Matrix Generation of C_3N_4

Dicyanocarbodiimide and Trinitreno-*s*-triazine Generated by Consecutive Photolysis of Triazido-*s*-triazine in a Low-Temperature Nitrogen Matrix**

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Since the publication of theoretical studies predicting that carbon nitride might be harder than diamond,[1] a considerable amount of research has been directed toward the preparation of pure C_3N_4.[2] In contrast, carbon nitride molecules with the C_3N_4 formula have seldom been studied. Dicyanodiazomethane, the only C_3N_4 isomer studied experimentally, has been converted into a dicyanomethylene (NC_3N).[3] Meanwhile, Schnick assumed that a C_3N_4 molecule would have a tricyanoazane $N(CN)_3$ structure.[4] With the aid of ab initio calculations, BelBruno et al. showed that there was a more stable isomer, dicyanocarbodiimide.[5] However, the existence of these molecules was never confirmed. In the present study, we have confirmed for the first time the generation of the quasilinear C_3N_4 molecule, dicyanocarbodiimide, in the matrix photolysis of triazido-*s*-triazine (**1**, Scheme 1). Triazide **1** has been studied as a precursor for high-spin trinitrene molecules. Indeed, generation of a triplet mononitrene and a quintet dinitrene was confirmed by electron spin resonance spectroscopy upon the photolysis of a single crystal of **1** at 4 K, although generation of the septet trinitrene was not confirmed.[6] Various reactive species and their products were formed upon the decomposition of **1**. Pulsed laser photolysis of **1** resulted in the formation of a nitrogen cluster ion N_5^+.[7] Generation of carbon nitride and carbon nanotubes by means of pyrolytic or detonative decomposition of **1** was reported.[8] Thus, the intermediates generated by the decomposition of **1** are quite intriguing. Herein, we report the consecutive photolysis of **1** in a low-temperature nitrogen matrix.

Crystallites of **1** were vaporized and codeposited with nitrogen onto a CaF_2 substrate at 20 K. Irradiation of the resulting matrix at 266 nm led to an instant decrease in the

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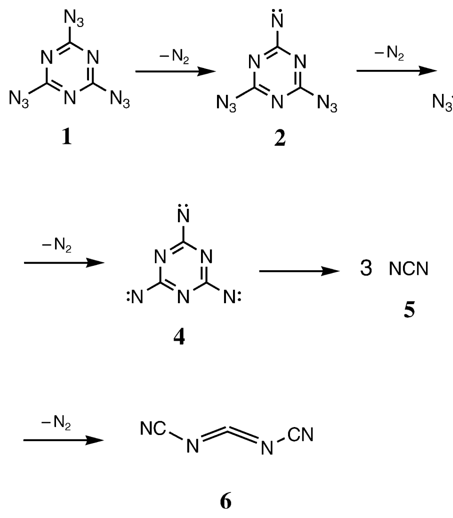

Scheme 1. Photoproducts generated successively in the photolysis of **1**.

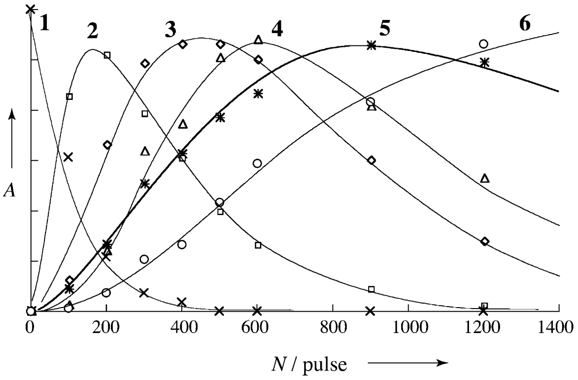

Figure 2. Dynamic behavior of the representative IR and UV/Vis absorption bands of the intermediates (**2**: IR 1339 cm^{-1}, **3**: IR 1438 cm^{-1}, **4**: IR 1326 cm^{-1}, **5**: UV/Vis 329 nm, **6**: IR 2271 cm^{-1}). *N* denotes the number of the irradiated laser pulses.

intensities of the IR bands of **1** and the concomitant growth of new IR bands ascribable to the photoproducts (Figure 1 a). The photolysis was also observed by UV/Vis absorption spectroscopy (Figure 1 b). The various IR and UV/Vis absorption bands ascribed to the photoproducts appeared successively indicating stepwise generation of several photoproducts. By analyzing the dynamic behavior of the IR and UV/Vis bands (Figure 2), we were able to group the bands into five sets.[9] Thus, we concluded that five intermediates were formed successively in the matrix.

The most prominent IR band of the first set was observed at 1339 cm^{-1}, and the dynamic behavior of this band was similar to that of the UV/Vis band at 344 nm. Previously reported results for the photolyses of the related species[6,10,11] indicate that the most probable candidate for the first photoproduct is the triplet mononitrene **2**. In the theoretical IR spectrum of **2** at the B3LYP/6-31G* level, the most intense band is at around 1340 cm^{-1} for all three isomers.[12] Previously reported results for an azido-*s*-triazine derivative[11] indicate that ring expansion of the nitrene produces didehydrotetrazepine. However, the characteristic IR band (around 1900 cm^{-1}) of didehydrotetrazepine was extremely weak in our case, indicating that subsequent photoreaction of the nitrene was preferred over ring expansion. Thus we assigned the first intermediate as triplet mononitrene **2**.

The second intermediate showed an intense IR band at 1438 cm^{-1}. This band corresponded to the prominent band at 1422 cm^{-1} in the theoretical IR spectrum of quintet dinitrene **3**, indicating that the second intermediate was formed by further loss of nitrogen from **2**.

Considering the observed stepwise loss of nitrogen, the third photoproduct may be septet trinitrene **4**, although generation of **4** was not confirmed in an earlier study.[6] In its theoretical IR spectrum, septet **4** shows only one discernible IR band between 800 and 4000 cm^{-1}, a band at 1298 cm^{-1}.[13] We assigned only one weak IR band, at 1326 cm^{-1}, to the third intermediate; we could not find other IR bands ascribable to this intermediate in this wavenumber region, particularly at around 2100 cm^{-1}. As the second intense IR band of **4**, an IR band was predicted at 747 cm^{-1} with intensity of 40 $km\,mol^{-1}$ (Figure 3 b). In the matrix experiment using a BaF_2 substrate in place of the CaF_2 substrate, which allowed the IR measurement between 600 and 4000 cm^{-1}, we could find out another IR band ascribable to **4** at 763 cm^{-1}. This band showed similar dynamic behavior to the band at 1326 cm^{-1} (Figure 3 a).

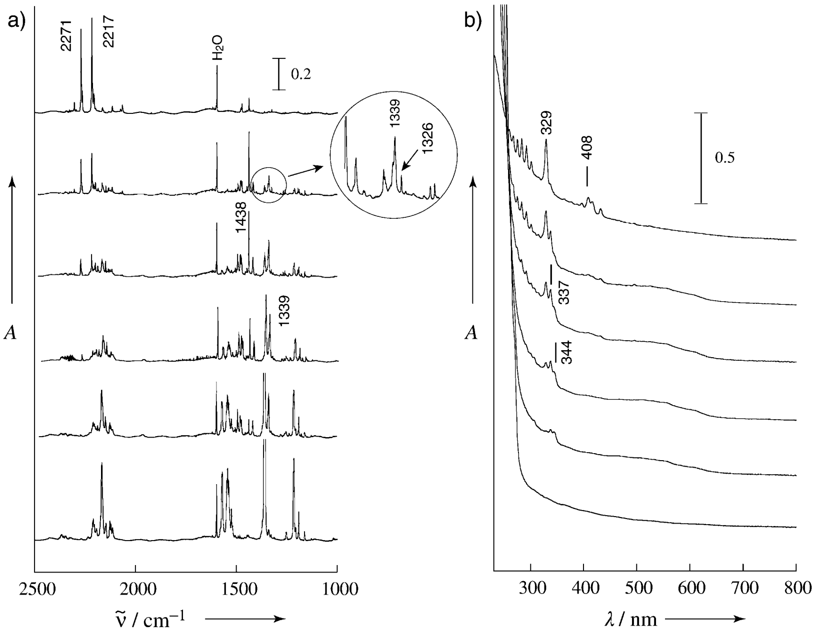

Figure 1. Observed a) FTIR and b) UV/Vis absorption spectra of a nitrogen matrix containing **1** upon irradiation at 266 nm with (bottom to top) 0, 100, 200, 300, 500, and 1200 FHG pulses from a Nd:YAG laser.

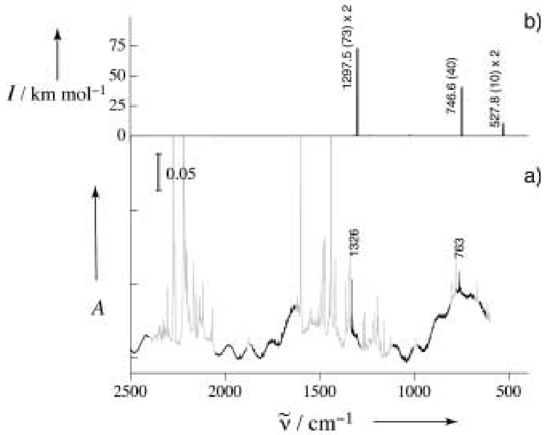

Figure 3. a) IR bands ascribable to trinitrene **4**. b) Calculated IR spectrum (B3LYP/6-31G* level, scaled by 0.9614) of **4**.

To confirm our identification of the photoproducts, we studied the ^{13}C isotopic shifts of their IR bands. We observed similar photoreactions, i.e. stepwise generation of five intermediates, in the photolysis of ^{13}C-labeled **1**. The observed spectra for the labeled photoproducts showed changes similar to those observed for the products of unlabeled **1**, although all corresponding IR bands were shifted to smaller wavenumbers (Table 1). The IR bands ascribed to the third intermediate shifted from 1326 and 763 cm^{-1} to 1299 and 746 cm^{-1}, respectively. The observed shift corresponded well to the theoretically predicted shift. Thus, we assigned the third intermediate as trinitrene **4**.

Table 1: Observed and calculated isotopic shifts of characteristic IR bands.

Compound	(^{12}C) [cm^{-1}]	(^{13}C) [cm^{-1}]	Δ [cm^{-1}]	Calcd Δ [cm^{-1}]	Calcd (^{12}C) [cm^{-1}]	Calcd (^{13}C) [cm^{-1}]
Mononitrene	1339	1307	−32	−25	1340[a]	1315[a]
				−24	1337[a]	1313[a]
				−25	1342[a]	1317[a]
Dinitrene	1438	1403	−35	−32	1422	1390
Trinitrene	1326	1299	−27	−28	1298	1270
	763	746	−17	−18	747	729
NCN	1475	1436	−39	−42	1517	1475
	1478	1440	−38			
					6	
Final compd.	2217	2160	−58	−60	2243	2183
	2271	2218	−53	−56	2314	2257

[a] IR bands predicted for three isomers of mononitrene.[12]

The IR bands of the fourth intermediate, which were difficult to analyze because they overlapped with the intense IR bands of **2**, appeared at around 1475 cm^{-1} after the disappearance of **2**. The fourth intermediate showed characteristic UV/Vis absorption bands: one intense peak at 329 nm accompanied by vibronic bands at 290–300 nm (Figure 1 b). We ascribed this characteristic UV/Vis spectrum to NCN (**5**) on the basis of the spectrum reported by Jacox et al. upon photolysis of N_3CN.[14] Trinitrene is a trimer of **5**. Considering that triazine can decompose into three HCN molecules,[15] decomposition of **4** into three molecules of **5** should be possible.

Upon further photoirradiation, NCN reportedly rearranges into CN_2, which shows an IR band at 1241 cm^{-1}.[14] However, it was not discernible in our study. Instead, two intense IR peaks appeared, at 2217 cm^{-1} and 2271 cm^{-1}, upon further irradiation (Figure 1 a) while the IR and UV/Vis bands of **5** decreased in intensity. These two new IR bands have never been observed in photolyses of N_3CN that generated **5**. In the matrix photolysis of **1**, the three molecules of **5** should stay in the same matrix cage, and, therefore, further photoirradiation would result in intermolecular reactions. Considering the sole photoproduct generated at the end of the sequence, the three molecules of **5** must form the final photoproduct. Among the calculated possible species, only one with the formula C_3N_4, dicyanocarbodiimide **6**, had two IR peaks at the corresponding wavenumbers. However, the calculated IR spectrum did not reproduce the intensities of these IR bands well. The observed ^{13}C isotopic shifts of the IR bands were 58 and 53 cm^{-1}. These shifts are larger than those for the species with a triazine ring and correspond well with the calculated isotopic shifts for **6**. Therefore, we assigned the final product as **6**. We propose the following mechanism for the generation of **6**: One of the three confined molecules of **5** is converted into CN_2 or a C atom, as in the photolysis of N_3CN.[16] The generated CN_2 or C atom immediately reacts with the other two molecules of **5**. The reaction of a C atom with two molecules of **5** forms **6** directly, whereas the reaction of CN_2 forms **6** by photoinduced nitrogen loss.

Experimental Section

Triazido-*s*-triazine (**1**) was synthesized by mixing a solution of cyanuric chloride (trichloro-*s*-triazine) in acetone and an aqueous solution of sodium azide according to the procedure described in ref. [11]. ^{13}C-Labeled **1** was synthesized from sodium azide and the ^{13}C isotopomer of cyanuric chloride (Isotec. Inc., 99.4 atom %) in which all ^{12}C was replaced by ^{13}C.

In the matrix isolation experiments crystallites of **1** were vaporized at 40–45 °C and codeposited with nitrogen (99.9999 %) onto a CaF_2 substrate at 20 K. Matrix-isolated **1** was photolyzed by using fourth-harmonic-generated (FHG) pulses of a Nd:YAG laser ($\lambda = 266$ nm, 10 Hz, 0.5 mJ cm^{-2} pulse^{-1}). A sample chamber with two pairs of windows, quartz for UV/Vis spectroscopy and KBr for FTIR measurements, enabled us to monitor the photolysis by FTIR and UV/Vis absorption spectroscopies simultaneously. Because of the strong absorption of the CaF_2 substrate, FTIR measurements were conducted between 800 and 4000 cm^{-1}.

The geometries of the compounds were optimized at the B3LYP/6-31G* level by using the Gaussian98 program package.[17] The nature of the stationary points was assessed by means of vibrational frequency analysis. Theoretical IR spectra were obtained by the vibrational frequency analysis: vibrational frequencies were scaled by 0.9614 on the basis of a literature report.[18] All calculations were done on the TACC Quantum Chemistry Grid/Gaussian Portal system at the Tsukuba Advanced Computing Center (TACC).

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