Interstellar Molecule CCCN May Be Formed by Charge-Stripping of $[CCCN]^-$ in the Gas Phase, and When Energized, Undergoes Loss of C with Partial Carbon Scrambling

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Deprotonation of $CH_2{=}CHCN$ with HO^- in the chemical ionization source of a VG ZAB 2HF mass spectrometer gives $CH_2{=}^-CCN$ which fragments through $[H^- (HCCCN)]$ to give $[CCCN]^-$. Similar reactions with $^{13}CH_2CHCN$ and $CH_2CH^{13}CN$ give $[^{13}CCCN]^-$ and $[CC^{13}CN]^-$. Collision induced dissociations of these anions, together with calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory indicate that the anions do not rearrange under conditions used to charge strip them to their neutrals. A comparison of the charge reversal ($^-CR^+$) and neutralization/reionization ($^-NR^+$) mass spectra of $[CCCN]^-$ indicate that neutral C_3N species (formed by charge stripping of the anion) decompose by loss of C. Experimental studies with the ^{13}C labeled analogues indicate that the loss of C occurs subsequent to or accompanying partial carbon scrambling of the CCCN backbone. Theoretical studies suggest that this scrambling may occur during equilibration of CCCN and CCNC via a decomposing "rhombic" C_3N intermediate.

Introduction

We have shown that CCCC, CCCO, and CCCS can be formed by charge stripping of $[CCCC]^{-\bullet}$, $[CCCO]^{-\bullet}$, and $[CCCS]^{-\bullet}$ in a collision cell of a mass spectrometer. These neutrals have all been detected in interstellar dust clouds.[1] When energized, CCCC undergoes partial scrambling of the atoms via a planar rhombic intermediate[2] while energized CCCO decomposes by loss of CO without scrambling of the carbon backbone.[3] We have now extended this study to investigate the interstellar molecule CCCN with a view to determine whether, when energized, it undergoes C scrambling (like CCCC) and/or rearranges to the less stable isomer CCNC. In this context, we have already reported that the energized neutral NCCCN undergoes atom scrambling.[4]

The neutral radical CCCN was tentatively identified in regions around the carbon rich star IRC +10206 by the presence of two doublets centered at 89 055 and 98 949 MHz.[5,6] This proposal was later confirmed by detection and identification of CCCN in low-pressure laboratory gas discharges.[7] CCCN was subsequently identified in Taurus dark clouds TMC1 and TMC2 and later in other interstellar regions.[8−13] It has been suggested that the reaction between the interstellar molecules CN and C_2H_2 on dust grains in interstellar regions may give CCCN (and HCCCN).[14] It has also been proposed that the isomer CCNC should be an interstellar molecule.[15,16] Although CCNC has not been detected in interstellar regions, precursor isomers of CCCN and CCNC, namely, HCCCN and HCCNC, are both interstellar molecules.[1] For example, HCCCN is a constituent of the atmosphere of Titan.[17,18] It has recently been proposed that CaCCCN could be an interstellar molecule,[19] and in this context, organometallic molecules containing CCCN bridges have been synthesized in the laboratory.[20]

There have been many theoretical studies on CCCN;[21−29] for example, it has been proposed that CCCN has a linear $^2\Sigma$ ground state with a first excited $A^2\Pi$ state 0.19 eV above the ground state.[24] The structure of the isomer CCNC has also been studied theoretically.[22,23] Rotational[24,30,31] and other spectroscopic properties of CCCN have been reported.[11,32] There have been reports of the heat of formation of CCCN,[33] and of several bond dissociation energies of this molecule.[22,34]

There have also been a number of reports of charged analogues of CCCN. Theoretical calculations have been reported for $[CCCN]^+$,[35−37] and the ion molecule chemistry of $[CCCN]^+$ has been studied extensively.[38−40] It has been suggested that, because of the high electron affinity of CCCN (4.59 eV),[41] the anion $[CCCN]^-$ could be a possible interstellar molecule.[40] $[CCCN]^-$ has been made by laser ablation[42] and by Cs^+ ion sputtering of graphite in the presence of N_2 or NO_2.[43] There have been a number of theoretical studies of $[CCCN]^-$ and its decomposition pathways.[44−48]

This paper describes the formation of CCCN and some ^{13}C labeled analogues from anionic precursors using the neutralization/reionization ($^-NR^+$) procedure (e.g., see refs 49 and 50). The formation of unlabeled CCCN from a cation precursor has been reported by Schwarz.[51]

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** represents the magnetic and electric sectors, respectively. The precursor anion $[CCCN]^-$ was formed in the chemical ionization source by reaction between $CH_2{=}CHCN$ with HO^- (from H_2O) to form $CH_2{=}^-CCN$ which then decomposes through intermediate $[H^- (HCCCN)]$ to yield $[CCCN]^-$ and H_2. Similar reactions of HO^- with $^{13}CH_2{=}CHCN$ and $CH_2{=}CH{-}^{13}CN$ yield $[^{13}CCCN]^-$ and $[CC^{13}CN]^-$, respectively, while reaction of DO^- (from D_2O) with $CH_2{=}CD{-}CN$ gave $CH_2{=}^-CCN$ exclusively, which decomposes to $[CCCN]^-$. Source conditions were as follows: source temperature, 100 °C; repeller voltage, −0.5 V; ion extraction voltage, 7 kV; mass resolution, $m/\Delta m \geq 1500$. Acrylonitrile (or labeled acrylonitrile as required) is added

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through the septum inlet (unheated) to give a pressure of 10^{-5} Torr measured in the source housing. Water (or D_2O) is then introduced through the septum inlet (unheated) to give a constant pressure of 10^{-4} Torr in the source housing. The estimated pressure in the ion source is 10^{-1} Torr.[2] 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 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 per ion.[52] Product anion peaks resulting from CID processes were recorded by scanning the electric sector.

Neutralization/reionization spectra ($^-NR^+$)[49,50] were performed for mass selected anions utilizing the dual collision cells located between the magnetic and the 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[53,54] were recorded using single-collision conditions in collision cell 1 (O_2, 80% transmission of 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 55 for a full description of this procedure.

B. Neutral Precursors. The neutral precursors $CH_2{=}CH{-}CN$, $CH_2{=}CD{-}CN$ ($D_1 > 99\%$), $^{13}CH_2{=}CH{-}CN$, and $CH_2{=}CH{-}^{13}CN$ ($^{13}C > 99\%$) were all commercially available and were used without further purification.

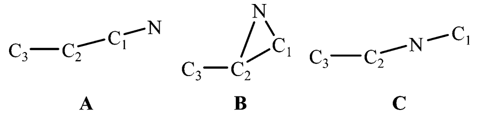
C. Theoretical Methods. Geometry optimizations were carried out with the Becke 3LYP method[56,57] using the 6-31+G(d) basis set[58] within the Gaussian 03 suite of programs.[59] Stationary points were characterized as either minima (no imaginary frequencies) or transition states (one imaginary frequency) 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. The calculated frequencies were also used to determine zero-point vibrational energies which were then scaled by 0.9804[60] and used as a zero-point correction for electronic energies. We have reported the success of this method in predicting geometries of unsaturated chain structures and that this method produces optimized structures, at low computational cost, that compare favorably with higher level calculations.[61] More accurate energies for the B3LYP geometries were determined using the CCSD(T) method including zero-point energy correction (calculated by vibrational frequencies at the B3LYP/6-31+G(d) level of theory). All calculations were carried out using the South Australian Partnership for Advanced Computing (SAPAC) facility.

Results and Discussion

The primary aim of this project is to form CCCN and ^{13}C labeled analogues from negative ions of known bond connectivity with a view to studying the behavior of energized CCCN. We chose unlabeled acrylonitrile as the precursor neutral to $[CCCN]^-$, because the labeled derivatives $^{13}CH_2{=}CH{-}CN$ and $CH_2{=}CH{-}^{13}CN$ are available and will readily form $[^{13}CCCN]^-$ and $[CC^{13}CN]^-$ respectively, as indicated by the process (forming $[CCCN]^-$) shown in eq 1. The deprotonation site shown in eq 1 is confirmed by the reaction between $CH_2{=}CD{-}CN$ and DO^- which gives exclusively $CH_2{=}^-C{-}CN$.

$$CH_2{=}CH{-}CN + HO^- \xrightarrow{-H_2O} CH_2{=}^-C{-}CN \rightarrow [H^-\,(HCCCN)] \rightarrow [CCCN]^- + H_2 \quad (1)$$

TABLE 1: Structures and Energies of the Isomeric Singlet Anions[a]



state	^1A	$^1A'$	$^1A'$
symmetry	C_1	C_S	C_S
energy (Hartrees)	−168.57243	−168.47161	−168.52221
energy relative to A	0	+63.3	+31.5
dipole moment (Debye)	2.6536	3.4899	3.1316
bond lengths (Å)			
NC_1	1.180	1.245	1.186
C_1C_2	1.365	1.619	
C_2C_3	1.256	1.266	1.322
NC_2		1.489	1.255
bond angles (degree)			
NC_1C_2	180.0	61.0	
$C_1C_2C_3$	180.0	151.6	
C_1C_2N		47.0	
C_2NC_1		72.0	180.0
C_3C_2N		161.4	180.0
dihedral angle (degree)			
$NC_1C_2C_3$	167.3	180.0	
$C_1NC_2C_3$			180.0

[a] Level of theory used: geometries, B3LYP/6-31+G(d); energies, CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d). Relative energies in kcal mol^{-1} with respect to A (0 kcal mol^{-1}).

Having prepared the three anions $[CCCN]^-$, $[^{13}CCCN]^-$, and $[CC^{13}CN]^-$, we find it is necessary to ascertain whether they are appropriate precursors of the radicals CCCN, $^{13}CCCN$, and $CC^{13}CN$. In order to do this, we have examined the collision induced (CID) mass spectra of the anions. The CID mass spectrum of $[CCCN]^-$ shows the parent anion as the base peak: the only fragment anions ≥0.5% of the base peak are those formed by losses of C (0.8%) and N (0.5%) from the parent. The corresponding fragment anions in the spectra of $[CC^{13}CN]^-$ are $-^{12}C$ (1.0%), $-^{13}C$ (0.05%) and −N (0.7%). This major loss of ^{12}C means that C scrambling and/or rearrangement of $[CC^{13}CN]^-$ to $[CCN^{13}C]^-$ is at best minimal.[63] The experimental data indicate that $[CCCN]^-$ formed as shown in eq 1 is stable under the collisional conditions necessary to effect Franck−Condon (a reviewer has indicated in this instance that the nomenclature “quasi-vertical” is more appropriate than “Franck-Condon”) charge stripping to neutral CCCN. Theoretical data are also in accord with this conclusion (see Table 1).

There are only three stable singlet $[C_3N]^-$ isomers, $[CCCN]^-$ (**A**), cyclic isomer (**B**), and $[CCNC]^-$ (**C**) at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory (see Table 1). The rearrangement of $[CCCN]^-$ through **B** to $[CCNC]^-$ is unlikely since **B** lies 63.3 kcal mol^{-1} above $[CCCN]^-$. Rearrangement through triplet $[CCCN]^-$ is not considered since the triplet is 83.7 kcal mol^{-1} above the ground state singlet [Table 1 and Table 5 (Supporting Information)].

The $^-CR^+$ (synchronous two electron stripping of $[CCCN]^-$ to $[CCCN]^+$)[53,54] and $^-NR^+$ (sequential two electron stripping, $[CCCN]^-$ to CCCN to $[CCCN]^+$)[49,50] spectra of $[CCCN]^-$ are shown in Figures 1 and 2. Both spectra show the recovery signal $[CCCN]^+$ as base peak with fragment cations corresponding to

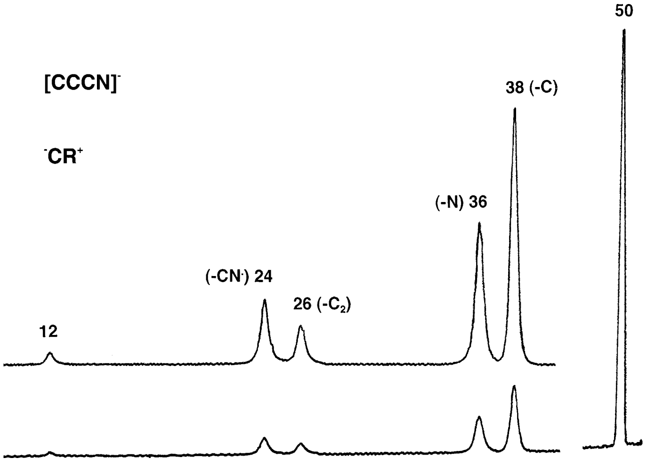


Figure 1. $^-$CR$^+$ spectrum of [CCCN]$^-$. For experimental details, see experimental section.

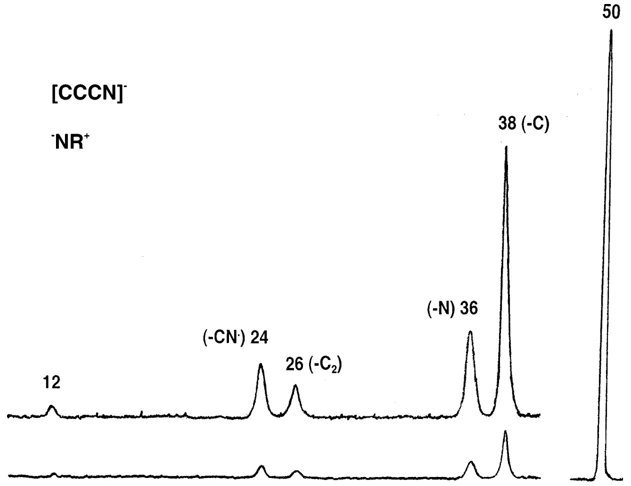


Figure 2. $^-$NR$^+$ spectrum of [CCCN]$^-$. For experimental details, see experimental section.

TABLE 2: $^-$CR$^+$ and $^-$NR$^+$ Spectra of [^{13}CCCN]$^-$ and [CC^{13}CN]$^-$ [a]

[^{13}CCCN]$^-$	
$^-$CR$^+$	51(100), 39(24.0), 38(14.5), 37(14.8), 27(1.3), 26(5.2), 25(9.0), 24(2.4), 13(0.5), 12(0.8).
$^-$NR$^+$	51(100), 39(27.5), 38(14.3), 37(13.0), 27(3.0), 26(8.5), 25(11.5), 24(5.0), 13(0.3), 12(0.7).
[CC^{13}CN]$^-$	
$^-$CR$^+$	51(100), 39(25.0), 38(7.7), 37(15.5), 27(4.8), 26(2.25), 25(4.9), 24(6.4), 13(0.5), 12(0.8).
$^-$NR$^+$	51(100), 39(26.5), 38(9.7), 37(10.5), 27(3.6), 26(2.25), 25(5.0), 24(5.0), 13(0.5), 12(0.9).

[a] *m/z* (relative abundance in %).

the losses of C and N and formation of CN$^+$ and C$_2{}^{+\bullet}$ The peak formed by loss of C in the $^-$NR$^+$ spectrum is more intense than the corresponding peak in the $^-$CR$^+$ spectrum. This means that whatever the structures of the neutral(s) C$_3$N formed by the Franck−Condon charge stripping of [CCCN]$^-$, these neutrals are losing more C than the corresponding positive ion(s) [C$_3$N]$^+$, which means that this process is (at least) comparable to that involving loss of C from the corresponding cation(s). This loss of C from the neutrals may allow us to determine whether the energized neutral C$_3$N radicals are undergoing carbon rearrangement prior to or during decomposition of C.

The $^-$CR$^+$ and $^-$NR$^+$ spectra of [^{13}CCCN]$^-$ and [CC^{13}CN]$^-$ are listed in Table 2. These spectra confirm that there is significant C scrambling, for example, in the losses of ^{12}C and ^{13}C and in the formation of ^{12}C^{12}C$^{+\bullet}$ versus ^{12}C^{13}C$^{+\bullet}$ and ^{12}CN$^+$ versus ^{13}CN$^+$. The $^-$NR$^+$ spectra show more loss of ^{12}C and ^{13}C than the $^-$CR$^+$ counterparts, confirming that the labeled neutral species are decomposing by loss of both ^{12}C and ^{13}C. These ratios ^{12}C:^{13}C are as follows: 62:38 ($^-$CR$^+$) and 66:34 ($^-$NR$^+$) from ^{13}CCCN and 76:24 ($^-$CR$^+$) and 73:27 ($^-$NR$^+$) from CC^{13}CN cation/neutral. The small but reproducibly different values observed in $^-$CR$^+$ and $^-$NR$^+$ spectra indicate that C scrambling processes are occurring for both neutral and cationic C$_3$N.

SCHEME 1

$$\mathrm{CCCN} \rightarrow \mathrm{C} + \mathrm{CCN} \quad (+\,139.5\ \mathrm{kcal\ mol^{-1}})$$
$$\mathrm{CCNC} \rightarrow \mathrm{C} + \mathrm{CNC} \quad (+\,115.6\ \mathrm{kcal\ mol^{-1}})$$
$$\mathrm{CCNC} \rightarrow \mathrm{C} + \mathrm{CCN} \quad (+\,117.0\ \mathrm{kcal\ mol^{-1}})$$

The calculated energies for the losses of C from CCCN and/or CCNC are shown in Scheme 1(calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory: experimental values are not known for all species shown in Scheme 1, so we are unable to compare computational and experimentally derived values). Losses of C from either end of CCNC are more energetically favorable than loss of C from CCCN. If C scrambling in CCCN is a consequence of direct isomerization to CCNC, then for the labeled neutrals, there should be mixtures of ^{13}CCCN and ^{13}CCNC (from ^{13}CCCN) and CC^{13}CN and CCN^{13}C (from CC^{13}CN). No combination of either pair of these decomposing isomer pairs can account for the experimental loss ratios ^{12}C:^{13}C from ^{13}CCCN and from CC^{13}CN which are approaching the theoretical ratio of 67:33 for complete randomization of carbon.

The experimental data indicate that partial carbon scrambling is occurring for both the energized neutral and its positive ion counterpart, but the data do not allow us to determine precisely how much scrambling is occurring for the neutral. The Franck−Condon energy {the difference in energy between ground state CCCN and that structure (of CCCN) with the same geometry as [CCCN]$^-$} is calculated to be only 1 kcal mol^{-1} at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory. The energy required to effect any of the various dissociation processes (Scheme 1) is significantly more than the Franck−Condon energy of this vertical process and presumably originates, at least in part, from subsequent collisions of the first formed neutral in the collision cell. Although we are ultimately interested in investigating possible scrambling mechanisms of neutral CCCN, it is instructive to consider the theoretical results of Ding et al.[37] with respect to interconversion of [CCCN]$^+$ to [CCNC]$^+$. These are shown pictorially in Figure 3 for the ground state triplet rearrangement.

The energy difference between [CCCN]$^+$ and the less stable isonitrile isomer [CCNC]$^+$ is 12 kcal mol^{-1} at the CCSD(T)/6-311G(d) level of theory, and there are two pathways for the nitrile/isonitrile interconversion. The first pathway goes through rhombic intermediate **D**, the second via three membered ring intermediate **E**. The barriers for both of these rearrangements are 43 and 45 kcal mol^{-1} respectively at this level of theory. Losses of C from the isomers [CCCN]$^+$ and [CCNC]$^+$ require the energies shown in Scheme 2 (CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory).

Both of the neutrals CCCN and CCNC have bent structures at the level of theory used in this study: previous calculations have reported that CCCN is linear.[21−29] Whether the calculated structure of CCCN is bent or linear depends upon the level of theory and the basis set used.[64] The latest report of the rotational

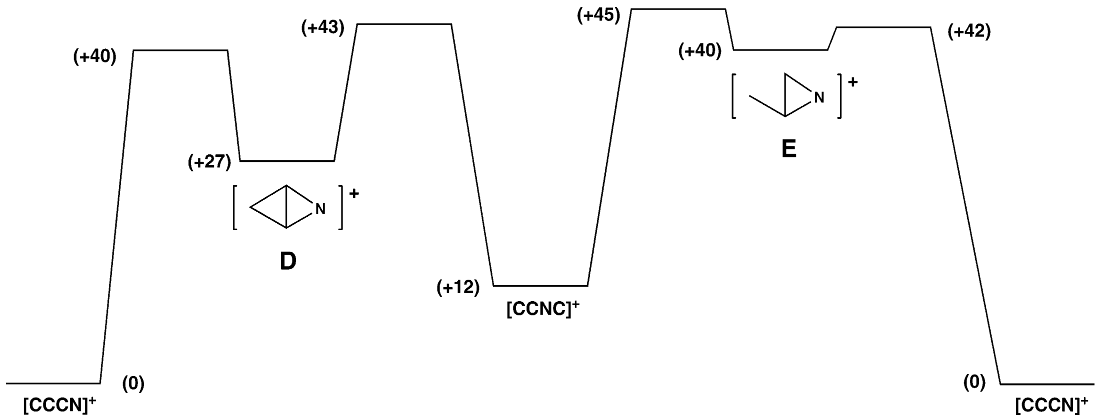


Figure 3. Reaction coordinate pathways for conversion of ground state triplet $[CCCN]^+$ to triplet $[CCNC]^+$ taken from Ding et al.[37] Relative energies in kilocalorie per mole. CCSD(T)/6-311G(d) level of theory.

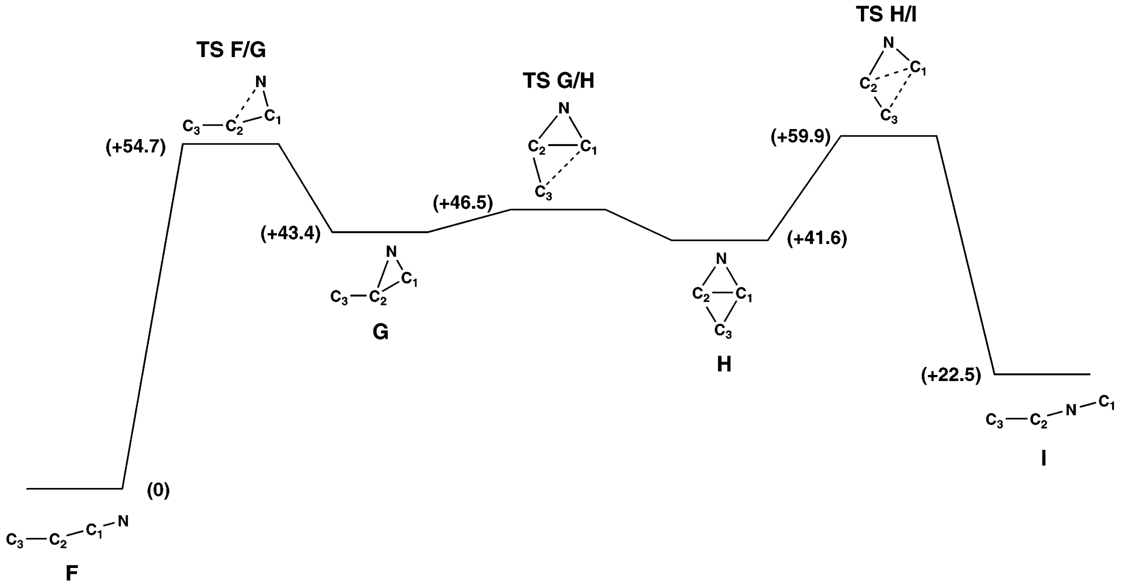


Figure 4. Reaction coordinate profile for interconversion of bent CCCN to CCNC. Relative energies in kilocalorie per mole. CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory. Formulas shown in the figure show bond connectivities only; for full structural details, see Tables 3 and 4.

SCHEME 2

$[CCCN]^+ \rightarrow C + [CCN]^+$	(+140.2 kcal mol^{-1})
$[CCNC]^+ \rightarrow C + [CNC]^+$	(+110.8 kcal mol^{-1})
$[CCNC]^+ \rightarrow C + [CCN]^+$	(+134.7 kcal mol^{-1})

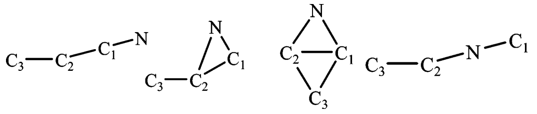
spectrum of CCCN indicates that the data best fit "a nearly pure $^2\Sigma$ (linear) electronic ground state."[31]

Our primary interest in this study is to determine the mechanism for the carbon equilibration of energized CCCN. We have undertaken reaction coordinate calculations for (i) the bent CCCN system at our usual B3LYP/6-31+G(d) level of theory [to compare with our previous studies on CCCC,[2] CCCO,[3] and CCCS[3] (which are all linear at this level of theory)], and (ii) linear CCCN at the B3LYP/6-311G(d)[33,64] level of theory. Results for the interconversion of bent CCCN to CCNC are shown in Figure 4, with full details of minima and transition states recorded in Tables 3 and 4. Results for linear CCCN are available as Supporting Information (Figure 5 and Tables 6 and 7). The data shown in Figures 4 and 5 are similar.

The rearrangement pathway shown in Figure 4 is different from those of the cation depicted in Figure 3: we have uncovered only one interconversion pathway for the neutrals. The rearrangement pathway (Figure 4) for CCCN shows some similarity to that of CCCC.[2] Both rearrangements proceed via "rhombic" intermediates (see **H**, Figure 4), and we previously attributed the C scrambling of energized CCCC to random cleavage of rhombic C_4.[2] The major difference between the two systems is energetic: C randomization via the triplet ground state of CCCC has a calculated barrier of only 28.6 kcal mol^{-1} (ref 2) whereas the maximum barrier shown in Figure 4 is 59.9 kcal mol^{-1}.

Partial scrambling can be seen for other processes in the $^-NR^+$ and $^-CR^+$ spectra apart from loss of C. This includes the formation of $[CC]^{+\bullet}$ and $[CN]^+$ (see Table 2). The ratio of formation of $[CC]^{+\bullet}$:$[C^{13}C]^{+\bullet}$ from ^{13}CCCN is 21:79 ($^-CR^+$), 30:70 ($^-NR^+$), and for CC^{13}CN, it is 57:43 ($^-CR^+$), 50:50 ($^-NR^+$). The ratio of formation of $[CN]^+$:$[^{13}CN]^+$ from ^{13}CCCN is 80:20 ($^-CR^+$), 74:26 ($^-NR^+$), and for CC^{13}CN, it is 30:68 ($^-CR^+$), 39:61 ($^-NR^+$). What is surprising is that there is more scrambling observed in each $^-NR^+$ spectrum for both of these processes. This must mean that there is some fragmentation of the neutral CCCN/CCNC system to give CC and CN even though a visual comparison of the $^-NR^+$ and $^-CR^+$ spectra (Figures 1 and 2) indicates only a clearly observable loss of C. The formation of CC plus CN from CCCN and CCNC are exothermic by 118.2 and 95.7 kcal mol^{-1} respectively (Supporting Information, Table 8). Again, comparison of the labeled $^-NR^+$ and $^-CR^+$ spectra (Table 2) do not allow a breakdown

TABLE 3: Structures and Energies of the Isomeric Doublet Neutral Minima[a]



	F	G	H	I
state	^2A	$^2A''$	$^2A''$	$^2A'$
symmetry	C_1	C_S	C_S	C_S
energy (Hartrees)	−168.41367	−168.34450	−168.34732	−168.37778
energy relative to F	0	+43.4	+41.6	+22.5
dipole moment (Debye)	0.8314	1.0160	1.0192	0.7712
bond lengths (Å)				
NC_1	1.177	1.279	1.379	1.198
C_1C_2	1.355	1.551	1.495	
C_2C_3	1.278	1.318	1.458	1.285
NC_2		1.390	1.379	1.293
C_1C_3			1.457	
bond angles (degree)				
NC_1C_2	178.5	57.9	57.2	
$C_1C_2C_3$	163.6	148.6	59.1	
C_1C_2N		51.2	57.2	
C_2NC_1		70.9	65.6	178.2
C_3C_2N		160.2	116.3	165.2
$C_1C_3C_2$			61.7	
$C_2C_1C_3$			59.2	
NC_1C_3			116.3	
dihedral angle (degree)				
$NC_1C_2C_3$	−179.8	180.0	180.0	
$C_1NC_2C_3$				180.0
$NC_2C_1C_3$			180.0	

[a] Level of theory: geometries, B3LYP/6-31+G(d); energies, CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d). Relative energies in kcal mol^{-1} with respect to F (0 kcal mol^{-1}).

of how much rearrangement is occurring within the equilibrating neutral CCCN/CCNC system. The overall scrambling in the $^-NR^+$ and $^-CR^+$ spectra for the losses of CC and CN is less than that observed for loss of C.

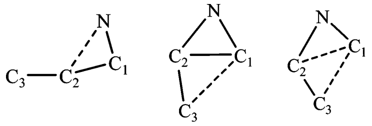
In conclusion, although we are not in a position to determine precisely how much carbon scrambling occurs through individual neutral and cationic CCCN in our $^-NR^+$ system, the combined scrambling through both is approaching statistical for the major loss of C. The most likely scenario for the carbon randomization of neutral CCCN involves equilibration with and random cleavage of bonds in the planar "rhombic" intermediate (Figure 4) to yield mixtures of CCCN and CCNC in which the carbons will be (ultimately) statistically randomized. Losses of carbon from these neutrals are most likely to occur by the decomposition pathways shown in Scheme 1. Carbon randomization of the initially formed cation $[CCCN]^+$ may also occur through the equilibrating and planar "rhombic" intermediate shown in Figure 3.

A reviewer has asked for a comparison of the results on the CCCC, CCCN, CCCO, and CCCS systems. All systems were investigated experimentally and calculations were carried out at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory.

In summary, the following is proposed:

1. CCCC undergoes cyclization to rhombic C_4 in an exothermic reaction (−10 kcal mol^{-1}) over a barrier of 29.5 kcal mol^{-1}. Loss of C comes from largely scrambled C_4 in a reaction endothermic by 122 kcal mol^{-1}.[2]

TABLE 4: Structures and Energies of the Doublet Neutral Transition States[a]



	TS F/G	TS G/H	TS H/I
state	^2A	$^2A''$	$^2A'$
symmetry	C_1	C_S	C_S
energy (Hartrees)	−168.32649	−168.33957	−168.31821
energy relative to F	+54.7	+46.5	+59.9
dipole moment (Debye)	1.6247	1.0311	0.8000
bond lengths (Å)			
NC_1	1.219	1.316	1.240
C_1C_2	1.458	1.576	1.811
C_2C_3	1.296	1.338	1.300
NC_2	1.725	1.377	1.534
C_1C_3		1.942	1.820
bond angles (degree)			
NC_1C_2	79.7	56.0	56.7
$C_1C_2C_3$	167.5	83.1	69.4
C_1C_2N	44.0	52.4	42.5
C_2NC_1	56.2	71.6	80.8
C_3C_2N	130.7	135.5	112.0
$C_1C_3C_2$		53.7	68.7
$C_2C_1C_3$		43.2	41.8
NC_1C_3		99.2	98.6
dihedral angle (degree)			
$NC_1C_2C_3$	−70.8	180.0	180.0
$C_1NC_2C_3$	164.4		
$NC_2C_1C_3$		180.0	180.0

[a] Level of theory: geometries, B3LYP/6-31+G(d); energies, CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d). Relative energies in kcal mol^{-1} with respect to *F* (0 kcal mol^{-1}).

2. CCCN rearranges to CCNC via rhombic C_3N (+41.6 kcal mol^{-1}) over a barrier of 54.7 kcal mol^{-1}. The partially scrambled neutral CCCN/CCNC system loses C. This loss of C is most favorable from CCNC [C + CNC (+115.6 kcal mol^{-1}); C + CCN (+117.6 kcal mol^{-1}).

3. Energized CCCO undergoes fragmentation to yield CC and CO (+79.8 kcal mol^{-1}) without scrambling of the skeleton. Theoretically, rearrangement through a rhomboid C_3O transition state requires an excess energy of +114.5 kcal mol^{-1}.[3]

4. CCCS undergoes minor fragmentation by loss of S (+144.6 kcal mol^{-1}) during the $^-NR^+$ time frame of a microsecond. Theoretically, the rearrangement of CCCS to an intermediate rhomboid C_3S is endothermic (+51.6 kcal mol^{-1}) with a barrier of 80.3 kcal mol^{-1}. No appropriate neutral fragmentation occurs which can be used as a probe to test for this rearrangement in the neutral.[3]

This concludes our investigations of interstellar neutrals, CCCX (X = C, N, O and S).

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Supporting Information Available: Geometries and energies of the triplet forms of three $[C_3N]^-$ isomers; energies and geometries of minima and transition states for the rearrangement of linear CCCN to CCNC at the B3LYP/6-311G(d,p) level of theory and the reaction coordinate for this rearrangement; energies for processes involving losses of CC and CN. This material is available free of charge via the Internet at http://pubs.acs.org.

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(64) We have repeated some calculations reported previously, namely, (i) CCCN is confirmed as linear at the MP2/6−311G(d,p) level of theory,[33] but (ii) at the B3LYP/6−311G(d) level of theory we find two minima, a stable linear structure (as reported),[27] and a bent structure (C_1C_2 1.263 Å; C_2C_3 1.353 Å; C_3N 1.167 Å: $C_1C_2C_3$ 162.1°, C_2C_3N 178.5°; dihedral angle 180°). The bent structure is the more stable by 6.5 kcal mol^{-1} [B3LYP/6−311G(d)] and 6.9 kcal mol^{-1} [CCSD(T)aug-cc-pVDZ//B3LYP/6−311G(d)]. CCCN is also bent (there is no stable linear form) at the B3LYP/6−311+G(d) level of theory (C_1C_2 1.266 Å; C_2C_3 1.351 Å; C_3N 1.167 Å; $C_1C_2C_3$ 162.9º; C_2C_3N 178.4°; dihedral angle 180°).