

Matrix isolation study on the 1:1 hydrogen-bonded complexes [H, C, N] $\cdots$ [H, C, N, O]

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ABSTRACT

[H, C, N] $\cdots$ [H, C, N, O] complexes were prepared by the photolysis of 1,2,5- and 1,3,4-oxadiazoles, utilizing the cage effect of the low-temperature, rigid Ar matrix. The complexes were characterized and identified by IR spectroscopy aided by quantum chemical computations. In the case of 1,2,5-oxadiazole HCN $\cdots$ HCN, HCN $\cdots$ HCNO, HCN $\cdots$ HNCO, and HCN $\cdots$ HOCN complexes were identified among the 220 nm photolysis products. The 220 nm photolysis of 1,3,4-oxadiazole generated HCN $\cdots$ HNCO and HCN $\cdots$ HOCN. Upon a secondary photolysis by a Hydrogen lamp, hydrogen isocyanide complexes, namely HCN $\cdots$ HNC, HNCO $\cdots$ HNC and HNC $\cdots$ HOCN could also be prepared and characterized spectroscopically. On the basis of product distribution, photodecomposition mechanisms are proposed.

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1. Introduction

Pseudohalogenides are among the most abundant molecular species in interstellar space. Several representatives of these compounds have already been identified in the interstellar medium (ISM), including HCN [1], HNC [2], HNCO [3], HCNO [4], and HOCN [5,6]. Since the ratio of the different isomers are sensitive to many parameters, the relative abundance of these compounds is considered as a sensitive indicator of the physical and chemical environments of ISM [7]. Furthermore, these compounds might be the precursors of complex organic molecules formed in space. As an example, many studies focused on exploring potential pathways of interstellar adenine formation from HCN [8,9].

H-bonded complexes are present on the surface of interstellar grains and in planetary atmospheres [10–12]. HCN ice was tentatively identified on Triton by analyzing the data recorded by AKARI infrared astronomy satellite [13]. It can be expected that after the launch of James Webb Space Telescope, the identification of H-bonded complexes or ices on the basis of their IR spectra might be

possible both in the ISM or in the atmospheres of exoplanets; therefore, extensive laboratory data acquisition is required for the analysis of future astronomical observations [14]. The formation a H-bonded complex can facilitate reactions between the monomers of the complex induced by different types of radiation. Matrix isolation spectroscopy is an important tool both for spectroscopic characterization of these complexes, and also for exploring the mechanism of radiation-induced reactions.

Among the astrochemically relevant complexes of HCN and HNC, HCN $\cdots$ HCN [15], O $\cdots$ HCN [16], O₃ $\cdots$ HCN [16], H₂O $\cdots$ HCN [17], HCN $\cdots$ HOH [17], H₂O $\cdots$ HNC [17], HNC $\cdots$ HOH [17], HNC $\cdots$ HCNS [18], S $\cdots$ HCN [19], OC $\cdots$ HCN [20], OC $\cdots$ HNC [20], OCO $\cdots$ HCN [21], and HCN $\cdots$ CO₂ [21] were characterized by IR spectroscopy in low-temperature inert matrices. It was shown by Mielke and Andrews that the broad-band UV photolysis of O₃ $\cdots$ HCN complex in solid Ar leads to O $\cdots$ HCN and HCNO as primary products, and (HNCO)₂ as a secondary product [16]. Feldman and coworkers observed the transformation of OC $\cdots$ HCN isolated in Ar and Kr matrices to OC $\cdots$ HNC upon X-ray irradiation [20]. The same group investigated the X-ray irradiation of HCN $\cdots$ CO₂ complexes in Ar and Kr matrices [21]. Upon the irradiation, CN and HNC were formed, and the subsequent annealing of the irradiated matrix lead to the formation of H₂CN, *trans*-HCNH and 'N-coordinated' *trans*-HCNH $\cdots$ CO₂ complex.

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The goal of the present study was to prepare and spectroscopically characterize binary H-bonded complexes between [H, C, N] and [H, C, N, O] isomers. The complexes were prepared *in situ* in Ar matrix from 1,3,4- and 1,2,5-oxadiazole (Scheme 1) by laser UV photolysis at 220 nm. The NH₂ substituted derivatives of these diazoles were recently used by us to prepare [NH₂, C, N, O] isomers by photolysis [22,23]. A subsequent photolysis at 121.6 nm, using an H-atom lamp, was used to induce further reactions and generate secondary molecular species or complexes. The identifications of the complexes were supported by *ab initio* computations.

2. Methods

2.1. Synthesis of the precursors

The glyoxime [24] and N,N'-diformylhydrazine [25] starting materials were prepared according to previously published methods, all other starting materials were obtained from commercial suppliers, and were used without further purification.

For the preparation of 1,2,5-oxadiazole [26,27] under a fume-hood a 500-mL two-necked flask was fitted with an adapter with two parallel necks and a thermometer extending almost to the bottom of the flask. The adapter was equipped with an overhead stirrer and a vertical recovery still head connected to an Allihn condenser fitted with a straight vacuum receiver and a 100-mL flask cooled with an ice bath. Finely grounded 42.50 g (0.483 mol) glyoxime and 62.50 g (0.625 mol) succinic anhydride were mixed and introduced into the reaction flask. The mixture was heated with a heat gun very carefully. It liquefied and a rapid reaction started at 150–160 °C with formation of dense fumes. The distillation was continued until the temperature reached 200 °C. When the apparatus was cooled down to ambient temperature, 20 mL water was added to the receiver. The distillate was extracted with three 30 mL portions of diethyl ether, dried over MgSO₄ and evaporated in a rotary evaporator. The crude material was distilled through a short-path distillation apparatus at atmospheric pressure. The pure product was collected in the 95–100 °C range. Yield: 6.07 g (0.087 mol, 17.9 mol%) colorless oily liquid. ¹H NMR (CDCl₃, 500 MHz): δ 8.27 (s, 2H, lit. τ = 1.81 (δ 8.19 ppm) in CCl₄ [26]). ¹³C NMR (CDCl₃, 126 MHz): δ 140.94 ppm.

To synthesize 1,3,4-oxadiazole [28] (see Scheme 1), 74.00 g polyphosphoric acid was introduced into a 250-mL round-bottom flask and stirred at 100 °C on an oil bath while 8.20 g P₄O₁₀ was added to the liquid. After 15 min 8.22 g (0.093 mol) N,N'-diformylhydrazine was added to the mixture. It was stirred for 4 h and then poured onto 400 g ice in a 1 L beaker. The resulting solution was neutralized by NaHCO₃ and extracted with four 120 mL portions of dichloromethane. Combined organic phase was dried over MgSO₄ and evaporated in a rotary evaporator. Yield: 0.97 g (0.014 mol, 14.8 mol%) colorless oily liquid. ¹H NMR (CDCl₃, 250 MHz): δ 8.52 (s, 2H; lit. 8.52 [28]). ¹³C NMR (CDCl₃, 63 MHz): δ 152.9 (lit. 152.7 [28]).

2.2. Spectroscopic measurements

The precursors were premixed with argon (Messer, 99.9999%) in a 1:1000–1:2000 ratio. For deposition the gas flow was kept at ~1

scm, the deposition time was 2.5–4 h. The mixture was condensed onto a 10 K CsI window, attached to a Janis CCS-350R cold head cooled by a CTI Cryogenics 22 closed-cycle refrigerator unit. The temperature of the cold window was controlled by a Lake Shore 321 thermostat equipped with a silicon diode thermometer. The cold window was set at 45° to the optical path of the spectrometer, and the irradiating laser beam was perpendicular to the optical path. The IR spectra were recorded by a Bruker IFS 55 spectrometer, using a Globar source and an MCT detector. The spectra were recorded at 1 cm⁻¹ instrumental resolution in the 4000–650 cm⁻¹ spectral region. Happ–Genzel apodization function, Mertz phase correction using phase resolution of 32 cm⁻¹, and a zero filling factor of 4 were applied.

2.3. Photolysis

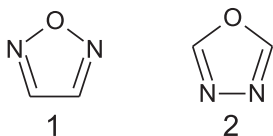
The UV photolysis at 220 nm was carried out by a second harmonic generation unit (GWU uvScan) attached to an optical parametric oscillator (VersaScan MB 240 OPO, GWU/Spectra Physics). The OPO was pumped by the third harmonic (355 nm) of a pulsed (10 Hz, 2–3 ns) Quanta Ray Lab 150 Nd:YAG laser (Spectra Physics). The pulse energy was between ~1 and 3 mJ. The laser beam was unfocused; its diameter was about 0.8 cm. An LPW 3860 low pass filter was placed between the sample and the detector of the IR spectrometer to make possible IR spectroscopic measurements during UV irradiation.

For secondary photolysis a microwave discharge H-lamp was used. A quartz tube with two ports on the side (F-shaped) was mounted to the LiF window of the cold head of matrix isolation setup. The lamp was powered by an EMS Microtron 200 Mk3 microwave generator (*P* = 100W), the discharge was ignited by a Tesla pistol. H₂ gas was entered into the quartz tube through the inlet closer to the window, while the other port of the lamp tube was connected to a turbomolecular pump. The pressure was measured between the pump and the outlet of the lamp and it was set to 0.4 mbar. It was shown by Lingterink et al. that for this applied geometry this pressure is the optimal to get the highest intensity of the astrophysically important Hydrogen Lyman-α radiation compared to the broad-band UV background [29].

2.4. Computational details

Quantum chemical computations were performed by the Gaussian09 program package [30]. Equilibrium structures, harmonic vibrational frequencies and intensities, and zero-point vibrational energy corrected bond dissociation energies of the complexes were computed at the B3LYP-D3/cc-pVTZ level of theory. The optimized geometries, the computed vibrational frequencies and intensities are summarized in Tables S1 and S2.

In order to get better estimates for vibrational frequencies, the equilibrium structures and harmonic frequencies of the monomers were also computed at the B3LYP-D3/cc-pVTZ level of theory. On the basis of comparison of computed harmonic frequencies of the monomers and experimental vibrational frequencies, available from literature, of the same species isolated in an Ar matrix, a scaling factor, *f* = 0.9869, was determined. A semi-empirical prediction for the Ar-matrix vibrational frequencies of the complex was obtained by adding the scaled computed vibrational wave-number shift (due to complexation) to the experimentally observed Ar-matrix vibrational wavenumbers of the monomers [31–35], according to Equation (1).



Scheme 1. 1,2,5-oxadiazole (1) and 1,3,4-oxadiazole (2).

$$\begin{aligned}\tilde{\nu}_{\text{complex,pred.}} &= \tilde{\nu}_{\text{monomer,Armatrix}} + (f \cdot \tilde{\nu}_{\text{complex,comp.}} \\ &\quad - f \cdot \tilde{\nu}_{\text{monomer,comp.}}) = \tilde{\nu}_{\text{monomer,Armatrix}} + \Delta\tilde{\nu}_{\text{shift,comp.}}\end{aligned}\quad (1)$$

3. Results and discussion

Among the possible [H, C, N, O] $\cdots$ [H, C, N] (and [H, C, N] $\cdots$ [H, C, N, O]) complexes only those ones were considered in the computations, which contains HNCO, HCNO or HOCN monomers. On the basis of former matrix isolation studies, other higher energy [H, C, N, O] isomers are unlikely formed in a detectable amount upon photolysis [35].

The computed structures of the complexes with H-bond dissociation energies and H-bond distances are shown in Fig. 1. The complexes can be divided into four groups based on the structure and the role of [H, C, N] species. This species can be either HCN (hydrogen cyanide) or HNC (hydrogen isocyanide), and it can be either donor or acceptor in H-bond with the [H, C, N, O] species. The comparison of the H-bond dissociation energy of a [H, C, N, O] $\cdots$ HCN complex to the H-bond dissociation energy of the corresponding [H, C, N, O] $\cdots$ HNC complex shows that the latter one is more stable for each pairs, indicating that HNC is more acidic than HCN. The difference between the H-bonding energy of a HCN $\cdots$ [H, C, N, O] and the corresponding HNC $\cdots$ [H, C, N, O] is very small in each case, showing that the basicity of HCN and HNC is similar. In the HNCO $\cdots$ [H, C, N], HCNO $\cdots$ [H, C, N], and HOCN $\cdots$ [H, C, N] series the latter complex has the largest dissociation energy, because of the stronger basicity of the N atom compared to O atom. Due to the acidic nature of the OH group, the stability of the [H, C, N] $\cdots$ HOCN

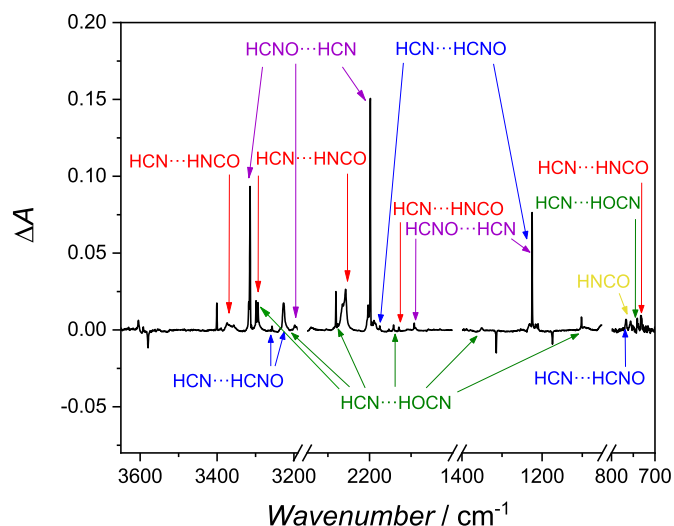


Fig. 2. Difference IR spectrum (after photolysis – before photolysis) of 220 nm photolysis 1,2,5-oxadiazole in Ar matrix.

complex is considerably larger compared to [H, C, N] $\cdots$ HNCO, and [H, C, N] $\cdots$ HCNO complexes.

Upon preparing the complexes we have utilized the cage effect, i.e., in the rigid Ar matrix the photoproducts cannot separate and they form a complex in the cage. The experimentally observed distribution of the complexes primarily determined by the photodecomposition pathways, which depend on the precursor and the wavelength of the photon. The primary photoproducts can also be unstable against the same UV radiation, and photoisomerization (or

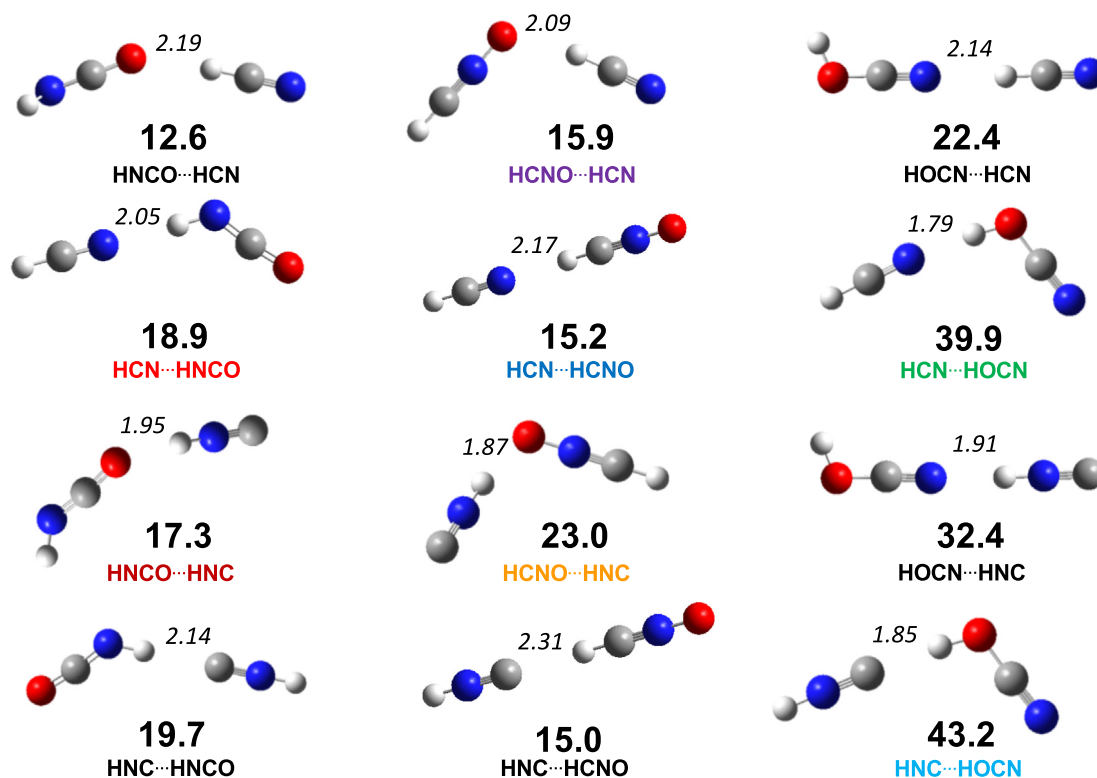


Fig. 1. Computed structure of [H, C, N] $\cdots$ [H, C, N, O] and [H, C, N, O] $\cdots$ [H, C, N] complexes with H-bond dissociation energies (bold, in kJ mol⁻¹) and H-bond distances (italics, in Å).

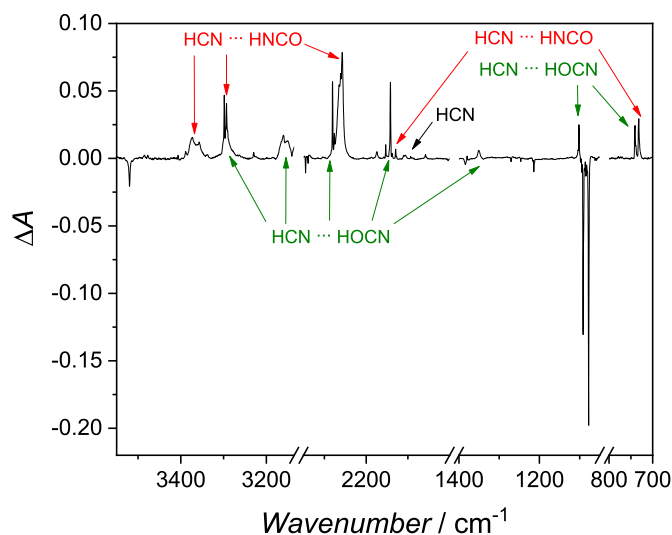


Fig. 3. Difference IR spectrum (after photolysis – before photolysis) of 220 nm photolysis 1,3,4-oxadiazole in Ar matrix.

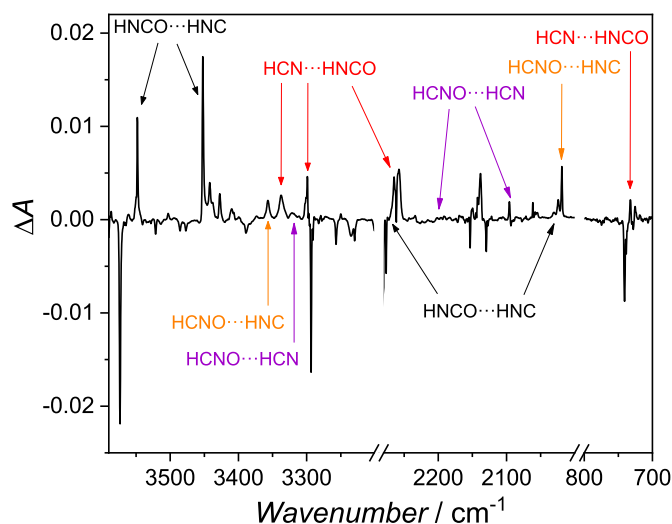


Fig. 4. Difference IR spectrum (after secondary photolysis – before secondary photolysis) of secondary, Hydrogen lamp photolysis 1,2,5-oxadiazole in Ar matrix.

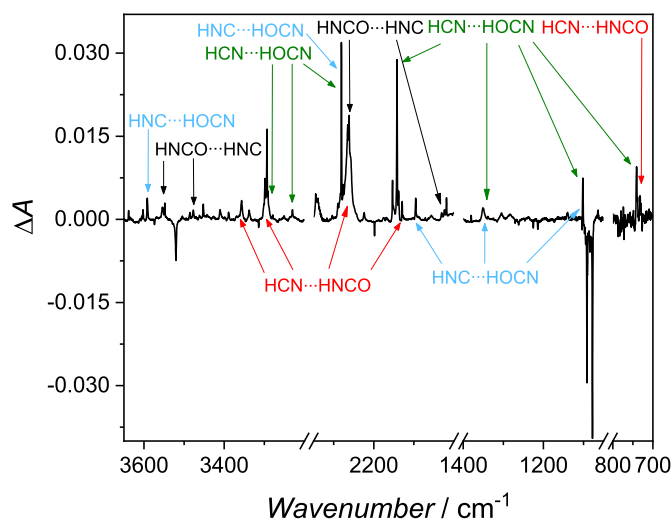


Fig. 5. Difference IR spectrum (after secondary photolysis – before secondary photolysis) of secondary, Hydrogen lamp photolysis 1,3,4-oxadiazole in Ar matrix.

further decomposition) might take place. The ratio of the $\text{HXYZ} \cdots \text{HVW}$ and $\text{HVW} \cdots \text{HXYZ}$, where $\text{X,Y,Z} = \{\text{C,N,O}\}$ and $\text{V,W} = \{\text{C,N}\}$, depends not only on the relative stability of the two complexes, but also on the photodecomposition pathway and geometry of the cage. As was pointed out by Barnes and Mielke [36], the matrix cage can stabilize metastable complexes, and it can distort the geometry of the complex. Therefore, the identification of the complexes needs some caution, and in some cases larger differences can be expected between the experimental IR spectrum of the complex embedded in an Ar host and the IR spectrum computed for the free complex.

The computed IR spectra of the precursors, i.e., 1,2,5- and 1,3,4-oxadiazole together with the experimental IR spectra of these species isolated in Ar matrix are shown in Figs. S1 and S2 of the Supporting Information. To produce complexes, the precursors were first irradiated by 220 nm UV light. The difference spectra as obtained by subtracting the spectrum recorded after the photolysis from the one recorded before the photolysis are shown in Figs. 2 and 3 for the two precursors. Secondary photolysis was carried out by a Hydrogen lamp, the corresponding difference spectra are displayed on Figs. 4 and 5. The computed spectra of the complexes plotted together with the experimental difference spectra are shown in Figs. S3–S6 of the Supporting Information.

To identify the complexes, the bands appeared upon photolysis were grouped on the basis of kinetic curves (i.e., intensity normalized to maximum intensity vs photolysis time). These curves are shown in the Supporting Information. The experimental frequencies and the relative intensities of each group of bands are compared to the computed (scaled and corrected) frequencies and the computed intensity of the complexes. The relative intensity changes upon secondary photolysis by a Hydrogen lamp further supported the identification, and, as will be discussed below, generated complexes not observed after the primary photolysis. Note that the noise level is relatively larger in the low-wavenumber region (below ca. 850 cm^{-1}). The theoretical prediction of the bands in this region might be worse than for larger frequencies. Therefore, the assignments are more uncertain in this region.

In the case of 1,2,5-oxadiazole the major product of the 220 nm photolysis is the $\text{HCNO} \cdots \text{HCN}$ complex (Fig. 2 and Table 1). The $\text{HCN} \cdots \text{HCNO}$ complex can also be identified (Table 2), but in a much less amount. In addition, $\text{HCN} \cdots \text{HNCO}$ and $\text{HCN} \cdots \text{HOCN}$ are also formed (Tables 3 and 4). It can be supposed that $\text{HCNO} \cdots \text{HCN}$ and $\text{HCN} \cdots \text{HCNO}$ are primary products formed by rupture of the O–C and the C–C bonds, according to Scheme 2. The computed energy difference between these two complexes are very small, see Fig. 1. Therefore, the higher abundance of the $\text{HCNO} \cdots \text{HCN}$ complex might be governed by the cage geometry, because the bent $\text{HCNO} \cdots \text{HCN}$ fits better into the cage established by the precursor than the $\text{HCN} \cdots \text{HCNO}$ complex. The $\text{HCN} \cdots \text{HNCO}$ and $\text{HCN} \cdots \text{HOCN}$ complexes might be secondary products, generated by photoisomerization from $\text{HCNO} \cdots \text{HCN}$ and $\text{HCN} \cdots \text{HCNO}$. This is supported by the kinetic curves corresponding to the 220 nm photolysis (Fig. S7), because the initial formation rate of $\text{HCNO} \cdots \text{HCN}$ and $\text{HCN} \cdots \text{HCNO}$ is considerably larger than that of $\text{HCN} \cdots \text{HNCO}$ and $\text{HCN} \cdots \text{HOCN}$. Among the monomers only a band of HCN and one of HNCO could be identified, indicating that the escape of a monomer from the H-bonded complex and from the cage has very low probability.

The 220 nm photolysis of 1,3,4-oxadiazole leads to the formation of $\text{HCN} \cdots \text{HNCO}$ and $\text{HCN} \cdots \text{HOCN}$ (Fig. 3). This can be explained by C–C and N–N bond ruptures, leading to HCN and a nitrene intermediate (Scheme 3). The nitrenes, even under matrix isolation conditions, rearrange e.g. by H atom shift [37]. The H atom can migrate both to the N or to the O atom. Therefore, the final product can be either HNCO or HOCN, both of which form a complex with HCN in the cage. This mechanism is in line with the kinetic curves

Table 1

Identification of the HCNO...HCN complex; computed vibrational wavenumbers ($\tilde{\nu}_{m, comp.}$) and intensities ($I_{m, comp.}$) of the monomers, Ar-matrix vibrational wavenumbers of the monomers ($\tilde{\nu}_{m, Ar matrix}$), computed vibrational wavenumbers ($\tilde{\nu}_{c, comp.}$) and intensities ($I_{c, comp.}$) of the complex, scaled wavenumber shift of the vibrational wavenumbers due to complexation ($\Delta\tilde{\nu}_{shift, comp.}$), predicted vibrational wavenumbers of the complex ($\tilde{\nu}_{c, pred.}$), and Ar-matrix vibrational wavenumbers ($\tilde{\nu}_{c, Ar matrix}$) and normalized relative intensities ($I_{c, Ar matrix}$) of the complex. All wavenumbers are in cm^{-1} , computed intensities are in km mol^{-1} .

Assignment	$\tilde{\nu}_{m, comp.}$	$I_{m, comp.}$	$\tilde{\nu}_{m, Ar matrix}^a$	$\tilde{\nu}_{c, comp.}$	$I_{c, comp.}$	$\Delta\tilde{\nu}_{shift, comp.}$	$\tilde{\nu}_{c, pred.}^c$	$\tilde{\nu}_{c, Ar matrix}^d$	$I_{c, Ar matrix}^d$
HCNO HCN bend	202.3	79.2	566	299.8 325.3	71.7 69.4	96.2 121.4	662.2 687.4		
HCNO CNO bend	561.2	0.1	536.9	556.7	2.3	−4.5	532.4		
HCNO CNO bend	568.4	1.4	538.2	562.4	1.9	−5.9	532.3		
HCN CN bend	761.4	72.7	721	825.3 848.0	30.6 53.0	63.1 85.5	784.1 806.5	^f	
HCNO NO stre	1291.6	127.0	1244.1	1272.4	165.3	−18.9	1225.2	1225	42
HCN CN stre	2199.5	1.3	2105 ^b	2190.0	43.7	−9.4	2095.6	2093	6
HCNO CN stre	2324.4	390.0	2192.7	2328.3	384.8	3.8	2196.5	2198	89
HCN HC stre	3449.3	60.7	3305	3347.1	362.7	−100.8	3204.2	3227,3208	− ^e
HCNO HC stre	3502.9	257.4	3317.2	3489.5	273.6	−13.2	3304.0	3314	100

^a From Refs. 31–35.

^b Site-split averaged wavenumber.

^c See Eq. (1).

^d This work, using 1,2,5-oxadiazole precursor.

^e Broad, overlapped with HCN...HNCO.

^f Uncertain, see text.

Table 2

Identification of the HCN...HCNO complex; computed vibrational wavenumbers ($\tilde{\nu}_{m, comp.}$) and intensities ($I_{m, comp.}$) of the monomers, Ar-matrix vibrational wavenumbers of the monomers ($\tilde{\nu}_{m, Ar matrix}$), computed vibrational wavenumbers ($\tilde{\nu}_{c, comp.}$) and intensities ($I_{c, comp.}$) of the complex, scaled wavenumber shift of the vibrational wavenumbers due to complexation ($\Delta\tilde{\nu}_{shift, comp.}$), predicted vibrational wavenumbers of the complex ($\tilde{\nu}_{c, pred.}$), and Ar-matrix vibrational wavenumbers ($\tilde{\nu}_{c, Ar matrix}$) and normalized relative intensities ($I_{c, Ar matrix}$) of the complex. All wavenumbers are in cm^{-1} , computed intensities are in km mol^{-1} .

Assignment	$\tilde{\nu}_{m, comp.}$	$I_{m, comp.}$	$\tilde{\nu}_{m, Ar matrix}^a$	$\tilde{\nu}_{c, comp.}$	$I_{c, comp.}$	$\Delta\tilde{\nu}_{shift, comp.}$	$\tilde{\nu}_{c, pred.}^c$	$\tilde{\nu}_{c, Ar matrix}^d$	$I_{c, Ar matrix}^d$
HCNO HCN bend	202.3	79.2	566	441.2 441.4	57.6 58.1	235.8 236.0	801.8 802.0		
HCNO CNO bend	561.2	0.1	536.9	596.4	14.5	34.8	571.7		
HCNO CNO bend	568.4	1.4	538.2	596.7	14.3	28.0	566.2		
HCN CN bend	761.6	72.7	721	770.3 770.9	35.4 34.5	8.6 9.1	729.6 730.1	766	26
HCNO NO stre	1291.6	127.0	1244.1	1273.8	206.8	−17.6	1226.5	1225	100
HCN CN stre	2199.5	1.3	2105 ^b	2214.4	7.6	14.7	2119.7		
HCNO CN stre	2324.4	390.0	2192.7	2308.5	265.6	−15.6	2177.1	2189	23
HCN HC stre	3449.3	60.7	3306	3376.1	878.9	−72.3	3233.7	3227	− ^e
HCNO HC stre	3502.9	257.4	3317.2	3438.4	50.1	−63.6	3253.6	3257	6

^a From Refs. 31–35.

^b Site-split averaged wavenumber.

^c See Eq. (1).

^d This work, using 1,2,5-oxadiazole precursor.

^e Broad, overlapped with HCN...HNCO.

Table 3

Identification of the HCN...HNCO complex; computed vibrational wavenumbers ($\tilde{\nu}_{m, comp.}$) and intensities ($I_{m, comp.}$) of the monomers, Ar-matrix vibrational wavenumbers of the monomers ($\tilde{\nu}_{m, Ar matrix}$), computed vibrational wavenumbers ($\tilde{\nu}_{c, comp.}$) and intensities ($I_{c, comp.}$) of the complex, scaled wavenumber shift of the vibrational wavenumbers due to complexation ($\Delta\tilde{\nu}_{shift, comp.}$), predicted vibrational wavenumbers of the complex ($\tilde{\nu}_{c, pred.}$), and Ar-matrix vibrational wavenumbers ($\tilde{\nu}_{c, Ar matrix}$) and normalized relative intensities ($I_{c, Ar matrix}$) of the complex. All wavenumbers are in cm^{-1} , computed intensities are in km mol^{-1} .

Assignment	$\tilde{\nu}_{m, comp.}$	$I_{m, comp.}$	$\tilde{\nu}_{m, Ar matrix}^a$	$\tilde{\nu}_{c, comp.}$	$I_{c, comp.}$	$\Delta\tilde{\nu}_{shift, comp.}$	$\tilde{\nu}_{c, pred.}^c$	$\tilde{\nu}_{c, Ar matrix}^d$	$I_{c, Ar matrix}^d$	$\tilde{\nu}_{c, Ar matrix}^e$	$I_{c, Ar matrix}^e$
HNCO HNC/ NCO bends	573.0	81.7	573.7	631.4	20.9	57.7	631.4				
HNCO NCO bend	636.0	3.9		654.9	0.0	18.7					
HCN CN bend	761.6	72.7	721	771.4 771.4	28.3 34.1	9.6 9.6	730.6 730.6	732	11	732	11
HNCO HNC/ NCO bends	801.1	207.6	769.8	844.1	251.8	42.5	812.3	^f		^f	
HNCO NC/CO s. stre	1335.5	0.3	1315.0	1339.4	10.3	3.9	1318.9				
HCN CN stre	2199.5	1.3	2105 ^b	2218.7	7.1	18.9	2123.9	2130	1	2130	2
HNCO NC/CO a.s. stre	2337.4	688.1	2259.0	2340.2	737.2	2.8	2261.8	2257	100	2257	100
HCN HC stre	3449.3	60.7	3306	3437.8	121.0	−11.4	3294.6	3294	6	3294	7
HNCO NH stre	3679.9	150.6	3511.3 ^b	3528.2	901.2	−149.7	3361.6	3354	38	3357	43

^a From Refs. 31–35.

^b Site-split averaged wavenumber.

^c See Eq. (1).

^d This work, using 1,2,5-oxadiazole precursor.

^e This work, using 1,3,4-oxadiazole precursor.

^f Uncertain, see text.

Table 4
Identification of the HCN...HOCN complex; computed vibrational wavenumbers ($\tilde{\nu}_{m, comp.}$) and intensities ($I_{m, comp.}$) of the monomers, Ar-matrix vibrational wavenumbers of the monomers ($\tilde{\nu}_{m, Ar\ matrix}$), computed vibrational wavenumbers ($\tilde{\nu}_{c, comp.}$) and intensities ($I_{c, comp.}$) of the complex, scaled wavenumber shift of the vibrational wavenumbers due to complexation ($\Delta\tilde{\nu}_{shift, comp.}$), predicted vibrational wavenumbers of the complex ($\tilde{\nu}_{c, pred.}$), and Ar-matrix vibrational wavenumbers ($\tilde{\nu}_{c, Ar\ matrix}$) and normalized relative intensities ($I_{c, Ar\ matrix}$) of the complex. All wavenumbers are in cm^{-1} , computed intensities are in km mol^{-1} .

Assignment	$\tilde{\nu}_{m, comp.}$	$I_{m, comp.}$	$\tilde{\nu}_{m, Ar\ matrix}^a$	$\tilde{\nu}_{c, comp.}$	$I_{c, comp.}$	$\Delta\tilde{\nu}_{shift, comp.}$	$\tilde{\nu}_{c, pred.}^c$	$\tilde{\nu}_{c, Ar\ matrix}^d$	$I_{c, Ar\ matrix}^d$	$\tilde{\nu}_{c, Ar\ matrix}^e$	$I_{c, Ar\ matrix}^e$
HOCN OCN bend	457.5	14.0		529.1	15.5	70.6					
HOCN OCN bend	514.1	3.4		649.8	95.6	133.9					
HCN CN bend	761.6	72.7	721	779.6	30.4	17.7	738.7	741	8	741	21
				779.7	34.4	17.8	738.8				
HOCN CO stre	1097.3	72.4	1081.3	1122.0	61.0	24.4	1105.7	1102	7	1102	16
HOCN COH bend	1249.1	94.0	1227.9	1362.6	77.0	112.0	1339.9	1351	6	1351	12
HCN CN stre	2199.5	1.3	2105 ^b	2234.8	16.3	34.8	2139.8	2142	5	2142	35
HOCN CN stre	2378.8	123.1	2286.3	2368.2	202.6	-10.4	2275.9	2281	18	2281	18
HCN HC stre	3449.3	60.7	3306	3438.5	19	-10.7	3295.3	3294	8	3294	20
HOCN OH stre	3757.3	147.1	3569.6	3372.7	1582.8	-379.6	3190.0	3160	100	3160	100

^a From Refs. 31–35.

^b Site-split averaged wavenumber.

^c See Eq. (1).

^d This work, using 1,2,5-oxadiazole precursor.

^e This work, using 1,3,4-oxadiazole precursor.

(Fig. S8); the two products show very similar concentration increase in time. Similarly to the photolysis of the other precursor, the free monomers are hardly produced, only a small amount of free HCN could be detected.

The 220 nm photolysis of the two precursors resulted in the formation of HNCO...HCN and HOCN...HCN. This observation can be rationalized both with energetic and geometric arguments. The HCN...HNCO and HCN...HOCN complexes less strongly bound than the HNCO...HCN and HOCN...HCN complexes. Furthermore, HNCO...HCN and HOCN...HCN have a more bent structure, fitting better into cage possessing the geometry determined by the precursor.

It was observed by Milligan and Jacox [34] that short-wavelength UV radiation induces HCN→HNC isomerization. In line with this, secondary photolysis by a Hydrogen lamp (121.6 nm) generated HCNO...HNC and HNCO...HNC (Fig. 4, Tables 5 and 6) in the case of 1,2,5-oxadiazole, and HNCO...HNC and HNC...HOCN (Fig. 4, Tables 6 and 7) for 1,3,4-oxadiazole. Former studies revealed that broad-band UV radiation can also induce the photoisomerization of [H, C, N, O] species. HOCN formation was observed both from HCNO and HNCO [31,32]. It is very likely that the radiation of the Hydrogen lamp can also change the ratio of the [H, C, N, O] species. However, it is hard to make any conclusion which paths are induced, because the precursor could not be completely bleached in the primary 220 nm photolysis, therefore the H lamp can generate species not only from the 220 nm photoproducts, but also from the remaining precursor molecules. The formation of HCNO...HNC and HNC...HOCN species and the lack of HNC...HCNO and HOCN...HNC again consistent both with energetic and geometric explanations, i.e., the more stable and more bent structures are observed (see Fig. 1). In the case of HNCO...HNC and HNC...HNCO both the H bond dissociation energies and the spatial requirements are predicted to be similar (Fig. 1); the formation of

HNCO...HNC and the lack of HNC...HNCO might be due to different efficiencies for photoisomerization paths leading to these species.

4. Summary

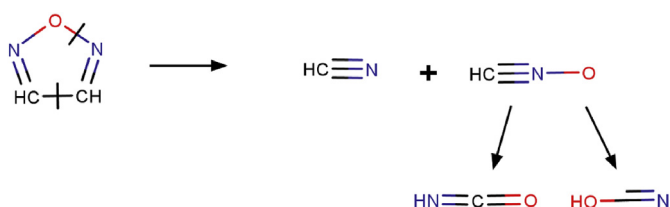
1,2,5- and 1,3,4-oxadiazoles were photolyzed in low-temperature Ar matrix, and the photolysis products were identified by IR spectroscopy aided by quantum chemical computations. Due to the cage effect of the low-temperature, rigid Ar matrix the major photolysis products were [H, C, N] ... [H, C, N, O] (and [H, C, N, O] ... [H, C, N]) complexes; only traces of some [H, C, N] and [H, C, N, O] isomers could be identified. 220 nm photolysis 1,2,5-oxadiazole generated HCNO...HCN, HCN...HCNO, HCN...HNCO, and HCN...HOCN complexes, while in the case of 1,3,4-oxadiazole HCN...HNCO and HCN...HOCN complexes were produced. Secondary photolysis by a Hydrogen lamp resulted in HCNO...HNC, HNCO...HNC, and HNC...HOCN complexes. It can be expected that these complexes are present in either planetary atmospheres or on the surface of interstellar grains. The present work can help the future astronomical identification of these molecular complexes.

Declaration of competing interest

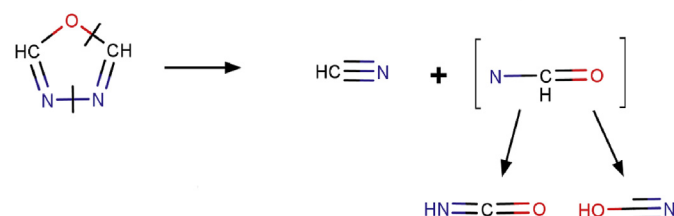
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Barbara Keresztes: Data curation, Formal analysis, Investigation. **István Pál Csonka:** Data curation, Formal analysis, Investigation, Writing - review & editing. **Győző György Lajgút:** Resources,



Scheme 2. 220 nm photolysis of 1,2,5-oxadiazole.



Scheme 3. 220 nm photolysis of 1,3,4-oxadiazole.

Table 5

Identification of the HCNO...HNC complex; computed vibrational wavenumbers ($\bar{\nu}_{m, comp.}$) and intensities ($I_{m, comp.}$) of the monomers, Ar-matrix vibrational wavenumbers of the monomers ($\bar{\nu}_{m, Ar matrix}$), computed vibrational wavenumbers ($\bar{\nu}_{c, comp.}$) and intensities ($I_{c, comp.}$) of the complex, scaled wavenumber shift of the vibrational wavenumbers due to complexation ($\Delta\bar{\nu}_{shift, comp.}$), predicted vibrational wavenumbers of the complex ($\bar{\nu}_{c, pred.}$), and Ar-matrix vibrational wavenumbers ($\bar{\nu}_{c, Ar matrix}$) and normalized relative intensities ($I_{c, Ar matrix}$) of the complex. All wavenumbers are in cm^{-1} , computed intensities are in km mol^{-1} .

Assignment	$\bar{\nu}_{m, comp.}$	$I_{m, comp.}$	$\bar{\nu}_{m, Ar matrix}^a$	$\bar{\nu}_{c, comp.}$	$I_{c, comp.}$	$\Delta\bar{\nu}_{shift, comp.}$	$\bar{\nu}_{c, pred.}^c$	$\bar{\nu}_{c, Ar matrix}^d$	$I_{c, Ar matrix}^d$
HCNO HCN bend	202.3	79.2	566	327.6	66.7	123.7	689.7		
				367.3	64.8	162.8	728.8		
HNC HNC bend	471.9	136.4	535	679.7	117.8	116.9	593.9		
				745.3	174.7	85.7	709.6		
HCNO CNO bend	561.2	0.1	536.9	551.5	3.4	−9.6	527.3		
HCNO CNO bend	568.4	1.4	538.2	558.7	7.2	−9.6	528.6		
HCNO NO stre	1291.6	127.0	1244.1	1262.5	173.8	−28.8	1215.3	1225	− ^e
HNC NC stre	2105.2	60.1	2031 ^b	2109.0	13.5	3.7	2034.7	2024	27
HCNO CN stre	2324.4	390.0	2192.7	2330.4	385.1	5.9	2198.6	2198	100
HCNO HC stre	3502.9	257.4	3317.2	3482.6	494.3	−20.1	3297.1	3298	42
HNC NH stre	3805.6	247.2	3602 ^b	3539.0	1038.4	−263.1	3338.9	3364	38

^a From Refs. 31–35.

^b Site-split averaged wavenumbers.

^c See Eq. (1).

^d This work, using 1,2,5-oxadiazole precursor.

^e Overlapped.

Table 6

Identification of the HNCO...HNC complex; computed vibrational wavenumbers ($\bar{\nu}_{m, comp.}$) and intensities ($I_{m, comp.}$) of the monomers, Ar-matrix vibrational wavenumbers of the monomers ($\bar{\nu}_{m, Ar matrix}$), computed vibrational wavenumbers ($\bar{\nu}_{c, comp.}$) and intensities ($I_{c, comp.}$) of the complex, scaled wavenumber shift of the vibrational wavenumbers due to complexation ($\Delta\bar{\nu}_{shift, comp.}$), predicted vibrational wavenumbers of the complex ($\bar{\nu}_{c, pred.}$), and Ar-matrix vibrational wavenumbers ($\bar{\nu}_{c, Ar matrix}$) and normalized relative intensities ($I_{c, Ar matrix}$) of the complex. All wavenumbers are in cm^{-1} , computed intensities are in km mol^{-1} .

Assignment	$\bar{\nu}_{m, comp.}$	$I_{m, comp.}$	$\bar{\nu}_{m, Ar matrix}^a$	$\bar{\nu}_{c, comp.}$	$I_{c, comp.}$	$\Delta\bar{\nu}_{shift, comp.}$	$\bar{\nu}_{c, pred.}^c$	$\bar{\nu}_{c, Ar matrix}^d$	$I_{c, Ar matrix}^d$	$\bar{\nu}_{c, Ar matrix}^e$	$I_{c, Ar matrix}^e$
HNC HNC bend	471.9	136.4	535	622.5	67.8	148.6	625.6				
				625.9	115.1	152.0	687.0				
HNCO HNC/ NCO bends	573.0	81.7	573.7	564.1	116.6	−8.7	565.0				
HNCO NCO bend	636.0	3.9		644.4	90.1	8.2					
HNCO HNC/ NCO bends	801.1	207.6	769.8	743.9	211.0	−56.4	713.4	^g		^g	
HNCO NC/CO s. stre	1335.5	0.3	1315.0	1344.8	9.1	9.2	1324.2				
HNC NC stre	2105.2	60.1	2031 ^b	2111.7	18.4	6.4	2037.4	2031	4	2031	3
HNCO NC/CO a.s. stre	2337.4	688.1	2259.0	2346.5	873.2	8.9	2267.9	2258	100	2258	100
HNCO NH stre	3679.9	150.6	3511.3 ^b	3695.7	1031.6	15.6	3491.6	3452	− ^f	3470	− ^f
HNC NH stre	3805.6	247.2	3602 ^b	3660	137.2	−143.7	3493.5	3548	− ^f	3548	− ^f

^a From Refs. 31–35.

^b Site-split averaged wavenumber.

^c See Eq. (1).

^d This work, using 1,2,5-oxadiazole precursor.

^e This work, using 1,3,4-oxadiazole precursor.

^f Broad, overlapped.

^g Uncertain, see text.

Table 7

Identification of the HNC...HOCN complex; computed vibrational wavenumbers ($\bar{\nu}_{m, comp.}$) and intensities ($I_{m, comp.}$) of the monomers, Ar-matrix vibrational wavenumbers of the monomers ($\bar{\nu}_{m, Ar matrix}$), computed vibrational wavenumbers ($\bar{\nu}_{c, comp.}$) and intensities ($I_{c, comp.}$) of the complex, scaled wavenumber shift of the vibrational wavenumbers due to complexation ($\Delta\bar{\nu}_{shift, comp.}$), predicted vibrational wavenumbers of the complex ($\bar{\nu}_{c, pred.}$), and Ar-matrix vibrational wavenumbers ($\bar{\nu}_{c, Ar matrix}$) and normalized relative intensities ($I_{c, Ar matrix}$) of the complex. All wavenumbers are in cm^{-1} , computed intensities are in km mol^{-1} .

Assignment	$\bar{\nu}_{m, comp.}$	$I_{m, comp.}$	$\bar{\nu}_{m, Ar matrix}^a$	$\bar{\nu}_{c, comp.}$	$I_{c, comp.}$	$\Delta\bar{\nu}_{shift, comp.}$	$\bar{\nu}_{c, pred.}^c$	$\bar{\nu}_{c, Ar matrix}^d$	$I_{c, Ar matrix}^d$
HNC HNC bend	471.9	136.4	535	522.7	125.4	50.2	527.2		
				523.3	131.0	50.8	585.8		
HOCN OCN bend	457.5	14.0		531.2	18.9	72.7			
HOCN OCN bend	514.1	3.4		511.5	1.6	−2.6			
HOCN CO stre	1097.3	72.4	1081.3	1124.0	61.8	26.4	1107.7	1102	50
HOCN COH bend	1249.1	94.0	1227.9	1376.3	59.1	125.6	1353.5	1351	42
HNC NC stre	2105.2	60.1	2031 ^b	2175.8	47.6	69.6	2100.6	2095	19
HOCN CN stre	2378.8	123.0	2286.3	2364.8	226.4	−13.8	2272.5	2281	100
HOCN OH stre	3757.3	147.1	3569.6	3225.2	1714.0	−525.1	3044.5	− ^e	− ^e
HNC HN stre	3805.6	247.2	3602 ^b	3791.5	319.6	−13.9	3588.1	− ^e	− ^e

^a From Refs. 31–35.

^b Site-split averaged wavenumbers.

^c See Eq. (1).

^d This work, using 1,2,5-oxadiazole precursor.

^e Overlapped with more intense bands of other complexes.

Investigation. **Gábor Bazsó:** Methodology. **György Tarczay:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Writing - original draft, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molstruc.2020.128535>.

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