Dimer Cations of Cyanoacetylene: Theoretical Isomers and Their Laboratory Production in the Absence and Presence of $C_{60}{}^{2+}$. Implications for Interstellar/Circumstellar Chemistry

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Cyanoacetylene dimer cations, $(HC_3N)_2{}^+$, were produced in a selected-ion flow tube in helium buffer at 0.35 $\pm$ 0.1 Torr and 294 $\pm$ 3 K either directly by the association of HC_3N^+ with HC_3N or indirectly in a sequence of reactions of $C_{60}{}^{2+}$ with two molecules of HC_3N. Two distinctly different isomers were identified by multiple collision-induced dissociation. The structures and energies of nine isomers of $(HC_3N)_2{}^+$ were computed at the B3LYP/6-31+G(d) and B3LYP/6-311++G(2df,p) levels together with selected energies of dissociation. A comparison of the latter with observed dissociation pathways and onset energies indicates that the $(HC_3N)_2{}^+$ formed directly is a solvated ion and that the $(HC_3N)_2{}^+$ produced in the presence of $C_{60}{}^{2+}$ is a cyclic dicyanocyclobutadiene cation. A mechanism is proposed for the formation of the cyclic isomer that involves a 2 + 2 cycloaddition of HC_3N to the charged terminus of a cyanoacetylene molecule anchored to C_{60} through a C–N bond. The results point toward a general gas-phase reaction route for the cyclization of cyanoacetylenes in the presence of doubly charged substrates and have implications for the dimerization of HC_3N and higher members of the homologous series of cyanopolyacetylenes in interstellar/circumstellar environments.

Introduction

The homologous cyanoacetylene molecules, $H(C{\equiv}C)_nCN$, with n up to 5, although not found naturally on earth, have been identified by radioastronomers to be present in various interstellar molecular clouds and in the envelopes of certain stars.[1] Various sources of radiant energy in these regions lead to the ionization of these molecules and so to chemistry initiated by $H(C{\equiv}C)_nCN^+$. Our early experimental studies of the chemistry initiated by the lowest member, $H-C{\equiv}C-CN^+$, showed that at least two molecules of cyanoacetylene add sequentially to HC_3N^+ in a helium bath at 0.341 Torr and 297 K by, what is expected to be, collisional-stabilized association, reaction 1.[2]

$$HC_3N(HC_3N)_n{}^+ + HC_3N + He \rightarrow$$
$$HC_3N(HC_3N)_{n+1}{}^+ + He \quad (1)$$
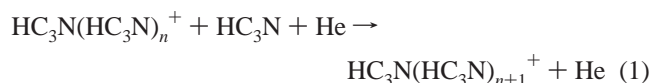
Similar association reactions have been reported to occur in an ion-cyclotron resonance (ICR) spectrometer for n up to 2 (at 10^{-6} Torr of cyanoacetylene) and in a high-pressure photoionization mass spectrometer for n up to 6 at a cyanoacetylene pressure of ca. 10^{-2} Torr.[3]

Results of experiments with $C_{60}{}^{2+}$ that are reported here suggest an unexpected alternate route for the formation of a dimer cation $(HC_3N)_2{}^+$ that itself appears *not* to add additional molecules of cyanoacetylene. Cyanoacetylene undergoes nucleophilic addition with $C_{60}{}^{2+}$ according to reaction 2. Reaction

$$C_{60}{}^{2+} + HC_3N + He \rightarrow C_{60}(HC_3N)^{2+} + He \quad (2)$$
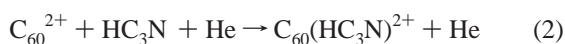
with a second molecule of cyanoacetylene produces charge-separated products according to reaction 3. One of these is a dimer cation of cyanoacetylene that exhibits a collision-induced

$$C_{60}(HC_3N)^{2+} + HC_3N \rightarrow C_{60}{}^+ + (HC_3N)_2{}^+ \quad (3)$$
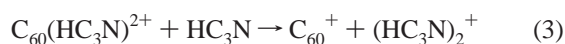
dissociation (CID) pattern completely different from that of the dimer cation produced in reaction 1. Apparently, distinctly different isomers of $(HC_3N)_2{}^+$ are produced in the *absence* and *presence* of $C_{60}{}^{2+}$. This remarkable result prompted us to investigate the potential energy surfaces of these isomers using ab initio molecular orbital calculations and so to provide insight into their energies, structures, and possible mechanisms of formation. Cyclic structures of $(HC_3N)_2{}^+$ appear to be particularly stable and this result has implications for the synthesis of cyclic neutral dimers of cyanoacetylene and higher members of the homologous series in the presence of doubly charged fullerene or related ions. Since mechanisms exist for the production of doubly charged fullerenes from neutral interstellar and circumstellar fullerenes,[4,5] reactions of type (3) may provide a route toward the formation of a variety of cyclic dimers of the cyanoacetylene family in these extraterrestrial environments.

Experimental Section

Experiments were performed with a selected-ion flow tube (SIFT) apparatus described previously.[6,7] The ions, $C_{60}{}^{2+}$ and $HC_3N^{\bullet+}$ were produced in a low-pressure ion source by electron-impact ionization of C_{60} vapor and HC_3N gas at electron energies between 60 and 100 and 25–45 eV, respectively. The cyanoacetylene was prepared from propiolic acid (98% Aldrich Chemical Co.) by converting the acid into an ester, and then into an amide and cyanide.[8]

In separate experiments the $C_{60}{}^{2+}$ and $HC_3N^{\bullet+}$ ions were selected and injected into helium buffer gas, thermalized by ca. 10^5 collisions with He atoms, and then allowed to react with cyanoacetylene added downstream. Rate coefficients were measured in the usual manner.[6,7] In separate experiments using 26% argon in helium as the buffer/collision gas the dimer ions produced by reactions 1 and 3 were subjected to multiple collision-induced dissociation just before entering the sampling nose cone.[9]
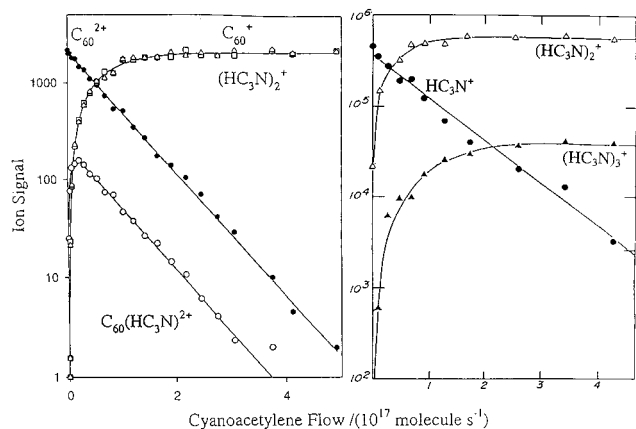
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Figure 1. (Left) Experimental data recorded for the reaction of C_{60}^{2+} with cyanoacetylene in helium buffer gas at 294 ± 3 K and 0.35 ± 0.01 Torr. Note that the product ion signal profiles for C_{60}^+ and $(HC_3N)_2^+$ overlap in intensity at all flows of cyanoacetylene. The C_{60}^{2+} ions were produced in a low-pressure ion source by electron impact ionization of C_{60} vapor at 80 eV. (Right) Experimental data recorded for the reaction of HC_3N^+ with cyanoacetylene in helium buffer gas at 298 K and 0.319 Torr.
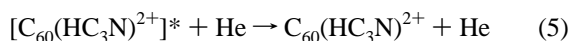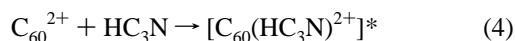
Theoretical Details

Standard ab initio molecular orbital calculations were carried out using the Gaussian 94 program.[10] Geometries were optimized using gradient techniques[11,12] at B3LYP[13-15] with a basis sets of 6-31+G(d) and 6-311++G(2df,p),[16-22] denoted B3LYP/6-31+G(d) and B3LYP/6-311++G(2df,p), respectively, for all ions studied. The optimized structures were characterized by harmonic frequency calculations, which showed them to be at minima; i.e., they have no imaginary frequencies. The frequency calculations also yielded both zero-point energies and the thermal corrections required to calculate the thermochemical properties at 298 K.

Results and Discussion

Experimental Results. Previously measured reaction profiles for the chemistry initiated by HC_3N^+ in HC_3N are shown in Figure 1.[2] The formation of the cyanoacetylene dimer cation, presumed to occur by collision-stabilized association, is very rapid and has a measured effective bimolecular rate coefficient $k = 1.2 \ (\pm 0.4) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.[2] Figure 1 also provides evidence for the slow formation of $(HC_3N)_3^+$ by the further reaction of $(HC_3N)_2^+$ with another HC_3N molecule.

The reaction profiles measured in this study for the chemistry initiated by C_{60}^{2+} in HC_3N are also shown in Figure 1. These profiles indicate that reactions 2 and 3 proceed in sequence and that both $C_{60}^{\bullet+}$ and $(HC_3N)_2^+$ do not react further with HC_3N, $k < 1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The effective bimolecular rate coefficient, k, for the primary addition reaction 2 is 7.3 $(\pm 2.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Reaction 2 presumably proceeds by collisional stabilization according to reactions 4 and 5. No electron transfer was observed to occur with HC_3N,

$$C_{60}^{2+} + HC_3N \rightarrow [C_{60}(HC_3N)^{2+}]^* \quad (4)$$

$$[C_{60}(HC_3N)^{2+}]^* + He \rightarrow C_{60}(HC_3N)^{2+} + He \quad (5)$$

as would be expected on the basis of the relative ionization energy of HC_3N (IE = 11.64 ± 0.01 eV)[23] and C_{60}^+ (IE = 11.39 ± 0.05 eV). IE (C_{60}^+) was deduced from a measurement of the appearance energy of C_{60}^{2+} obtained from direct double
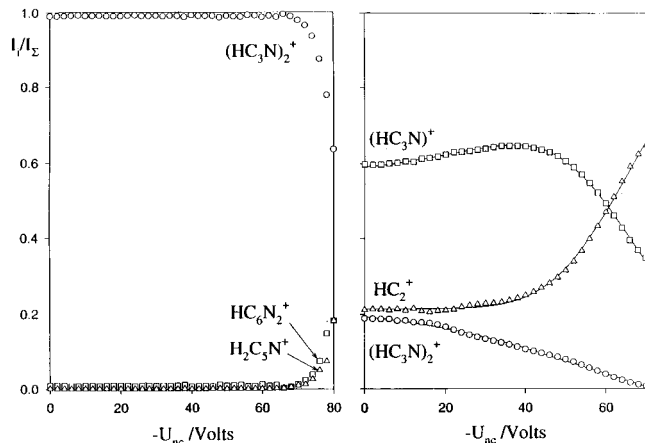

Figure 2. Results of multi-CID experiments of dimer formed in the presence of C_{60}^{2+} and a HC_3N flow of 5.0×10^{17} molecules s^{-1} (left) and the absence of C_{60}^{2+}, at a HC_3N flow of 1.0×10^{17} molecules s^{-1} (right). 26% argon in helium was used as the buffer/collision gas. (Left) The rise in $HC_6N_2^+$ corresponds to loss of H from the dimer cation, and the rise in $H_2C_5N^+$ corresponds to loss of CN.

ionization of C_{60} using synchroton radiation, AE(C_{60}^{2+}) = 19.00 ± 0.03 eV,[24] and IE(C_{60}) = 7.64 ± 0.02 eV.[25]

The secondary bimolecular reaction of $C_{60}(HC_3N)^{2+}$ with HC_3N results in charge separation, reaction 3, and occurs extremely rapidly, $k = 7.7 \ (\pm 2.6) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, essentially at the collision rate calculated according to the combined variational transition state theory−classical trajectory study of Su and Chesnavich,[26] $k = 7.7 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. Such a high rate is possible because of the large polarizability (5.32 Å^3, from bond and group polarizabilities)[27] and dipole moment ($\mu_D = 3.72$ D)[28] of cyanoacetylene. We have observed such charge-separation reactions previously for reactions between C_{60}^{3+} and other nitriles, RCN (where R = C_2H_3, C_2H_5, CH_2CN, and CN).[29]

The CID spectrum of the dimer cation formed from HC_3N^+ and HC_3N is shown in Figure 2. The $(HC_3N)_2^+$ fragments at very low nose-cone voltages to eliminate HC_3N, and the HC_3N^+ ion fragments further at higher voltages to eliminate CN according to reactions 6 and 7, respectively.

$$(HC_3N)_2^+ + He \rightarrow HC_3N^+ + HC_3N + He \quad (6)$$

$$HC_3N^+ + He \rightarrow HC_2^+ + CN + He \quad (7)$$
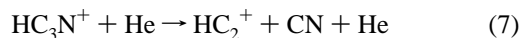
The CID spectrum of the dimer cation formed in the *presence* of C_{60}^{2+} is also shown in Figure 2. It looks completely different. $(HC_3N)_2^+$ begins to dissociate only at very high nose-cone voltages, greater than 70 V, and eliminates both H and CN according to reaction 8. Clearly, the $(HC_3N)_2^+$ ions formed in

$$(HC_3N)_2^+ + He \rightarrow HC_6N_2^+ + H + He \quad (8a)$$

$$\rightarrow H_2C_5N^+ + CN + He \quad (8b)$$
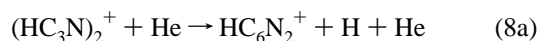
the absence and presence of C_{60}^{2+} are completely different.

Theoretical Results. Ab initio molecular-orbital calculations were directed toward an investigation of various possible isomers of the dimer cation $(HC_3N)_2^+$ and the energetics of their possible modes of dissociation with the hope of elucidating the nature of the two isomers identified experimentally. Two levels of theory were employed: B3LYP/6-31+G(d) and B3LYP/6-311++G(2df,p). Results of the calculations are summarized in Tables 1 and 2.

TABLE 1: Total Electronic Energies (in Hartrees), Unscaled Zero-Point Vibrational Energies and Thermal Energies (in kcal mol⁻¹) and Relative Energies (in kcal mol⁻¹)

	B3LYP/6-31+G(d)			relative energies at 298 K
structure	electronic energies	ZPE	thermal energies	
I	−338.859 18	37.3	4.4	0
II	−338.857 44	37.1	4.5	1.0
III	−338.847 78	36.2	5.0	6.7
IV	−338.789 34	35.4	5.4	42.9
V	−338.780 44	35.9	4.5	48.1
VI	−338.743 03	35.5	4.7	71.4
$HC_3N + HC_3N^{\bullet+}$	−338.748 05	33.2	4.9	66.1
HC_3N	−169.581 21	16.9	2.4	
$HC_3N^{\bullet+}$	−169.166 84	16.3	2.5	

**TABLE 2: Total Electronic Energies (in Hartrees) and Relative Energies (in kcal mol⁻¹) from Structure Optimizations**

	B3LYP/6-311++G(2fd,p)	
structure	electronic energies	relative energies at 298 K[a]
I	−338.932 41	0
II	−338.931 49	0.5
III	−338.926 04	3.5
IV	−338.870 70	37.8
V	−338.854 23	47.8
VI	−338.816 22	71.4
$HC_3N + HC_3N^{\bullet+}$	−338.829 36	61.4
HC_3N	−169.623 64	
$HC_3N^{\bullet+}$	−169.205 72	

[a] Using ZPE and thermal energies from B3LYP/6-31+G(d) calculations.

Structures with an Energy Minimum. The $(HC_3N)_2^+$ structures that have been optimized at B3LYP/6-31+G(d) and B3LYP/6-311++G(2df,p) are shown in Figure 3. The minima on the potential energy surface (PES) for $(HC_3N)_2^{\bullet+}$ are presented in Figure 4 for both levels of theory. The predicted bond lengths for the optimized geometries are slightly shorter with the larger basis set, but in general, the structures remain essentially unchanged from one basis set to the next. The relative order of stability of the dimer cations is the same at the two levels of theory, but the energy differences are slightly smaller at B3LYP/6-311++G(2df,p). The energy of the reactants $HC_3N + HC_3N^+$ is 64.7 kcal mol⁻¹ above the global minimum at B3LYP/6-311++G(2df,p). Two other dimer structures (not shown in Figure 3) were investigated at B3LYP/3-21G(d): an eight-membered heavy-atom ring is 150 kcal mol⁻¹ above structure **I** and a four-membered ring containing a nitrogen and three carbon atoms is 141 kcal mol⁻¹ above structure **I**. Both of these structures are very high in energy compared with those shown in Figure 3.

The ion at the global minimum is structure **I**, a π-radical containing a four-membered ring system with cyano groups cis to each other. The stability of this ion can be attributed to the extensive resonance charge delocalization that is possible over four ring-carbon atoms and a terminal nitrogen atom. The (H)C−C(CN) bond length of 1.391 Å is indicative of a bond intermediate between a double and a single bond and this is consistent with the extensive charge delocalization. The (NC)C−C(CN) bond of 1.542 Å is relatively long due in part to ligand−ligand repulsion between the cis CN groups. The trans-substituted cyclobutadienyl cation, structure **II**, is only slightly higher on the PES by 1.0 kcal mol⁻¹ at B3LYP/6-31+G(d) and
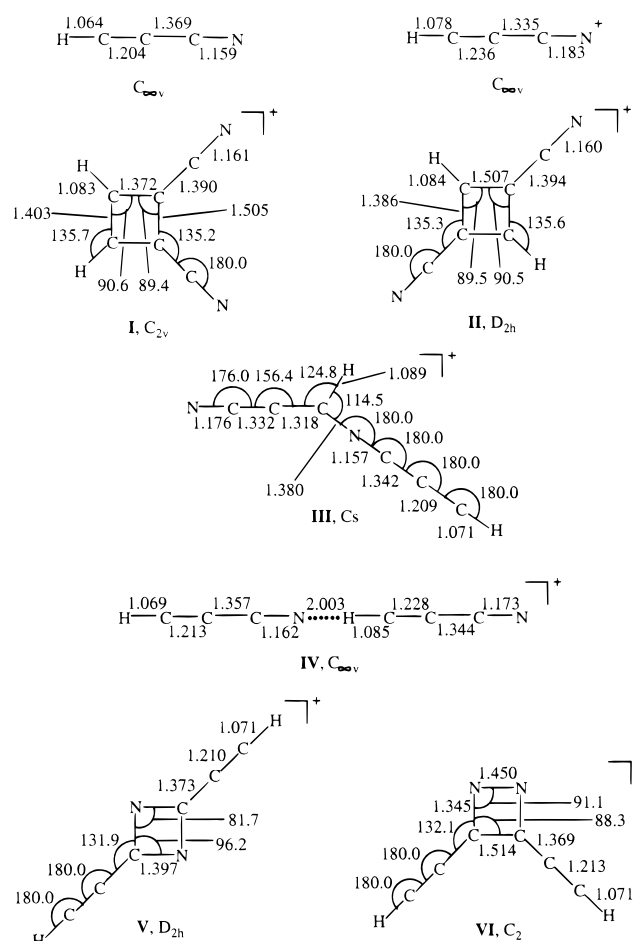
Figure 3. Structure optimizations at B3LYP/6-311++G(2df,p).

Isomers at Minima on the Potential Energy Surface for $(HC_3N)_2^+$
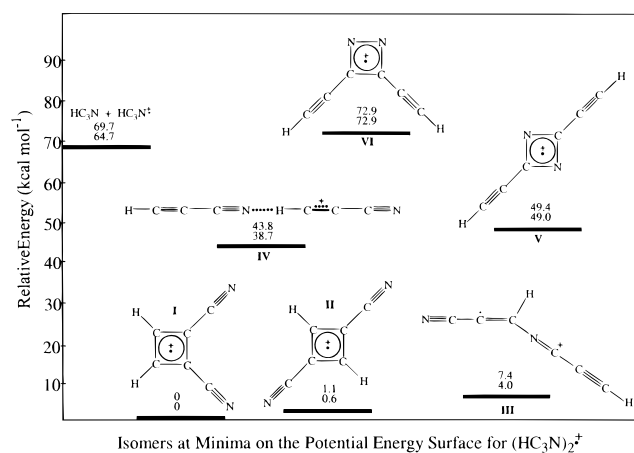
Figure 4. Calculated minima on the potential energy surface for $(HC_3N)_2^+$ at B3LYP/6-31+G(d) (top numbers) and B3LYP/6-311++G-(2df,p) (bottom numbers).

0.5 kcal mol⁻¹ at B3LYP/6-311++G(2df,p). Again, the positive charge can be delocalized over the heavy-atom centers in the dimer.

The lowest noncyclic dimer on the PES is structure **III**, only 6.7 kcal mol⁻¹ above the global minimum. Here the lone pair of electrons on the nitrogen in neutral cyanoacetylene attacks the "empty" p-orbital on the carbon in the cyanoacetylene cation and forms a dimer cation with the positive charge formally located on the nitrogen. A bonding pair of π-electrons can be moved onto the nitrogen carrying the positive charge, resulting in the charge being formally located on the adjacent carbon.

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The π-system of structure **III** also allows the dimer cation to delocalize the positive charge to the terminal carbon atom, and we attribute the stability of this ion to delocalization of the charge onto these three centers.

Structure **IV** is a weakly bound linear dimer of $(HC_3N)_2^+$ and is 42.9 kcal mol^{-1} above the global minimum on the B3LYP/6-31+G(d) PES (37.8 kcal mol^{-1} above the global minimum on the B3LYP/6-311++G(2df,p) PES). The geometrical parameters of structure **IV** resemble the individual monomers, HC_3N^+ and HC_3N with a long solvating N···H bond of 2.011 Å; viz., the (HC_3N^+)···(HC_3N) interaction leaves the fragment structures essentially unchanged.

Structures **V** and **VI** have four-membered rings containing nitrogen. Structure **V** is planar and delocalizes the positive charge over four carbon atoms and two nitrogen atoms in the dimer cation framework. Structure **VI** is slightly above the reactants $HC_3N^+ + HC_3N$ in energy but is at a minimum on the $(HC_3N)_2^{•+}$ PES at both levels probed. It has a puckered ring and only a 2-fold axis of rotation. Structure **VI** formed in
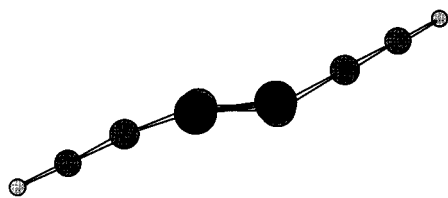
Structure **VI**, C$_2$

the gas phase is likely to dissociate into a stable N$_2$ molecule and a linear HC≡C−C≡C−C≡CH]$^+$ cation. The dissociation is exothermic by more than 50 kcal mol^{-1} at B3LYP/6-31+G-(d).

Dissociation Energies. The observation of dissociation (6) and the computed stability of structure **IV** suggest that structure **IV** can be assigned to the $(HC_3N)_2^+$ dimer cation produced in reaction 1. However, it is not possible to assign a structure to the $(HC_3N)_2^+$ isomer formed in reaction 3 only on the basis of the energies of the various isomers computed. The observation in the CID experiments of the dissociation (8) for this isomer to produce CN and H is consistent with an assignment of structure **I**, **II**, or **III**.

The energetics for the loss of CN$^+$, CN, and H were explored for each of the structures **I**, **II**, and **III** at B3LYP/6-31+G(d) and B3LYP/6-311++G(2df,p). The results are summarized in Tables 3−5. Both the singlet and triplet states of the daughter cations were investigated for the loss of H and CN. Homolytic cleavage of H and CN will lead to the triplet, which then can relax to the singlet through thermalizing collisions in the He bath gas. The endothermicity for CN$^+$ loss for each of the three structures is at least 130 kcal mol^{-1} higher than that for any other dissociation pathway at both levels of theory. The calculations also indicate that for both structures **I** and **II** the energy change associated with loss of H and CN is almost identical within 15 kcal mol^{-1}, just as is observed experimentally for the $(HC_3N)_2^+$ dimer cation formed in the presence of C_{60}^{2+}. In sharp contrast, the energy change associated with the lowest energy loss of H from structure **III** is 48 kcal mol^{-1} lower than the energy change associated with the loss CN. There are two possible sources for H loss in structure **III**, loss from a terminal C and loss from a central C. The latter, at 102.3 kcal mol^{-1}, has a lower-energy threshold since it forms a more stable ion. The 48 kcal mol^{-1} difference in dissociation energy between homolytic H loss and CN loss is not consistent with experi-

TABLE 3: Calculated Bond Energies at 298 K for Dissociations of the Parent Ion, Structure I, at B3LYP/6-31+G(d) and B3LYP/6-311++G(2df,p)

Dissociation Products	D_o^{298} (kcal mol^{-1})
	109.4 *96.4*
	119.9 *106.8*
	113.5 *104.6*
	127.4 *118.2*
	265.5 *257.2*

mental observations, and so structure **III** can be eliminated as a possible structure for the dimer cation formed in the presence of C_{60}^{2+}.

For each of the dissociations investigated, the puckered singlet state is energetically preferred over the planar triplet state by at least 10 kcal mol^{-1} at both B3LYP/6-31+G(d) and B3LYP/6-311++G(2df,p). Previous theoretical studies have determined that cyano groups can function either as a π-donor or as a π-acceptor depending upon the environment, although when it is adjacent to a cationic center it generally functions as a π-donor.[30] π-Donation from the cyano groups to the four-membered ring increases the π-population and, as the singlet is a 2π-homoaromatic system, this interaction destroys the aromaticity and is destabilizing. In the case of the triplet, any increase over the 3π-electrons that are formally in the ring is also potentially destabilizing, as it makes the system closer to having a 4π-antiaromatic occupancy. The fact that substitution by CN favors the singlet relative to the triplet indicates that this destabilization is smaller in the singlet than in the triplet.

Formation of Dimer Cations. Formation of the dimer cation in reaction 1 may be viewed as a weak interaction between the lone pair of electrons on the nitrogen of a solvating cyanoacetylene molecule and the positive end of the cyanoacetylene cation. Our experimental data suggest the occurrence of a second solvation reaction under SIFT conditions.

Possible mechanisms for the formation of dimer cations with structures **I**, **II**, and **III** in the sequential reaction of two cyanoacetylene molecules to C_{60}^{2+} are shown in Figure 5. The first adduct, $C_{60}(HC_3N)^{2+}$, is formed by nucleophilic attack of C_{60}^{2+} by the lone pair of electrons on the nitrogen of the incoming HC$_3$N molecule. Upon C−N covalent-bond formation

TABLE 4: Calculated Bond Energies at 298 K for Dissociations of the Parent Ion, Structure II, at B3LYP/6-31+G(d) and B3LYP/6-311++G(2df,p)

Dissociation Products	D_o^{298} (kcal mol^{-1})
H$^\bullet$ + [singlet cyclobutadiene cation, CN, NC substituents, H]	107.7 / *95.1*
H$^\bullet$ + [triplet cyclobutadiene cation, CN, NC substituents, H]	118.4 / *104.9*
CN$^\bullet$ + [singlet cyclobutadiene cation, CN, H substituents, H]	111.6 / *103.3*
CN$^\bullet$ + [triplet cyclobutadiene cation, CN, H substituents, H]	128.5 / *119.8*
CN$^+$ + [cyclobutadiene, CN, H substituents, H]	269.2 / *261.6*

TABLE 5: Calculated Bond Energies at 298 K for Dissociations of the Parent Ion, Structure III, at B3LYP/6-31+G(d) and B3LYP/6-311++G(2df,p)^a

| Dissociation Products	D_o^{298} (kcal mol^{-1})
H$^\bullet$ + NC—C≡C—N$^+$≡CC$_2$H (singlet)	52.5 / ---
H$^\bullet$ + NC—$\overset{\bullet}{C}$=$\overset{\bullet}{C}$—N$^+$≡CC$_2$H (triplet)	102.3 / ---
H$^\bullet$ + NC—$\overset{\bullet}{C}$=C(H)—N$^+$=C$_2$C: (singlet)	143.5 / *131.4*
H$^\bullet$ + NC—$\overset{\bullet}{C}$=C(H)—N$^+$=C$_2$C$^\bullet$ (triplet)	134.8 / *122.0*
CN$^\bullet$ + :C=C(H)—N$^+$=CC$_2$H (singlet)	118.2 / *108.9*
CN$^\bullet$ + $^\bullet\overset{\bullet}{C}$=C(H)—N$^+$=CC$_2$H (triplet)	150.3 / *141.2*
CN$^+$ + :C=C(H)—N=$\overset{\bullet\bullet}{C}C_2$H	301.3 / *292.6*

^{a} The energy quoted is obtained from a single-point calculation at B3LYP/6-31+G(d) with geometry and frequency calculations performed at B3LYP/DZVP. The lower channel to H loss is an upper limit because of convergence problems in the calculations and should be accurate to within 2 kcal mol^{-1}.

this charge becomes delocalized through the π-system; one of the resonance structures localizes the charge on the terminal carbon of the cyanoacetylene ligand. This latter resonance structure may be preferred because of Coulomb repulsion between the terminal charge and the charge remaining on the C$_{60}$. Figure 5 shows two plausible pathways by which the second nucleophilic attack of HC$_3$N can lead to dimer formation. Pathway **A** leads to the formation of the open-chain dimer of (HC$_3$N)$_2^{\bullet+}$, structure **III**. In this pathway the second cyanoacetylene attacks through the lone pair on the nitrogen at the terminal carbon of the ligand, resulting in the positive charge being formally transferred to the *attacking* nitrogen. Subsequent homolytic bond cleavage of the C$_{60}$–nitrogen bond then results in the formation of the charge-separated product ions. Pathway **B** involves a 2 + 2 cycloaddition and a similar cleavage as in pathway **A**, producing C$_{60}^{\bullet+}$ and a cyclic dimer, structure **II**, upon homolytic bond cleavage of the C$_{60}$–nitrogen bond. The π-system of the second cyanoacetylene must be coplanar with the π-system of the coordinated cyanoacetylene to follow this pathway. There are two possible alignments, cis and trans; calculations indicate that these have almost identical energies. The trans isomer has been selected arbitrarily in Figure 5. The CID results indicate that path **B** is preferred under SIFT conditions. It is also interesting to note that the dicyanocyclobutadiene cation formed in the homolytic bond cleavage at the fullerene surface does not add another cyanoacetylene molecule, as was the case for the dimer cation produced in reaction 1.

The C$_{60}^{2+}$ cation has a number of attributes that favor the 2 + 2 cycloaddition mechanism shown in Figure 5. The C$_{60}$ surface provides atomic sites suitable for covalent bonding. The initial C–N bond formation at the C$_{60}$ surface is favored by

the double charge on C$_{60}^{2+}$ and the high dipole moment of the approaching HC$_3$N nucleophile (3.72 D),[15] which leads to a strong electrostatic interaction sufficient to overcome any barrier associated with the rehybridization of the C atom on the C$_{60}$ surface required for bonding. The covalent C–N bond results from electron-pair donation to a localized positive charge site on the C$_{60}$ surface at close internuclear separations. Coulombic repulsion between the remaining charge on C$_{60}$ and the charge transferred to the substituent favors charge localization at the terminus of the anchored HC$_3$N nucleophile that then becomes the favored site of attack by the second incoming HC$_3$N molecule.

Implications for Interstellar/Circumstellar Chemistry. Several mechanisms are available for the double ionization of C$_{60}$ in interstellar and circumstellar environments.[4,5] These include sequential photoionization, direct double ionization with cosmic rays, and an electron transfer/electron detachment reaction with He$^+$ ions. The observations and calculations with cyanoacetylene reported here suggest the possible transformation of *any two* members of the homologous series of cyanopolyacetylenes into derivatized cyclobutadiene cations in the presence of C$_{60}^{2+}$ in two sequential reactions according to the overall reaction 9.

$$C_{60}^{2+} + 2H(C_2)_nCN \rightarrow C_{60}^+ + c\text{-}C_4H_2((C_2)_{n-1}CN)_2^+ \quad (9)$$
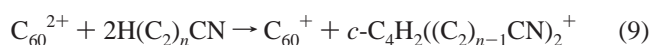
An analogous role can be conceived, reaction 10, for related doubly charged PAH cations that are thought to be formed in

Dimer Cations of Cyanoacetylene
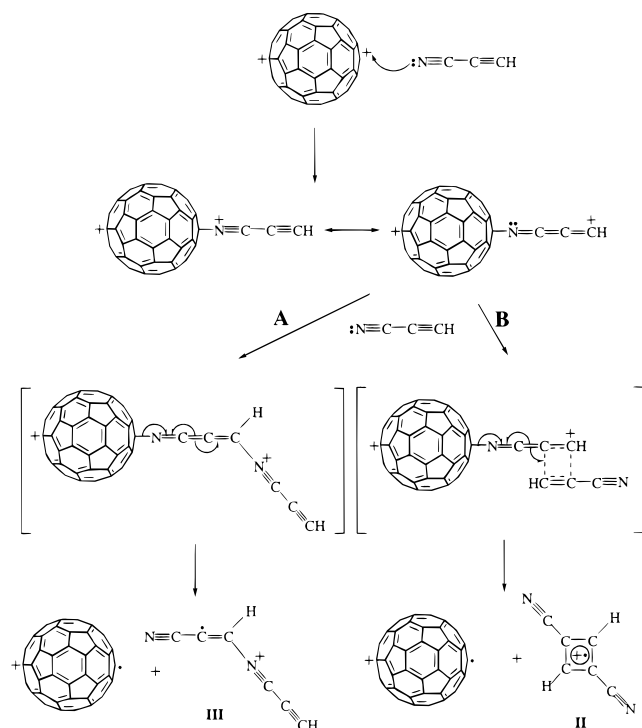
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Figure 5. Possible pathways to the formation of structures **II** and **III** in the presence of C_{60}^{2+}.

$$PAH^{2+} + 2H(C_2)_nCN \rightarrow$$
$$PAH^+ + c\text{-}C_4H_2((C_2)_{n-1}CN)_2^+ \quad (10)$$

a manner similar to the formation of C_{60}^{2+} in interstellar and circumstellar environments.[31,32] Indeed, any doubly charged substrate capable of bonding to the N-atom terminus in the cyanopolyacetylene molecule should allow a similar transformation according to reaction 11.

$$X^{2+} + 2H(C_2)_nCN \rightarrow X^+ + c\text{-}C_4H_2((C_2)_{n-1}CN)_2^+ \quad (11)$$
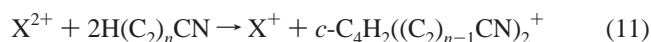
Neutralization of the $c\text{-}C_4H_2((C_2)_{n-1}CN)_2^+$ product ions of reactions 9−11 by electron transfer from a species of low ionization energy such as metal atoms or by radiative recombination with electrons, for example, would then finally establish the derivatized neutral cyclobutadiene. At B3LYP/6-31+G(d), our calculations indicate an ionization energy for structure **I** of 8.83 eV. The synthesis overall results in the transformation of two cyanopolyacetylene molecules into a derivatized cyclobutadiene in the presence of a doubly charged molecule or molecular cluster and an available electron.

Conclusions

Experiments have shown that distinctly different isomers of the dimer $(HC_3N)_2^+$ cation can be generated in the gas phase in the *absence* and *presence* of C_{60}^{2+}. Observed CID spectra, together with computed dissociation energies, indicate a solvated-ion structure and a derivatized cyclic butadiene structure for the two $(HC_3N)_2^+$ dimers, repectively. Fomation of the derivatized cyclic butadiene cation can be attributed to the ability of C_{60}^{2+} to provide a chemical *anchor* for the first cyanoacetylene molecule. Coulombic repulsion then acts to localize one of the charges on the terminus of the cyanoacetylene substituent and promotes a 2 + 2 cycloaddition with a second incoming

cyanoacetylene molecule. This mechanism provides a general means to convert two acyclic cyanides into a cyclic cyanide. Such conversions ought to be possible in interstellar/circumstellar environments containing cyanopolyacetylenes and doubly charged molecular species capable of N-bonding. The resulting cyclic cation can then be neutralized by electron transfer or radiative recombination with electrons.

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