Kurzmitteilung / Short Communication

Mass-Spectrometric Characterization of Isomeric NNCCN and NCNCN Ions and Neutrals

César A. Muedas, Detlev Sülzle[+], **and Helmut Schwarz***

Institut für Organische Chemie der Technischen Universität Berlin,
Straße des 17. Juni 135, W-1000 Berlin 12, F.R.G.

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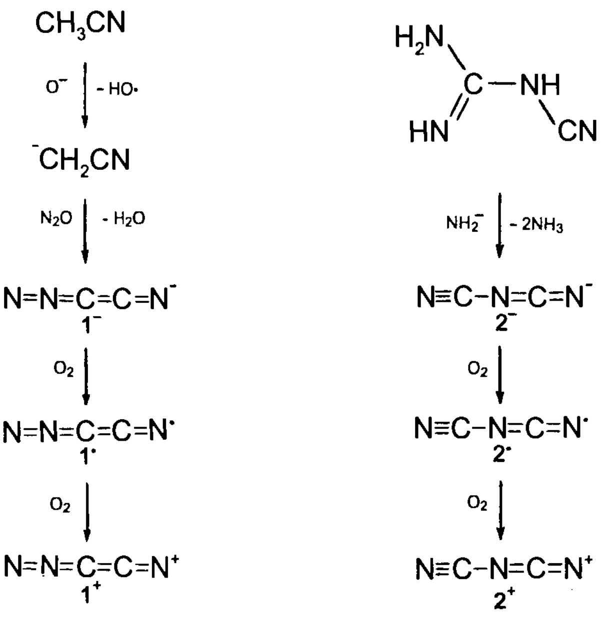
Neutralization-reionization mass spectrometry as well as charge reversal and collisional activation experiments serve to distinguish and assign the connectivities NNCCN and NCNCN to isomeric pairs of anions, neutral radicals and cations of C_2N_3. Loss of N_2 to generate C_2N^+ is the critical discriminant, and the assignment is further substantiated by subjecting these fragment ions to collisional activation experiments by using tandem-mass spectrometry facilities.

Recent work in our laboratory has dealt with the study of cumulenes of cosmochemical and theoretical relevance[1]. Particularly challenging is the prospect of distinguishing isomeric structures in heteroatom-containing species. The use of tandem-mass spectrometry is once again utilized in this report for the characterization of two isomers of C_2N_3, namely NNCCN and NCNCN as such neutrals and their corresponding cations and anions in the gas phase.

Results and Discussion

Scheme 1 depicts our approach to the generation of two isomers of C_2N_3 in our tandem mass spectrometer. The formation of di-

Scheme 1



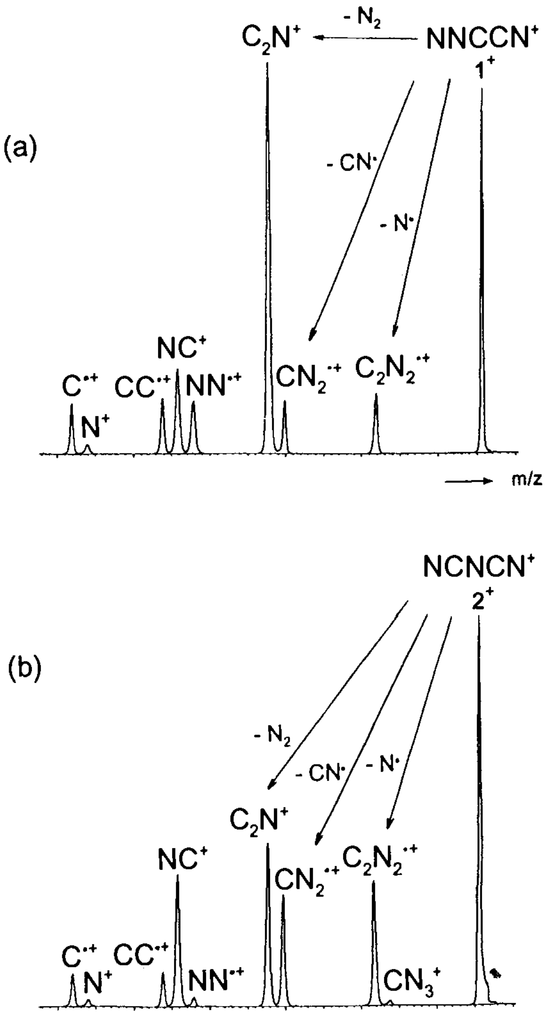


Figure 1. CR mass spectra of: a) $C_2N_3^-$ from deprotonation and diazotization of CH_3CN; b) $C_2N_3^-$ from deprotonation and deamination of cyanoguanidine

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[+] Present address: Schering AG, Postfach 650311, W-1000 Berlin 65, F.R.G.

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azocyanomethanide ($\mathbf{1}^-$) is a straightforward diazotization reaction typical of a primary carbanion[2]. On the other hand, cyanoguanidine behaves as a suitable precursor for dicyanomethanide ($\mathbf{2}^-$) when treated with ammonia in the ion source, i.e., collisions with the reagent gas result in concomitant deprotonation and deamination (for details, see Experimental).

Each anion of $m/z = 66$ is mass-selected from the source by double-focusing and submitted to charge reversal (CR)[3]. The corresponding cations render the fragmentation patterns shown in Figure 1. Clear differences are observable in the relative intensities of the fragment peaks, most pronounced for the loss of dinitrogen leading to $m/z = 38$ [C_2N^+] and in the abundance of $m/z = 28$ [$N_2^{\cdot+}$]. A minor, though distinct feature is the weak signal at $m/z = 54$ [CN_3^+] arising from NCNCN$^+$ exclusively.

Both $\mathbf{1}^-$ and $\mathbf{2}^-$ undergo efficient neutralization and reionization to their cations ($^-$NR$^+$ experiments)[4]. The NR spectra (Figure 2), vis-à-vis the CR ones, establish the correspondence of identical connectivities for each anion/radical/cation set. The noticeable intensity of the recovery signals supports the existence of the radicals $\mathbf{1}^{\cdot}$ and $\mathbf{2}^{\cdot}$ as solitary species in the gas phase within the timescale of the $^-$NR$^+$ measurements (ca. 1 µs).

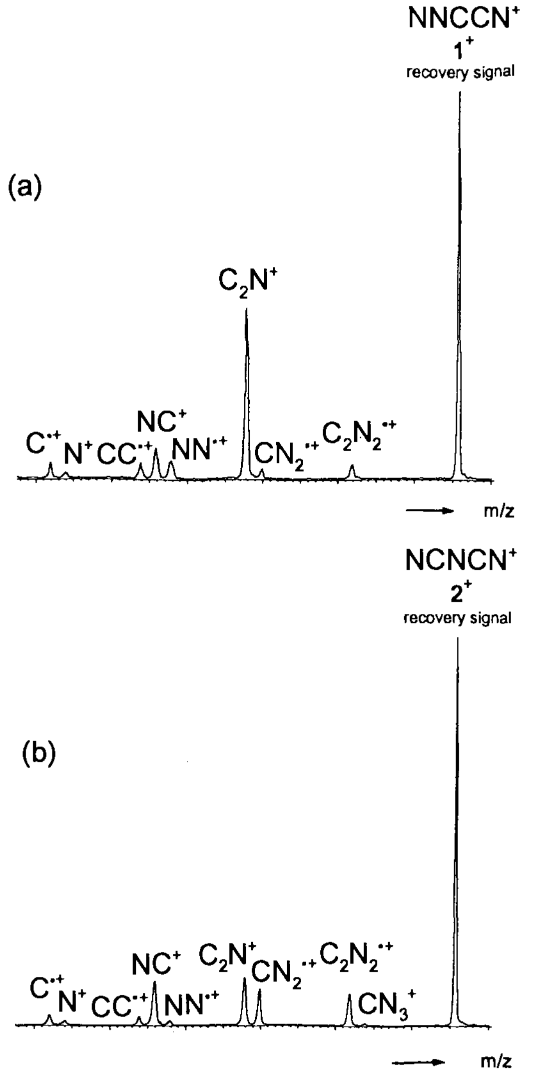

Figure 2. $^-$NR$^+$ mass spectra of (a) NNCCN$^-$ ($\mathbf{1}^-$) and (b) NCNCN$^-$ ($\mathbf{2}^-$)

Complementary evidence for the assignment of structures NNCCN and NCNCN (ions and neutrals) is provided by collisional activation (CA) analysis of isobaric fragment ions selected from the CR experiment, i.e., CR/CA experiments.

Starting from $\mathbf{1}^-$, the ion $C_2N_2^{\cdot+}$ ($m/z = 52$) can be due to NNCC$^{\cdot+}$ or NCCN$^{\cdot+}$; from $\mathbf{2}^-$, however, $m/z = 52$ should be NCNC$^{\cdot+}$. As the spectra in Figure 3 show, the intensity of CC$^{\cdot+}$ is markedly higher coming from NNCC$^{\cdot+}$ or NCCN$^{\cdot+}$ (Figure 3a) where the CC moiety is already present. Similarly, we note the intensive signal for NN$^{\cdot+}$ in Figure 3a as compared with Figure 3b. Interestingly, the signal for CC$^{\cdot+}$ from NCNC$^{\cdot+}$ points to significant structural reorganization prior to dissociation. This observation is in agreement with a previous report on the abundant loss of N_2 from NCNC$^{\cdot+}$[5].

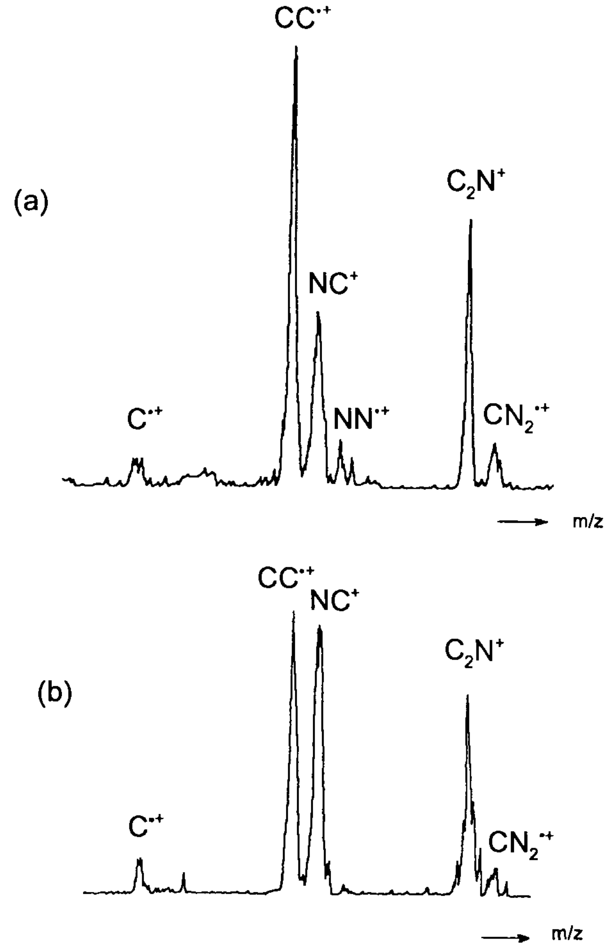

Figure 3. CR/CA mass spectra of isomeric $C_2N_2^{\cdot+}$ ions generated from (a) NNCCN$^-$ ($\mathbf{1}^-$) and (b) NCNCN$^-$ ($\mathbf{2}^-$) by loss of an N atom

Selection and analysis of m/z 40 [$CN_2^{\cdot+}$] reveals the difference between NNC$^{\cdot+}$ and NCN$^{\cdot+}$ (Figure 4). The former ion is predicted to display a strong signal for $N_2^{\cdot+}$, as is the case for its parent ion NNCCN$^+$. This is indeed borne out in Figure 4a. Even if $CN_2^{\cdot+}$ is in each case a mixture, the different intensities for $N_2^{\cdot+}$ are consistent with $CN_2^{\cdot+}$ originating in distinct isomers, one of which does contain a prevalent N–N connnectivity.

The fragmentation of $m/z = 38$ [C_2N^+] (Figure 5) is identical irrespective of the starting parent ion $\mathbf{1}^-$ or $\mathbf{2}^-$. This result aids on the explanation of how extrusion of N_2 may occur, i.e., C_2N^+ must consist in both cases of the same contributors (CCN^+ and CNC^+, or identical mixtures of these two). The isomer $NNCCN^+$, regardless of the way N_2 is eliminated, can give rise to CCN^+ only, and therefore CCN^+ must be the major component in $m/z = 38$. Consequently, the formation of CCN^+ from $NCNCN^+$, will necessarily involve a formal 1,3-elimination of N_2 as the major pathway. Moreover, "clean" CCN^+ has been characterized in CR/CA experiments on $NCCCN^-$ and does present exactly the same pattern as in the fragmentation of C_2N^+ here observed[6]. Therefore, we propose that additional, not yet fully understood decomposition pathways are operative in the N_2 dissociation from $\mathbf{1}^-$ and $\mathbf{2}^-$ under CR conditions.

A third precursor to $C_2N_3^-$ was also found in 1*H*-1,2,4-triazole. CR and $^-NR^+$ experiments were similarly performed as above. The spectra (Figure 6) point to $m/z = 66$, in this case, as being nearly identical to NCNCN ions and radical. The differences may be attributed to an $NCNCN^-$ in an electronic state different from that of $\mathbf{2}^-$. In fact, this occurrence is limited to the CR experiment as the $^-NR^+$ spectra given in Figures 2b and 6b are identical, i.e., notwithstanding the electronic state in which $NCNCN^-$ is generated, the neutral is cool and long-lived enough to be always reionized to $NCNCN^+$ by identical channels. The weakness of the iso-

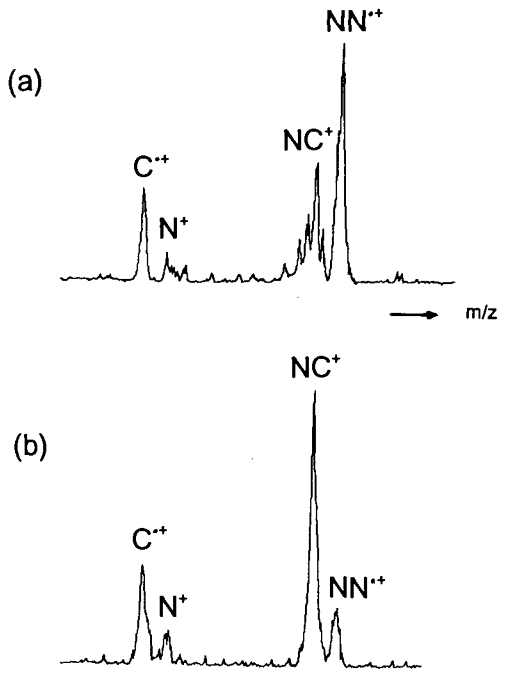

Figure 4. CR/CA mass spectra of isomeric $CN_2^{\cdot+}$ ions generated from (a) $NNCCN^-$ ($\mathbf{1}^-$) and (b) $NCNCN^-$ ($\mathbf{2}^-$) by loss of CN•

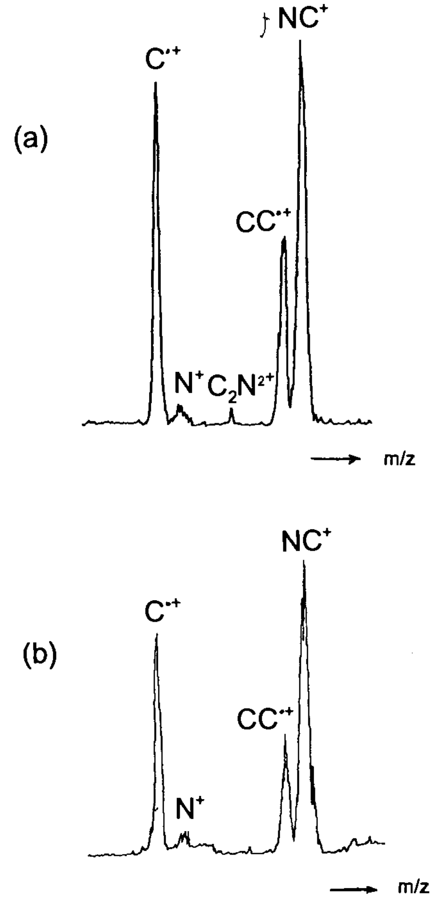

Figure 5. CR/CA mass spectra of isomeric C_2N^+ ions generated from (a) $NNCCN^-$ ($\mathbf{1}^-$) and (b) $NCNCN^-$ ($\mathbf{2}^-$) by loss of N_2

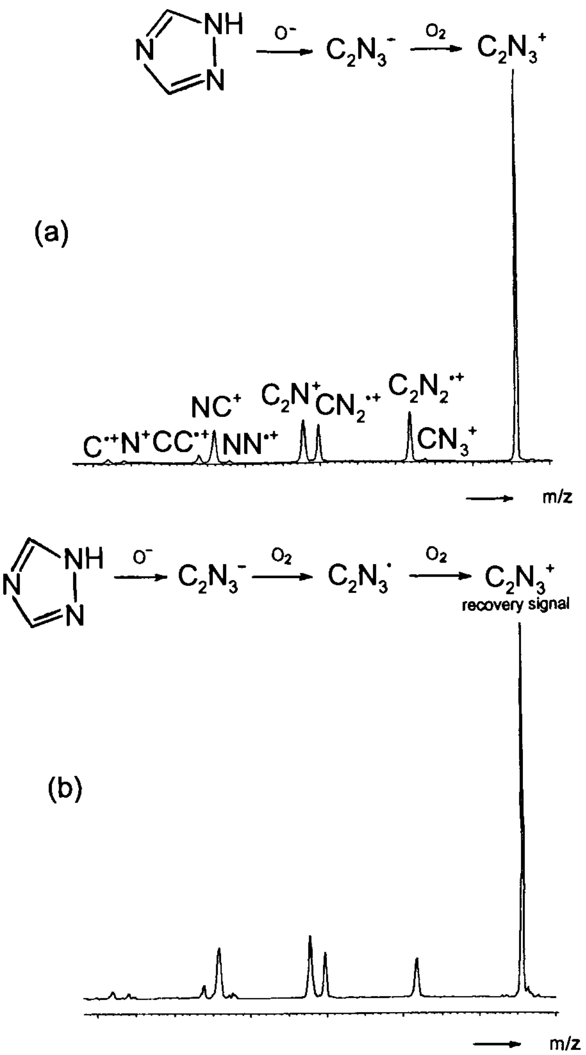

Figure 6. CR (a) and $^-NR^+$ (b) mass spectra of $C_2N_3^-$ ions generated by deprotonation of 1*H*-1,2,4-triazole

baric fragment ions of interest, unfortunately, precludes further CR/CA measurements.

The results here presented shed light on the existence of two distinguishable isomers of C_2N_3 with the connectivities NNCCN and NCNCN in their anions, radicals and cations. These cumulenes constitute adequate precursors to tetra- and triatomic ions whose collisional-activation analysis further supports the structural assignment of the parent isomers and helps understand the mechanism of dinitrogen extrusion from them.

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Experimental

All the reactions to generate $C_2N_3^-$ are carried out in the chemical ionization (CI) source of the Berlin four-sector mass spectrometer of *BEBE* configuration[7]. Acetonitril (Merck) is injected into the CI source by a capillary jet, cyanoguanidine (Aldrich) and 1*H*-1,2,4-triazole (Aldrich) access the source by a mobile probe insert, heated within the range of 100–175°C. The reagent gases enter through independent inlets. The total pressure in the source is ca. 10^{-7} bar at a temperature of 200°C.

For the CR experiments, the beam of m/z = 66 anions, selected by *B*(1) and *E*(1), is forced to collide with O_2 [80% transmittance (*T*)]. The ions of permutated charge, along with the fragments derived from them, are recorded by scanning *B*(2). The $^-NR^+$ experiments consist of consecutive neutralization and reionization with O_2 as target gas at 80% *T* in each step. Mass selection and scanning are analoguous to the CR case. The CR/CA measurements proceed as the CR experiments but followed by selection of a fragment ion of interest (derived from m/z = 66) with *B*(2), further collision of it with He at 80% *T*, and final scanning with *E*(2). In all cases, signal-averaging techniques are controlled by an AMD Intectra data system.

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