

Matrix Isolation of Two Isomers of N_4CO^{**}

Xiaoqing Zeng, Helmut Beckers, and Helge Willner*

Inorganic molecules containing polynitrogen chains are known as intrinsically unstable high-energetic compounds. Tetranitrogen (N_4) was merely detected as a gaseous metastable molecule with a lifetime of microseconds by neutralization–reionization mass spectrometry,^[1] and only a few derivatives of N_4 with open-chain structures— N_4O ,^[2] N_4O_2 ,^[3] and $[N_3NFO][SbF_6]$ ^[4]—have been spectroscopically identified. A catenated pentanitrogen unit is found in the N_5^+ ion.^[5] Its structure and chemistry was recently explored by Christe et al., and the N_5 unit exhibits a bent structure with C_{2v} symmetry as shown by X-ray crystallography.

Concerning the hexanitrogen compounds, numerous theoretical calculations have been devoted to the two isomers of N_6 , diazide and hexazine, but none of them were identified experimentally up to now.^[6] To the contrary, its isoelectronic analogue, diisocyanate ($OCN-NCO$), was prepared by photolysis and flash pyrolysis of oxalic acid diazide, $O_2C_2(N_3)_2$, and characterized by matrix IR spectroscopy.^[7] Only the C_{2h} symmetrical conformer was computationally found to be a minimum,^[8] and the initially formed nitrene intermediate was not observed. Our recent synthesis of pure carbonyl diazide, $OC(N_3)_2$,^[9] encouraged us to conduct a similar experiment in seeking azido isocyanate, N_3-NCO , an even closer analogue to N_6 .

Gaseous $OC(N_3)_2$ exhibits two broad absorptions at $\lambda_{\max} = 232$ and 198 nm. Irradiation of Ar matrix-isolated $OC(N_3)_2$ with UV light ($\lambda = 255$ nm, interference filter) was performed, and the appearance of new IR bands at the expense of those of $OC(N_3)_2$ was observed. Formation of CO was evidenced by a weak band at 2140.6 cm^{-1} (Figure S1 in the Supporting Information), and strong new bands in the region of N_3 and NCO stretching modes appeared upon photolysis. To distinguish the different carriers of these bands, subsequent irradiation of the matrix with visible light ($\lambda \geq 455$ nm) was performed. No decomposition of $OC(N_3)_2$ was observed under these conditions, and the IR difference spectrum before and after $\lambda \geq 455$ nm photolysis is shown in Figure 1b. The good agreement between the observed and calculated spectra (B3LYP/6-311 + G(3df), using a scaling factor of 0.9679)^[10] for triplet $N_3C(O)N$ (Figure 1a, Table 1) suggested its formation upon UV photolysis ($\lambda = 255$ nm) of $OC(N_3)_2$. The

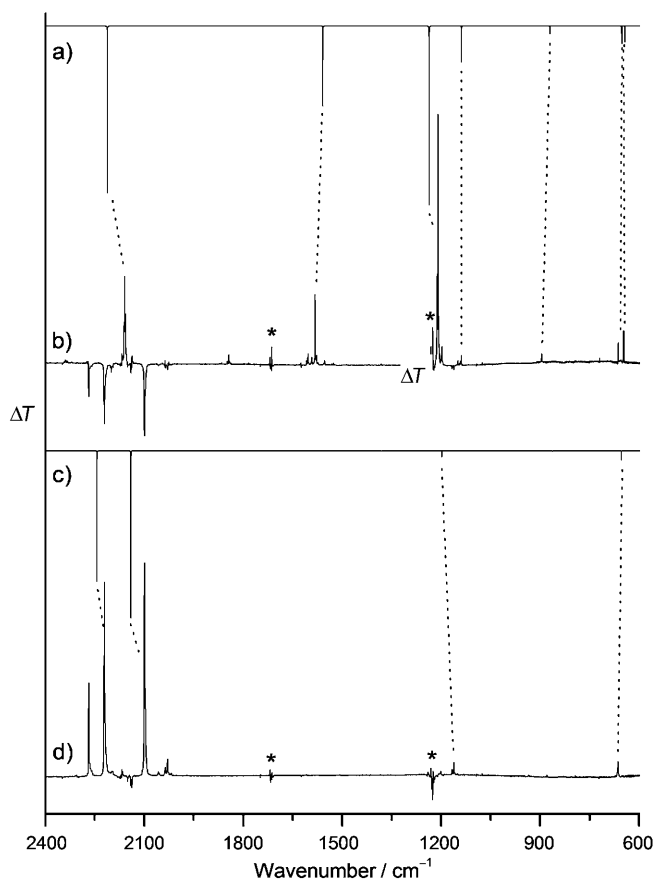


Figure 1. a,c) Calculated IR spectra of a) *anti*- $N_3C(O)N$ ($^3A''$) and c) N_3-NCO (B3LYP/6-311 + G(3df), a scaling factor of 0.9679 was applied). b) IR difference spectrum recorded before and after visible light irradiation ($\lambda \geq 455$ nm) of the UV photolysis ($\lambda = 255$ nm) products of Ar matrix-isolated $OC(N_3)_2$. d) IR difference spectrum recorded before and after subsequent UV/Vis irradiation ($\lambda \geq 335$ nm) of (b). Features marked with asterisks are due to different matrix site occupancies of $OC(N_3)_2$.

nitrene $N_3C(O)N$ was depleted upon visible irradiation ($\lambda \geq 455$ nm, Figure 1b).

In principle, two nitrene conformers can be formed which adopt a *syn* and *anti* orientation of the azide group with respect to the C–N bond. In fact, weak satellites at 1602.6 cm^{-1} (Ar matrix) and 1602.9 cm^{-1} (Ne matrix) of the strong bands for the C=O stretching vibration at 1581.7 cm^{-1} (Ar matrix) and 1582.5 cm^{-1} (Ne matrix) might suggest the formation of a second nitrene conformer. However, the absence of any such features for the other nitrene bands indicates the presence of only one conformer. The preference for *anti*- $N_3C(O)N$ ($^3A''$) comes from various DFT calculations (Figure S2 and Table S2), which predict this conformer to be energetically slightly more stable than the *syn* conformer. The

[*] Dr. X. Zeng, Dr. H. Beckers, Prof. Dr. H. Willner
Bergische Universität Wuppertal, FB C–Anorganische Chemie
42097 Wuppertal (Germany)
Fax: (+49) 202-439-3053
E-mail: willner@uni-wuppertal.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. X.Z. acknowledges a fellowship from the Alexander von Humboldt Foundation.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201005177>.

Table 1: Calculated and experimental IR wavenumbers (cm^{-1}) of $\text{N}_3\text{C}(\text{O})\text{N}$.

Calculated ^[a]				Experimental ^[b]		Assignment ^[c]
<i>syn</i>		<i>anti</i>		Ar matrix	Ne matrix	<i>anti</i>
$^3\text{A}''$	$^1\text{A}'$	$^3\text{A}''$	$^1\text{A}'$	$^3\text{A}''$	$^3\text{A}''$	
2197 (509)	2224 (429)	2212 (412)	2228 (426)	2159.7 (55)	2159.9 (68)	$\nu_1, \nu(\text{N}_3)_{\text{asym}}$
1551 (264)	1698 (445)	1558 (193)	1727 (486)	1581.7 (35)	1582.5 (47)	$\nu_2, \nu(\text{CO})$
1257 (362)	1327 (123)	1236 (454)	1321 (65)	1209.1 (100)	1204.0 (100)	$\nu_3, \nu(\text{N}_3)_{\text{sym}}$
1101 (72)	1247 (147)	1138 (94)	1227 (157)	1138.5 (9)	1138.8 (11)	$\nu_4, \nu(\text{CN})$
821 (19)	884 (16)	871 (17)	889 (7)	894.6 (6)	897.6 (7)	$\nu_5, \nu(\text{C}-\text{N}_3)$
614 (30)	626 (15)	652 (42)	641 (12)	664.8 (17)	662.7 (11)	$\nu_6, \delta(\text{N}_3)_{\text{ip}}$
607 (28)	582 (25)	643 (37)	582 (19)	646.5 (19)	651.8 (14)	$\nu_{10}, \delta(\text{N}_2\text{CO})_{\text{oop}}$

[a] Calculated (B3LYP/6-311 + G(3df)) frequencies (scaled by 0.9679). Absolute intensities [km mol^{-1}] are given in parenthesis. A complete list of all the calculated IR fundamentals of singlet and triplet $\text{N}_3\text{C}(\text{O})\text{N}$ species is given in Table S1. *Syn/anti* orientation of the azide group with respect to the C–N bond (Figure S2). [b] Band positions at the most intense matrix sites with relative integrated intensities [%] in parenthesis. [c] Assignments correspond to the more stable *anti* conformer of $\text{N}_3\text{C}(\text{O})\text{N}$ ($^3\text{A}''$).

anti preference is also consistent with Scheme S1 that assumed the favorable formation of *anti*- $\text{N}_3\text{C}(\text{O})\text{N}$ from the more abundant *syn-syn* conformer of $\text{OC}(\text{N}_3)_2$.^[9]

Further experiments were performed using ^{15}N -labeled $\text{OC}(\text{N}_3)_2$ which was prepared from 1- ^{15}N sodium azide. Three isotopomers of doubly ^{15}N -labeled $\text{OC}(\text{N}_3)_2$ were identified in the matrix spectrum, from which four isotopologues of $\text{N}_3\text{C}(\text{O})\text{N}$ with equal molar ratio were expected to be formed upon photolysis (Scheme S2). The expected doublet-like splitting with nearly equal intensity was clearly observed for the N_3 vibrational modes ν_1 , ν_3 , and ν_5 in the ^{15}N -labeling experiment (Figure S3). An ^{15}N -isotopic shift was also observed for the CO stretching mode (ν_2), indicating vibrational coupling to the N_3 stretching modes (Table S3).

The UV photolysis ($\lambda = 255 \text{ nm}$) products of Ne matrix-isolated $\text{OC}(\text{N}_3)_2$ exhibits several absorptions below 800 nm (Figure 2). Upon subsequent visible photolysis ($\lambda \geq 455 \text{ nm}$), the major broad band at 430 nm and further weak features at around 660 nm and 330 nm disappeared simultaneously, while two additional bands at 438 and 272 nm increased. This photolysis behavior indicates that these transitions are due to different species, and the former bands (660, 450, and 330 nm) were assigned to $\text{N}_3\text{C}(\text{O})\text{N}$. The weak absorption at $\lambda_{\text{max}} = 660 \text{ nm}$ for $\text{N}_3\text{C}(\text{O})\text{N}$ ($^3\text{A}''$) is consistent with a calculated vertical transition at 740 nm ($f = 0.0004$) using the TD-DFT

B3LYP/6-311 + G(3df) method. This band shows a regular average vibrational spacing of 466 cm^{-1} (Table S4), which resembles those of triplet carbonyl nitrene $\text{FC}(\text{O})\text{N}$ at $\lambda_{\text{max}} = 572 \text{ nm}$ ($\Delta\tilde{\nu} = 465 \text{ cm}^{-1}$).^[11] The strongest transition for $\text{N}_3\text{C}(\text{O})\text{N}$ ($^3\text{A}''$) is predicted at 484 nm ($f = 0.0208$), consistent with the observation of the strong broad band at $\lambda_{\text{max}} = 430 \text{ nm}$ (Figure 2). In addition, three weak transitions observed at 344, 325, and 308 nm are also assigned to $\text{N}_3\text{C}(\text{O})\text{N}$ ($^3\text{A}''$) (Table S4) based on their photolytic behavior. During the photolysis of the diazide, NCO radicals were also formed as evidenced by their characteristic visible absorptions at 438 nm ($0 \leftarrow 0$) and the vibrational progression at 414, 398, and 383 nm (Figure 2c).^[11]

Once the formation of $\text{N}_3\text{C}(\text{O})\text{N}$ ($^3\text{A}''$) from $\text{OC}(\text{N}_3)_2$ by UV photolysis ($\lambda = 255 \text{ nm}$) was ascertained, it may photoisomerize to the title compound $\text{N}_3\text{-NCO}$ through Curtius-type rearrangement. This is indeed proved by the appearance of new IR bands upon visible irradiation ($\lambda \geq 455 \text{ nm}$) of the matrices containing $\text{N}_3\text{C}(\text{O})\text{N}$ ($^3\text{A}''$) (Table 1). Experimental IR band positions are compared to calculated ones for $\text{N}_3\text{-NCO}$ in Table 2. Two strong bands at 2220.8 ($\tilde{\nu}_{\text{calcd}} = 2244 \text{ cm}^{-1}$) and 2099.1 ($\tilde{\nu}_{\text{calcd}} = 2141 \text{ cm}^{-1}$) were assigned to the asymmetric stretches of the NCO and N_3 moieties, respectively. The first band split into three components in ^{15}N -labeling experiments (Figure S4) with ^{15}N -isotopic shifts of

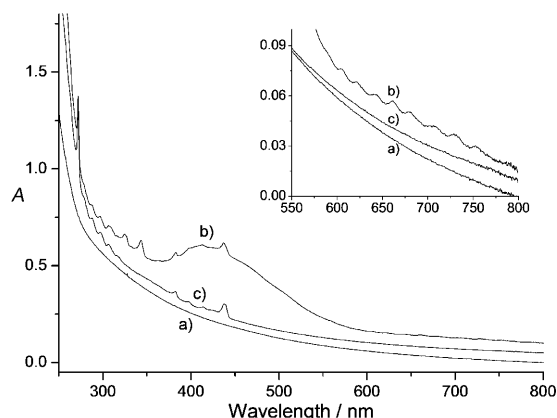


Figure 2. UV/Vis spectrum of Ne matrix-isolated $\text{OC}(\text{N}_3)_2$: a) before photolysis, b) after UV photolysis ($\lambda = 255 \text{ nm}$), c) after subsequent Vis photolysis ($\lambda \geq 455 \text{ nm}$).

Table 2: Calculated and experimental IR wavenumbers [cm^{-1}] of $\text{N}_3\text{-NCO}$.

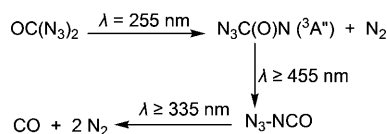
Calculated ^[a]		Experimental ^[b]		Assignment
		Ar matrix	Ne matrix	
		2267.8 (33)	2266.7 (38)	$\nu_3 + \nu_5$
2244 (810)	2220.8 (79)	2223.8 (74)		$\nu_1, \nu(\text{NCO})_{\text{asym}}$
2141 (1066)	2099.1 (100)	2102.2 (100)		$\nu_2, \nu(\text{N}_3)_{\text{asym}}$
1380 (3)				$\nu_3, \nu(\text{NCO})_{\text{sym}}$
1197 (39)	1160.7 (4)	1165.9 (4)		$\nu_4, \nu(\text{N}_3)_{\text{sym}}$
861 (5)				$\nu_5, \nu(\text{N}-\text{N})$
652 (63)	663.7 (6)	668.5 (5)		$\nu_6, \delta(\text{NCO})_{\text{ip}}$
603 (2)				$\nu_7, \delta(\text{N}_3)_{\text{ip}}$

[a] Calculated (B3LYP/6-311 + G(3df)) frequencies (scaled by 0.9679). Absolute intensities [km mol^{-1}] are given in parenthesis. A list of all the calculated IR data of $\text{N}_3\text{-NCO}$ is given in Table S6. [b] Band positions of the most intense matrix sites with relative integrated intensities [%] in parenthesis.

1.0, 8.6, and 14.3 cm^{-1} , while the second band shows two components with ^{15}N -isotopic shifts of 7.6 and 23.7 cm^{-1} (Table S5). Additional two weak bands at 1160.7 and 663.7 cm^{-1} were assigned to the symmetric stretching mode of the N_3 group and the in-plane bending mode of NCO group, respectively. The stretching mode of the N–N bond linking the two pseudo halogen moieties ($\tilde{\nu}_{\text{calcd}} = 861\text{ cm}^{-1}$) was predicted to be very weak (Table 2) and has not been observed. A strong band at 2267.8 cm^{-1} showed a similar photolytic behavior, indicating that the carrier of this band is also $\text{N}_3\text{-NCO}$. It is tentatively assigned to the ($\nu_3 + \nu_5$) combination band, which probably gains intensity through a Fermi resonance with ν_1 (2220.8 cm^{-1}). Attempts to accumulate $\text{N}_3\text{-NCO}$ in the cryogenic matrix by prolonged photolysis failed, because it decomposed to form carbon monoxide when exposed to UV light of $\lambda = 255\text{ nm}$.

Upon irradiation of matrix-isolated $\text{N}_3\text{-NCO}$ with UV/Vis light ($\lambda \geq 335\text{ nm}$), CO was formed as the only IR detectable species (Figure 1c, 2140.6 cm^{-1}). Its photolytic behavior implies an electronic band of $\text{N}_3\text{-NCO}$ above 335 nm. This was confirmed by TD-DFT calculation, which predicted a weak transition at 366 nm ($f = 0.0004$). An additional absorption at 272 nm can be assigned to $\text{N}_3\text{-NCO}$, whose intensity increased with visible irradiation ($\lambda \geq 455\text{ nm}$) of $\text{N}_3\text{C(O)N}$ ($^3\text{A}''$), and decreased after subsequent UV/Vis irradiation ($\lambda \geq 335\text{ nm}$). It corresponds to a predicted vertical transition at 279 nm ($f = 0.0005$) for $\text{N}_3\text{-NCO}$.

The photochemistry studied herein is summarized in Scheme 1. Starting from $\text{OC(N}_3)_2$ two isomers of N_4CO were isolated, the azido carbonyl nitrene, $\text{N}_3\text{C(O)N}$, which re-



Scheme 1. Photochemistry of $\text{OC(N}_3)_2$ in Ar matrices at 16 K.

arranged upon visible light irradiation ($\lambda \geq 455\text{ nm}$) through a Curtius-type rearrangement to azido isocyanate, $\text{N}_3\text{-NCO}$. Further loss of N_2 by near-UV irradiation yielded CO and N_2 . No other intermediates, for example, the long-sought diazirinone, N_2CO ,^[12] or its isomers,^[13] were observed under our experimental conditions.

The novel carbonyl nitrene was proved to adopt a triplet ground state by its characteristic IR and UV spectra. However, according to CBS-QB3 calculations (Table S1), the calculated singlet–triplet energy gap is rather small ($\Delta E_{\text{S-T}} < 20\text{ kJ mol}^{-1}$). It is worth to mention that alkyl and aryl carbonyl nitrenes usually have closed-shell singlet ground states.^[14] Such singlet carbonyl nitrenes shows structural and spectroscopic properties which are very different from those of the triplet species, as the former ones have much shorter, double bond-like C=N bonds and unusually small NCO angles of about 90° (Figure S2).^[11]

In general, the photo-rearrangement of the nitrene $\text{N}_3\text{C(O)N}$ might give access to two different chain-like isomers, $\text{N}_3\text{-NCO}$ and $\text{N}_3\text{-OCN}$, which have been explored

theoretically using various DFT methods (Tables S2, S6, and S7). Only the former one was observed experimentally, and the nitrene–isocyanate rearrangement was found to be exothermic by 157.3 kJ mol^{-1} at the B3LYP/6-311 + G(3df) level of theory (Table S1). $\text{N}_3\text{-OCN}$ was found to be higher in energy than $\text{N}_3\text{-NCO}$ by 173.4 kJ mol^{-1} at the same level of theory. The calculated structures of the interpseudo-halogens $\text{N}_3\text{-NCO}$ (Figure 3) and $\text{N}_3\text{-OCN}$ are similar to those of the

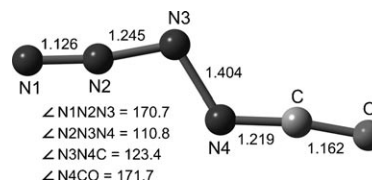


Figure 3. Calculated structure of $\text{N}_3\text{-NCO}$ at the B3LYP/6-311 + G(3df) level of theory. Bond lengths and angles are given in [Å] and [deg], respectively.

isoelectronic analogues N_6 ^[6] and OCN-NCO ^[8a] concerning the *anti* arrangement of their two pseudohalogen moieties with respect to the central N–N bond, which minimize their mutual repulsion. At the B3LYP/6-311 + G(3df) level of theory the predicted length of the weak N–N bond in $\text{N}_3\text{-NCO}$ is 1.404 Å, which is between those predicted for OCN-NCO (1.372 Å) and the experimentally unknown diazide $\text{N}_3\text{-N}_3$ (1.439 Å) at the same level. The latter bond is, however, still considerably shorter than the corresponding N–O bond of $\text{N}_3\text{-OCN}$ (1.501 Å). Even if formed, the very weak N–O bond in $\text{N}_3\text{-OCN}$ might facilitate its rearrangement to the more stable $\text{N}_3\text{-NCO}$ under the experimental conditions.

Experimental Section

Caution! Carbonyl diazide, $\text{OC(N}_3)_2$, was found to be an extremely explosive and shock sensitive compound in liquid and solid state. Although we did not experience any explosions during this work, safety precautions must be taken, including face shields, leather gloves, and protective leather clothing, particularly in the case of handling pure $\text{OC(N}_3)_2$ in solid and liquid state.

Sample preparation: Carbonyl diazide, $\text{OC(N}_3)_2$, was prepared from FC(O)Cl and NaN_3 according to literature procedure^[9] and purified by repeated fractional condensation in vacuum. For the preparation of ^{15}N -labeled $\text{OC(N}_3)_2$, $1\text{-}^{15}\text{N}$ sodium azide (98 at % ^{15}N , EURISO-TOP GmbH) was used. The purity of the sample was verified by FT-IR spectroscopy.

Matrix isolation and photolysis: Matrix IR spectra were recorded on a FT-IR spectrometer (IFS 66v/S Bruker) in reflectance mode using a transfer optic. A KBr beam splitter and an MCT detector were used in the region of 5000 to 550 cm^{-1} . For each spectrum 200 scans at a resolution of 0.25 cm^{-1} were co-added. The gaseous sample was mixed by passing the argon gas through a glass U-trap containing ca. 10 mg of $\text{OC(N}_3)_2$, which was kept in an ethanol bath at a temperature of -65°C . By adjusting the flow rate of Ar or Ne (2 mmol h^{-1}), a small amount of the resulting mixture ($\text{OC(N}_3)_2$ /inert gas ca. 1:1000 estimated) was deposited within 30 min onto the matrix support (Rh-plated Cu block) at 16 K (Ar matrix) or 5 K (Ne matrix) in high vacuum. Details of the matrix apparatus have been described elsewhere.^[15] Photolysis experiments were carried out with a high-pressure mercury arc lamp (TQ 150, Heraeus) by conducting the light

through water-cooled quartz lenses and an interference filter $\lambda = 255$ nm or cut off filters $\lambda \geq 335$ and $\lambda \geq 455$ nm (Schott).

Theoretical studies: The structures of all stationary points were fully optimized with DFT (B3LYP,^[16] BP86,^[17] MPW1PW91^[18]) and CBS-QB3^[19] methods. The 6-311 + G(3df) basis set was used for all the DFT calculations. Time-dependent (TD) DFT (B3LYP/6-311 + G(3df)) calculations^[20] were performed for the prediction of UV/Vis spectra. Quantum chemical calculations were carried out using the Gaussian03 software package.^[21]

Received: August 18, 2010

Revised: October 1, 2010

Published online: December 5, 2010

Keywords: azides · matrix isolation · nitrenes · photoisomerization · vibrational spectroscopy

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