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Elusive Diazirinone, N_2CO**

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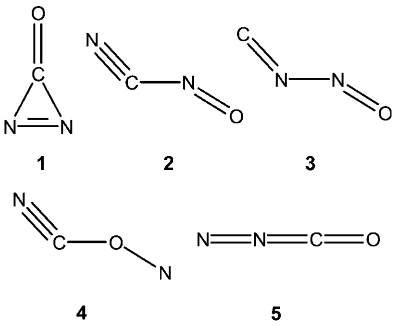
Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 70th birthday

Diazirinone, N_2CO (**1**, Scheme 1), and its isoelectronic analogues tetranitrogen (N_4)[1] and dicarbon dioxide (C_2O_2)[2] are of fundamental interest since they may be viewed as dimers of the very stable diatomic molecules CO and N_2. Thus, they represent a very special class of molecules. The consequent metastability also serves to make their preparation and detection challenging. However, experimental detection of such species affords an opportunity to study molecules at the limit of chemical stability.



Scheme 1. Isomers of N_2CO.

N_2CO (**1**) was calculated to be 400 kJ mol^{-1} higher in energy than N_2 and CO, but a significant dissociation barrier of 108 kJ mol^{-1} was also predicted at the coupled-cluster level of theory.[3,4] The cyclic isomer **1** was calculated to be the most stable of the N_2CO species on the singlet potential energy surface (PES); it is thermodynamically more stable than NCNO (**2**), CNNO (**3**), and NCON (**4**), all of which have been observed in cryogenic Ar matrices at 15 K.[5]

Formation of triplet NNCO (**5**) has been claimed in a neutralization–reionization mass spectrometry study starting from mixtures of N_2^+ + CO or N_2 + CO^+.[6] Observation of **1** in the reaction of *p*-nitrophenoxychlorodiazirine with halide salts was recently reported.[7–10] However, subsequent work[11] strongly suggested that an IR feature attributed in the previous study[7] to cyclic N_2CO was in fact due to condensed-phase CO. Thus, to date, diazirinone remains an undetected species.[12]

Our recent studies of pure carbonyl diazide, $OC(N_3)_2$,[13] stimulated investigations of its photolytic decomposition reactions. UV photolysis ($\lambda = 255$ nm) of low-temperature matrix-isolated $OC(N_3)_2$ results in carbonyl nitrene $N_3C(O)N$, which undergoes a Curtius rearrangement to give the N_6 analogue N_3–NCO upon visible-light ($\lambda \geq 455$ nm) irradiation.[14] N_3–NCO decomposed to CO and N_2 when irradiated with UV/Vis light ($\lambda \geq 335$ nm). In these experiments, none of the N_2CO isomers were observed, probably because of their photolytic destruction under the experimental conditions.

Herein, we report on the thermal decomposition of gaseous $OC(N_3)_2$ through low-pressure pyrolysis, both in the pure form and diluted with noble gases. In the low-pressure pyrolysis of the pure diazide at 400 °C, the pyrolysis products were directed through two U-traps held at 173 and 77 K (liquid nitrogen). Unreacted diazide remained in the former trap, while the trap at 77 K contained a small amount of a yellow solid. Its gas-phase IR spectrum displays two prominent bands in the region from 1800 to 2100 cm^{-1} (Figure 1). The positions (Q centers) at 2044 and 1865 cm^{-1} and relative intensities are in excellent agreement with values predicted for the most intense vibrational bands of cyclic **1** (Table 1). Furthermore they exhibit the expected A-type band contour with a P–R separation of 25 cm^{-1} (calc.: 24.7 cm^{-1}).[15,16] At room temperature in an IR cell, the intensities of these bands

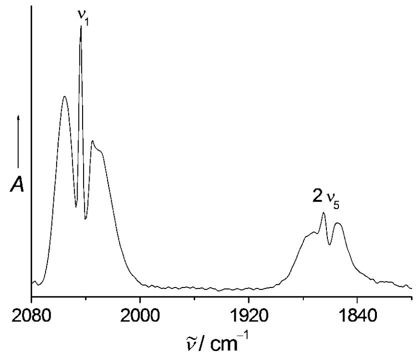


Figure 1. Gas-phase IR spectrum of diazirinone (N_2CO) in the region of the ν_1 and $2\nu_5$ bands (resolution 2 cm^{-1}, 298 K).

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Table 1: Calculated and experimental IR frequencies [cm^{-1}] of diazirinone (**1**).

Calculated[a]	Experimental[b]		Isotopic shifts[a,b]						Assignment
ν_i	ν_i	ν_i	$\Delta\nu_i(^{14}N^{15}N)$		$\Delta\nu_i(^{15}N^{15}N)$		$\Delta\nu_i(^{13}C)$		
	Ne matrix	Ar matrix	expt.	calc.	expt.	calc.	expt.	calc.	
2939 (7.0)	2936.5 (1)	2925.0 (1)	12.0	12.1	23.9	23.7	54.6	53.7	a_1: $\nu_1 + \nu_3$
2046 (316.7)	2042.3 (100)[c]	2033.6 (100)	5.1	4.5	9.4	8.7	52.6	54.9	ν_1, C=O stretch
1860 (120.7)	1863.0 (32)[c]	1857.4 (34)	10.3	11.1	23.4	23.0	34.5	39.7	$2\nu_5$
1325 (0.2)	–	–	–	20.2	–	41.0	–	0.3	ν_2, N=N stretch
903 (5.2)	904.6 (3)	902.1 (3)	8.0	8.0	15.6	15.1	2.9	3.0	ν_3, NCN s-stretch
565 (28.7)	564.5 (6)	564.4 (10)	0.8	0.8	1.5	1.5	17.2	16.9	b_1: ν_4, out of plane bend
961 (11.3)	961.9 (4)	959.6 (6)	7.5	7.6	15.2	15.3	17.6	17.8	b_2: ν_5, NCN as-stretch
529 (11.9)		528.7 (3)	4.5	4.5	9.0	8.6	5.9	5.7	ν_6, OCN rock

decreased with a first-order rate corresponding to a half-life of about 1.4 h (Figures S1 and S2 in the Supporting Information). The only decomposition product observed by IR spectroscopy was CO.

When the thermal decomposition products of $OC(N_3)_2$ (highly diluted in Ar with an estimated ratio of 1:1000) were quenched in an Ar matrix at 16 K, the formation of carbon monoxide (2140.0 cm^{-1}) among with traces of N_3–NCO (2219.7 and 2099.5 cm^{-1}) can be ascertained by their characteristic IR bands.[14] However, some diazide still survived even at furnace temperatures of 500 °C, and a few new bands appeared in the pyrolysis products (Figure S3 in the Supporting Information). Comparison with the IR spectrum of cyclic **1** predicted by high-level CCSD(T)/ANO2 anharmonic frequency calculations suggested that almost all of the new bands can be attributed to this novel species (Table 1).

To further support the assignments of the new bands, the pyrolysis products were irradiated with UV/Vis light ($\lambda \geq$ 335 nm). Two bands at 2033.6 and 1857.4 cm^{-1}, along with some much weaker features partly due to N_3–NCO, disappeared completely after 20 min of irradiation (Figure 2, lower trace). Only carbon monoxide was detected as a photolysis product.

The strongest band observed at 2033.6 cm^{-1} (Ar matrix) can be confidently assigned to the C=O stretching mode of **1**. It is noted that the unusually high C=O stretching frequency and the high intensity of the second strongest band at 1857.4 cm^{-1}, assigned to $2\nu_5$, are well predicted by the anharmonic calculations (Table 1). These two curiosities are the manifestation of a strong Fermi resonance[17] between these two vibrational levels.[11] Because solid Ne forms weaker interacting matrices, we repeated these experiments with Ne matrices at 5 K. The two bands appeared at 2042.3 and 1863.0 cm^{-1}, very close to the gas-phase values of 2044 and 1865 cm^{-1}, respectively.

After we had detected the two strongest bands of cyclic **1**, we searched for the two weak C–N stretches (ν_3 and ν_5) around 900 cm^{-1} (Table 1), and two weaker bands (ν_4 and ν_6) using a liquid-helium-cooled Bolometer detector. All of these bands were found and assignments have been further confirmed by ^{15}N- and ^{13}C-labeling experiments (Table 1). Significantly, starting from ^{15}N-disubstituted $OC(N_3)_2$, three isotopomers (N_2CO, $^{15}NNCO$, and $^{15}N_2CO$) were formed with the relative abundances of 1:2:1, respectively. This intensity pattern, clearly resolved in the ^{15}N-labeling experiment for all bands but ν_4, which is not sufficiently resolved, (Figure 2, middle trace), unequivocally proves the presence of two symmetrically equivalent N atoms in the molecule.

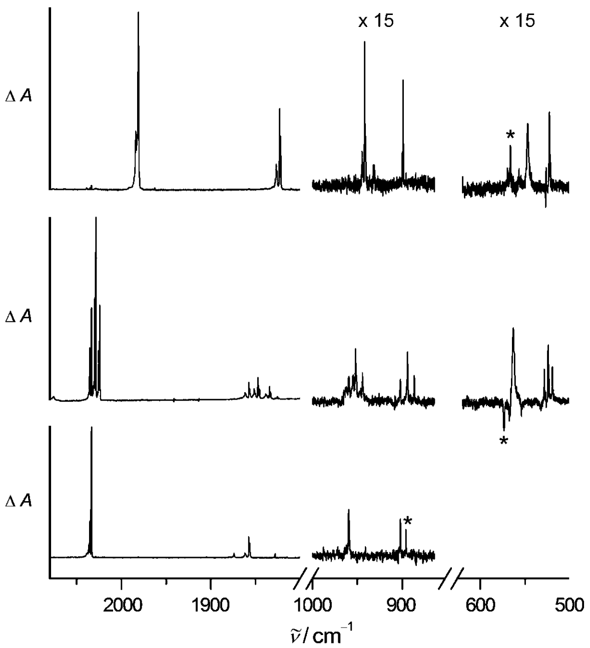
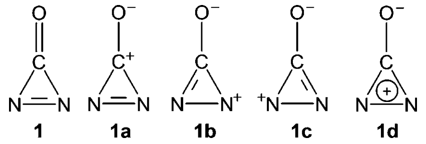


Figure 2. IR difference spectra recorded before and after UV/Vis irradiation ($\lambda \geq 335$ nm) of the pyrolysis (500 °C) products of $OC(N_3)_2$ isolated in solid Ar (lower trace), with ^{15}N-labeling (middle trace), and ^{13}C labeling (upper trace). Features marked by asterisks are caused by a change of the matrix site population of $OC(N_3)_2$ upon irradiation.

The structures and energies of five CON_2 isomers (Scheme 1) were calculated at the DFT B3LYP/6-311 + G-(3df) level of theory (Table S1 in the Supporting Information). Generally, the results are consistent with earlier theoretical studies.[3,4] The stability of **1** relative to the others has been attributed in part to its aromatic character, which can be represented by the resonance structures **1a**–**d** (Scheme 2). The aromatic stabilization energy was estimated to be 25.1 kJ mol^{-1} by B3LYP/6-311 + G* calculations, which is much lower than that of cyclopropenone (102.6 kJ mol^{-1}).[4]

In summary, thermal decomposition of $OC(N_3)_2$ provides an experimental route to the novel high-energy metastable diazirinone molecule. All IR fundamentals with the exception of the very weak N=N stretching mode have been observed in



Scheme 2. Lewis resonance structures of diazirinone (**1**).

cryogenic matrices, and assignments have been supported by ^{15}N and ^{13}C isotopic shifts. In agreement with the predicted high decomposition barrier of 108 kJ mol^{-1},[4] cyclic **1** was found to be rather kinetically stable with a half-life of about 1.4 h in the gas phase at ambient temperature in an IR cell. Its slow decomposition to the very stable dinitrogen and carbon monoxide molecules makes N_2CO an interesting candidate for further studies, which are currently underway.

Experimental Section

Caution! Carbonyl diazide, $OC(N_3)_2$, was found to be an extremely explosive and shock-sensitive compound in the liquid and solid states.[13] Although we did not experience any explosions during this work, safety precautions must be taken, including face shields, leather gloves, and protective leather clothing.

Carbonyl diazide, $OC(N_3)_2$, was prepared from FC(O)Cl and NaN_3 (> 99 %, Merck) according to the reported procedure[13] and purified by repeated fractional condensation in vacuum. For the preparation of ^{15}N-labeled $OC(N_3)_2$, 1-^{15}N sodium azide (98 atom % ^{15}N, Euriso-Top GmbH) was used. For the preparation of ^{13}C-labeled $OC(N_3)_2$, $F^{13}C(O)Cl$ was used, which was prepared from ClF and ^{13}CO (> 99 % atom ^{13}C, Deutero GmbH) as described in the literature.[18] The purity of the samples was checked by gas-phase FTIR spectrometry.

At a vacuum line a glass container with roughly 100 mg of $OC(N_3)_2$ was immerged in a cold bath at −15 °C. In a dynamic vacuum the diazide vapor passed through a glass tube heated to 400 °C (6 mm o.d., 3 mm i.d., heated zone 30 mm long), and the pyrolysis products were directed through U-traps held at −100 and −196 °C. The formation of volatile products (CO and N_2) passing the −196 °C trap was indicated by a Pirani vacuum meter. Diazirinone was trapped at −196 °C, and unreacted diazide at −100 °C. The reaction was repeated several times until all the diazide had decomposed (yield ca. 0.5 mg). Gas-phase IR spectra (2 cm^{-1} resolution) were recorded using a glass cell (20 cm optical path lengths), attached to the vacuum line, equipped with two silicon windows, and placed in the sample compartment of a Bruker Vector22 spectrometer (KBr beamsplitter).

Infrared spectra of matrix-isolated diazirinone were recorded on an FTIR spectrometer (IFS 66v/S Bruker) in reflectance mode using a transfer optic. A KBr beam splitter and a MCT detector were used in the region of 5000–530 cm^{-1} and a Ge-coated 6-μm Mylar beam splitter with liquid-helium-cooled Si bolometer in the region of 700–180 cm^{-1} (CsI window). For each spectrum 200 scans at a resolution of 0.25 cm^{-1} were coadded. The gaseous samples were obtained by passing argon gas through a glass U-trap containing approximately 10 mg of $OC(N_3)_2$, which was kept in an ethanol bath at −65 °C. At a flow rate of 2 mmol h^{-1} of Ar or Ne, the resulting mixture ($OC(N_3)_2$/inert gas $\approx$ 1:1000 estimated) was passed through a quartz furnace with a nozzle (1 mm, i.d.), which was heated to about 500 °C over a length of roughly 10 mm with a platinum wire (0.25 mm, o.d.), prior to deposition on the matrix support. A typical spectrum is shown in Figure S3. Spectra of isotopic labeled species are depicted in an expanded scale in Figure S4. Details of the matrix apparatus have been described elsewhere.[19] Photolysis experiments were carried out using a high-pressure mercury arc lamp (TQ 150, Heraeus), water-cooled quartz lenses, and a cut-off filter ($\lambda \geq 335$ nm, Schott).

Structures, vibrational frequencies, and anharmonic force field corrections were computed for diazirinone using the coupled-cluster singles and doubles model, together with a perturbative treatment of triple excitations [CCSD(T)],[20] as implemented in the CFOUR software package.[21] The basis set used was the atomic natural orbital basis ANO2, which is based on Taylor and Almlöf's natural atomic orbitals,[22] truncated to 5s4p3d2f1g on each atom. Cubic and quartic force constants were calculated by numerical differentiation of analytic second derivatives calculated at displaced points, following the approach of Stanton et al.[23] DFT calculations of all the isomers of CON_2 species were also performed, and the results and corresponding references are given in the Supporting Information.

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