How Does Energized NCCCCCN Lose Carbon in the Gas Phase? A Joint Experimental and Theoretical Study

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How Does Energized NCCCCCN Lose Carbon in the Gas Phase? A Joint Experimental and Theoretical Study

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Neutral NCCCCCN may be prepared in a collision cell of a VG ZAB 2HF mass spectrometer by charge stripping of (NCCCCCN)$^{•-}$, formed in the ion source by the process NCCCCH(OEt)(CN) + HO$^-$ → H$_2$O + NCCCC$^-$(OEt)(CN) → (NCCCCCN)$^{•-}$ + EtO$^•$. A comparison of the neutralization/reionization ($^-$NR$^+$) and charge reversal ($^-$CR$^+$) spectra of (NCCCCCN)$^{•-}$ indicate that some neutrals NCCCCCN are energized and rearrange to an isomer which decomposes by loss of carbon. An ab initio study at the CCSD(T)/cc-pVTZ//B3LYP/6-311+G(3df) level of theory indicates that (i) triplet NCCCCCN is the ground state with a T/S energy gap of −14.9 kcal mol^{-1}; (ii) the structures of triplet and singlet NCCCCCN need to be described by molecular obital theory, and a simple valence bond approach cannot be used for this system; and (iii) there are several possible routes by which an energized neutral may lose carbon, but the major route involves the triplet nitrile to isonitrile rearrangement NCCCCCN → CNCCCCN → NCCCCN + C.

Introduction

Small unsaturated molecules are of much interest to chemists and astrophysicists. For example the following nitrogen-containing linear heterocumulenes have been detected in interstellar or circumstellar dust clouds: C$_3$N, HC$_3$N, C$_3$N, HC$_5$N, HC$_7$N, HC$_9$N, and HC$_{ll}$N.[1] Diheterocumulenes of the general structure NC$_n$N have also been studied but not, as yet, identified in interstellar regions. We are particularly interested in such systems where n is an odd number: examples are as follows. High-level calculations for NCN have found a linear $^3\Sigma_g^-$ ground state with a C−N bond length of 1.233 Å in excellent agreement with the value of 1.231 Å determined experimentally.[2,3] The transient dicyanocarbene NCCCN is accessible by photolysis or pyrolysis of dicyanomethane,[4] and electron spin resonance shows the ground state to be a triplet.[5] NCCCN is a reactive species, inserting into aliphatic C−H bonds and adding across C=C bonds.[6] The NCCCN system has been studied theoretically, with the ground state being a triplet.[7−10] Neutral NCCCN can be made by charge-stripping of (NCCCN)$^-$ in the gas phase, and ^{13}C labeling shows that energized NCCCN rearranges to NCCNC via the intermediacy of a four-membered C$_{2v}$ symmetrical transition state.[10]

The radical species NCCCCCN has been identified in gas matrices,[11−14] for example, following discharge of dicyanoacetylene.[11] The electronic spectrum of NCCCCCN has been determined in the gas phase by cavity ring down spectroscopy in a supersonic plasma.[15] High-level theoretical calculations have been carried out on C$_n$N$_2$ systems (including NCCCCCN)[16−18] and also the corresponding anions.[19] It appears that the triplet is the ground state of NCCCCCN,[14,16] and it has been shown that for NC$_n$N systems where n is an odd number, the linear structures are mainly cumulenic, whereas when n is even, the structure is essentially an alternating triple bond single bond

system.[17] Higher nitrogen containing cumulenes (both neutrals and anions) have also been studied theoretically.[16−20]

In previous studies we have shown, by using the neutralization/reionization technique[21,22] to form and study the structures of cumulenes, that such systems may undergo carbon scrambling of the cumulene backbone. Cumulenes CCCC[23] and CCCN[24] undergo cyclization to rhomboid four membered ring systems. Ring cleavage of the rhomboid systems causes rearrangement within the skeleton of the cumulene. In contrast, energized NCCCN does not cyclize to a "rhomboid" species but scrambles the carbon atoms by a nitrile to isonitrile interconversion via a three center transition state, followed by further rearrangement of the backbone via four membered transition state.[10]

This paper reports (1) a specific synthesis of NCCCCCN by charge-stripping of anion (NCCCCCN)$^{•-}$, itself formed by an unequivocal synthesis, and (2) a neutralization/reionization study that indicates that energized NCCCCCN decomposes by loss of C, and high-level theoretical calculations which uncover the mechanism for the loss of C, and show that "rhomboid" intermediates are not formed in this system.

Experimental Section

A. Mass Spectrometric Methods. The experiments were performed using a two-sector modified VG ZAB 2HF mass spectrometer with **BE** configuration, where **B** and **E** represent magnetic and electric sectors, respectively. The precursor anion (NCCCCCN)$^{•-}$ was formed in the chemical ionization source by reaction between NCCCCH(OEt)(CN) with HO$^-$ (from H$_2$O) to form (NCCCCCN)$^-$. Source conditions were as follows: source temperature, 100 °C; repeller voltage, −0.5 V; ion extraction voltage, 7 kV; mass resolution, $m/\Delta m$ ~1500. The precursor molecule is added through the septum inlet (at 50 °C) to give a pressure of 10^{-5} Torr measured in the source housing. Water is then introduced through the septum inlet to give a constant pressure of 10^{-4} Torr in the source housing. The estimated pressure in the ion source is 10^{-1} Torr. Collision induced (CID) spectra were determined using the magnetic sector to select the parent anion, and utilizing argon as the collision gas in the first collision cell following the magnetic

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sector. The pressure of argon in the first cell was maintained such that 80% of the parent ion beam was transmitted through the cell. This corresponds to an average of 1.1−1.2 collisions/ion.[25] Product anion peaks resulting from CID processes were recorded by scanning the electric sector.

Neutralization/reionization spectra ($^-$NR$^+$)[21,22] were performed for mass selected anions utilizing the dual collision cells located between the magnetic and electric sectors. Neutralization of anions was effected by collisional electron detachment using O_2 at 80% transmission (of the ion beam) as collision gas in the first collision cell, while reionization to cations was achieved by collision of neutrals with O_2 (80% transmission) in the second collision cell. To detect a reionization signal due to the parent neutral, the neutral species must be stable for the 1 μs time frame of this experiment. Charge reversal ($^-$CR$^+$) spectra[26−28] were recorded using single collision conditions in collision cell 1 (O_2, 80% transmission of the main beam). Comparison of $^-$CR$^+$ and $^-$NR$^+$ data for a given parent anion provides information concerning the neutral formed from the parent anion: see ref 23 for a full description of this procedure.

B. Synthetic Precursor. Cyanopropiolaldehyde (NCCCC-HO)[29] was converted to the diethylacetal [NCCCCH(OEt)$_2$] using the ethanol/*p*-toluene sulfonic acid method[30] in 63% yield [EI MS: M$^{•+}$ (*m/z* 153), 20%; M$^{•+}$−EtO$^•$ [(*m/z* 108), 100%]. ^{1}H NMR (600 MHz): δ 5.3 (^{1}H, s), 3.65 (4H, multiplet), 1.2 (6H, triplet). The acetal was allowed to react with NC$^-$ (under dry N$_2$) by a standard method[31] to give 1,3-dicyano-l-ethoxyprop-2-yne [NCCCH(OEt)(CN)] as a dark liquid (crude yield, 75%) [EI MS: M$^{•+}$ (*m/z* 134), 75%; M$^{•+}$−EtO$^•$, 100%], which was unstable on standing. A sample of the crude product, immediately on formation, was introduced into the ion source of the ZAB 2HF mass spectrometer together with HO$^-$ (see Mass Spectrometric Methods) to yield (NCCCCCN)$^{•-}$ as the only abundant anion.

C. Theoretical Methods. Geometry optimizations were carried out with the Becke 3LYP method[32,33] using the 6-311+G(3df) basis set within the GAUSSIAN 03 suite of programs.[34] Stationary points were characterized as either minima (no imaginary frequencies) or transition states (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures. The minima connected by a given transition structure were confirmed by intrinsic reaction coordinate (IRC) calculations. We have reported the success of this method in predicting geometries of unsaturated chain structures, and that this method produces optimized structures that compare favorably with higher level calculations.[35] More accurate energies for the B3LYP geometries were determined using the CCSD(T) method with cc-pVTZ basis set,[36−38] including unscaled zero-point energy correction (calculated by vibrational frequencies at the B3LYP/6-311+G(3df) level of theory). The data of bond orders were analyzed with Gaussian natural bond orbital (NBO). All calculations were carried using the South Australian Partnership for Advanced Computing (SAPAC) Facility.

Results and Discussion

A. Formation of the Precursor Anion (NCCCCCN)$^{•-}$. The synthesis of neutrals NCC$_n$CN where *n* is an even number is straightforward since they are available by charge-stripping of readily available dicyano(poly)acetylene radical anions in the gas phase. When *n* is odd, unequivocal syntheses are not so simple; e.g., see ref 10. In the case of NCCCCCN, the synthesis of the neutral from which the anion was derived was achieved as shown in sequence 1 (Scheme 1). 3-Cyano-

SCHEME 1
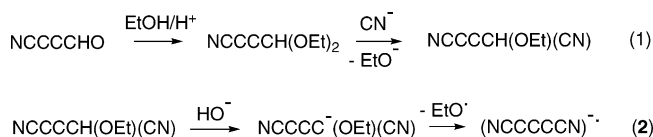
prop-2-yne-1-al was converted to the diethyl acetal which then underwent an S$_N$2 reaction with the cyanide anion to give the required neutral 1,3-dicyano-3-ethoxyprop-2-yne (sequence 1). Insertion of this neutral into the chemical ionization source of the mass spectrometer, followed by reaction with the hydroxyl anion, effected deprotonation followed by loss of an ethoxyl radical to yield (NCCCCCN)$^{•-}$ (*m/z* 88) (sequence 2, Scheme 1).

The next problem to be addressed is whether (NC-CCCCN)$^{•-}$ is a suitable precursor for the formation of neutral NCCCCCN. In other words, will (NCCCCCN)$^{•-}$ survive the collisional conditions necessary to effect Franck−Condon vertical electron stripping to the required neutral in the first collision cell of the mass spectrometer? In principle, this question may be answered by a consideration of the collision-induced mass spectrum of (NCCCCCN)$^{•-}$. The CID MS/MS of (NCCCCCN)$^{•-}$ is simple. The parent ion (*m/z* 88) is the base peak (100% relative abundance) of the spectrum, with only low-abundance fragment peaks observed due to the ions *m/z* 74 (-N, 0.01%) and *m/z* 26 (NC$^-$, 0.02%). There is no fragment ion produced which is indicative of rearrangement of the skeleton of the (NCCCCCN)$^{•-}$. For example, there is no ion formed by loss of C from the parent anion.

B. $^-$CR$^+$ and $^-$NR$^+$ Spectra of (NCCCCCN)$^{•-}$. Having determined that (NCCCCCN)$^{•-}$ is a suitable precursor for neutral NCCCCCN, the next step is to determine the charge reversal mass spectrum of (NCCCCCN)$^{•-}$ [conversion of the anion to the corresponding cation by synchronous two electron stripping ($^-$CR$^+$)][26−28] and the neutralization/reionization mass spectrum of the same anion [sequential charge stripping of two electrons proceeding through the neutral which has a lifetime of some 10^{-6} s before it is ionized in the second collision cell ($^-$NR$^+$)].[21,22] If there are differences between the two spectra, these are a consequence of dissociation and/or rearrangement of the first formed neutral before conversion to the cation(s).[23]

The $^-$CR$^+$ and $^-$NR$^+$ spectra of (NCCCCCN)$^{•-}$ are shown in Figures 1 and 2. The two spectra are similar with the exception of a more pronounced peak due to the decomposition (*m/z* 88 − C) in the $^-$NR$^+$ spectrum. Although this is a low-abundance peak, the process forming it is likely to require significant excess energy, and its presence attests to some rearrangement of the initially formed neutral radical NCCCCCN (possibly to CNCCCCN) in the first of the collision cells prior to ionization of the neutral(s) in the second collision cell.

Theoretical Study

A. Structure of NCCCCCN. Triplet NCCCCCN is the ground state by 14.9 kcal mol^{-1} with respect to singlet NCCCCCN at the CCSD(T)/cc-pVTZ//B3LYP/6-311+G(3df) level of theory, results which are compatible with previous theoretical studies. Triplet NCCCCCN is linear, whereas singlet NCCCCCN is bent (angle C$_1$C$_2$C$_3$ is 141°; see Supporting Information Tables 1 and 3). However, triplet NCCCCCN has an unusual structure with bond connectivities and bond lengths shown as follows.. Reported bond lengths are as follows: CC (single, 1.54; double, 1.34; triple, 1.20 Å); CN (single, 1.47; double, 1.30; triple, 1.16 Å).[39]

1.17 1.27 1.33
N–C–C–C–C–C–N
1.33 1.27 1.17
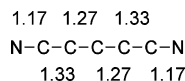
Chuchev and BelBruno[17] propose that triplet NCCCCCN has a linear cumulenic structure that may be described by using valence-bond resonance structures: unfortunately these resonance structures are bent and inappropriate for this system. The simplest linear valence-bond formulation is :N•=C=C=C=C=•N:, but this is also not correct since the theoretical treatment indicates the CN bonds to be triple bonds with all the CC bonds being double bonds with some triple bond character. A similar problem arises for singlet NCCCCCN (see Supporting Information Table 3). These are systems where the simple valence bond approach is not appropriate and/or where the bond lengths[39] of conventional CC and CN systems are not adequate to describe cumulene systems of this type.

This dilemma can be resolved by a consideration of the data shown in Figure 3. This figure displays the 3D HOMO and NHOMO shapes as well as the corresponding energies of the triplet and singlet NCCCCCN structure at the B3LYP/6-311+G(3df) level of theory. The HOMO and NHOMO orbitals
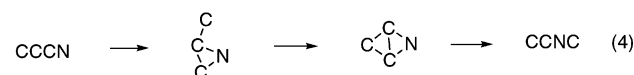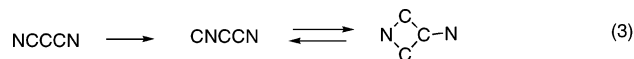

Figure 1. $^-$CR$^+$ spectrum of (NCCCCCN)$^{•-}$, VG ZAB 2HF mass spectrometer.

Figure 2. $^-$NR$^+$ spectrum of (NCCCCCN)$^{•-}$, VG ZAB 2HF mass spectrometer.
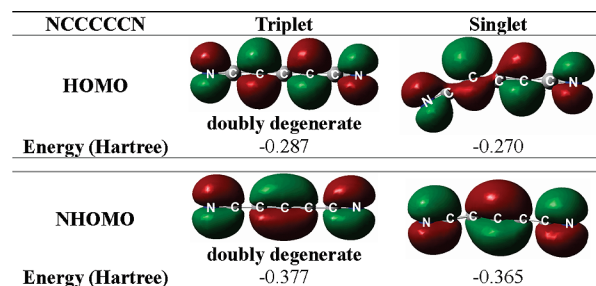
Figure 3. 3D HOMOs and NHOMOs of triplet and singlet NCCCCCN.

SCHEME 2

of the triplet structure are both doubly degenerate; the degenerate orbitals are orthogonal with identical electron distribution, which result in its stability and linearity compared to the singlet. There is significant distribution of the HOMO electrons on the terminal N atoms (N_1 and N_2), and certain NHOMO electrons delocalize between these two N atoms and their adjacent C atoms (C_1 and C_5). This contributes to the abnormally short CN bond length. Distribution of the electrons on C_2 and C_4, and among the three C atoms in the middle (C_2, C_3, and C_4) can be determined (see Figure 3) for the HOMO and NHOMO, respectively, leading to the bond lengths of C_2–C_3 and C_3–C_4 being 0.06 Å shorter than those of C_1–C_2 and C_4–C_5. For the singlet structure, the HOMO electron distribution on C_2 is more than that of C_4; repulsion between electrons in molecular orbitals causes this structure to be bent. Like the triplet, the singlet shows a distribution similar to that of the NHOMO electrons, with the structure exhibiting a similar C–C bond length trend; i.e., the two middle C–C bonds are shorter. The bond order analysis by NBO shows that C_1C_2 and C_4C_5 bonds in both singlet and triplet structures are single bonds, while CN bonds are triple bonds. On the basis of these results, it can be suggested that the bond lengths of conventional CC and CN systems are not adequate to describe these two structures. As a consequence, a simple valence bond treatment is not appropriate to describe the structures of triplet and singlet NCCCCCN.

B. Nitrile to Isonitrile Rearrangements of Triplet and Singlet NCCCCCN. There are two types of nitrile to isonitrile rearrangements that have been described for nitrogen-containing cumulene systems previously. These are shown in Scheme 2.

The rearrangement of NCCCN is shown in eq 3, where the initial cumulene rearranges via a three-membered transition state to form CNCCN which then proceeds to a four-membered transition state (shown in eq 3), ring-opening of which causes scrambling of the carbons.[10] In contrast, CCCN first forms a three membered ring intermediate, which ring closes to give a rhombic intermediate, the ring-opening of which randomizes the carbons (eq 4).[24]

Can NCCCCCN rearrange to an isonitrile which can then lose carbon? Since the triplet/singlet gap of NCCCCCN is only -14.9 kcal mol^{-1}, rearrangements of both triplet and singlet are considered. These are summarized in Figures 4 and 5, with full details of geometries and energies recorded in Supporting Information Tables 1−4.
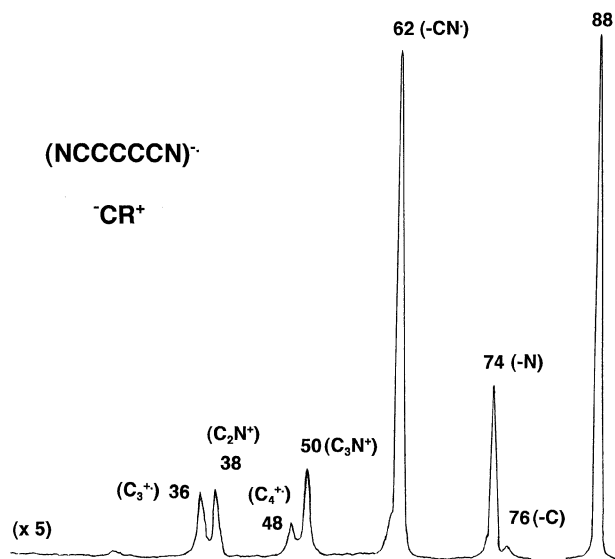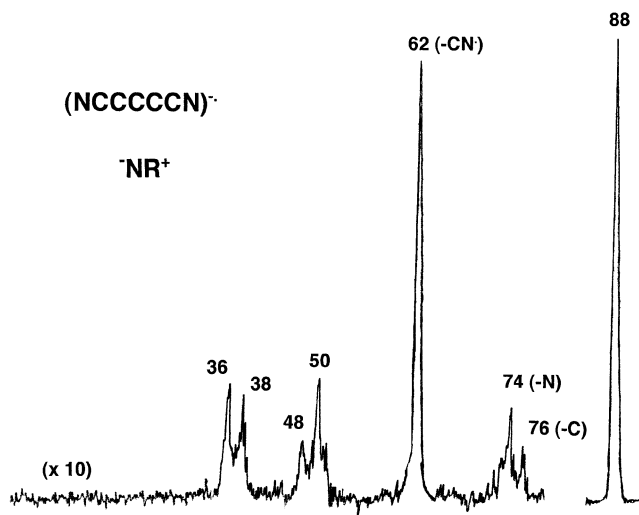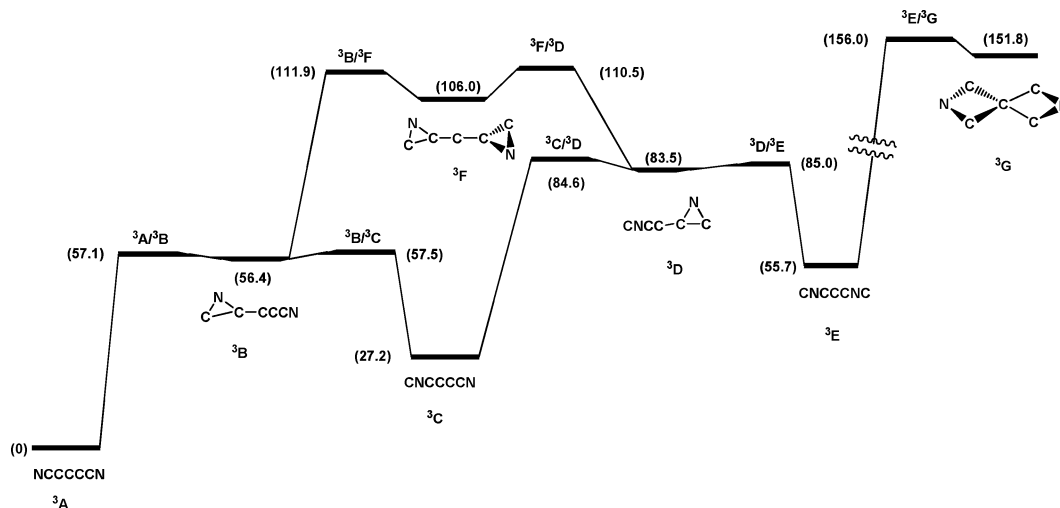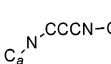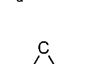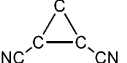
Figure 4. Rearrangement coordinate profiles of triplet NCCCCCN. The nitrile to isonitrile processes and related rearrangements. CCSD(T)/cc-pVTZ//B3LYP/6-311+G(3df) level of theory. Relative energies (ΔE, kcal mol^{-1}).
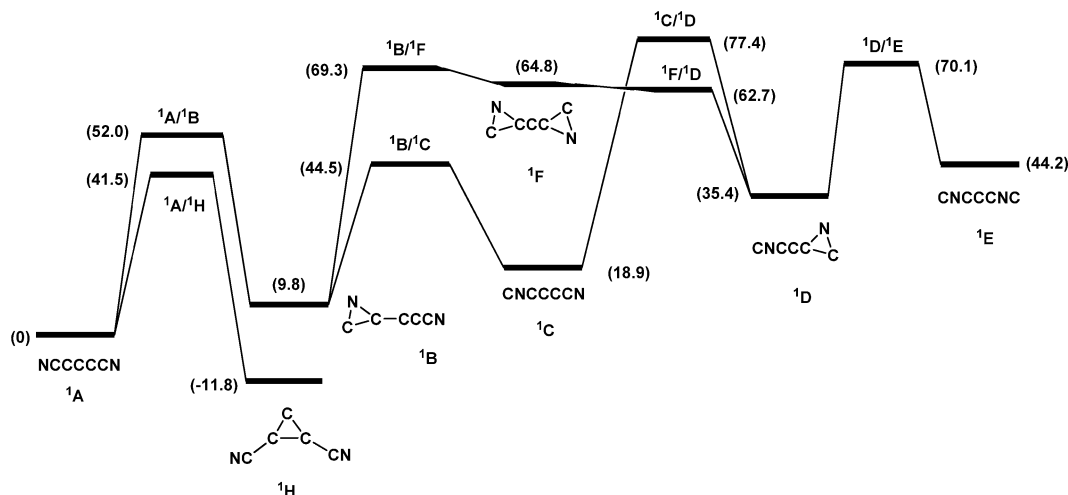
Figure 5. Rearrangement coordinate profiles of singlet NCCCCCN. The nitrile to isonitrile processes and the formation of ^{1}H. CCSD(T)/cc-pVTZ//B3LYP/6-311+G(3df) level of theory. Relative energies (ΔE, kcal mol^{-1}).

The reaction coordinate profiles of the conversion of triplet and singlet NCCCCCN to the isonitrile CNCCCCN (**C**) and the bis-isonitrile CNCCCNC (**E**) are shown in Figures 4 and 5. Neither triplet nor singlet rearrangements proceed through rhombic intermediates of the type formed from CCCCN.[24] Rhombic structures are not stable at the level of theory used for this investigation. Processes which are energetically feasible for both triplet and singlet NCCCCCN are those which form the mono-isonitrile via three membered ring intermediates. For the triplet, the process ^{3}**A** to ^{3}**B** to ^{3}**C** is endothermic by 27.2 kcal mol^{-1} with the highest energy transition state (^{3}**B**/^{3}**C**) in this sequence lying at +57.5 kcal mol^{-1}. All of the processes which lead to the bis-isonitrile (^{3}**E**) in Figure 4 have significant barriers ($\leq$ 84 kcal mol^{-1}) and, as a consequence, are energetically unfavorable. For the singlet (Figure 5), the analogous process ^{1}**A** to ^{1}**B** to ^{1}**C** is endothermic by 18.9 kcal mol^{-1} and the highest energy transition state (^{1}**A**/^{1}**B**) in this sequence is +52.0 kcal mol^{-1}. Formation of the bis-isonitrile (^{1}**E**; +44.2 kcal mol^{-1}) is more energetically favorable than for the triplet, but the formation of ^{1}**E** still requires an excess energy of +69.3 kcal mol^{-1} (to proceed over transition state ^{1}**B**/^{1}**F**). There are no four-center or "rhombic" transition states or intermediates

**TABLE 1: Loss of C from NC$_5$N Isomers**

[of the type shown in eq 3 (for NCCCN)] following CNCCCCN (either ^{3}**C** or ^{1}**C** in Figures 4 and 5).

In Table 1 are listed energies required to effect loss of C from those triplet or singlet isomers of NC$_5$N shown in Figures 4 and 5. Losses of C from triplet and singlet isonitriles respectively have the following energy requirements: from triplet

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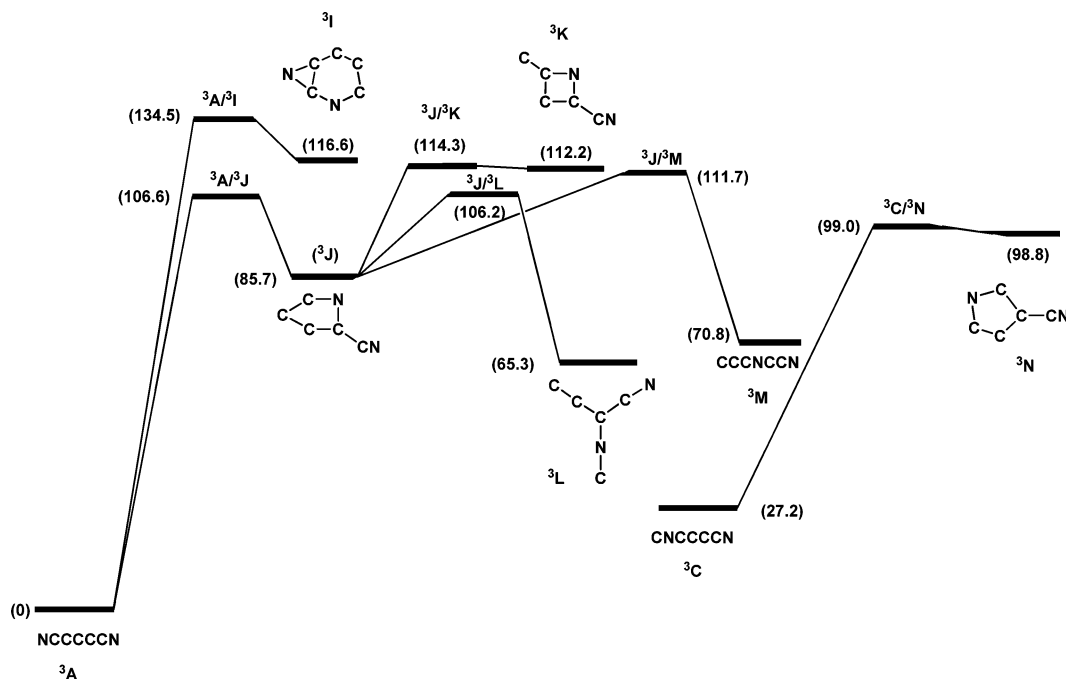
Figure 6. Rearrangement coordinate profiles of triplet NCCCCCN. High-energy rearrangements. CCSD(T)/cc-pVTZ//B3LYP/6-311+G(3df) level of theory. Relative energies (ΔE, kcal mol⁻¹).
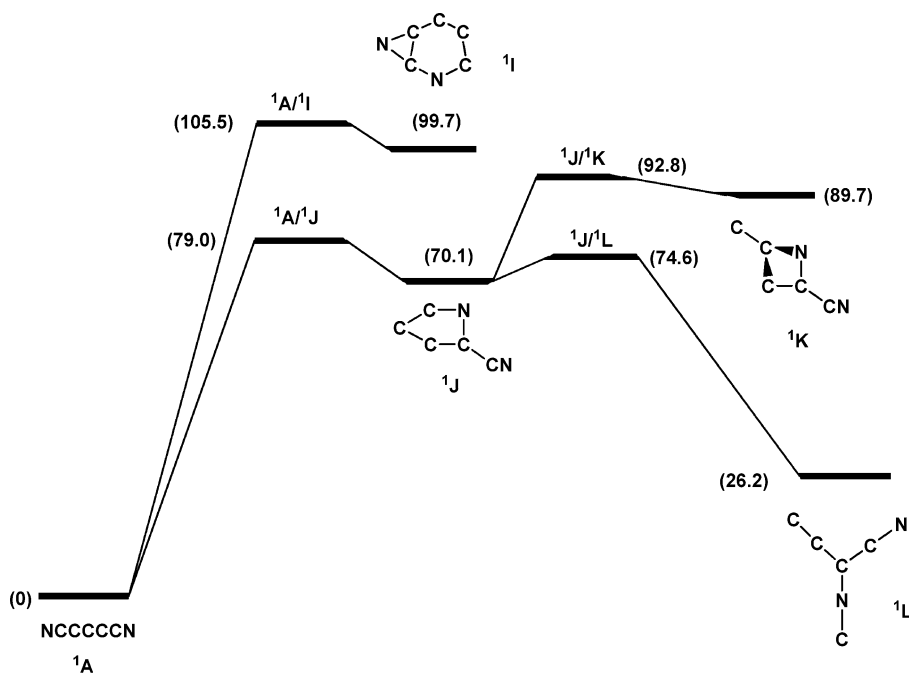

Figure 7. Rearrangement coordinate profiles of singlet NCCCCCN. High-energy rearrangements. CCSD(T)/cc-pVTZ//B3LYP/6-311+G(3df) level of theory. Relative energies (ΔE, kcal mol⁻¹).

and singlet CNCCCCN (+93.3 and +101.6 kcal mol⁻¹, respectively); from triplet and singlet CNCCCNC (+88.4 and +105.4 kcal mol⁻¹, respectively).

We conclude from the above data that (i) interconversion of both triplet and singlet NCCCCCN to the corresponding isonitrile CNCCCCN is feasible, (ii) the energy required for the losses of carbon from triplet and singlet CNCCCCN is comparable for that required for the similar rearrangements/decompositions of CCCCN[24] and NCCCN,[10] and (iii) rearrangements to the triplet and singlet bis-isonitriles CNCCCNC are too energy demanding to be considered as a viable sequence for this system.

C. C₂,₄ Three-Membered Ring Cyclization of Singlet NCCCCCN. On Figure 5 is shown an exclusive and unexpected reaction of singlet NCCCCCN which is competitive with the nitrile to isonitrile rearrangements of both triplet and singlet NCCCCCN shown in Figures 4 and 5. This involves the formation of cyclic and symmetrical species ¹H. There is no corresponding species on the triplet potential surface. Reaction ¹A to ¹H (Figure 5) is exothermic (−11.8 kcal mol⁻¹) with a barrier to the transition state of +41.5 kcal mol⁻¹, making this process competitive with ³A to ³C (Figure 3) and ¹A to ¹C (Figure 5).

TABLE 2: C$_5$N$_2$ Isomers Shown in Figures 3−6 (Relative Energies, kcal mol^{-1})

NCCCCCN	N=C–CCCCN	CNCCCCN	CNCC–C(=N)(C)	CNCCCNC
^{3}A (0)	^{3}B (+56.4)	^{3}C (+27.2)	^{3}D (+83.5)	^{3}E (+55.7)
^{1}A (0)	^{1}B (+9.8)	^{1}C (+18.9)	^{1}D (+35.4)	^{1}E (+44.2)
T/S (−14.9)	T/S (+31.7)	T/S (−6.6)	T/S (+33.2)	T/S (−3.4)
(N=C–C–C–C–C–N)	(N,C,C,C,C,N ring)	(NC–C–C–CN)	(N,C,C,N,C ring)	(C–N / C–C–C / CN)
^{3}F (+106.0)	^{3}G (+151.8)		^{3}I (+116.6)	^{3}J (+85.7)
^{1}F (+64.8)		^{1}H (−11.8)	^{1}I (+99.7)	^{1}J (+70.1)
T/S (+27.1)			T/S (+2.0)	T/S (+0.7)
(C–N / C–C / C–C–CN)	CCCNCCN	(C–C–C–N / N–C ring)	(N–C / C–C–CN ring)	
^{3}K (+112.2)	^{3}M (+70.8)	^{3}L (+65.3)	^{3}N (+98.8)	
^{1}K (+87.7)	^{1}M (+51.4) ^{a}	^{1}L (+26.2)	^{1}N (+63.8) ^{a}	
T/S (+9.6)	T/S (+4.5)	T/S (+24.2)	T/S (+20.1)	

^{a} These two structures are not shown in Figures 5 and 7; listed in the table for completeness.

Could ^{1}**H** lose carbon as shown in eq 5 [in this case the geometry of ^{1}**H** (Supporting Information Table 1) closely matches the valence bond structure shown in eq 5]? The energy required to effect this decomposition is 68.0 kcal mol^{-1} (at the CCSD(T)/cc-pVTZ//B3LYP/6-311+G(3df) level of theory; see Table 1). Presumably the electron-withdrawing capability of the two nitrile groups of ^{1}**H** reduces the energy requirement for cleavage of the two CC single bonds [it is of interest to compare this value of 68.0 kcal mol^{-1} with the energy necessary to remove a carbon from triplet ground state cyclic C$_3$ (136.3 kcal mol^{-1} at the level of theory used in this study)]. So not only is formation of ^{1}**H** more favorable than either of the triplet or singlet nitrile to isonitrile processes, but also the loss of carbon from ^{1}**H** is significantly more favored than losses of carbon from either triplet or singlet CNCCCCN (+93.3 and +101.6 kcal mol^{-1}, respectively).

$$N\equiv C-C\equiv C-C\equiv N \;+\; C \qquad (5)$$

^{1}**H**
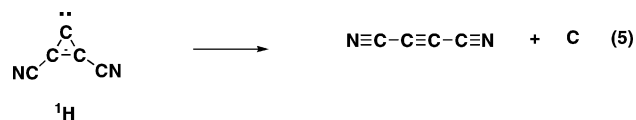
D. Mechanism for Loss of C from NCCCCCN. The T/S gap between triplet and singlet NCCCCCN is −14.9 kcal mol^{-1}. The consequence is that collision-induced charged stripping of (NCCCCCN)$^{\bullet-}$ will form triplet NCCCCCN predominantly, and the lowest energy loss of carbon from a species on the triplet potential surface is from the triplet mono isonitrile (which requires an extra 93.3 kcal mol^{-1} to effect loss of carbon). However singlet NCCCCCN undergoes a facile rearrangement to ^{1}**H** (−11.8 kcal mol^{-1}; Figure 5) followed by favorable loss of carbon as outlined above. However singlet NCCCCCN is a minor product from the charge-stripping of (NCCCCCN)$^{\bullet-}$.

The only way that ^{1}**H** can be the major precursor of carbon loss in this system is if intersystem crossing can occur between the triplet and singlet potential surfaces, specifically in this case if triplet NCCCCCN (^{3}**A**) can readily interconvert to singlet NCCCCCN (^{1}**A**). Intersystem crossing data for the triplet and singlet NCCCCCN interconversion (^{3}**A**/^{1}**A**) were obtained at the CASSCF/6-311+G(d) level of theory using a standard method.[40-43] The spin−orbit coupling constant (SOC) for ^{3}**A**/^{1}**A** at the CASSCF/6-311+G(d) level of theory (CASSCF is

contained in the Gaussian 03 package) was computed at the crossing point using a one-electron approximation. The HOMO and LUMO in all cases are π orbitals; thus, the active spaces chosen for the triplet NCCCCCN involve six electrons in eight orbitals, which include π and the corresponding antibonding orbitals. The calculated SOC is 0.4 cm^{-1}, a value so low that spin inversion between the two states is highly unfavorable. We conclude that the loss of carbon identified from a comparison of the $^-$CR$^+$ and $^-$NR$^+$ spectra of (NCCCCCN)$^-$ is due predominantly to decomposition of triplet CNCCCCN to yield NCCCCN and C.

E. Other Rearrangements of Triplet and Singlet NCCCCCN. Other rearrangement processes of triplet and singlet NCCCCCN are summarized in Figures 6 and 7 with detailed geometry and energy data for minima and transition states shown in Figures 6 and 7 being listed in Supporting Information Tables 3 and 4. For ease of illustration, all isomers shown in Figures 4−7 are depicted in Table 2 in the order of the identification lettering used in Figures 4−7. The relative energy of each species is indicated relative to either triplet or singlet NC-CCCCN, both considered as a nominal 0 kcal mol^{-1}. Many of the isomers are high-energy species. There are no stable rhombic isomers on either potential surface. The only four membered ring containing minima are the planar and rectangular ^{3}**K**, the nonplanar species ^{1}**K**, and the bicyclic orthogonal species ^{3}**G**. Triplet/singlet energy gaps are indicated for each structure as appropriate. A negative number indicates the triplet to be the ground state. A positive number indicates the singlet to be the ground state. Where both stable triplet and singlet states exist for a particular isomer, a linear structure has a triplet ground state except **M**, while an isomer containing a cyclic moiety has a singlet ground state. Considering now all cyclization reactions shown in Figures 4−7 compared in terms of relative energies: for the triplet potential surface 3 < 5 < 4 ≈ 6/3 (i.e., three membered ring cyclization is more favorable than five membered ring cyclization, etc.), while for the singlet potential surface, 3 (C$_2$C$_4$) < 3 (C$_2$N) < 5 < 4 < 6/3.

Conclusions

(1) Neutral NCCCCCN can be prepared in the collision cell of the VG ZAB 2HF mass spectrometer by collision-induced vertical charge-stripping of anion (NCCCCCN)$^{\bullet-}$.

(2) A comparison of the $^-$NR$^+$ and $^-$CR$^+$ spectra of (NCCCCCN)$^{\bullet-}$ indicates that some neutral NCCCCCN are energized and undergo rearrangement to an isomer which can decompose by loss of C.

(3) An ab initio study at the CCSD(T)/cc-pVTZ//B3LYP/6-311+G(3df) level of theory indicates that the triplet of NC-CCCCN is the ground state with a T/S energy gap of −14.9 kcal mol^{-1}.

(4) A study of the theoretical triplet and singlet potential surfaces indicates that the major rearrangement which proceeds or accompanies the loss of C is the triplet three-membered nitrile to isonitrile rearrangement, which occurs without carbon scrambling of the CNCCCCN backbone (apart from a change in position of the nitrile C).

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Supporting Information Available: Tables S1 and S2, triplet neutral C_5N_2 potential surface, and Tables S3 and S4, singlet neutral C_5N_2 potential surface. This material is available free of charge via the Internet at http://pubs.acs.org.

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