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Photochemical Formation of Diazenecarbaldehyde (HNNCHO) and Diazenecarbothialdehyde (HNNCHS) in Low-Temperature Matrices

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Abstract

The photochemical decomposition of 1,2,4-oxadiazole-3,5-diamine and 1,2,4-thiadiazole-3,5diamine was investigated in low-temperature Ar and Kr matrices at different wavelengths. The analysis of matrix-isolation infrared (MI-IR) spectra aided by high-level quantum chemical computations showed that these photochemical reactions yield not only [NH₂, C, N, X] (X=O, S) isomers, but the bands of a novel, formerly unobserved species were also observed. The comparison of computed IR spectra of potential products with the observed spectra suggests that these species are the diazenecarbaldehyde (HNNCHO) and diazenecarbothialdehyde (HNNCHS). Neither of the reactive HNNCHO and HNNCHS molecules was observed experimentally before. Both molecules are identified in the matrix as a complex with the other photoproduct, NH₂CN. Comparison of the present experiments with former photochemical experiments on 1,2,5-oxadiazole-3,4-diamine and 1,2,5-thiadiazole-3,4-diamine and the analysis of the rate of formation of the different photoproducts indicate that HNNCHO and HNNCHS are formed in a different reaction path than H₂NNCX and H₂NC(NX) (X = O, S), and not by photoisomerization from these latter products.

Introduction

The matrix isolation (MI) method is one of the oldest and most powerful tools for preparation and spectroscopic characterization of reactive molecules, radicals, and reaction intermediates.^{1–3} Another advantage of the method is that the most frequently used low-temperature inert matrices (Ne, Ar, Kr, N₂, and para-H₂) provide a very weakly interacting environment, therefore the spectral transitions are very close to those of the free molecules; or in case of a photolysis that results in by-products, the molecules are prepared in a relatively simple bimolecular complex form. ⁴ Due to the latter advantage MI spectra can be straightforwardly correlated both with spectra obtained by quantum chemical computations or by astrophysical observations. Therefore, it is not surprising that MI spectroscopy has been extensively applied to generate and characterize reactive molecules with astrochemical interest.^{5–35}

An interesting group of reactive astrochemical molecules are pseudohalogenide compounds. Many of these species have already been identified in the interstellar medium (ISM).³⁶⁻⁴² These compounds play an important role in astrophysical studies because they have several low-energy structural isomers, and the identification and the determination of the relative abundance of the different forms in the ISM can provide details about the physical conditions and chemical evolution of these astrophysical objects.⁴³ Amino substituted pseudohalogenides are also interesting potential astrochemical molecules. Among these, aminoisocyanate (H₂NNCO) was prepared in a 10 K Ar matrix,⁴⁴ cyanamide-N-sulfide (H₂NCNS) was investigated in the gas phase by collisional activation and neutralizationreionization mass spectrometry.⁴⁵ Furthermore, it was shown recently that H₂NCNX, H_2NNCX , and $H_2NC(NX)$ (X = O, S), can be generated in inert matrices by the photolysis of 1,2,5-oxadiazole-3,4-diamine (1) and 1,2,5-thiadiazole-3,4-diamine (2) (see Scheme 1).³⁰ Although that study provided the first experimental observation and characterization of four of these molecules, H₂NCNO, H₂NNCS, and the two cyclic isomers, H₂NC(NO) and $H_2NC(NS)$, interestingly, some low-energy structures including, e.g., the thermodynamically most stable [NH₂, C, N, S] isomer, H₂NSCN was not observed among the products. Furthermore, in that study, tautomers of [NH₂, C, N, S] structures, *i.e.*, [NH, H, C, N, S] isomers containing unsaturated HN=N- or HN=C< moieties were not detected either. The identification of these structures would be interesting because these are reactive intermediates in organic chemistry, and they can be important precursors of biomolecules in the ISM. As an example, methanimine, ⁴⁶ cyanomethanimine, ⁴⁷ ketenimine, ^{48,49} and ethanimine ⁵⁰ were

detected in the ISM in the last few years. The amine and imine forms can convert into each other by tautomerization driven by shocks in the interstellar and circumstellar clouds.⁴⁸ The observation of ethanimine establishes a precursor to alanine formation, which is one of the most common amino acid in proteins.⁵⁰



Scheme 1. Structure of 1: 1,2,5-oxadiazole-3,4-diamine, 2: 1,2,5-thiadiazole-3,4-diamine, 3: 1,2,4-oxadiazole-3,5-diamine, 4: 1,2,4-thiadiazole-3,5-diamine.

The purpose of the present work was to explore whether new isomers, including [NH, H, C, N, X] can be prepared in matrices by tuning the structure (*i.e.*, using structural isomers) of the precursors and the photon wavelength used for photolysis. Therefore, here we report the photolysis of 1,2,4-oxadiazole-3,5-diamine (**3**) and 1,2,4-thiadiazole-3,5-diamine (**4**) (Scheme 1) under MI conditions.

Methods

Precursors

3 was prepared following a literature method, by the reaction of hydroxylamine hydrochloride and sodium dicyanamide in a 1:1 ratio, in methanol solvent.⁵¹ The byproduct sodium-chloride was filtered, then the solvent from the filtrate was evaporated under reduced pressure. The crude product was recrystallized from water.

4 was obtained as a commercial product (Sigma-Aldrich, 97%) and it was used in the experiments without further purification.

The precursors were stored in closed flasks in dark at room temperature. At these conditions no decomposition or other side reaction was observed.

Spectroscopic Measurements

A home-built Knudsen-cell was used to evaporate the precursors into the vacuum chamber. For **3** the evaporation temperature was 351 K for IR and 349 K for UV measurements. These values were 350 K and 343 K for **4**, respectively. At these conditions neither the decomposition of the precursors nor any other side-reactions were observed. The evaporated precursors were mixed with Ar (Messer, 99.9999%) or Kr (Messer, 99.998%) before deposition. The gas-flow was kept at ~0.04 mmol min⁻¹ during the deposition for MI-IR, and ~0.01 mmol min⁻¹ for MI-UV investigations. The distance between the orifice of the Knudsen cell and the window was ~5 cm, and the chamber was continuously pumped during deposition. The sample–noble-gas mixtures were condensed onto a CsI window for MI-IR and onto a BaF₂ window for MI-UV measurements. Based on our previous measurements, to achieve matrices with good optical qualities, the temperature of the CsI window was kept at 10 K for the measurements in argon, and at 18 K for the measurements the BaF₂ window was kept at 12 K. The windows were cooled by closed-cycle helium cryostats, and the temperature was monitored by a silicon diode thermometer.

The MI-IR spectra were recorded by a Bruker IFS 55 Fourier transform infrared (FT-IR) spectrometer equipped with a Globar source, a KBr beamsplitter, and an MCT detector. At least 512 scans were accumulated at 1 cm⁻¹ resolution in the 3800–600 cm⁻¹ spectral window. Happ–Genzel apodization function, Mertz phase correction using phase resolution of 32 cm⁻¹, and a zero filling factor of 4 were applied.

Absorption MI-UV spectra were measured by a Varian Cary3E spectrometer, using 5 nm min^{-1} scan rate, 0.333 nm step size, and 1 nm spectral bandwidth. Data were collected in the 350–190 nm spectral region.

In the case of the MI-UV studies, the matrix was irradiated by a Cathodeon HPK 125 W highpressure mercury lamp through a quartz window mounted on the vacuum chamber. For selective photolysis a Melles Griot interference filter (FWHM 10 nm) was used to select the appropriate line and to block the other emissions of the lamp. Broad-band UV (BBUV) photolysis was carried out using the mercury lamp without filter.

In the MI-IR studies the photolysis was carried out by a second harmonic generation unit (GWU uvScan) attached to an optical parametric oscillator (VersaScan MB 240 OPO, GWU/Spectra Physics). The OPO was pumped by the third harmonic (355 nm) of a pulsed (10 Hz, 2–3 ns) Quanta Ray Lab 150 Nd:YAG laser (Spectra Physics). The laser output

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energies were measured as 50 $\mu J/pulse$ at 213 nm, 150 $\mu J/pulse$ at 220, 250, and 260 nm, and 400 $\mu J/pulse$ at 240 nm.

Computational Details

The quantum-chemical computations were carried out by the CFour⁵² and the Gaussian09⁵³ quantum chemistry packages. The equilibrium structures of the investigated molecules have been computed at the B3LYP^{54,55}/aug-cc-pVTZ^{56,57} and the frozen-core (fc) CCSD(T)⁵⁸/cc-pVTZ, while the structure and energy of the complexes at the B3LYP/aug-cc-pVTZ and the fc MP2⁵⁹/cc-pVTZ levels of theory. In the fc CCSD(T) and MP2 computations the core electrons (1s electrons of N, C, and O, and 1s, 2s, and 2p electrons of S) were not correlated.

Geometry optimizations – which in case of the complexes were started from many different starting orientations of the monomer and the cyanamide molecule – were followed by harmonic vibrational frequency computations in order to confirm that the structures are minima on the potential energy surface (PES).

Anharmonic corrections to the harmonic vibrational wavenumbers were computed by vibrational perturbation theory (VPT2)^{60,61} at the B3LYP/aug-cc-pVTZ level.

Experimental and Computational Results

MI-IR and MI-UV spectra of the precursors

The baseline corrected MI-IR spectra of **3** and **4** isolated in Ar and in Kr matrices are shown together with the computed IR spectra in Figure S1 and Figure S2 of the Supporting Information. For both precursors a very good agreement was observed between the computed and the experimental results, considering both the vibrational wavenumbers and the intensities (see Table S1–S2). In the case of the oxadiazole molecule each band with computed intensity larger than 10 km mol⁻¹ was observed, while for the thiadiazole precursor each computed fundamental band was observed in the investigated region. In addition, a few, very small bands were observed in the spectra recorded after deposition, which are not predicted by harmonic frequency computations. The intensity of each of them is smaller than the weakest band listed in Table S1 and Table S2. These bands can be combination bands or overtones. Since the primary aim of this work was to study the photolysis products of the precursors, the complete assignment of these bands was not attempted.

To choose the appropriate wavelengths for the photolysis, the MI-UV spectra of the precursors isolated in Ar matrix were recorded. The MI-UV spectrum of **3** and **4** is shown in Figures 1 and 2, respectively.



Figure 1. a) MI-UV spectrum of **3** isolated in an Ar matrix at 12 K. b) MI-UV spectrum recorded after BBUV photolysis of **3**.



Figure 2. a) MI-UV spectrum of **4** isolated in an Ar matrix at 12 K. b) MI-UV spectrum recorded after 254 nm photolysis of **4**. c) MI-UV spectrum recorded after 254 nm and BBUV photolysis of **4**.

As in the case of 1 and 2, the absorption maximum of 4 is shifted to longer wavelengths compared to 3. The difference between the maxima of the bands is \sim 40 nm. 4 was photolyzed using a 254 nm irradiation, which resulted in the decrease of the UV band of the precursor. For both precursors complete decomposition was observed after 15 minutes, using broad-band UV (BBUV) irradiation (*i.e.*, unfiltered radiation of the mercury lamp).

Photolysis of 1,2,4-oxadiazole-3,5-diamine (3)

The photolysis of **3** was carried out at 213 nm, which is the shortest available wavelength of our laser system. This wavelength is very close to the maximum position of the band in the MI-UV spectrum. In another experiment 220 nm radiation was used, which is near the long-wavelength edge of the absorption band (see Figure 1). The IR bands of the different photolysis products are clearly visible in the difference spectra (*i.e.*, the spectrum recorded after deposition is subtracted from the spectra recorded after different photolysis times; see Figures 3–4).



Figure 3. Difference spectra as obtained by subtraction of the spectrum recorded immediately after deposition from the spectrum recorded after 220 nm photolysis of **3** in an Ar matrix a) after 25 min photolysis b) after 35 min photolysis c) after 100 min photolysis. (At these selected times the products were present in the largest quantity.) The band of CO is marked with asterisk.



Figure 4. Difference spectra as obtained by subtraction of the spectrum recorded immediately after deposition from the spectrum recorded after a) 100 minutes 220 nm photolysis of $\mathbf{3}$ b) 100 minutes 213 nm photolysis of $\mathbf{3}$ c) 3 hours 239 nm photolysis of $\mathbf{1}$ d) 3 hours 213 nm photolysis of $\mathbf{1}$ in an Ar matrix. The band of CO is marked with asterisk.

On the basis of the rate of intensity change, the bands appeared upon photolysis can be divided into three groups (see Figures S3–S5 of the Supporting Information).

Based on our previous study,³⁰ the bands at 3246.8/3254.8, 3143.7/3138.9, 2336.7/2332.3, and 1323.4/1320.0 cm⁻¹ together with their site bands, belong to the H₂NCNO : H₂NCN. Similarly, the bands at 2267.6/2272.0, 2223.0/2218.6, 1035.4/1034.4, 829.5/828.4 cm⁻¹ together with their site bands are assigned to the H₂NNCO : H₂NCN complex. (Although the position of the band observed at 3246.8/3254.8 cm⁻¹ correlates well with the previously observed values for H₂NCNO : H₂NCN (see Table S3), and it was clearly seen that the relative intensity of this band changed together with the other bands of H₂NCNO : H₂NCN complex, because this band is broad and it has low intensity, its integration was not carried out in this study.) As seen from the Tables S3–S4 there is only a 1–3 cm⁻¹ difference between the former and the current observations; the largest differences are 5.5, and <1 cm⁻¹ for the two complexes, respectively. This small difference can be explained by the fact that from the different precursors (*i.e.*, constitutional isomers) the photoproduct complexes can have slightly different structures in the matrix cages. These observations support our former identification of the H₂NCNO : H₂NCN and H₂NNCO : H₂NCN complexes and the assignments of their MI-IR spectra.

After the initial 220 nm photolysis, a subsequent 250 nm irradiation was also carried out. In this case the decrease of the bands of $H_2NNCO : H_2NCN$ complex was observed. In addition to the previously assigned bands of this complex some formerly non-observed low-intensity bands could also be identified (see Figure S6 and the bands marked with asterisks in Table S4). The observation of these small bands was possible on one hand due to the relatively large amount of the complex compared to the previous investigation on 1.³⁰ On the other hand, in the case of 1 the precursor has intense bands at almost the same positions, where the new, small bands are observed in the present experiments. These bands of 1 prevented the observation of these low-intensity bands.

Comparing our previous investigations carried out for 1 and the present experiments, some differences are observed. In the former experiment a third isomer of the $[NH_2, C, N, O]$ structures, $H_2NC(NO)$, was also observed in the case of the 239 nm irradiation. The formation of this isomer as a result of irradiation at 213 nm was not observed neither in the previous nor in the present study. On the basis of quantum chemical computations (see Supplementary Material of Ref. 30) this cyclic isomer has an absorption band between 200–220 nm. Therefore, the irradiation likely results in isomerization to more stable forms or to fragmentation.

The photolysis of **3** at 213 nm resulted in the monotone growth of the bands belong to H_2NCNO , and H_2NNCO complexes (see Supporting Information), while in the case of **1** the bands of H_2NCNO reached their maximum intensities at around 45 minutes photolysis time. The intensity of bands of the H_2NCNO complex showed a maximum at ~30 minutes photolysis time in case of 220 nm irradiation. Although in each experiment the formation rate of H_2NCNO is larger than that of H_2NNCO , comparing the absorbance ratios of the H_2NNCO and H_2NCNO bands at the photolysis time when the bands of H_2NCNO have maximum intensity, a notable difference was observed. Namely, the ratio of H_2NNCO and H_2NCNO was 5–6 times larger in the case of the photolysis of **3** at 220 nm, than for the **1** photolyzed at 213 nm.

In addition to the above mentioned and already assigned bands, some additional bands were also observed in the case of the photolysis of **3**. These were observed at 2137.6, 1744.9, 1408.5, 820.4, and 652.1 cm⁻¹ in Ar and at 2131.8, 1740.0, 1409.5, 831.9, and 653.7 cm⁻¹ in Kr together with some site-split bands. Among these, the band at 2137.6/2131.8 cm⁻¹ belongs to the CO molecule.⁶² Carbon-monoxide is a stable photoproduct which may be generated from one of the primary photoproducts. The other newly observed bands show the same intensity change as a function of photolysis time both at 213 and at 220 nm (see Figures S3– S5). Therefore these bands belong to the same species. Among these bands, the most intense is the one at 1744.9 cm⁻¹ in Ar (1740.0 cm⁻¹ in Kr). Considering the computed anharmonic vibrational wavenumbers for the [NH₂, C, N, O] monomers and [NH₂, C, N, O] : H₂NCN complexes, only the H₂NC(NO) and the H₂NC(NO) : H₂NCN complexes have computed bands around 1800 cm⁻¹. As it is discussed above, the formation of this ring-structure isomer is not expected during the irradiation at around 220 nm. Furthermore, in our former study³⁰ the corresponding band of the $H_2NC(NO)$ isomer was identified at 1790 cm⁻¹ in Ar, which is far from the band observed in the present study. In addition, the other unidentified, newly observed bands do not match with the computed bands of $H_2NC(NO)$. As a conclusion the newly observed bands cannot be assigned to [NH₂, C, N, O] isomers.

Another possibility could be that these bands belong to a tautomer of the precursor. According to our vibrational harmonic frequency computations (see Table S5 in the Supporting Information), the assignments to the tautomers of the precursor can be excluded.

A third possibility is that the carrier of these bands is one of tautomers of the $[NH_2, C, N, O]$ isomers. Therefore, the structure and IR spectra of [NH, H, C, N, O] isomers were computed. Here we present the computational results for two low-energy forms, nitrosomethanimine (HNCHNO) and diazenecarbaldehyde (HNNCHO) including their stereoisomers (Figure 5 and Tables and S6), the results for iminomethanimine oxide (HNCNHO), isocyanic acid oxime (HNCNOH), 1-(hydroxymethanidylene)diazen-1-ium (HNNCOH), and *trans*-1,2-oxaziridin-3-imine (HNC(O)NH) isomers are summarized in the Supporting Information (Figure S7 and Tables S7–S8). Each of the last four isomers have two computed bands with larger than 100 km mol⁻¹ computed intensity values in the experimentally observed region, i. e.: 1268, and 1080 cm⁻¹ for HNCNHO; 2083, and 990 cm⁻¹ for HNCNOH; 1297, and 935 cm⁻¹ for HNNCOH; 1882, and 1172 cm⁻¹ for HNC(O)NH. These large intensity values ensure that these isomers can be observable by IR spectroscopy, if at least ~1% of the precursor is converted to these species.



Figure 5. Structure of some low-energy [NH, H, C, N, O] isomers with ZPVE corrected relative energies (in kJ mol⁻¹) as computed at the B3LYP/aug-cc-pVTZ (normal characters) and fc CCSD(T)/cc-pVTZ (bold characters) levels of theory. (The *ct* HNCHNO structure is not a minimum in the fc CCSD(T)/cc-pVTZ calculations.) The relative energy of the most stable [NH₂, C, N, O] isomer, the H₂NNCO (see Ref. 30) was chosen to be 0 kJ mol⁻¹.

In the case of HNCHNO four structures could be located on the potential energy surface (PES) at the B3LYP/aug-cc-pVTZ level. They mostly differ in their HNCH (denoted by first *c* or *t* letter, as they stand for *cis* and *trans*) and NCNO (denoted by second *c* or *t* letter, abbreviating *s*-*cis* and *s*-*trans*) torsion angles. Among these, at the CCSD(T)/cc-pVTZ level of theory the *ct* structure was found as a saddle point and not a minimum on the PES. (Therefore *ct* is not listed in Table S6.) The computed ZPVE corrected isomerization barriers at the B3LYP/aug-cc-pVTZ level of theory are: 200.8 ($cc \rightarrow tc$), 87.3 ($ct \rightarrow tt$), 3.6 ($cc \rightarrow ct$), and 13.9 ($tc \rightarrow tt$) kJ mol⁻¹. For HNNCHO both computational levels predict four minimum energy structures, which mainly differ in the HNNC torsion angle (denoted by the first *c* or *t* letter, as standing for *cis* and *trans*) and by NNCO torsion angle (denoted by the second *c* or *t*

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letter, abbreviating *s-cis* and *s-trans*). *cc* HNCHNO and *tc* HNNCHO are distorted from the planar structure (see Table S6). (For the potential energy scan for HNNCHO see Figure S8.) In these cases there are two energetically equivalent minima on the PES; the two structures corresponding to these two minima are mirror images of each other. The computed ZPVE corrected isomerization barriers for HNNCHO at the B3LYP/aug-cc-pVTZ level of theory are: 169.7 ($ct \rightarrow tt$), 63.2 ($cc \rightarrow tc$), 9.6 ($ct \rightarrow cc$) kJ mol⁻¹. The $tc \rightarrow tt$ barrier is only 0.6 kJ mol⁻¹ without ZPVE correction, while with ZPVE correction the energy of the computed transition structure is 0.4 kJ mol⁻¹ below the *tc* structure. This indicates that *tc*-HNNCHO can only be observed if the cage or a complex formation with the other reaction product stabilizes this structure. Furthermore, it can be concluded that the distortion around the NCNO and the NNCO coordinates, respectively in the two isomers, requires very low energy; therefore both the matrix cage and the complex formation can easily and significantly distort the molecules from their equilibrium structure along this torsion.

The ZPVE corrected relative energy order of the other investigated [NH, H, C, N, O] isomers (in kJ mol⁻¹) are: HNCNOH (145.0), *t*–HNC(O)NH (159.1), HNNCOH (199.3), HNCNHO (255.7) at the fc CCSD(T)/cc-pVTZ level of theory. (See these structures and their computed IR spectra in the Supporting Information.)

tt HNCHNO	tc HNCHNO	cc HNCHNO	Assig	nment	
3248 (2.0)	3194 (6.4)	3314 (3.0)	NH str.		
2977 (10)	3069 (11)	2941 (23)	СН	str.	
1648 (22)	1642 (9.5)	1638 (24)	NC	str.	
1543 (35)	1541 (33)	1544 (26)	NO	str.	
1332 (38)	1343 (23)	1344 (30)	HNCH def.		
1190 (19)	1161 (80)	1154 (57)	HNCH def.		
1065 (68)	1053 (74)	1052 (6.7)	HNCH def.		
960 (62)	763 (24)	875 (33)	NCNO def.		
804 (24)	757 (25)	758 (11)	de	ef.	
558 (1.8)	708 (23)	602 (22)	def.		
354 (21)	324 (13)	347 (8.4)	def.		
132 (3.6)	152 (0.6)	136 (21)	def.		
tc HNNCHO	cc HNNCHO	ct HNNCHO	tt HNNCHO Assignment		
3128 (5.6)	2924 (57)	2742 (58)	3153 (0.9) NH str.		
2865 (56)	2815 (5.5)	2589 (94)	2829 (47) CH str.		
1785 (170)	1774 (82)	1811 (154)	1794 (137) CO str.		
1564 (16)	1552 (21)	1546 (28)	1533 (11) NN str.		
1454 (45)	1462 (53)	1456 (69)	1433 (60) HNN bend.		
1357 (2.8)	1325 (15)	1325 (10)	1325 (1.8) OCH bend.		
1029 (56)	1101 (25)	1046 (14)	1068 (16)	HNNC def.	
1017 (33)	775 (47)	941 (59)	981 (52)	HCNN def.	
828 (39)	774 (15)	847 (49)	809 (29)	def.	

Table 1. Computed^a vibrational wavenumbers (in cm⁻¹) and infrared intensities (in km mol⁻¹) of the HNCHNO and the HNNCHO isomers.

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512 (7.3)	739 (64)	599 (0.5)	604 (5.0)	def.
336 (7.2)	394 (22)	428 (22)	413 (9.7)	def.
$34^{b}(4.6)$	105 ^b (52)	121 (6.3)	99 (5.7)	def.

^afc CCSD(T)/cc-pVTZ harmonic wavenumbers corrected by B3LYP/aug-cc-pVTZ anharmonic contributions. IR intensities obtained by the harmonic approximation at fc CCSD(T)/cc-pVTZ level of theory are given in brackets.

Considering the computed wavenumbers of fundamental vibrational transitions for the [NH, H, C, N, O] species (see Tables 1 and S8 of the Supporting Information), only three HNNCHO isomers have a computed band in the $1700-1800 \text{ cm}^{-1}$ region, and the *ct* HNNCHO isomer has an intense band at 1811 cm^{-1} . Although there is a quite good agreement for the bands observed at 1744.9/1740.0, 1408.5/1409.5, and $820.4/831.9 \text{ cm}^{-1}$ in Ar/Kr, the computation does not predict a band near the experimentally observed one at $652.1/653.7 \text{ cm}^{-1}$ for the *tc* and *cc* structures, while for the other two isomers the computed intensity of the band at ~ 600 cm^{-1} is very low. Furthermore for each HNNCHO isomer there is at least one medium intensity computed band which cannot be identified in the spectra.

A possible reason of these differences is that the decomposition of the precursor at matrix isolation conditions can result in complexes in the matrix cage. To justify this, several complex structures were also computationally studied.

The computed structures of the HNNCHO : H_2NCN complexes are shown in Figure 6. (The complexes are denoted by C(O)-*xy*, where *x* stands for the HNNC torsion angle, and can be *c* or *t*, while *y* is the number of the structure. The NNCO torsion is not referred in the name of the complexes, because, as it is mentioned above, along this torsion the PES is shallow, the HNNCHO molecules can significantly distort as a consequence of complex formation.) As seen from the figure, altogether seven complexes were found, in the case of the *tc*-like monomer structure only one complex was found, which can be explained by the very small barrier between the *tc* and the *tt* structures.

The most stable complex is C(O)-t2, while the best agreement between the computed and the measured values is obtained for the C(O)-t1 structure. The computed wavenumbers of the fundamental vibrational modes and intensities together with the assignments to the experimentally observed bands for these two complexes are given in Table 2. (For the computed anharmonic values of these two isomers, and computed IR spectra of the other isomers see the Supporting Information.)

Altogether four vibrational fundamentals could be observed. Although the computations predict some further intense bands (*e.g.*, the NH stretching modes above 3000 cm^{-1}) that are

^b Vibrational perturbation theory predicted too large anharmonic corrections, therefore the harmonic values are presented.

not observed experimentally, the computed intensity and wavenumber of these modes are very sensitive to the structure of the complex, therefore they are most likely broad features in the experimental spectra, and they cannot be observed in the background noise, or they overlap with bands of other products.



Figure 6. Structures of HNNCHO : H₂NCN complexes as obtained at the MP2/cc-pVTZ level of theory together with ZPVE corrected relative energies (in kJ mol⁻¹) as computed at the B3LYP/cc-pVTZ (normal characters) and MP2/cc-pVTZ (bold characters) levels of theory. The relative energy of the most stable complex (C(O)-t2) was chosen to be 0 kJ mol⁻¹.

Table 2. Computed and experimental wavenumbers of fundamental vibrational transitions (in cm⁻¹), computed IR intensities (in km mol⁻¹) and experimental relative IR absorbances (in parentheses) of HNNCHO : H_2NCN in the 3800–600 cm⁻¹ region.

Computed ^a		Experin	mental ^b		
C(O)- <i>t</i> 1	C(O)- <i>t</i> 2	Ar matrix	Kr matrix	Assignment	
3482 (93)	3512 (98)	-	-	NH ₂ as str. of H ₂ NCN	
3355 (108)	3401 (55)	-	-	NH ₂ symm. str. of H ₂ NCN	
3183 (0.7)	3164 (72)	-	-	NH str. of HNNCHO	
2943 (17)	2864 (47)	-	-	CH str. of HNNCHO	
2214 (62)	2217 (72)	_ ^d	_d	CN str. of H ₂ NCN	
1746 (110)	1779 (112)	1744.9, 1739.0, 1733.7 ^c (100)	1740.0, 1736.6, 1733.7° (100)	CO str. of HNNCHO	
1596 (28)	1580 (45)	-	-	NN str. of HNNCHO	
1500 (20)	1501 (36)	-	-	HNH bending of H ₂ NCN	
1427 (33)	1451 (46)	1408.5 (sh. 1406.4) (13)	1409.5 (29)	NNH bending of HNNCHO	
1359 (1.0)	1321 (1.6)	-	-	OCH bending of HNNCHO	

1194 (4.2)	1181 (3.5)	-	-	HNH bending of H ₂ NCN
1073 (5.7)	1080 (5.0)	-	-	NC str. of H ₂ NCN
1027 (18)	1101 (16)	-	-	def. of HNNCHO
974 (73)	852 (22)	-	-	def. of HNNCHO
847 (28)	1013 (84)	820.4 (3.0)	831.9 (4.9)	def. of HNNCHO
610 (218)	664 (196)	652.1 (sh. 652.8), 677.9 ^e (7.6)	653.7, 652.2 ^e (21)	HNH bending of $H_2NCN(t1) / def.$ of HNNCHO(t2)

^aMP2/cc-pVTZ harmonic vibrational transitions corrected by B3LYP/cc-pVTZ anharmonic contributions (in cm⁻¹) and harmonic MP2/cc-pVTZ IR intensities (in km mol⁻¹). ^bBands obtained after 220 nm irradiation. The relative intensity of the most intense band of

HNNCHO:H₂NCN was chosen to be 100. [°]Site split bands.

^dThe bands of the complexed H_2NCN are assigned to corresponding bands of the H_2NCNO : H_2NCN and H_2NNCO : H_2NCN complexes that are formed in much larger amounts (see Supporting Information).

^eSite split band or Fermi resonance, see Table S19.

As seen in Figure 4, the identified HNNCHO : H_2NCN complex was generated only from **3** by irradiation (at both 213 nm and 220 nm), while the photolysis of **1** did not result in this complex (either at 213, or at 239 nm). As it is mentioned above, in the case of 220 nm photolysis of **3**, the amount of HNNCHO : H_2NCN (Figure S5) had a maximum at ~30 min irradiation, while H_2NNCO : H_2NCN was monotonously growing till the end, or only slightly decreased at the end (~100 min) of irradiation. These observations prove that HNNCHO is not a photoisomerization product of H_2NNCO , but it is generated from **3** in an independent reaction path.

Photolysis of 1,2,4-thiadiazole-3,5-diamine (4)

On the basis of the MI-UV spectrum of **4** (see Figure 2) the photolysis was carried out near the maximum position of the MI-UV band, namely at 240, 250, and 260 nm in Ar and at 250 nm in Kr. These photolysis experiments resulted in several new bands in the IR spectra with different relative absorbance *vs.* photolysis time curves (see Figures 7 and S9–S12). Based on these curves, the bands appeared upon the photolysis experiments can be divided into four groups.



Figure 7. Difference spectra as obtained by subtraction of the spectrum recorded immediately after deposition from the spectrum recorded after 250 nm photolysis of **4** in an Ar matrix a) after 20 min photolysis b) after 100 min photolysis c) after 30 min photolysis d) after 10 min photolysis (At these selected times the products were present in the largest quantity.)

The position of these bands of three of these groups agrees very well with the previously reported vibrational wavenumbers of the H₂NCNS : H₂NCN and the H₂NNCS : H₂NCN complexes, and the H₂NC(NS) molecule (see Tables S10–S12 in the Supporting Information). For the H_2NCNS : H_2NCN complex three, while for the H_2NNCS : H_2NCN complex six bands (together with their site bands) were observed, so all of the previously observed bands were detected in the present experiments (see Tables S10-S11 and Figure 7). In the present experiments, only two bands of the H2NC(NS) molecule were observed, and their intensities were smaller than in the case of the 280 nm photolysis of **2**. The smaller amount of this ringstructure isomer can be explained by the shorter irradiation wavelengths used compared to the ones applied in the previous study.³⁰ When 2 was irradiated at 221 nm, the formation of the ring-structure isomer was not observed in a detectable amount. This is in line with the computations (see Supplementary Material of Ref. 30), which predict absorption bands for the ring-isomer at 229 and 208 nm. In the case of $H_2NC(NS)$, the largest difference between the previously reported vibrational wavenumbers and the present ones is not larger than 0.5 cm⁻¹ (see Table S12 of the Supporting Information), which is smaller than the instrumental resolution. In the case of the two complexes somewhat larger differences, $1-3 \text{ cm}^{-1}$, were observed. As in the case of the O-analogue, this can be explained by the slightly different structures that can form in the matrix cage from the two different precursors. Based on this, the observed differences also support the previous identification of these molecules, and also support that the H₂NCNS and H₂NNCS are present in a complex formed with the other photoproduct, the cyanamide molecule.

Along with the bands identified above, upon the 240, 250 and 260 nm irradiations of **4**, some further bands appeared in the MI-IR spectra, namely at 3522.3 (with a site band at 3516.9), 3413.9 (with a site band at 3418.4), 1617.4, 1442.2, 1250.6, 1012.9 (with a site band at 1006.1), and 891.7 cm⁻¹ in Ar, and at 3519.3 (with a site band at 3512.1), 3405.3 (with a site band at 3409.7), 1614.7, 1439.7, 1246.2, 1016.2 (with a site band at 1010.7), and 888.8 cm⁻¹ in Kr. These bands were not observed in the photolysis of **2**. All of these bands show the same relative intensity change as the function of time, which is shown in Figures S9–S12 for four of these bands at 1617.4, 1442.2, 1250.6, and 1012.9 (with a site band at 1006.1) cm⁻¹ in Ar, and 1614.7, 1439.7, 1246.2, 1016.2 (with a site band at 1010.7) cm⁻¹ in Kr. (The bands at 3522.3/3519.3 cm⁻¹ in Ar/Kr overlap with the bands of the generated H₂NC(NS) isomer, while the edge of the bands at 3413.9/3405.3 cm⁻¹ overlap with one of the bands of the precursors, the 891.7/888.8 cm⁻¹ band has very small absorbance, therefore these bands cannot be accurately integrated, and their absorbance *vs.* time curve is not plotted in the Figures. By visual inspection it was clear, that especially at the beginning of the photolysis, these bands have the same behavior like the other four bands.)

Similarly to the O-analogue, on the basis of comparison of the experimental wavenumbers and intensity values of these new bands and that of the computed ones for the [NH₂, C, N, S] isomers and [NH₂, C, N, S] : H₂NCN complexes (see Ref. 30), no good match was observed in any case. Unlike in the case of the O-analogues, among the S-containing isomers H₂NSCN has the lowest energy. It is interesting to note, that this isomer (and that of its O-analogue) was not observed in any of the photolysis experiments. According to the computation (see Ref. 30) H₂NSCN has only one medium intensity band in the observed region at 842 cm⁻¹, the computed intensities of the other bands are smaller than 30 km mol⁻¹, which is a possible explanation for the lack of its observation both in the earlier³⁰ and in the present experiments. Furthermore, the tautomers of the precursor can also be excluded as the carriers of these bands (see computed structures and IR spectra in Table S13 of the Supporting Information).

As it was observed in the case of **3**, photolysis may result in a tautomer of the pseudohalogen molecules, so the unidentified bands may belong to one of the [NH, H, C, N, S] isomers. To justify this, some low-energy isomers were investigated from this family. Here were present the results for thionitrosomethanimine (HNCHNS) and diazenecarbothialdehyde (HNNCHS) (see Figure 8 and Tables 3 and S14). Similarly to the O-analogue, both of these two species have stereoisomers, which are connected by isomerization barriers (in kJ mol⁻¹ at the ZPVE corrected B3LYP/aug-cc-pVTZ level of theory) of 92.3 ($cc \rightarrow tc$), 91.9 ($ct \rightarrow tt$), 2.1 ($tc \rightarrow tt$), and 6.4 ($cc \rightarrow ct$) for HNCHNS, while 37.1 ($cc \rightarrow tc$), 171.6 ($ct \rightarrow tt$), 2.4 ($tt \rightarrow tc$), 3.1

 $(ct \rightarrow cc)$ for HNNCHS. (For the potential energy scan of HNNCHS see Figure S14.) The structures and computed IR spectra of other constitutional isomers, including iminomethanimine sulfide (HNCNHS), *N*-(iminomethylene)thiohydroxylamine (HNCNSH), 1-(mercaptomethanidylene)diazen-1-ium (HNNCSH), 1-thioformyldiazen-1-ium (HNNHCS), and *trans*-1,2-thiaziridin-3-imine (HNC(S)NH) are presented in the Supporting Information (Figure S13 and Tables S15–S16). The relative energy order of these latter isomers (with their energies relative to H₂NSCN in kJ mol⁻¹ at the CCSD(T)/cc-pVTZ level of theory): HNCNSH (35.1), *t*-HNC(S)NH (97.1), HNCNHS (142.1), HNNCSH (180.8), HNNHCS (263.6).



Figure 8. Structure of some low-energy [NH, H, C, N, S] isomers with ZPVE corrected relative energies (in kJ mol⁻¹) as computed at the B3LYP/aug-cc-pVTZ (normal characters) and fc CCSD(T)/cc-pVTZ (bold characters) levels of theory. The relative energy of the most stable [NH₂, C, N, S] isomer, the H₂NSCN (see Ref. 30) was chosen to 0 kJ mol⁻¹.

tt HNCHNS	tc HNCHNS	ct HNCHNS	cc HNCHNS	Assignment	
3267 (4.8)	3243 (1.3)	3306 (5.1)	3317 (3.6)	NH str.	
2943 (11)	3024 (8.3)	2887 (22)	2887 (22) 2910 (21)		
1587 (11)	1576 (31)	1583 (18)	1582 (56)	NC str.	
1352 (43)	1354 (26)	1355 (13)	1356 (32)	HNCH def.	
1213 (74)	1193 (73)	1216 (44)	1200 (34)	HNCH def.	
1073 (58)	1079 (29)	1052 (2.8)	1069 (37)	HNCH def.	
1043 (5.4)	1034 (53)	1052 (5.1)	1025 (6.7)	HCNS def.	
956 (30)	843 (16)	916 (50)	860 (29)	HNCH def.	
852 (31)	798 (13)	805 (31)	790 (44)	HNCH def.	
488 (6.6)	574 (40)	525 (5.7)	580 (12)	HNCN def.	
309 (2.7)	293 (3.0)	334 (8.3)	297 (26)	def.	
106 (0.3)	107 (3.2)	102 (3.5)	145 (25)	def.	
tc HNNCHS	cc HNNCHS	ct HNNCHS	tt HNNCHS	Assignment	
3136 (2.7)	3007 (3.8)	2864 (35)	3158 (0.5)	NH str.	
2982 (6.8)	2960 (22)	2801 (51)	2958 (5.7)	CH str.	
1545 (6.2)	1531 (17)	1502 (23)	1484 (4.3)	NN str.	
1436 (72)	1447 (53)	1447 (112)	1439 (19)	HNN bend.	
1310 (51)	1301 (14)	1314 (42)	1314 (60)	HCS bend.	
1085 (48)	1074 (22)	1116 (15)	1098 (14)	CS str.	
961 (29)	941 (90)	964 (64)	969 (5.8)	HNNC def.	
882 (6.4)	867 (17)	946 (3.6)	946 (16)	def.	
809 (21)	803 (6.5)	771 (7.7)	770 (53)	def.	
479 (22)	579 (14)	523 (1.5)	512 (6.5)	def.	
334 (0.72)	321 (20)	331 (5.1)	335 (3.4)	def.	
121 (1.8)	175 (28)	76 (0.003)	83 (0.6)	def.	

Table 3. Computed^a vibrational wavenumbers (in cm⁻¹) and infrared intensities (in km mol⁻¹) of [NH, H, C, N, S] isomers.

^afc CCSD(T)/cc-pVTZ harmonic wavenumbers corrected by B3LYP/aug-cc-pVTZ anharmonic contributions. IR intensities obtained by the harmonic approximation at fc CCSD(T)/cc-pVTZ level of theory are given in brackets.

From the [NH, H, C, N, S] isomers, the most intense unidentified band at 1442.2/1439.7 in Ar/Kr agrees the best with a computed intense band of the four HNNCHS isomers. For the other bands, at 1617.4/1614.7, 1250.6/1246.2, 1012.9/1016.2, and 891.7/888.8 cm⁻¹ the agreement between the experiment and computations is not as good as it is expected at this level of theory. Furthermore, the computations do not predict transitions for the four free HNNCHS monomers (and nor for the other monomers) at around 3500 cm⁻¹, but two bands were also observed in this region. It can be assumed that the photolysis resulted in a HNNCHS complex.

As in the case of the O-analogue, the computed vibrational transitions of these complexes (see Figure 9 for the structures and Tables 4 and S17 for the computed wavenumber and intensity values) correlate better with the above-mentioned bands than the computed IR bands of the free molecule (see Table 4). In this case seven fundamental transitions could be assigned. The best agreement is obtained for the C(S)-c3 complex. For this complex the largest deviations

between computation and experiment of 49 and 53 cm⁻¹ were obtained for the bands at 892 and 1251 cm⁻¹ in Ar, but the position of these bands is very sensitive to the structure of both the monomer (*i.e.*, *cis* or *trans*) and to the that of the complex (see Tables 4 and S17). Considering the computed IR spectrum of the C(S)-*c*3 complex, only one medium intense (>50 km mol⁻¹) band was not observed in our experiments. The generated H₂NNCS : H₂NCN complex has an absorption band at ~2260 cm⁻¹ (see Table S11) which likely overlap with the band of C(S)-*c*3 expected at 2218 cm⁻¹. The assignment of HNNCHS further supports the identification of HNNCHO in the previously discussed analogous reaction.



Figure 9. Structures of HNNCHS : H_2NCN complexes as obtained at the MP2/cc-pVTZ level of theory together with ZPVE corrected relative energies (in kJ mol⁻¹) as computed at the B3LYP/cc-pVTZ (normal characters) and MP2/cc-pVTZ (bold characters) levels of theory. The relative energy of the most stable complex (C(S)-*t*3) was chosen to be 0 kJ mol⁻¹

Table 4. Computed and experimental wavenumbers of fundamental vibrational transitions (in
cm ⁻¹), computed IR intensities (in km mol ⁻¹) and measured relative IR absorbances (in
parentheses) of HNNCHS : H_2NCN in the 3800–600 cm ⁻¹ region.

1 /	=		0		
Com	puted ^a	Experi	mental ^b	Aggignmont	
C(S) - c3	C(S) - t3	Ar matrix	Kr matrix	Assignment	
2482 (88)	2400 (110)	3522.3,	3519.3,	NH og str of H NCN	
5462 (88)	5499 (110)	3516.9° (s)	3512.1° (s)	NH_2 as str. of H_2NCN	
2201 (00)	2278 (84)	3413.9,	3405.3,	NH ₂ symm. str. of	
3391 (90)	5576 (64)	3418.4^{c} (s)	3409.7 ^c (s)	H ₂ NCN	
2895 (18)	3163 (66)	-	-	CH str. of HNNCHS	
2838 (28)	2982 (4.6)	-	-	NH str. of HNNCHS	
2218 (58)	2210 (67)	- ^d	_ ^d	CN str. of H ₂ NCN	
1486 (42)	1488 (32)	-	-	NN str. of HNNCHS	
1576 (26)	1562 (24)	1617.4 (m)	1614.7 (m)	HNH bending of	
13/0 (30)	1303 (34)	1017.4 (m)	1014.7 (m)	H ₂ NCN	
1415 (77)	1421 (12)	1442.2 (a)	1420 7 (s)	NNH bending of	
1413 (77)	1421 (12)	1442.2 (8)	1439.7 (8)	HNNCHS	
1204 (17)	1211 (27)	1250.6 (m)	1246.2 (m)	SCH bending of	
1304 (17)	1311 (37)	1230.0 (w)	1240.2 (w)	HNNCHS	
1127(74)	1160 (2.7)			HNH bending of	
1137 (7:4)	1109 (2.7)	-	-	H ₂ NCN	
1186 (4.2)	1075 (4.7)	-	-	NC str. of H ₂ NCN	
1078 (5.0)	1124 (10)	-	-	def. of HNNCHS	
971 (55)	1014 (7.6)	1012.9,	1016.2,	def of HNNCHS	
7/1 (55)	1014 (7.0)	1006.1° (w)	$1010.7^{\rm c}({\rm w})$		
941 (19)	973 (24)	891.7 (vw)	888.8 (vw)	def. of HNNCHS	
742 (9.6)	807 (49)	-	-	def. of HNNCHS	

^aMP2/cc-pVTZ harmonic vibrational transitions corrected by B3LYP/cc-pVTZ anharmonic contributions (in cm⁻¹) and harmonic MP2/cc-pVTZ IR intensities (in km mol⁻¹).

^bBands obtained after 240 nm irradiation in Ar and 250 nm irradiation in Kr. The exact integration of the observed bands was not possible. s: strong, m: medium, w: weak, vw: very weak

^cSite split bands.

^dThe bands of the complexed H_2NCN are assigned to corresponding bands of the H_2NCNS : H_2NCN and H_2NNCS : H_2NCN complexes that are formed in much larger amounts (see Supporting Information).

As in the case of the O-analogue, the formation of HNNCHS was observed only when 4 was used as the precursor regardless to the wavelength used. Furthermore, the amount of HNNCHS showed a maximum at an early photolysis time, while the intensity maximum of the bands of $H_2NC(NS)$ observed later, and the concentration of H_2NNCS is increasing till the end of the experiment. This means that, similarly to the O-analogue, the HNNCHS is not a photoisomerization product of H_2NNCS or $H_2NC(NS)$.

Conclusions

In this study the UV laser photolysis of 1,2,4-oxadiazole-3,5-diamine (3) and 1,2,4thiadiazole-3,5-diamine (4) was studied. The photochemistry of these species is compared to that of the previously studied structural isomers of these precursors, 1,2,5-oxadiazole-3,4diamine (1) and 1,2,5-thiadiazole-3,4-diamine (2). First, the MI-UV spectra were measured to choose the appropriate wavelengths for the photolysis, which were 213, and 220 nm for the O-analogue, and 240, 250, and 260 nm for the S-analogue. In order to facilitate the spectrum analysis, the normalized absorbances of the bands appearing upon the irradiation were plotted as the function of the photolysis time. These studies showed that the bands appearing upon photolysis can be grouped into three and into four different photoproducts of 3 and 4, respectively. Comparing these groups of bands with our previous results for the photolysis of 1 and 2, two groups of bands were assigned to the $H_2NCNX : H_2NCN, H_2NNCX : H_2NCN$ (X = O, S) complexes, and a third group of bands of the S-analogue with H₂NC(NS). In both cases the group of bands that remained unidentified was not observed when the other precursors were used in the experiments. On the basis of quantum chemical computations, it was excluded that these bands belong to tautomers of the precursors, or to formerly unobserved [NH₂, C, N, X] isomers, but these bands correlated best with the most intense computed vibrational bands of HNNCHO and HNNCHS. In both cases the agreement between computations and experimental observations was much better when the IR spectra were computed for the complexes of these molecules with the by-product of the photolysis, H₂NCN. Since the structure of the complexes can be affected significantly by the cage of the matrix, the identification of the complexes are only tentative. In the case of O-analogue the best agreement between the observed and computed IR spectra was obtained for C(O)-t1, while for the S-analogue for the C(S)-c3 complex.

Considering the formation rate curves, it was concluded that HNNCHO and HNNCHS are not photoisomerization products of H_2 NNCO and H_2 NNCS, respectively, but they are formed in a different reaction path. Since HNNCHO and HNNCHS are not observed in the photolysis of **1** and **2**, their formation path possibly goes through a tautomer of **3** and **4**. The most likely first step in the decomposition of the ring is the NO bond cleavage. A second possibility is that in the case of **3** and **4** very reactive nitrenes ($H_2NC(N)O$ and $H_2NC(N)S$) are formed together with NH₂CN. These nitrenes might rearrange to HNNCHX. Because of the different constitution of the precursors, these nitrenes cannot be formed from **1** and **2**. Unfortunately, none of these possible intermediate nitrenes could be identified. (For the computed IR spectra

of singlet and triplet nitrenes see Supporting Information.) A third possibility is that in the first step of the photolysis a cyclic H-bonded intermediate is formed. In the case of **3** and **4** the geometric arrangement of this intermediate can facilitate a double H-transfer leading to the formation of HNNCHO and HNNCHS, respectively. A similar mechanism in a different intermediate formed from **1** and **2** might also explain why carbodiimide was observed in the photolysis of **1** and **2**, but not for **3** and **4**. In order to understand the reaction paths we are currently investigating the photolysis of mono amino substituted analogues of the precursors and we are carrying out supplementary quantum chemical computations.

Both for **3** and **4** the destruction of the diazenes was observed at the end of long UV irradiations. Possible decomposition products could be H_2CX and N_2 , but the bands of H_2CO^{63} or H_2CS^{64} were not observed in our experiments. Most likely at our photolysis wavelengths the final product is the H_2NNCX : H_2NCN complex, and the complexes of diazenes also isomerize to these species. In a relatively small amount CO was also identified as a final photoproduct of **3**.

Although we are aware of some theoretical studies for HNNCHO,^{65–67} neither HNNCHO nor HNNCHS was observed experimentally earlier. These novel molecules can be important as being reactive intermediates in organic chemistry and they are also potential astrochemical species.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. The MI-IR spectra and the computed IR spectra of the precursors; the computed and the experimentally observed wavenumbers of fundamental vibrational transitions with their intensities of the H₂NCNX : H₂NCN, H₂NNCX : H₂NCN, (X = O, S) complexes, and the H₂NC(NS) isomer; the computed IR spectra of the tautomers of the precursors; the computed structures and IR spectra of some [NH, H, C, N, X] (X = O, S) monomers other than HNCHNX and HNNCHX, the computed anharmonic wavenumbers for the C(O)-*t*1, C(O)-*t*2, C(S)-*c*3, and C(S)-*t*3 complexes, potential energy scans for HNNCHX; normalized absorbances *vs.* photolysis time curves for the bands obtained during the photolysis of the precursors (213 nm in Ar, 220 nm in Kr for **3**, 240, 260 nm in Ar and 250 nm in Kr for **4**); and difference spectra for the photolysis of **3** (at 220 and 250 nm in Ar).

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Notes

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