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Photochemical Synthesis of the Cyanodiacetylene HC_5N: A Cryogenic Matrix Experiment

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The reactivity of intermolecular complexes cyanoacetylene:acetylene and dicyanoacetylene:acetylene, trapped in solid argon matrixes at 10 K and irradiated with vacuum UV, has been studied. FTIR measurements, together with ^2H, ^{15}N, ^{13}C labeling experiments and with density functional theory (DFT) calculations (B3LYP/aug-cc-pVTZ), pointed to the formation of cyanodiacetylene HC_5N (cyanobutadiyne). This synthetic route is potentially important for chemical models of the Titan's atmosphere.

Introduction

Ever since its first detection[1] 3 decades ago in the molecular cloud Sagittarius B2, cyanodiacetylene HC_5N has become increasingly interesting as an astrochemical object. To date, the presence of this compound has been reported in about 20 interstellar sources. Likewise, the isotopomeric (^2H- and ^{13}C-bearing) species[2,3] have been detected in space.

The interest in cyanopolyynes stems primarily from their current status of the heaviest unambiguously identified gaseous components of the interstellar medium. Such very long rod-shaped species are also very interesting from the purely spectroscopic point of view. With regard to the Titan's atmosphere, the possible importance of cyanodiacetylene was suggested by Coll et al.[4] following the detection of this compound in irradiated CH_4/N_2 mixtures. Winnewisser et al.[5−7] produced HC_5N, treating the mixture of C_2H_2 and HCN (or C_2H_2 and acrylonitrile, CH_2CHN) with radiofrequency discharges. Alexander et al.[8] and Bizzocchi et al.[9] found laboratory routes to macroscopic samples of HC_5N. Very recently, Guillemin et al.[10] reported on the elegant, reproducible and highly efficient preparative organic synthesis of cyanodiacetylene, which led to large quantities of the pure compound, and opened up the way to missing spectroscopic investigations. Following this synthesis, Bénilan et al.[11] measured frequencies and absolute intensities of both IR and vaccum-UV absorption bands in broad frequency ranges. Prior to the latter work, microwave rotational spectra of HC_5N were analyzed in detail, and high-resolution measurements of ν_2 and ν_7 vibrational bands were reported.[8,12,13] More recently, Degli Esposti et al.[14] extended the study of millimeter range HC_5N spectra to 15 excited vibrational states. Apart from the experimental work, advanced theory was indispensable[9,13,15] to predict the HC_5N geometry together with spectroscopic parameters such as rotational constants and anharmonic vibrational frequencies.

The dominant mechanism for the cyanopolyynes formation in space most probably involves the collisions of electrically neutral radicals with closed-shell molecules. This was shown in recent kinetic models[16] and was demonstrated by Balucani et al.[17] in a crossed molecular beam experiment, which consisted of the cyanoacetylene production out of acetylene and ground-state cyano radicals $CN^\bullet$.

Highly unsaturated linear molecules HC_3N (**1**),[18] C_4N_2 (**2**),[19] and C_2H_2 (**3**)[20] were found in Titan's atmosphere. This moon is submitted to UV photons, solar wind, and cosmic rays, which give rise to the rich photochemistry and radiation chemistry. Numerous experiments on the photolysis of C_2H_2[21] are reported in the literature. Lauter et al.[21c] studied the dissociation dynamics of acetylene irradiated at 193.3 nm and at 121.6 nm (Lyman-α) under collision-free conditions; both wavelengths led to the formation of H atoms along with $C_2H^\bullet$ radicals. For HC_3N and C_4N_2, literature data suggest gas-phase reactions $HC_3N \rightarrow H^\bullet + C_3N^\bullet$ and $C_4N_2 \rightarrow CN^\bullet + C_3N^\bullet$ as major UV photolysis channels.[22] UV irradiations of HC_3N in Ar matrixes yielded three isomers:[23,24] HC_2NC, HNC_3, C_2NCH. Similar experiments with C_4N_2[22,25] resulted in the formation of isomeric species NC_3-NC, CNC_2NC and C_3NCN. In matrix experiments involving **1** we found the wavelength range $\lambda > 180$ nm to be much less photochemically effective than $\lambda > 120$ nm[22] (consistent with the respective UV absorption spectrum[26]). For both **1** and **2**, the main process at $\lambda > 180$ nm, as inferred from the preferential formation of isonitriles, was the breaking of a C−CN bond (leading to isonitriles). In addition to the isonitrile HC_2NC, the imine HNC_3 was abundantly produced from **1** at $\lambda > 120$ nm.

Our recent study[27] demonstrated that the cryogenic co-deposition of **3** with **1** or with **2** induced the formation of respective complexes **1**:**3** or **2**:**3**. The measured vibrational frequency differences between separated and complexed molecules pointed, when compared with the results of theoretical calculations, to linear structures of both **1**:**3** and **2**:**3**. In addition to these $C_{\infty v}$ species, characterized by a hydrogen bond between the cyano group nitrogen and one of the hydrogens of **3**, a T-shaped **1**:**3** complex was predicted, in which the hydrogen of cyanoacetylene interacted with the π-electronic system of acetylene. Energies of the linear complex **1**:**3** and of the T-shaped one were (at the applied B3LYP/6-31G** theory level) identical within 0.1 kJ/mol. Indeed, matrix-isolation measurements showed the coexistence of both structures.

Here we report on a new way of cyanodiacetylene synthesis, which consists of the UV irradiation of molecular complexes

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1:**3** and **2**:**3**. The goal was to show a chemical route of potential importance for the formation of cyanopolyynes in the atmosphere of Titan, the extensively studied Saturn's moon.

^{13}C-, ^{15}N-, and ^{2}H-isotopic versions of reactants were used along with those of natural isotopic contents, and the assignment of products was possible via vibrational spectroscopy. Although the results of state-of-the-art quantum chemical calculations[9,13,15] are available for HC_5N, we were obliged to obtain a uniform set of predictions for all isotopomers under study; this has been carried out at the density functional theory (DFT) level.

Experimental Details

Pure cyanoacetylene **1** and dicyanoacetylene **2** were synthesized using slightly modified procedures of Moureu and Bongrand,[28,29] starting from methyl propiolate and dimethyl acetylenedicarboxylate, respectively. The ^{15}N-cyanoacetylene **1^{15}N** was prepared by the introduction of ^{15}N-enriched ammonia (Cambridge Isotope laboratories, 98%) at the appropriate stage of the synthesis. All cyanoacetylene compounds were distilled in vacuo prior to each experiment.

Pure acetylene (**3**), acetylene-d_2 (**3D**), and acetylene-$^{13}C_2$ (**3^{13}C**) were supplied by Air Liquide (purity $\geq$ 99.6%), CDN Isotop (purity 99.6%), and Sigma-Aldrich Chimie (99%), respectively, and were used without further purification.

Matrix Isolation Experiments. The details of apparatus and experimental techniques used to obtain argon matrixes in our laboratory have already been described.[30] Gas mixtures were prepared using standard manometric techniques at the following ratios: **1**/**3**/Ar (2/1/750), **1**/**3D**/Ar (2/1/750), **1^{15}N**/**3**/Ar (2/1/750), **2**/**3**/Ar (2/1/500), **2**/**3D**/Ar (2/1/500), **2**/**3^{13}C**/Ar (2/1/500). Such concentrations guaranteed a sizable formation of molecular complexes.

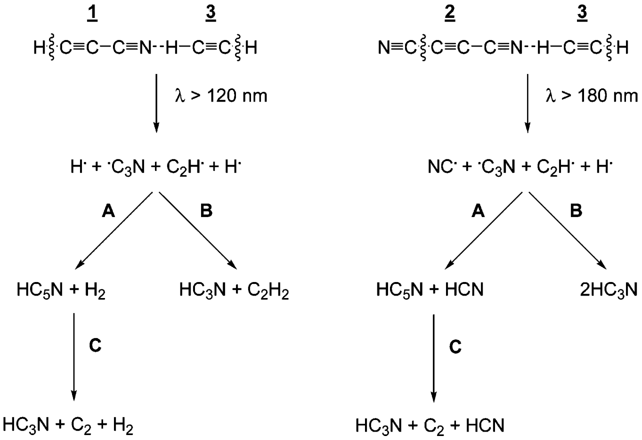
Gas mixtures were sprayed onto a highly polished gold-platted copper surface cooled to 20 K within a closed-cycle helium cryostat (CTI-Cryophysics). A Fourier transform IR spectrometer (Nicolet series II Magna system 750) was used to record the spectra in the range 4000−650 cm^{-1}, with a resolution of 0.125 cm^{-1}.

Irradiation Techniques. All cryogenic samples were irradiated using a microwave discharge H_2 lamp (Opthos Instruments), which simulated the interstellar radiation field and was adapted directly onto the sample chamber. The spectral flux of the lamp (operated with a steady flow of hydrogen, at 0.9 mbar) was confined in the range 3−10 eV, being dominated by two bands centered on 120 and 160 nm, approximately.[31]

Two types of VUV broad-band irradiations were employed, depending on photolyzed compounds. The flux of the lamp was transmitted either through an MgF_2 window ($\lambda > 120$ nm) or through the quartz window ($\lambda > 180$ nm), for samples involving cyanoacetylene and dicyanoacetylene, respectively.

Details of Calculations. Quantum chemical calculations were carried out with Gaussian 03 Rev. C.02 suite of programs.[32] The equilibrium structure of HC_5N and the corresponding harmonic frequencies of molecular vibrations (as given by analytical second derivatives of the total energy, with respect to nuclear positions) were predicted using the density functional theory (DFT)[33] with the B3LYP hybrid exchange-correlation functional,[34] the correlation-consistent polarized valence triple-ζ basis set augmented by s, p, d, and f functions (aug-cc-pVTZ),[35] and standard convergence criteria. Vibrational frequencies were scaled down with a uniform factor of 0.96 to partly account for the anharmonicity, incomplete inclusion of electron correlation effects or deficiencies in the applied basis set. Published values of B3LYP scaling factors for stretching modes are close to 0.96 (see for example the work of Scott and Radom,[36] of Palflox,[37] or the extensive comparative studies by Halls et al.[38]). The adequacy of this scaling factor was also verified (e.g., by Kolos and Sobolewski[24b]) for unsaturated carbon−nitrogen chains.

SCHEME 1: Proposed Routes for the Photolysis of Ar Matrix-Isolated Complexes 1:3 and 2:3



Results

Our IR spectra of co-deposited **1**(**1^{15}N**)/**3**(**3D**) or **2**/**3**(**3D**)-(**3^{13}C**), measured in Ar matrixes at 10 K, show the presence of isolated molecules **1**,[39] **2**[40] and **3**[41] (or their isotopomers) along with corresponding molecular complexes. All these species could undergo the photolysis when subjected to VUV irradiations. The knowledge of photoproducts[22−24] arising from decompositions of **1**, **2**, and **3** suggested the recombination of $C_2H^{\bullet}$ and $C_3N^{\bullet}$ radicals (previously created within complexes) as the most probable channel for the formation of HC_5N (**4**). Both wavelength ranges, $\lambda > 120$ nm and $\lambda > 180$ nm, could be used to produce $C_2H^{\bullet}$ from **3**. However, as pointed out in the Introduction, the yield of $C_3N^{\bullet}$ production from **1** is expected to be higher with $\lambda > 120$ nm. Generally, $\lambda > 120$ nm radiation proved more effective than $\lambda > 180$ nm in the photolysis of both **1** and **2**. On the other hand, recent experiments on the photoreactivity of complex **2:3**[42] gave evidence for yet another process at $\lambda > 120$ nm, competitive to the creation of HC_5N, namely the recombination of $C_3N^{\bullet}$ radicals into dicyanodiacetylene NC_6N (followed by an isomerization of the latter compound). For that reason, photolysis experiments presented here were accomplished at wavelength ranges $\lambda > 120$ nm and $\lambda > 180$ nm, for complexes **1**:**3** and **2**:**3**, respectively (Scheme 1).

Irradiation of 1:3 at $\lambda > 120$ nm. During the irradiation of **1**/**3**/Ar matrixes at $\lambda > 120$ nm, IR bands due to **1**, **3** and **1**:**3** complexes decreased in intensity. This was accompanied by the build-up of new spectral features, most of which resulted from the photolysis of separated molecules **1** and **3**. Specifically, cyanoacetylene yielded its three higher energy isomers (HNC_3, HC_2NC, $HCNC_2$),[23,24] together with species CN^-,[23,43] $CN^{\bullet}$,[44] and possibly C_3N^-.[23] Acetylene decomposition led to the formation of C_4H_2,[45] $C_4H^{\bullet}$,[46] C_4[47] and $C_2H^{\bullet}$.[45a−c,48]

Difference spectra (after − before photolysis; Figure 1) depict the photolysis effects found in samples **1**/Ar, **1**/**3**/Ar, and **3**/Ar. Only two bands appeared during the irradiations of **1**/**3**/Ar, which were present neither in photolyzed **1**/Ar nor in **3**/Ar. These bands, originating most likely from the photolyzed **1**:**3** complex, appeared at frequencies 2248.5 and 2186.5 cm^{-1} and displayed the same evolution during irradiations. We attributed them, correspondingly, to ν_2 and ν_3 modes of HC_5N **4**, on the basis of the study by Haas et al.,[12] who measured the wavenumbers 2256.1 and 2188 cm^{-1} in the gas phase.

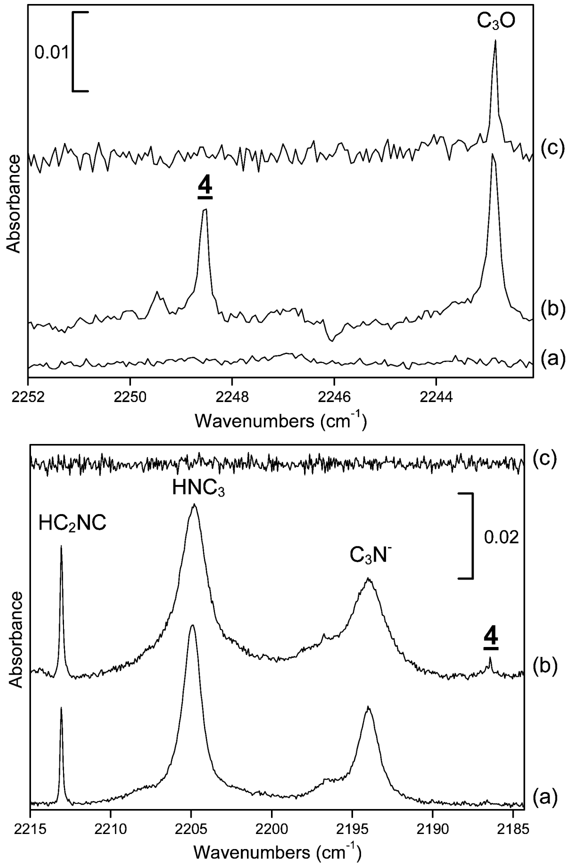


Figure 1. FTIR difference spectra (after-before photolysis) showing the creation of photoproducts at $\lambda > 120$ nm: (a) **1**/Ar matrix, 17 h of irradiation; (b) **1**/**3**/Ar, 21 h; (c) **3**/Ar, 35 h. C_3O originates from dioxygen, present in the matrix as an impurity.

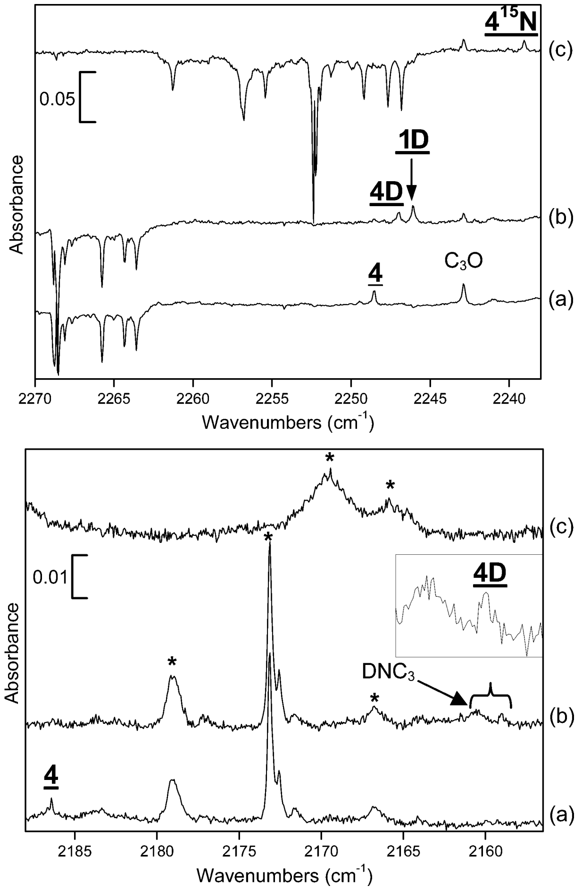


Figure 2. FTIR difference spectra (after-before photolysis) showing the product bands arising in Ar matrixes following the photodecomposition of **1:3** complexes (and of their isotopic modifications) at $\lambda >$ 120 nm: (a) **1:3** complexes, 21 h of irradiation; (b) **1**:**3D**, 26 h; (c) $\mathbf{1^{15}N}$:**3**, 27 h. Asterisked bands, resulting from the photolysis of uncomplexed molecules, are not attributed.

Further studies were done to confirm the identification of **4**. First, we replaced cyanoacetylene with dicyanoacetylene (see below). Second, we carried out the isotopic substitution experiments, starting with deuterated acetylene, D_2C_2 (**3D**). A **1**/**3D**/Ar matrix was irradiated at $\lambda > 120$ nm. Spectral features recognized as due to DC_5N (**4D**) indeed appeared (in addition to those resulting from the photolysis of separated **1** and **3D** molecules), but we could also see the emergence of yet another product, DC_3N (**1D**), with bands at 2600.8, 2246.1 and 1964.6 cm^{-1} (representing C−D, C≡N, and C≡C stretching modes,[49] respectively). This important reaction route, indicated by the presence of **1D**, was too difficult to detect in **1**/**3**/Ar experiments, where the corresponding product, **1**, was identical with one of the reactants.

Available CCSD(T) predictions[15] (and DFT results listed in Table 1) permitted us to identify as many as 4 fundamental bands due to **4D**: 2588.8, 2247.0, 2159.0 and 1950.5 cm^{-1} (Figure 2). The ν_1 (C−D stretch) of DC_5N was easily identified, being not (unlike the corresponding HC_5N band) masked by a very strong ν_1 feature of the parent **1**. Furthermore, the appearance of the fourth mode of **4D** (not detected in **4**) matched the CCSD(T) result, according to which the IR intensity of ν_4 should be ca. 100 times higher in **4D** than it was in **4** (at our DFT level, this intensity increase was 50-fold). The H-to-D isotopic shifts of ν_2 and ν_3 cyanodiacetylene bands, supplied by **1**/**3**/Ar and **1**/**3D**/Ar experiments, are in reasonable agreement with CCSD(T) predictions[15] involving the harmonic approximation, and with our DFT results.

The second isotopic experiment engaged ^{15}N-labeled cyanoacetylene. Irradiations of the $\mathbf{1^{15}N}$/**3**/Ar sample produced, in addition to the usual evidence for the photolysis of separated monomers, only one absorption band, at 2239.0 cm^{-1} (Figure 2). On the basis of the ^{14}N-to-^{15}N frequency shift, which agreed with the theoretical value (Table 2), the band was easily assigned

TABLE 1: Vibrational Frequencies (cm^{-1}) for HC_5N and DC_5N, As Measured Following the Photolysis of 1:3(3D) and 2:3(3D) Complexes in Ar Matrixes, and Compared to DFT Values (Harmonic, Downscaled by 0.96)[a]

	experiment			theory B3LYP aug-cc-pVTZ[d]				
	HC_5N	DC_5N		HC_5N		DC_5N		
modes	ν_H (cm^{-1})	ν_D (cm^{-1})	$\nu_H - \nu_D$	ν_H (cm^{-1})	I	ν_D (cm^{-1})	I	$\nu_H - \nu_D$
ν_1	3317.3[c]	2588.8[b]/2589.3[c]	**728.0**[c]	3320.9	120	2581.6	52	**739.3**
ν_2	2248.5[b]/2249.7[c]	2247.0[b]/2248.3[c]	**1.5**[b]/**1.4**[c]	2255.2	98	2254.9	100	**0.3**
ν_3	2186.5[b]/2186.5[c]	2159.0[b]/2159.0[c]	**27.5**[b]/**27.5**[c]	2191.9	2	2169.3	5	**22.6**
ν_4		1950.5[b]/1956.1[c]		2061.3	≪1	1950.6	10	**110.7**

[a] See Table 3 for experimental IR intensities. [b] From cyanoacetylene-containing complexes. [c] From dicyanoacetylene-containing complexes. [d] IR intensities I in km/mol.

TABLE 2: Vibrational Frequencies (cm^{-1}) for $HC_5{}^{15}N$ and $H^{13}C_2C_3N$, As Measured Following the Photolysis of $1^{15}N$:3 and 2:$3^{13}C$ Complexes in Ar Matrixes, and Compared to DFT Values (Harmonic, Downscaled by 0.96)[a]

	experiment[b]						theory, B3LYP aug-cc-pVTZ[c]					
	$HC_5{}^{15}N$[d]			$H^{13}C_5N$[e]			$HC_5{}^{15}N$			$H^{13}C_5N$		
modes	ν (cm^{-1})	I	$\Delta\nu$	ν (cm^{-1})	I	$\Delta\nu$	ν (cm^{-1})	I	$\Delta\nu$	ν (cm^{-1})	I	$\Delta\nu$
ν_1				3288.9	35	**28.4**	3320.9	120	**0**	3303.5	120	**17.4**
ν_2	2239.0	100	**9.5**	2248.1	100	**1.6**	2246.2	98	**9**	2254.6	96	**0.6**
ν_3	-		-	2181.5	39	**5**	2179.4	$\ll$1	**12.5**	2173.9	2	**18**
ν_4							2056.3	<1	**5**	2004.7	1	**56.6**

[a] $\Delta\nu$ values are isotopic frequency differences related to the normal isotopomer. [b] IR intensities I of most intense bands arbitrarily taken as 100. [c] IR intensities I in km/mol. [d] From $1^{15}N/3$/Ar mixture irradiation. [e] From $2/3^{13}C$/Ar mixture irradiation.

to the ν_2 mode of **$4^{15}N$**. The fact that the detectable **$4^{15}N$** spectrum was reduced to just one band found the explanation in DFT results. Indeed, spectral features due to ν_3 and ν_4 modes of **$4^{15}N$** are expected to be very weak. Moreover, the ν_1 band was unavoidably concealed by the intense C−H stretching fundamental of the parent **$1^{15}N$**.

Irradiation of 2:3 at λ > 180 nm. Photolysis of the **2**/**3**/Ar mixture at λ > 180 nm resulted in the decrease of bands assigned to **2**, **3**, and to the complex species **2:3**. Apart from the irradiation products coming from separated molecules **2** and **3**, the characteristic bands of HC_3N **1** appeared at 3313.6, 2268.4 and 2076.6 cm^{-1}. We observed also the appearance of a band at 3305.8 cm^{-1} in the acetylene C−H stretch range, recognized as ν_1 of HCN.[50] In addition to these, product bands at 3317.3, 2249.7 and 2186.5 cm^{-1} (Figure 3) developed, assigned by us to cyanodiacetylene **4**. Noteworthy, this experiment presented no obstacles to the detection of the C−H stretching band (ν_1) of **4**. The knowledge of its frequency, and of the ν_1 value previously measured for **4D** in the **1**/**3D**/Ar experiment, gave us the corresponding H-to-D isotopic shift, which agreed well with the CCSD(T) theoretical prediction,[15] and with the value given by DFT, listed in Table 1.

Next, the **2**/**3**/Ar study was extended with experiments engaging isotopically labelled acetylene, either D_2C_2 (**3D**) or $H_2{}^{13}C_2$ (**$3^{13}C$**). Photolysis of **2**:**3D** led to the development of DC_3N bands at 2600.8, 2245.5 and 1964.4 cm^{-1}, DCN[51] bands at 2622.7 and 1946.7 cm^{-1}, and the features centered at 2589.3, 2248.3, 2159.0 and 1956.1 cm^{-1} (Figure 4), which we assigned to **4D**. In Table 3, cyanodiacetylene fundamentals observed following the photolysis of dicyanoacetylene-based **2:3** (**2:3D**) complexes are compared to those resulting from cyanoacetylene-bearing species **1:3** (**1:3D**). Generally, vibrational frequencies of **4** (**4D**) were slightly, yet measurably, sensitive to the identity of the $^{\bullet}C_3N$ moiety donor (either mono- or dicyanoacetylene), which can be explained by the inequality of matrix sites in both cases.

The photolysis of **2**:**$3^{13}C$** (Figure 4) resulted in the development of three absorption bands, situated at 3288.9, 2248.1 and 2181.5 cm^{-1}, which we assigned to the $H^{13}C_2C_3N$ (**$4^{13}C$**) isotopomer of cyanodiacetylene. Moreover, we observed the growth of an additional band in the CN stretching region, at 2264.5 cm^{-1}. This feature, shifted by 4.5 cm^{-1} toward lower frequencies with regard to the ν_2 band of HC_3N, can be tentatively identified as coming from the isotopomer $H^{13}C_2CN$ (**$1^{13}C$**). Although the agreement with DFT predictions is rather poor in this case, the proposed assignment is strongly supported by the fact that we did not detect any spectral traces of normal isotopomeres **1** and **4** when photolyzing **2**:**$3^{13}C$** complexes; instead, the red-shifted bands (presumably of **$1^{13}C$** and **$4^{13}C$**) were observed, with intensities similar to those in previous experiments involving **2**:**3**.

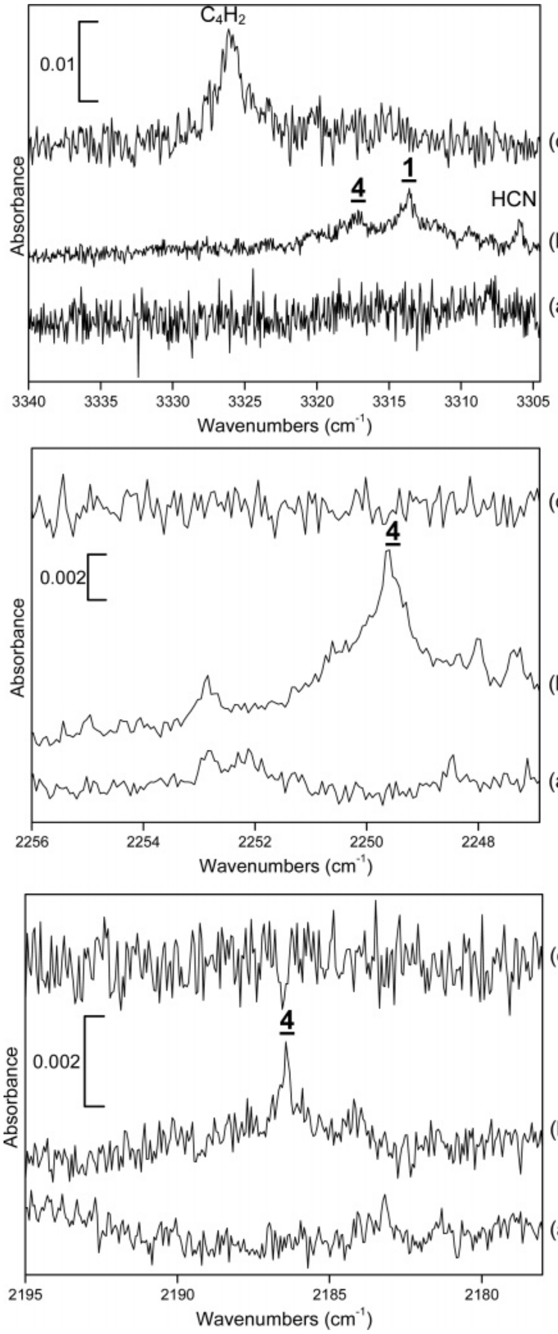


Figure 3. FTIR difference spectra (after − before photolysis) showing the creation of photoproducts at λ > 180 nm: (a) **2**/Ar matrix, 26 h of irradiation; (b) **2**/**3**/Ar, 22 h; (c) **3**/Ar, 13 h.

Discussion

The compounds responsible for the synthesis of cyanodiacetylene in irradiated matrixes are most likely the neighboring

TABLE 3: Cyanodiacetylene (4, 4D) Vibrational Frequencies (Ar Matrixes) Measured Following the Photolysis of Complexes 1:3(3D), Compared to Those Coming from the Photolysis of 2:3(3D)[a]

	HC_5N					DC_5N				
	1/3/Ar		2/3/Ar			1/3D/Ar		2/3D/Ar		
modes	ν_{H1} (cm^{-1})	*I*	ν_{H2} (cm^{-1})	*I*	$\nu_{H2} - \nu_{H1}$	ν_{D1} (cm^{-1})	*I*	ν_{D2} (cm^{-1})	*I*	$\nu_{D2} - \nu_{D1}$
ν_1			3317.3	30		2588.8	19	2589.3	21	**0.5**
ν_2	2248.5	100	2249.7	100	**1.2**	2247.0	100	2248.3	100	**1.3**
ν_3	2186.5	22	2186.5	32	**0**	2159.0	22	2159.0	27	**0**
ν_4						1950.5	35	1956.1	55	5.6

[a] Frequency differences in rightmost columns for each isotopomer reflect inequality of matrix sites originating from cyano- and dicyanoacetylene-containing molecular complexes. IR intensities *I* of most intense bands arbitrarily taken as 100.

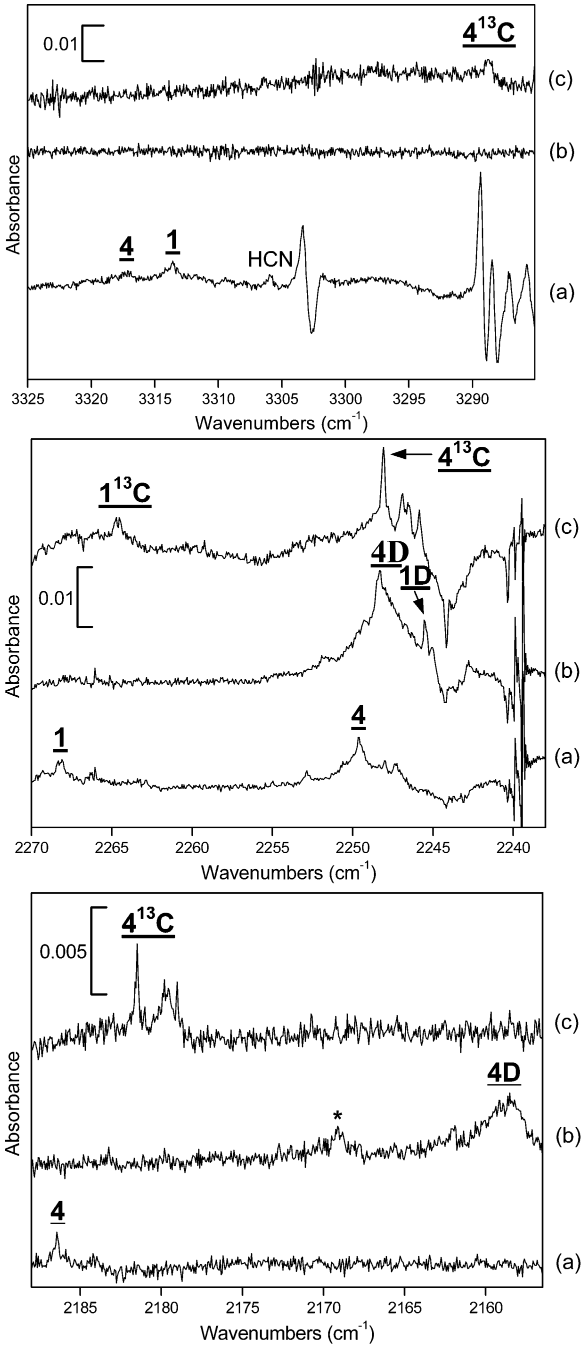


Figure 4. FTIR difference spectra (after − before photolysis) showing the product bands arising in Ar matrixes following the photodecomposition of **2:3** complexes (and of their isotopic modifications) at $\lambda >$ 180 nm: (a) **2:3** complex, 26 h of irradiation; (b) **2:3D**, 24 h; (c) **2:3^{13}C**, 24 h. Asterisked bands, resulting from the photolysis of uncomplexed molecules, are not attributed.

molecules **1** (or **2**) and **3**, loosely bound in bimolecular complexes **1:3** and **2:3**. Absorptions of energetic vacuum-UV photons by either of the two chromophores present within a complex destruct or modify the original intermolecular bonding. Furthermore, the creation of transient molecular fragments, like $H^\bullet$, $C_2H^\bullet$, $C_3N^\bullet$ and $CN^\bullet$ takes place. The matrix cage effect, together with the close vicinity of potential reactants, stimulates recombination reactions between the radicals, or the reactions between radicals and closed-shell molecules.

At $\lambda > 120$ nm, C−H bonds can cleave in **1** and in **3**. At $\lambda > 180$ nm, the opening of one C−H bond is expected in **3**, and the major process for **2** consists of the breaking of one C−CN bond. During the irradiation of complexes **1:3** and **2:3** (and of their isotopic modifications) at, respectively, $\lambda > 120$ nm and $\lambda > 180$ nm, we observed the formation of the same product: cyanodiacetylene. It is presently not possible to elucidate the sequence of particular intra- and intermolecular geometry changes leading to disparate processes within our matrix-isolated molecular complexes. However, it is reasonable to envisage the cyanodiacetylene molecule as created via the recombination of $C_2H^\bullet$ and $C_3N^\bullet$ (Scheme 1, path A). The transient presence of this pair of radicals implies also the emergence of a complementary pair − that of two $H^\bullet$ atoms for **1:3**, or of $H^\bullet$ and $CN^\bullet$ for **2:3**, with corresponding recombination reactions. We had no technical means to detect small quantities of matrix-isolated H_2. However, we did observe the creation of HCN from photolyzed **2:3**. This is consistent with path A.

Still, the evidence acquired from isotopic studies excludes the simplest picture, in which stable products would correspond to all possible “exchanges of radicals” between the components of a given bimolecular complex. Deuterated cyanoacetylene **1D** appeared in the photolysis of both **1:3D** and **2:3D** complexes. Formally, this compound could be formed following the recombination of the acetylene $D^\bullet$ atom with $C_3N^\bullet$ (Scheme 1, path B). On the other hand, for the **1:3D** photolysis, such a path would involve the existence of a complementary pair, $C_2D^\bullet$ and $H^\bullet$, probably combining into C_2HD. Monodeuterated acetylene was not observed, which makes route B unlikely. Further arguments against it come from the photolyzed complex **2:3^{13}C**. Path B implies two alternative recombination reactions leading to cyanoacetylene: either $C_3N^\bullet + H^\bullet$ or $^{13}C_2H^\bullet + CN^\bullet$, and thus the production of HC_3N along with $H^{13}C_2CN$. Only one isotopomer, $H^{13}C_2CN$, was in fact detected.

Given these pieces of evidence, it is rational to propose the photolysis of HC_5N (Scheme 1, path C), as the most likely route toward cyanoacetylene in our experiments. This would require the feasibility of photoreaction $HC_5N \rightarrow HC_3N + C_2$ at both wavelength ranges used ($\lambda > 120$ nm and $\lambda > 180$ nm).

It is of interest to compare our IR measurements of **4** photochemically generated in solid Ar, to the gas-phase vibrational spectrum of cyanodiacetylene, thus far the most

TABLE 4: Major IR Absorption Features of Gaseous Cyanodiacetylene, Compared to Those Detected in UV-Irradiated Ar Matrixes Containing C_4N_2/C_2H_2 Complexes

	HC_5N			
	gas phase[a]		Ar matrix[b]	
mode	ν (cm^{-1})	I^d	ν (cm^{-1})	I^e
ν_1 C−H stretch[c]	3333 R 3322 P	100	3317.3	30
$2\nu_5$ overtone	2339 R 2330 P	11	not found	
ν_2 C≡N stretch	2257 R 2248 P	52	2249.7	100
ν_3 C≡C stretch	2192.5 R 2182.5 P	11	2186.5	32
$2\nu_7$ overtone	1276 R 1267 P	30	not found	
ν_7 bend	642.2	75	out of range	

[a] Reference 11. [b] Values obtained from **2:3** photolysis. [c] In resonance with $\nu_3 + \nu_5$. [d] Intensities, relative to ν_1 (the strongest band in the gas phase; ca. 280 atm^{-1} cm^{-2}) arbitrarily taken as 100. [e] Intensities, relative to ν_2 (the strongest band in the matrix) arbitrarily taken as 100.

TABLE 5: IR Frequencies and Intensities of Cyanoacetylene Absorption Bands (Ar-1 = Gas Phase Molecules Trapped in Solid Argon; Ar-2 = Molecules Photochemically Produced within C_4N_2/C_2H_2 Complexes in Solid Argon)

	HC_3N					
	gas phase[a]		Ar-1[b]		Ar-2	
mode	ν (cm^{-1})[c]	I^d	ν (cm^{-1})	I^d	ν (cm^{-1})	I^d
ν_1 C−H stretch	3336 R 3318 P	100	3315	100	3314	50
ν_2 C≡N stretch	2279 R 2263 P	14	2269	12	2268	100
ν_3 C≡C stretch	2085 R 2068 P	3	2076	6	2076	6
$2\nu_5$ overtone	1322 R 1305 P	25	1318	15	not found	
ν_5 CCH bend	663	73	665	59	not found	

[a] Reference 52. [b] Reference 23. [c] Maxima of rotational branches. [d] Relative intensities in comparison to the strongest band arbitrarily taken as 100.

complete one, obtained at Créteil at Laboratoire Inter-Universitaire des Systèmes Atmosphériques[11] (Table 4). Though the weak feature $2\nu_5$, missing from present matrix spectra of **4**, is most likely hidden in noise due to the absorption by atmospheric CO_2, reasons for the absence of $2\nu_7$ band have to be more complex. A possible explanation is suggested by the IR spectrum of HC_3N, resultant from the photodecomposition of HC_5N (Scheme 1, path C). Table 5 lists major IR features of molecule **1**; an intense bending band ν_5, normally observed in HC_3N gas, and in **1**/Ar matrixes (at 667 cm^{-1}), was missing (together with its first overtone) from the spectrum of HC_3N newly created from **4**. We may speculate that molecule **4**, once formed out of recombining transients $C_2H^\bullet$ and $C_3N^\bullet$, occupies a tight matrix site, i.e., the one not allowing for much bending movement. This site is expected to be strongly influenced by the vicinity of another reaction product, H_2 or HCN (Scheme 1, path A; cf. Table 3). Thus the microenvironment of any given molecule **4** (or, once **4** is photolyzed, of its daughter species **1**) is probably different from energetically relaxed noble gas cages emerging in standard matrix isolation experiments, which may be reflected in a sizable suppression of molecular bending motions.

Conclusions

Combined with theoretical predictions, the outcome of reported IR-spectroscopic measurements gives evidence to the formation of cyanodiacetylene in UV-induced reactions within Ar matrix-isolated bimolecular complexes: cyanoacetylene: acetylene and dicyanoacetylene:acetylene. The similarity of processes observed for both complexes pointed (together with the results of ^2H, ^{15}N, and ^{13}C isotope substitution studies) to the recombination of short-living $C_2H^\bullet$ and $C_3N^\bullet$ radicals as the most likely route toward HC_5N. Additionally, the photodecomposition of HC_5N, with HC_3N being a product, was observed. Reactions disclosed in this study may be significant for the chemistry of Titan's atmosphere, where acetylene and cyanoacetylene are important constituents.

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