On the Generation of Polycarbon Nitride Radicals $C_nN^\cdot$ (n = 2–5) by Neutralization-Reionization Mass Spectrometry☆

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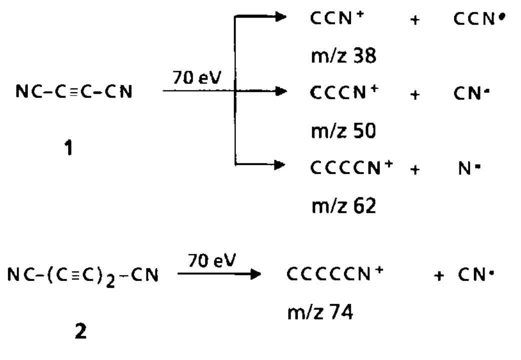
The title radicals, thought to be of prime importance in the genesis of interstellar organic molecules, are accessible in the gas phase by neutralization of the corresponding C_nN^+ ions (n = 2–5) using tandem mass spectrometry methods (neutralization-reionization mass spectrometry). Collision-induced dissociation reactions of mass-selected C_nN^+ are in keeping with the connectivity of a "carbon rod" bearing a nitrogen atom at one terminus.

In a series of papers we have recently demonstrated that the *even*-numbered polycarbon molecules :C=C=S[1], S=C=C=S[2], O=C=C=S[3], S=C=C=C=C=S[1], O=C=C=C=C=S[4], O=C=C=C=C=O[5], and S=C=C=C=C=C=C=S[6] are indeed stable molecules in the gas phase[7]. All these – and many other elusive molecules – became accessible from the corresponding radical ions by using the technique of neutralization-reionization mass spectrometry (NRMS)[8].

In this paper we report on the successful gas-phase generation and characterization of the whole series of polycarbon nitrides $C_nN^\cdot$ (n = 2–5) and their corresponding cations C_nN^+ (n = 2–5) by using tandem mass spectrometry techniques[9]. Several of these species have been discussed in the past in quite a different context. For example, both theory and experiment indicate the existence of two isomers of C_2N^+ and $C_2N^\cdot$, i.e. the connectivities $CCN^{+/\cdot}$ and $CNC^{+/\cdot}$[10]. For C_3N^+ a combined experimental/theoretical study[11] points to two minima on the potential energy surface: The more stable species corresponds to $CCCN^+$ with a cyclic isomer ca. 1 eV higher in energy. For the isocyanid form $CCNC^+$, which is predicted to lie 0.15–0.5 eV above the ground state, no conclusive experimental support is available. Numerous studies are concerned with the possible existence of $C_3N^\cdot$ isomers. For example, ab initio MO calculations[12] and laboratory-based experiments[13] support the detection and assignment of the cyanoethynyl radical $CCCN^\cdot$ as an interstellar species[14]. While the higher numbered carbene ions C_nN^+ ($n \geq 4$) were generated by several techniques and their gas-phase chemistry probed using ion/molecule reactions[15], no data exist to the best of our knowledge for the corresponding radicals $C_nN^\cdot$. The latter, as several other polycarbon molecules having the general structure $X(C_n)Y$ (X, Y: lone electron pair, H_2, O, S; $n \geq 2$), are believed to play a crucial role in the genesis of interstellar organic compounds[16].

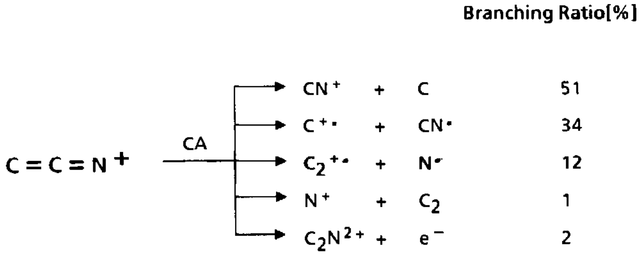
As reported earlier[17] 70-eV electron impact ionization of dicyanoacetylene (**1**) or dicyanodiacetylene (**2**) affords by direct cleavage processes the complete series C_nN^+ ions (Scheme 1).

Scheme 1



The mass selection of a given C_nN^+ species (n = 2–5) by using $B(1)E(1)$ in a tandem experiment[18], followed by collisional activation[19] of the 8-keV translational energy beam with helium as collision gas [80% transmission (T)], afforded collisional activation (CA) mass spectra which clearly reflect the connectivity of the species of interest. This is exemplified by the CA mass spectrum of C_2N^+ (m/z 38). The decomposition pattern given in Scheme 2, and in particular the signal corresponding to $C_2^{+\cdot}$ (m/z 24), is only compatible with the connectivity CCN^+ and not with that of the isomeric, thermochemically more stable[10h] form CNC^+. Obviously, C_2N^+ is formed from $\mathbf{1}^{+\cdot}$ without structural reorganization[20].

Scheme 2



Structurally characteristic CA fragmentation patterns are also observed for the other C_nN^+ species. For example, the CA spectrum of C_3N^+ contains the following signals: C_2N^+ (85%), $C_3^{+\cdot}$ (7%), CN^+ (2%), $C_2^{+\cdot}$ (5%), and $C^{+\cdot}$ (1%). For C_4N^+ we obtain under

Chem. Ber. **124** (1991) 1481–1483 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1991 0009–2940/91/0606–1481 $ 3.50+.25/0

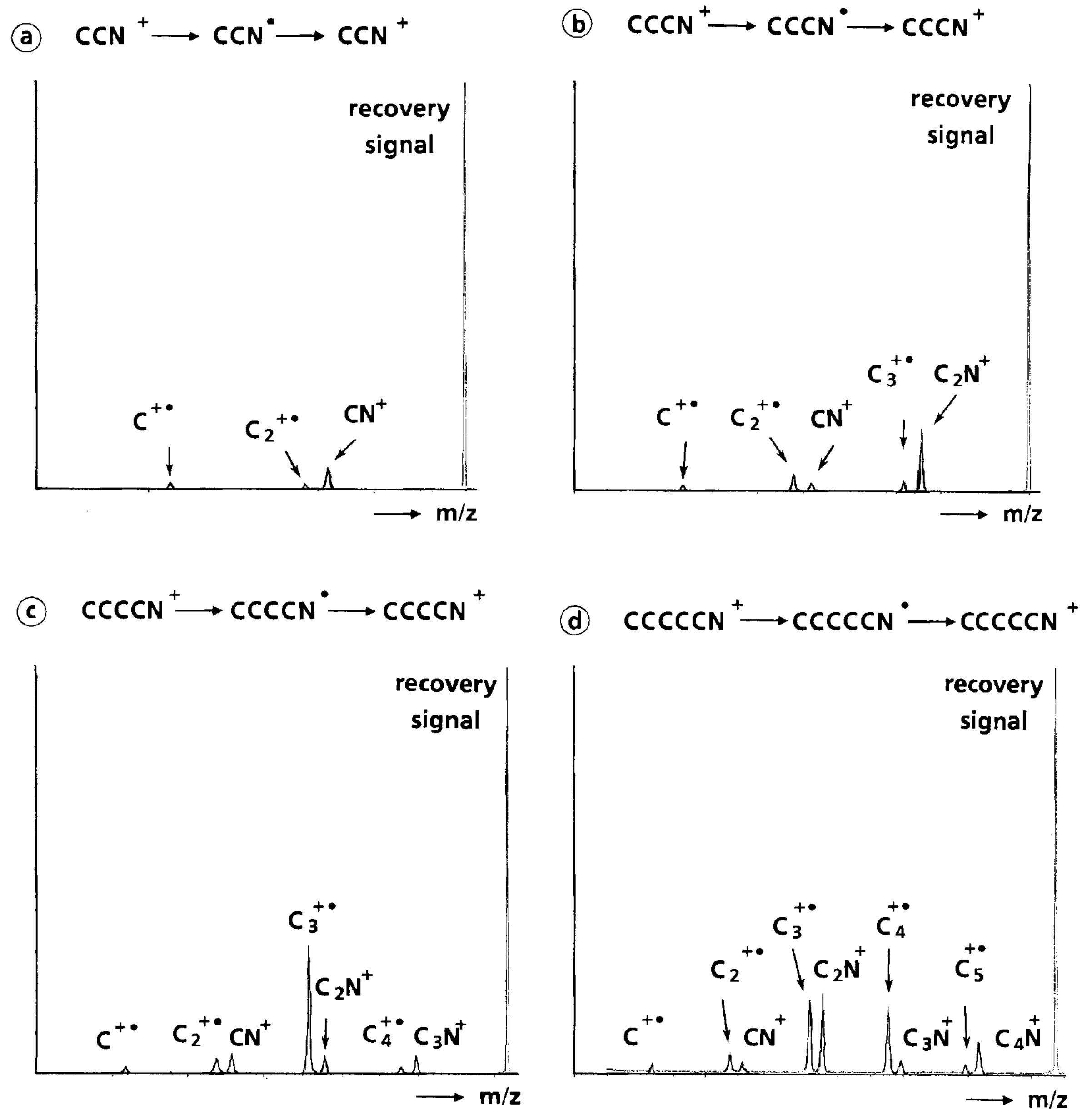


Figure 1. NR mass spectra (xenon/oxygen) of C_nN^+: (a) C_2N^+; (b) C_3N^+; (c) C_4N^+; (d) C_5N^+

CA conditions signals for C_3N^+ (7%), $C_4^{+\bullet}$ (4%), C_2N^+ (8%), $C_3^{+\bullet}$ (78%), CN^+ (1%), $C_2^{+\bullet}$ (2%), and $C^{+\bullet}$ (< 1%). Analogously, the CA spectrum of C_5N^+ is also dominated by direct bond-cleavage processes giving rise to the following ionic species: C_4N^+ (23%), $C_5^{+\bullet}$ (4 %), C_3N^+ (3%), $C_4^{+\bullet}$ (22%), C_2N^+ (40%), and $C_3^{+\bullet}$ (7%); CN^+, $C_2^{+\bullet}$, and $C^{+\bullet}$ are of less importance (< 1%). We note the preferred loss of C_3 from C_5N^+, which under collision-free conditions amounts to > 96%. Interestingly, loss of C_3 is also the major process for the dissociation of cationic and anionic all-carbon clusters $C_n^{+\bullet}/C_n^{-\bullet}$[21], and this has been ascribed to the particular thermochemical stability of the C_3 cluster[22]. Similarly, the particular stability of $C_3^{+\bullet}$[23] together with the favorable heat of formation of $CN^\bullet$ accounts for the dominance of this particular dissociation path in the CA and metastable-ion spectrum of C_4N^+ (78% and > 95%, respectively).

If the mass-selected C_nN^+ species are subjected to an NRMS experiment[8,9] (xenon 80% T/oxygen 80%T), one obtains in all cases very abundant recovery signals (Figure 1a–d); moreover, the fragmentation pattern is often close if not identical with the one observed in the CA mass spectra. The fact that the relative intensities of the signals in the NR spectra (Figure 1) and the CA mass spectra (see text) for C_nN^+ do not exactly match is due to reionization of smaller neutral fragments generated by either collision-induced dissociation (in the collision cell) of C_nN^+ or, alternatively, by fragmentation of a fraction of the $C_nN^\bullet$ molecules prior to reionization. In any case, we can safely conclude that the polycarbon nitride radicals $C_nN^\bullet$ ($n = 2-5$) are stable molecules in the gas phase. The connectivity of both the radicals and the cations C_nN^+ most likely corresponds to a "carbon rod" bearing a nitrogen atom at one terminus.

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[☆] Dedicated to Professor *Hans A. Staab* on the occasion of his 65th Birthday.

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