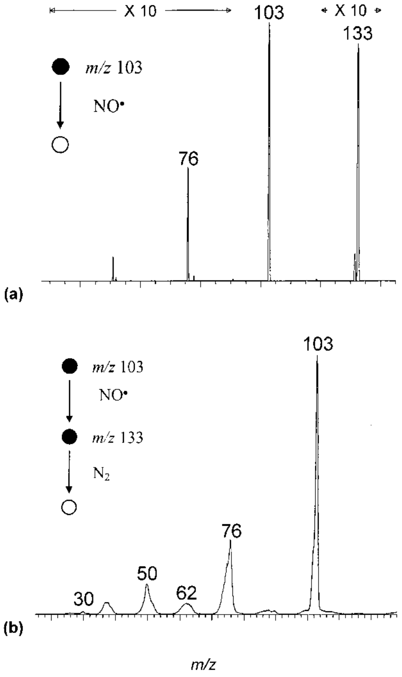


Figure 5. Ion−molecule reaction of ions **c** with nitric oxide (B scan) (a) and CA spectrum (nitrogen) of the *m*/*z* 133 ions (b).

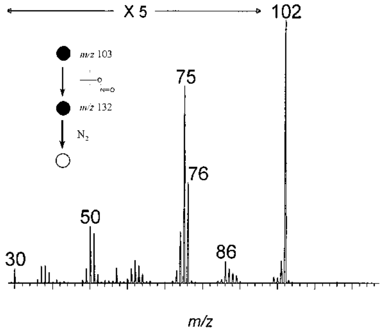


Figure 6. CA spectrum (nitrogen collision gas) of the *m*/*z* 132 ions produced in an ion−molecule reaction between ions **c** and *tert*-butyl nitrite.

the $C_7H_5N^{•+}$ radical cations, but a clear differentiation of these ions was nevertheless possible. The major reaction of the benzonitrile ion was charge exchange forming an acetone ion (*m*/*z* 58), while the carbenic ions reacted by proton transfer to form protonated acetone (*m*/*z* 59). The ionization energy of acetone (9.7 eV) is indeed similar to that of benzonitrile (9.6 eV) and, given the fact that the ions are not thermalized in our experiments, mildly endothermic electron transfer is possible. The fact that ion **c** reacts as a Brønstedt acid toward acetone is firmly confirmed by using perdeuterated acetone with the expected mass shift of the *m*/*z* 59 peak to *m*/*z* 65.

Dimethyl disulfide (DMDS) has been frequently used as an efficient reagent for distonic ions by its ability to transfer a thiomethyl radical to the radical site.[11,28] Attachment of $CH_3S^•$ (*m*/*z* 150, 3%) is nevertheless not a prominent reaction for ion **c**, which prefers to transfer a proton to DMDS (*m*/*z* 95, 60%). Charge exchange is also detected (*m*/*z* 94, 37%), indicating that the ionization energy of **c** is probably not too different from that of DMDS (8 eV[29]). In contrast, the conventional ion **d** reacts only via charge exchange.

5. Neutralization−Reionization Experiments. The neutralization−reionization (NR, NH_3/O_2)[30] mass spectra of benzonitrile ions **d** and distonic ions **c** (generated from 2-cyanobenzaldehyde) are compared in Figure 7. Very similar NR mass spectra were obtained with using DMDS as the electron donor (Figure 8). The NR spectra clearly distinguished the isomeric ions. In particular, ion **d** showed a very intense recovery signal at *m*/*z* 103, whereas the recover ion from **c** was weak. In contrast, NR of ion **c** showed an enhanced peak at *m*/*z* 27. It is therefore proposed that the neutral molecule formed by reduction of ion **c** is less stable and decomposes partly during the flight by loosing CHN.

The neutral molecule produced in the vertical reduction process of ion **c** is formally a carbene bearing an α-keteneimine substituent. Such a reactive intermediate could be stabilized by cyclization into an iminobenzocyclopropene structure as pro-

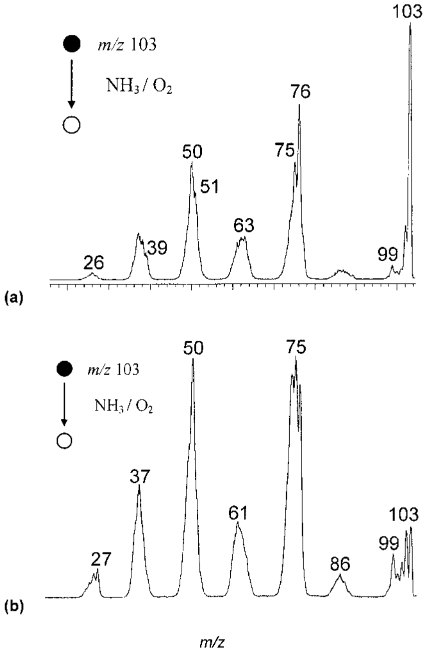


Figure 7. NR mass spectra (NH_3/O_2) of benzonitrile radical cations **d** (a) and of $[M-CO]^{•+}$ ions **c** of 2-cyanobenzaldehyde.

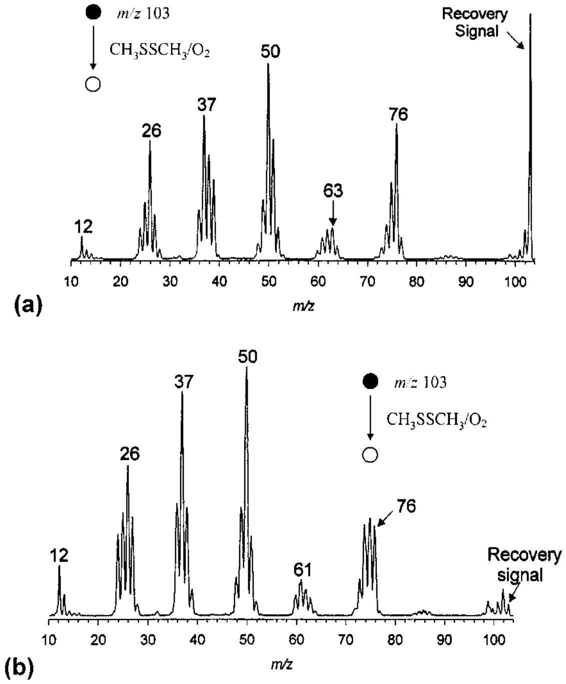


Figure 8. NR mass spectra (CH_3SSCH_3/O_2) of benzonitrile radical cations **d** (a) and of $[M-CO]^{•+}$ ions **c** of 2-cyanobenzaldehyde.

SCHEME 6

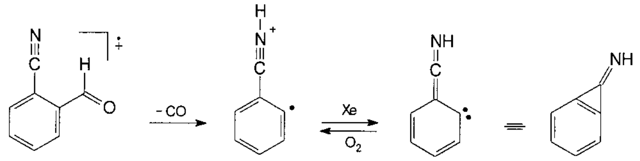


TABLE 2: Calculated Proton Affinities (at 0 K) of Benzonitrile at Nitrogen and Ring Carbon Atom Sites[a]

protonation site	B3LYP/6-31+G(d,p)	B3LYP/6-311++G(3df,2p)
N	824	828
C_{para}	712	707
C_{meta}	704	699
C_{ortho}	713	708

[a] Geometries are obtained from B3LYP/6-31+G(d,p) optimizations. Values are corrected for ZPEs. The given values correspond to the PA's at 0 K. To obtain the PA's at 298 K, a correction of 6 kJ mol^{-1} needs to be added to the PA (0 K). Thus, the PA (N, 298 K) amounts to 830−834 kJ mol^{-1}.

posed in Scheme 6, and this is supported with DFT calculations presented below.

6. Density Functional Theory Calculations. Having established the existence of various isomers of ionized benzonitrile, we have attempted to derive some useful quantitative parameters using ab initio calculations with the Gaussian 98 suite of programs.[31] Ion and neutral geometries were optimized using density functional theory[32] with Becke's hybrid functional B3LYP[33] and the 6-31+G(d,p) basis set and characterized by harmonic vibrational frequencies. The zero-point energies (ZPE) were estimated at this level. Single-point electronic energies were subsequently determined at these geometries with the larger 6-311++G(3df,2p) basis set. For open-shell systems, the unrestricted formalism (UB3LYP) was employed. We have selected this method because it is computationally economical as compared with the molecular orbital correlated methods and can provide comparable energetic results.[5d,34] In addition, use of the DFT method allows us to avoid the problem of spin contamination, which could be severe in some doublet and triplet electronic states. In general, the ordering of relative energies is not changed in using both the 6-31+G(d,p) and 6-311++G-(3df,2p) bases; the largest deviation amounts to about 10 kJ mol^{-1}.

First of all, let us consider the proton affinities (PA's) of benzonitrile at nitrogen and carbon sites whose theoretically estimated values are shown in Table 2. The calculated PA (at 298K) at nitrogen of 830−834 kJ mol^{-1} is found to be larger than in the experimental estimate of 812−820 kJ mol^{-1}.[17] Such an oversestimation lies, however, within the expected accuracy of the B3YLP functional. Ring carbon PA's are consistently lower by ca.120 kJ mol^{-1} irrespective of the relative ring position. Hence, ring protonation appears unlikely and the N-protonated benzonitrile should be the dominant isomer.

The distonic radical cations **a**−**c** are calculated to be ca. 45, 48, and 49 kJ mol^{-1}, respectively, less stable than the conventional benzonitrile ion **d** (Table 3). The ion structures show no exceptional bond lengths and angles, except perhaps for the fact that the C≡N−H moiety remains linear, even in the ortho-carbene isomer (Figure 9). Note that cyclization that would give rise to a three-membered cycle is endothermic and does not occur.[35] The energy of the transition state for the isomerization converting the distonic ion **c** into the conventional ion **d** by a 1,4- hydrogen shift is rather high, being 396 kJ mol^{-1} above **c**, in qualitative agreement with the significant differences found in the CA and NR spectra and the different reactivities in the ion−molecule reactions. Interconversion of the nonclassical ions **a**−**c** can be realized through 1,2-hydrogen shifts within the ring and requires somewhat lower energies. The calculated barriers for the **a**−**b** and **b**−**c** isomerizations were 313 and 308 kJ mol^{-1}, respectively. These are smaller than the threshold energies for dissociations and can thus explain the overall similarity of the CA spectra of these ions.

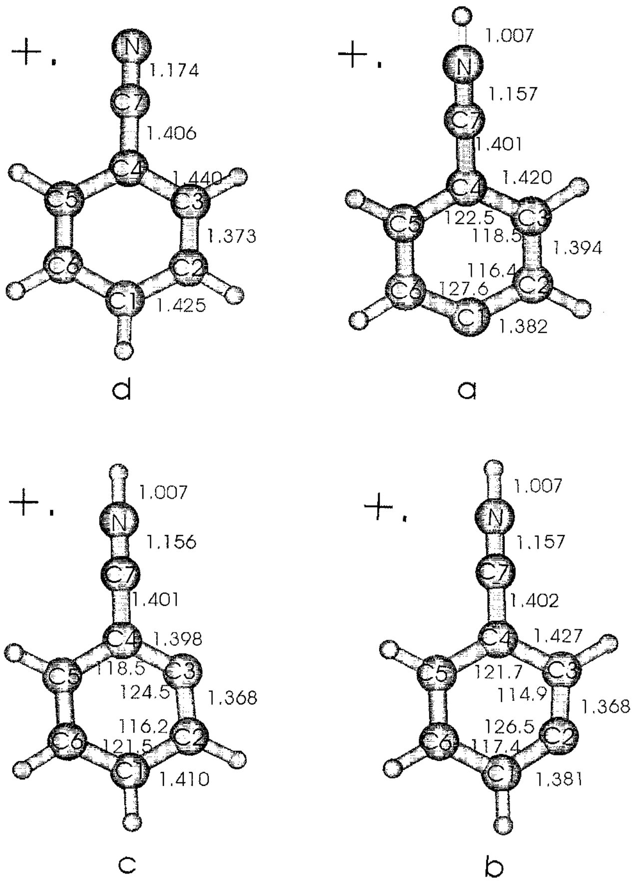


Figure 9. Selected UB3LYP/6-31++G(d,p) optimized structures of $[C_7H_5N]^{\bullet+}$ radical cations. Bond lengths are given in angstroms and bond angles in degrees.

While the spin densities in the radical cations **a**, **b,** and **c** are mainly located on the carbene centers, the positive net charge from Mulliken population analysis is localized on the para-carbon atom rather than in the nitrilium group. This indicates a clear separation of charge and spin sites in these ions. In the benzonitrile ion **d**, the spin density is equally shared by N (0.34), C-4 (0.36), and C-1 (0.38), while the positive charge is located mainly at C-4. An electron was apparently removed from the ring electron rather than from the nitrile function.

Relevant calculated adiabatic ionization energies (IE_a) are summarized in Table 4. As already observed for other systems, separation of charge and radical sites induces a dramatic decrease of the ionization energies and offers an explanation for the inefficient charge exchange in ion−molecule reactions of ion **c**. The calculated IE_a of benzonitrile amounts to 9.5 eV (9.62 eV experimental[17]), whereas those of the carbene isomers are 5.8 eV (ion **a**), 6.1 eV (ion **b**), and 7.3 eV (ion **c**).

A consequence of such small IE_as is that for the neutral counterparts, the energy gaps between benzonitrile and its hydrogen-shift isomers are greatly increased at the expense of the latter. Figure 10 shows the selected geometrical parameters of the neutral isomers in both lower-lying singlet and triplet

TABLE 3: Relative Energies of Ionized Forms of Benzonitrile (kJ mol^{-1})[a]

species	B3LYP/6-31+G(d,p)	B3LYP/6-311++G(3df,2p)
benzonitrile ion **d**	0.0	0.0
distonic (carbene) ion **a**	54	45
distonic (allene) ion **b**	57	48
distonic (carbene) ion **c**	58	49

[a] Geometries obtained from B3LYP/6-31+G(d,p). Relative energies are corrected for zero-point energies.

TABLE 4: Calculated Adiabatic Ionization Energies (IE$_a$, eV) of Benzonitrile and Its Isomers[a]

resulting ion	B3LYP/6-31+G(d,p)	B3LYP/6-311++G(3df,2p)
benzonitrile ion **d**	9.4	9.5
distonic (carbene) ion **a**	5.8	5.8
distonic (allene) ion **b**	6.1	6.1
distonic (carbene) ion **c**	7.3	7.3

[a] Geometries obtained from B3LYP/6-31+G(d,p). IE values are corrected for ZPEs.

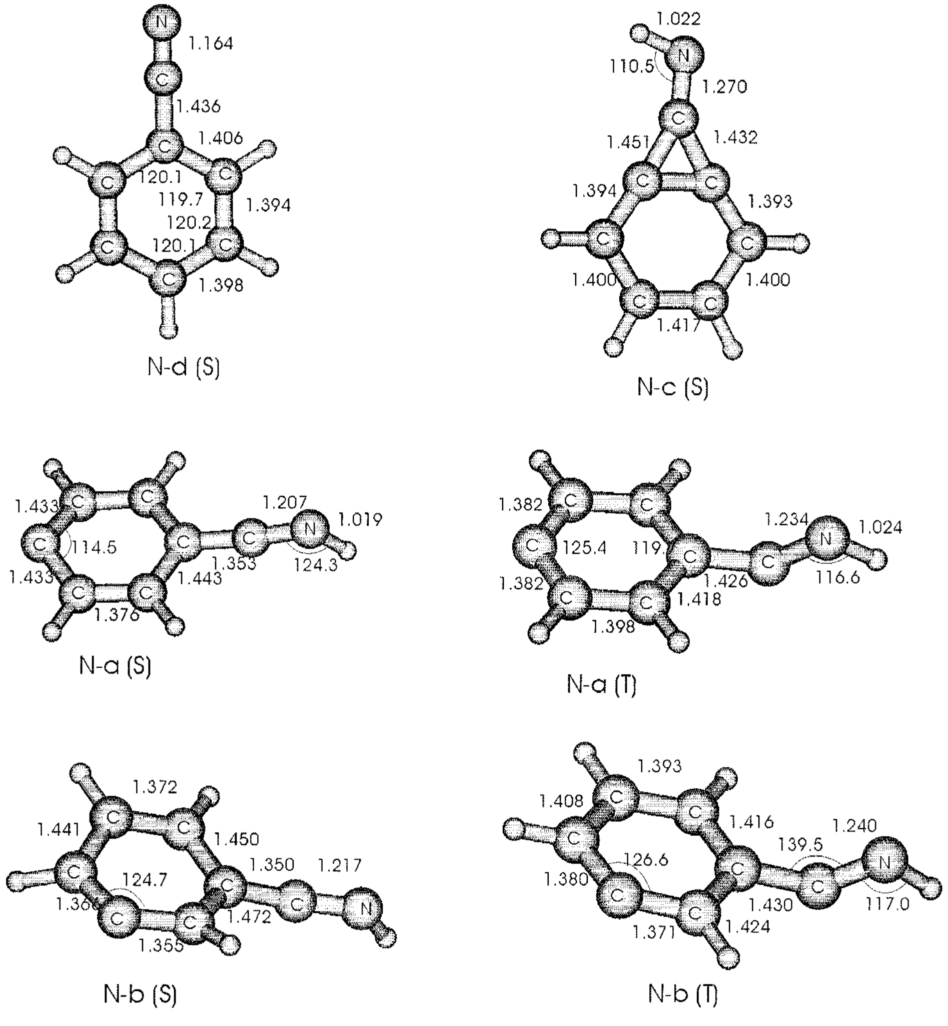


Figure 10. Selected B3LYP/6-31++G(d,p) optimized structures of [C_7H_5N] neutrals. Bond lengths are given in angstroms and bond angles in degrees.

TABLE 5: Relative Energies of Benzonitrile and Its Neutral Hydrogen-Shift Isomers (kJ mol^{-1})[a]

species	B3LYP/6-31+G(d,p)	B3LYP++G(3df,2p)
benzonitrile **N-d(S)**	0	0
carbene-para singlet **N-a(S)**	400	397
carbene-para triplet **N-a(T)**	364	367
allene-meta singlet **N-b(S)**	376	373
allene-meta triplet **N-b(T)**	366	369
iminocyclopropene singlet **N-c(S)**	257	260
iminocyclopropene triplet **N-c(T)**	503	509

[a] Geometries obtained from B3LYP/6-31+G(d,p). Relative energies are corrected for ZPEs.

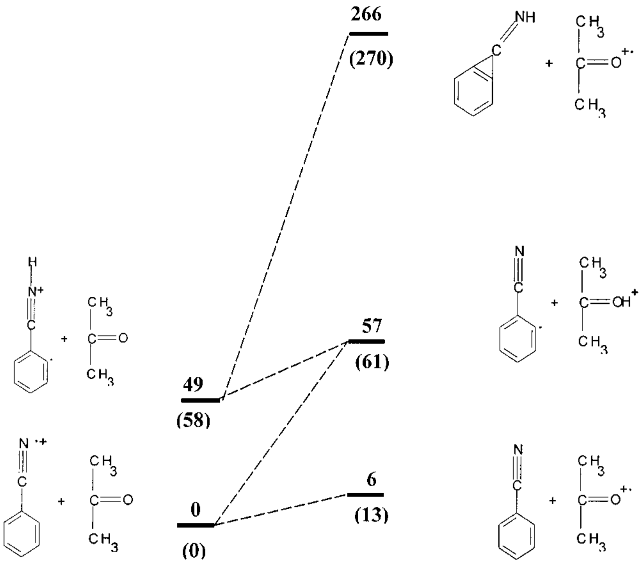


Figure 11. Relative energies for the protonation and charge exchange reactions of ions **c** and **d**. Values given in kJ mol^{-1} are obtained from (U)B3LYP/6-311++G(3df,2p)//B3LYP/6-31+G(d,p) + ZPE.

electronic states, whereas the relative energies are summarized in Table 5. A carbene counterpart of ion **c** was not a local energy minimum but underwent a ring closure to the three-membered cyclopropene imine **N-c(S),** which was 260 kJ mol^{-1} less stable than benzonitrile **N-d(S).** The triplet carbene **N-c(T)** (not shown in Figure 9) was substantially higher in energy (500 kJ mol^{-1}). The meta-carbene isomer **N-b** can be regarded as a cyclic and bent allene in which both closed-shell singlet **N-b(S)** and triplet **N-b(T)** structures are almost degenerate but with a small preference for the triplet state. The para-carbene isomer **N-a** is the only one in which the carbene atom is flanked by two vinyl groups. As a consequence, the triplet state **N-a(T)** is found to be the ground electronic state lying 30 kJ mol^{-1} below the singlet carbene **N-a(S).** Both triplet structures **N-a(T)** and **N-b(T)** are comparable in energy, being about 370 kJ mol^{-1} less stable than neutral benzonitrile **N-d(S)** (cf. Table 5). The higher lying isomers exhibit in both states distorted geometrical shapes (Figure 10).

Finally, some of the results regarding the ion−molecule reactions can be supported by quantum chemical calculations. For instance, the relative energies shown in Figure 11 fully confirm that a proton transfer from distonic ions **c** to acetone is only slightly endothermic (3 kJ mol^{-1} at the B3LYP/6-311++G(3df,2p) level), while a charge exchange forming neutral iminobenzocyclopropene **N−c (S)** is 212 kJ mol^{-1} endothermic and therefore energetically prohibited. The energetics is reversed for benzonitrile ion **d** where charge exchange is found to be ca. 50 kJ mol^{-1} more favorable than proton transfer.

In summary, tandem mass spectrometry (CA, NR, MS^3) indicated that distonic (carbenic) isomers of ionized benzonitrile can be produced in the gas phase by protonation−deiodination of iodobenzonitriles. These results were also supported by ion−molecule reactions in a quadrupole collision cell of a hybrid mass spectrometer. Density functional theory calculations indicated that the distonic isomers were less stable than ionized benzonitrile by only 50 kJ mol^{-1} and were protected against isomerizations and fragmentations by large energy barriers. The distonic radical cations include either carbene or bent allene structures whose corresponding neutrals possess very low ionization energies.

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