Cyanocarbene, Isocyanocarbene, and Azacyclopropenylidene: A Matrix-Spectroscopic Study**

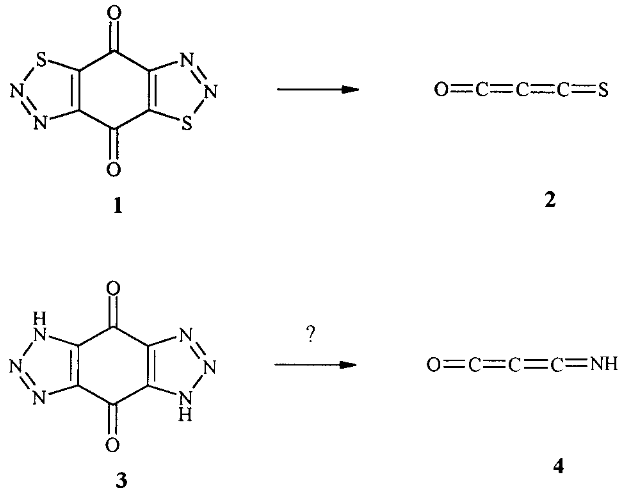
Günther Maier,* Hans Peter Reisenauer, and Katja Rademacher

Abstract: Matrix-isolated cyanoketene (**5**) was obtained by flash vacuum pyrolysis of the precursor **3** and by the photoinduced addition of carbon monoxide to cyanocarbene (**6**), which was generated by irradiation of diazoacetonitrile (**7**). The reaction **6**→**5** could be reversed by exciting **5** with UV light ($\lambda < 200$ nm). Matrix-isolated **6** was isomerized to isocyanocarbene (**8**) and azacyclopropenylidene (**9**) by irradiation with light of selected wavelengths. The photochemical interconversions of the three C_2HN isomers were completely reversible. The UV/Vis and IR spectra of **8** and **9** are reported for the first time. The identification of both carbenes is based on the good agreement between the experimental and theoretical IR spectra, which were obtained by density functional calculations (B3LYP/6-311++G**). From the IR spectra it can be concluded that **8** has a singlet ground state and a strongly bent structure.

Keywords: carbenes · matrix isolation · photochemistry · pyrolysis

Introduction

During our investigations of heterocumulenes,[1] we sought a precursor molecule of matrix-isolated iminopropadienone (**4**). In 1992 Wentrup et al.[2] showed by means of neutralization–reionization mass spectroscopy that **4** has a finite lifetime in the gas phase. However, attemps to identify **4** by matrix isolation techniques failed.[3] Since the thermolysis or photolysis of the *p*-quinone derivative **1** leads to C_3OS (**2**; Scheme 1),[4] it seemed conceivable that the structurally related 4,8-dihydrobenzobistriazole-4,8-dione (**3**) would show the same fragmentation to yield iminopropadienone (**4**).



Scheme 1. Precursor molecules for **2** and **4**.

We failed to isolate the target molecule **4**, but obtained cyanoketene (**5**) instead. The photochemistry of **5** opened a route to the C_2HN isomers. The history of these highly reactive carbenes began in 1964 with the first spectroscopic detection of cyanocarbene (**6**) by Bernheim et al. by means of matrix-isolation ESR spectroscopy.[5a] From the early ESR,[5a–c, 6] matrix IR,[7] and microwave[8] studies, a triplet ground state and a linear or nearly linear structure were derived, in contrast to the results of many theoretical calculations that predicted a bent structure.[9a–c] Since then additional results from microwave[10a–c] and gas-phase IR[11] studies, and ab initio calculations[12] have led to the quasilinearity of cyanocarbene being generally accepted. The other conceivable C_2HN isomers have attracted less attention. Aoki et al.[13] and Schwarz et al.[14] calculated geometries and energies of various cyanocarbene isomers in their lowest singlet and triplet states by high level ab initio and density functional methods. To our knowledge, the only experimental investigation is the neutralization–reionization mass spectrometric study by Schwarz et al.[14] On the basis of the fragmentation pattern of C_2HN ions, they claimed to have proved the existence of isocyanocarbene (**8**) and iminovinylidene carbene.

Results and Discussion

Matrix photolysis and flash vacuum thermolysis of precursor 3: 4,8-Dihydrobenzobistriazole-4,8-dione (**3**)[15] was obtained as one of the products of the diazotization of hexaaminoben-

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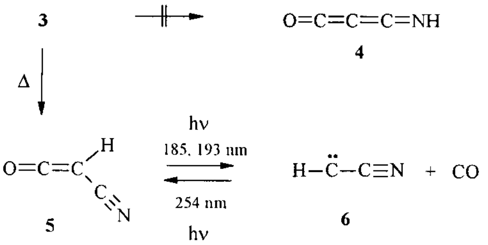
[**] Heterocumulenes, Part 11. For Part 10, see ref. [1].

zene. Matrix-isolated samples were prepared by sublimation of the compound at 280 °C and deposition on a CsI window at 12 K together with a large excess of argon. On irradiation with a low-pressure mercury lamp (254 nm), **3** proved to be rather photostable. Only a small decrease of its IR bands was observed. Some new, very broad, small bands that appeared between 2300 and 2000 cm^{-1} were not sufficient for any reliable assignment.

The flash vacuum pyrolysis of **3** was more successful. The compound was pyrolyzed at 460–740 °C in a quartz tube (8 × 50 mm, $p < 10^{-4}$ mbar), which was directly connected to the vacuum shroud of a cryostat, and the products were trapped at 12 K on a spectroscopic window together with a large excess of argon. The resulting matrix was probed by FTIR spectroscopy. At the optimized thermolysis temperature of 680 °C, cyanoketene (**5**) was formed in a very clean reaction (Scheme 2). The identification of **5** is mainly based on the very strong band for the asymmetric CCO stretching vibration at 2162.8 cm^{-1} and a much weaker band for the CN stretching at 2240.2 cm^{-1}. These two characteristic bands were also reported by Wentrup et al., who obtained **5** independently from two other precursors.[3] By comparison of our IR data with those calculated by the density functional method B3LYP/6-311 + + G**,[16] we were able to assign four additional IR bands to **5** (Figure 1, Table 1; see below). These are the overtone of the ketene band at 4306.3 cm^{-1}, the CH stretching vibration at 3076.7 cm^{-1}, the HCC in-plane bending vibration at 1364.4 cm^{-1}, and the out-of-plane bending vibration of the hydrogen atom at 552.8 cm^{-1}. However, no indications were found for formation of iminopropadienone (**4**). According to B3LYP/6-311 + + G** calculations, **4** should exhibit a strong IR band at around 2250 cm^{-1} (calculated position: 2376 cm^{-1}, calculated intensity: 3209 km mol^{-1}). According to this calculation, **4** is only 8 kcal mol^{-1} higher in engergy than **5**, but a reaction pathway leading to the thermodynamically most stable C$_3$HNO isomer, namely, cyanoketene (**5**), is preferred in the thermal fragmentation of **3**.



Scheme 2. Thermolysis of **3**.

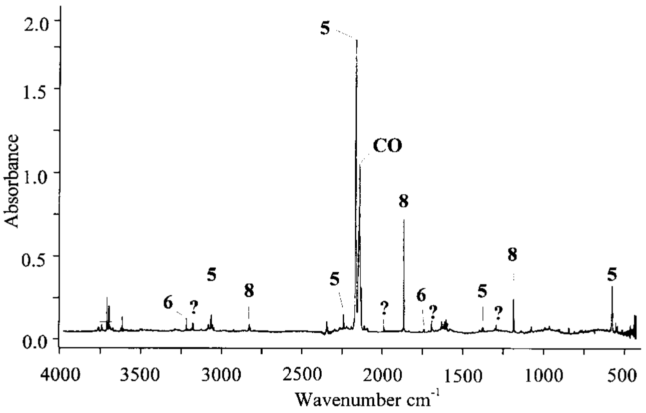


Figure 1. IR spectrum of cyanoketene (**5**) in an argon matrix. The spectrum was recorded after photolysis of matrix-isolated diazoacetonitrile (**7**) in the presence of CO (0.4 %) for 2 h at $\lambda = 254$ nm.

Matrix photolysis of cyanoketene: Since there are numerous examples for photochemically induced rearrangements of matrix-isolated molecules to isomers that are higher in energy, the question arose whether **4** might be obtained from **5** by photochemical excitation. This was not the case. Matrix-isolated **5** was stable towards irradiation with the 254 nm line of a low-pressure mercury lamp. When the 185 nm line of the mercury lamp or the 193 nm radiation of an Ar/F excimer laser was used for photolysis, the IR bands of **5** disappeared and those of carbon monoxide and cyanocarbene (**6**) grew. The carbene **6** was identified by its IR bands at 3229, 1735, 1179 and 458 cm^{-1}.[7] Besides these bands, an additional, rather prominent band appeared at 2090 cm^{-1}. Since no other band showed an identical change in intensity, this absorption must be the most intense band of an as-yet unkown photo-

Table 1. Cyanoketene (**5**). Experimentally observed IR-bands (cm^{-1}; Ar matrix, 12 K; relative intensity in parentheses) and calculated harmonic vibrational transitions (BLYP/6-311 + + G**).

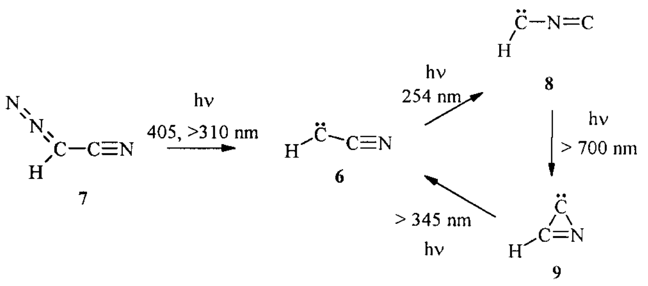
5 exptl[a]	**5** exptl[b]	**5** calcd	[^{13}C]**5** exptl[c]	[^{13}C]**5** calcd	[D]**5** exptl[d]	[D]**5** calcd	approx. description	sym	
4306.3	–	–	–	–	–	–	overtone	a′	$2\nu_1$
3076.7(2)	3074.2	3178(3)	3073.6	3178	2273.7	2354	CH str.	a′	ν_1
2240.2(3)	2240.3	2334(3)	2237.5	2331	2235.3	2323	CN str.	a′	ν_2
2162.8(100)	2164.0	2244(100)[e]	2108.5	2185	2155.8	2240	CCO str.	a′	ν_3
1364.4(1)	1364.0	1403(1)	1362.5	1403	1325.5	1364	CH bend	a′	ν_4
–	–	1140(< 1)	–	1138	–	965	CH bend	a′	ν_5
–	–	978(< 1)	–	975	–	863	CCC str.	a′	ν_6
–	–	661(< 1)	–	649	–	659	CCC bend	a′	ν_7
552.8(9)	553.1	603(6)	552.3	600	539.3	575	CH bend	a″	ν_{10}
–	–	524(< 1)	–	512	–	511	CCO bend	a″	ν_{11}
–	–	424(< 1)	–	420	–	411	NCC bend	a′	ν_8
–	–	404(< 1)	–	404	–	339	NCC bend	a″	ν_{12}
–	–	147(< 1)	–	147	–	146	CCC bend	a′	ν_9

[a] Pyrolysis of **3**. [b] Photoaddition of CO to **6**. [c] Photoaddition of ^{13}CO to **6**. [d] Photoaddition of CO to [D]**6**. [e] Absolute intensity 883 km mol^{-1}.

product of **5**. If, after some time of exposure to radiation of wavelength 193 nm, the excitation wavelength was changed to 254 nm, the bands of **6** vanished completely and those of cyanoketene **5** reappeared. This indicates that the back reaction, that is, the addition of CO to **6**, is initiated by light of this wavelength. During irradiation at 254 nm, the unkown band at 2090 cm^{-1} also gained in intensity, and an additional absorption, which was later on identified as the strongest band of isocyanocarbene (**8**; see below), appeared at 1860 cm^{-1}

Matrix photolysis of diazoacetonitrile: These observations led us to an independent approach to the generation of matrix-isolated **5**. We irradiated diazoacetonitrile (**7**),[17] isolated together with various amounts of carbon monoxide, in an argon matrix at 254 and 405 nm, and obtained **6** along with ketene **5** in yields that depended on the concentration of CO (Figure 1). By using ^{13}CO or deuterodiazoacetonitrile we were able to introduce a ^{13}C label in the carbonyl position of **5** or a deuterium atom. The recorded shifts of the IR bands were in good agreement with the calculated values (Table 1). With regard to the nature of the species with a band at 2090 cm^{-1} that was observed upon irradiation of **5** (formed from **6** and CO), the isotopic shifts did not provide a final answer. No band shift was observed with deuterodiazoacetonitrile. This observation rules out isocyanoketene as the unknown species, our most favored guess, because the expected isotopic shift should be small (a few wavenumbers, as is the case for **5**) but observable. The failure to identify the new compound was one of the reasons for carrying out an independent study of the photochemistry of pure matrix-isolated **6**.

Cyanocarbene (**6**): Cycanocarbene (**6**) and deuterocyanocarbene ([D]**6**), isolated in solid argon and nitrogen at 12 K, were obtained from **7** and [D]**7** according to the procedure of Dendramis and Leroi.[7] The precursor **7** was evaporated at −40 °C and deposited with a large excess of the matrix gas on a CsI or BaF_2 window at 12 K. Spectra were recorded in the range of 190–1100 nm and 4000–220 cm^{-1}. By irradiation with the light from a high-pressure mercury lamp in combination with a monochromator (405 nm) or a cutoff filter ($\lambda >$ 310 nm), nitrogen was split off to give triplet **6** (Scheme 3).



Scheme 3. Formation of **6** and its irradiation products.

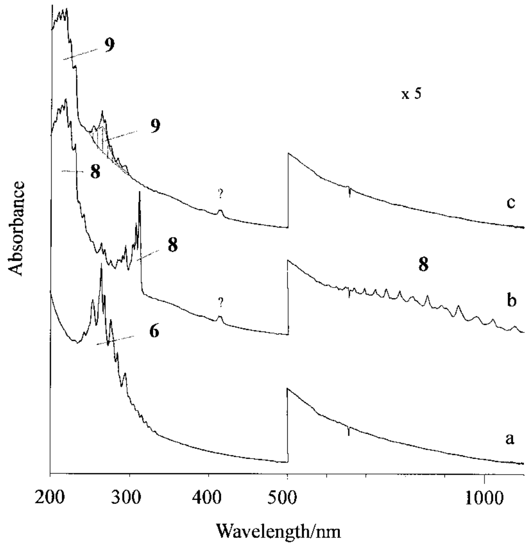


Figure 2. UV/Vis spectra of a) cyanocarbene (**6**), b) isocyanocarbene (**8**), and c) azacyclopropenylidene (**9**) in an argon matrix. The spectra were recorded after a) 1 h irradiation of matrix-isolated diazoacetonitrile (**7**) at $\lambda > 310$ nm, b) after an additional 0.5 h of irradiation at $\lambda = 254$ nm, and c) after an additional 4 h of irradiation at $\lambda > 700$ nm.

The UV/Vis spectrum of **6** (Figure 2a) was practically identical with that of Dendramis and Leroi.[7] It shows a complicated pattern of bands between 340 and 240 nm, in which at least two different band systems appear to overlap (340–300 nm, vibrational progression: ca. 550 cm^{-1}, and 295–240 nm, vibrational progression: ca. 1100 cm^{-1}).

To understand the matrix IR spectrum of cyanocarbene (Figure 3), which is consistent with triplet **6** (Table 2) but not with singlet **6** (Table 3), the microwave and gas phase IR data must be taken into account.[10c, 11] These experiments

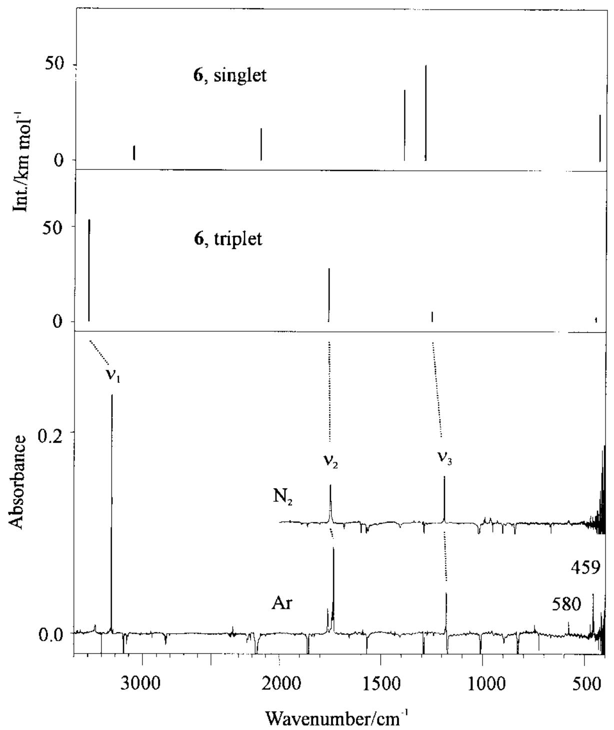


Figure 3. Comparison of the experimental (Ar, N_2, 12 K) and calculated (B3LYP/6-311++G**, harmonic approximation) IR spectra of cyanocarbene (**6**). Top: Calculated spectrum of singlet **6**. Middle: Calculated spectrum of triplet **6**. Bottom: Difference spectrum of the photoreaction **9**→**6** ($\lambda > 345$ nm, 1 h).

Table 2. Cyanocarbene (**6**), triplet ground state. Experimentally observed IR bands (cm^{-1}; Ar and N_2 matrix, 12 K; peak areas relative to the strongest band in parentheses) and calculated harmonic vibrational transitions (B3LYP/6-311++G**).

exptl (Ar)	exptl (N_2)	calcd	approx. description	sym	
3229.4(100)	3213.3	3399(100)[a]	HC str.	a′	ν_1
1763.0(11)	–	–	–		
1734.9(59)	1750.3	1760(53)	CCN asym str.	a′	ν_2
1178.6(16)	1189.2	1251(10)	CCN sym str.	a′	ν_3
–	–	448(6)	CCN ip bend	a′	ν_4
–	–	446(1)	CCN oop bend	a″	ν_6
–	–	283(96)	HCC bend	a′	ν_5
580.0(6)	–				
459.0(33)	–				

[a] Absolute intensity 53 km mol^{-1}

Table 3. Cyanocarbene (**6**), lowest singlet state. Calculated harmonic vibrational transitions (cm^{-1}; B3LYP/6-311++G**, relative intensity in parentheses).

calcd	approx. description	sym	
3074(15)	CH str.	a′	ν_1
2097(33)	CN str.	a′	ν_2
1087(74)	CC str.	a′	ν_3
930(100)[a]	HCC bend	a′	ν_4
433(49)	CCN bend	a′	ν_5
317(15)	CCN bend	a″	ν_6

[a] Absolute intensity 50 km mol^{-1}

Table 5. Deuterocyanocarbene ([D]**6**), triplet ground state. Experimentally observed IR bands (cm^{-1}; Ar and N_2 matrix, 12 K; peak areas relative to the strongest band in parentheses) and calculated vibrational transitions (B3LYP/6-311++G**,harmonic apporximation).

exptl (Ar)	exptl N_2	calcd	approx. description	sym	
2424.0(66)	2432.3	2534(74)	DC str.	a′	ν_1
1729.0(100)	1739.5	1750(100)[a]	CCN asym str.	a′	ν_2
1149.2(14)	1148.5	1208(23)	CCN sym str.	a′	ν_3
1127.7(9)	–	–	–	–	
–	–	446(20)	CCN ip bend	a′	ν_4
–	–	436(11)	CCN oop bend	a″	ν_6
–	–	215(88)	DCC bend	a′	ν_5
404.9(13)	–	–			
317.7(38)	–	–			

[a] Absolute intensity 27 km mol^{-1}

provide strong evidence that **6** must be regarded as quasilinear. This phenomenon is also found for structurally related molecules such as fulminic acid (HCNO). The term quasilinear[18] means that the pattern of the energy levels of such a molecule resembles neither those of a linear nor those of a bent limiting case. The harmonic approximation that is used in the standard ab initio calculations of vibrational spectra and in the normal coordinate analysis perfomed by Dendramis and Leroi[7] is not appropriate for the bending motions, but may still be valid for the stretching vibrations. These considerations provide an explanation for the fact that good agreement between the calculated and experimental IR bands (Figure 3, Table 2) is found for the three stretching vibrations, but not for the bending vibrations. We believe that the bands observed in the low-wavenumber region are propably not fundamental vibrations, but arise from transitions to vibrational energy levels (580 cm^{-1}: $3\nu_5$, $l=1$; 459 cm^{-1}: $2\nu_5$, $l=0$; see Table 4) that originate from the quasilinearity of **6**. They correlate fairly well with the energy levels deduced from the rotational spectra measured by McCarthy et al.[10c]

Our arguments for this assumption are as follows: First, we did not find the very weak band at 369.5 cm^{-1} reported by Dendramis and Leroi (denoted an uncertain band), which they assigned to the CCN bending vibration. Instead we registered a weak band at 580.0 cm^{-1}, which must be assigned to **6** because it showed the same variations in intensity during the photolyses as the other bands of **6**. Its counterpart in the spectrum of [D]**6** is at 404.9 cm^{-1} (Table 5), in accordance with earlier experiments.[7] This large band shift definitely rules out an assignment to the CCN deformation vibration, for which the expected H/D shift should be not more than a few wavenumbers. The frequency ratio $\tilde{\nu}_D/\tilde{\nu}_H$ (404.9/580.0 = 0.698) is very low and approximately equal to that of the second band in the low-wavenumber region, at 459.0 (**6**) and 317.7 cm^{-1} ([D]**6**), (317.7/459.0 = 0.692; Tables 2, 4, and 5). Therefore, a large contribution from the motion of a hydrogen atom must be involved in both transitions, as would be the case for the HCC bending vibration (denoted as ν_5 for the linear and quasilinear cases) and its overtones. Second, another interesting observation on changing the matrix material from argon to nitrogen must also be considered. While the bands of the three stretching vibrations $\nu_1-\nu_3$ are shifted by only about 10 cm^{-1}, which is a quite usual value for a change of the matrix material from argon to nitrogen, both bands in the low-wavenumber region (**6**: 580, 459 cm^{-1}; [D]**6**: 405, 318 cm^{-1}) could no longer be detected in a nitrogen matrix (Figure 3). This behavior is untypical for an ordinary fundamental vibration of a normal molecule. Small molecules such as HCl, H_2O, and CH_4 may freely rotate in solid argon

Table 4. Energies (in cm^{-1}; uncertainties in parentheses) of the low-lying vibrationally excited states of **6** and [D]**6**.

vibr. state[a]	gas phase MW[a] H	D	D/H	gas phase IR[b] H	Ar matrix[c] H	D	D/H	tentative[c] assignment
ν_5,$l=1$	145(±15)	90(±15)	0.62(±0.17)	187(±20)	–	–		
$2\nu_5$,$l=2$	340(±15)	215(±15)	0.63(±0.07)		–	–		
ν_4	365(±15)	367(±15)	1.00(±0.08)	383(±20)	–	–		
$l=0$	435(±20)	311(±15)	0.71(±0.07)		459.0	317.7	0.692	$2\nu_5$,$l=0$
$l=0$	525(±20)				–	–		
$l=0$	540(±20)				–	–		
$3\nu_5$,$l=3$	625(±20)	400(±20)	0.64(±0.05)		–	–		
					580.0	404.9	0.698	$3\nu_5$,$l=1$

[a] Ref. [10c]. [b] Ref. [11]. [c] This work.

but not in nitrogen; therefore, rotational fine structure of the IR bands is observable in an argon, but not in a nitrogen matrix.

Isocyanocarbene (**8**): When irradiation of the matrix with the 254 nm emission of a low-pressure mercury lamp was continued, which possibly promotes **6** from the triplet ground state to an electronically excited triplet state that corresponds to the UV absorption at this wavelength (Figure 2a), the bands of **6** gradually decreased and were finally replaced by new bands in the UV, near-IR, and mid-IR regions. Comparison of these IR bands with those calculated for singlet and triplet isocyanocarbene (**8**) (Figure 4, Table 6) left little doubt that a simple nitrile/isonitrile rearrangement took place. This is confirmed by the IR spectrum of the deuterated isotopomer [D]**8** (Table 7). Furthermore, the fact that good agreement between theory and experiment is found for the singlet but not for the triplet state (Table 8) shows that **8** has a singlet ground state. This result is important because the singlet/triplet gap of **8** calculated by ab initio and density functional methods is very small. According to a SDCI + Q/D95** calculation the singlet state is more stable by 0.4 kcal mol^{-1},[13] while other methods slightly favor the triplet state (e.g., B3LYP/6-311 + G**[14] by 3.0 kcal mol^{-1}).

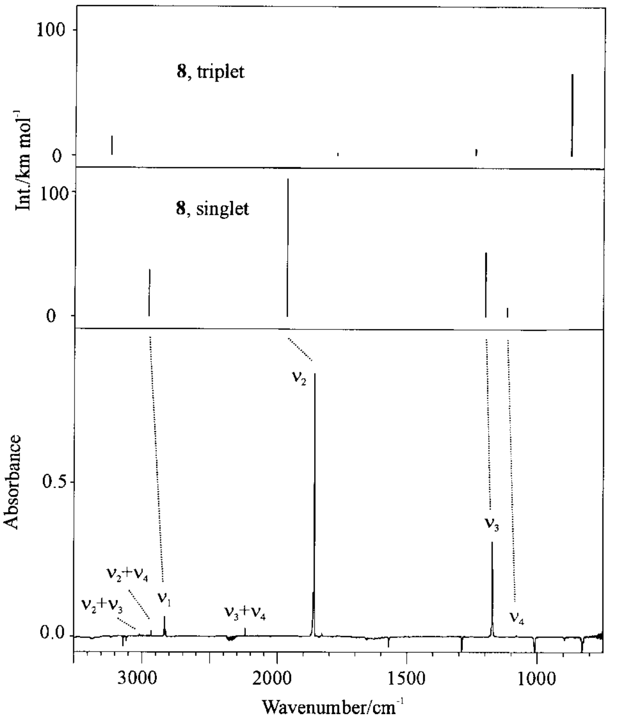


Figure 4. Comparison of the experimental (Ar, 12 K) and calculated (B3LYP/6-311 ++ G**, harmonic approximation) IR spectra of isocyanocarbene (**8**). Top: calculated spectrum of triplet **8**. Middle: calculated spectrum of singlet **8**. Bottom: difference spectrum of the photoreaction **6**→**8** (λ = 254 nm, 0.5 h).

Table 6. Isocyanocarbene(**8**), singlet ground state. Experimentally observed IR-bands (cm^{-1}; Ar and N_2 matrix, 12 K; peak areas relative to the strongest band in parentheses) and calculated harmonic vibrational transitions (B3LYP/6-311 ++ G**).

exptl (Ar)	exptl (N_2)	calcd	approx. description	sym	
3687.7(2)	3717.0	–	–	a′	$2\nu_2$
3018.8(1)	3043.8	–	–	a′	$\nu_2+\nu_3$
2933.4(2)	2958.7	–	–	a′	$\nu_2+\nu_4$
2834.5(20)	2852.8	2956(34)	C–H str.	a′	ν_1
2240.6(4)	2261.7	–	–	a′	$\nu_3+\nu_4$
1859.5(100)	1874.2	1935(100)[a]	C=N str.	a′	ν_2
1829.4(1)	1844.0	1904	^{13}C=N str.		
1173.5(39)	1182.9	1201(46)	C–N str.	a′	ν_3
1080.5(1)	1090.9	1118(8)	HCN bend	a′	ν_4
–	–	394(7)	CNC bend	a′	ν_5
–	–	274(1)	CNC bend	a″	ν_6

[a] Absolute intensity 112 km mol^{-1}

Table 7. Deuteroisocyanocarbene [D]**8** singlet ground state. Experimentally observed IR bands (cm^{-1}; Ar and N_2 matrix, 12 K; peak areas relative to the strongest band in parentheses) and calculated harmonic vibrational transitions (B3LYP/6-311 ++ G**).

exptl (Ar)	exptl (N_2)	calcd	approx. description	sym	
3681.4(4)	3711.0	–	–	a′	$2\nu_2$
2933.6(2)	2957.7	–	–	a′	$\nu_2+\nu_3$
2157.5(2)	–	–	–	a′	$2\nu_3$
2110.9(12)	2124.8	2172 (31)	C–D str.	a′	ν_1
1980.3(3)	1955.1	–	–	a′	$\nu_3+\nu_4$
1856.4(100)	1871.2	1928 (100)[a]	C=N str.	a′	ν_2
1827.0(1.5)	1841.6	1896	^{13}C=N str.		
1082.9(6)	1091.6	1126(1)	C-N str.	a′	ν_3
904.5(20)	911.2	916(31)	DCN bend	a′	ν_4
–	–	375(9)	CNC bend	a′	ν_5
–	–	268(6)	CNC bend	a″	ν_6

[a] Absolute intensity 93 km mol^{-1}

Table 8. Isocyanocarbene (**8**), lowest triplet state. Calculated harmonic vibrational transitions (cm^{-1}; B3LYP/6-311 ++ G**, relative intensities in parentheses).

calcd	approx. description	sym	
3236(23)	CH str.	a′	ν_1
1775(4)	NC str.	a′	ν_2
1240(9)	CN str.	a′	ν_3
873(100)[a]	HCN bend	a′	ν_4
403(< 1)	CNC bend	a″	ν_6
353(4)	CNC bend	a′	ν_5

[a] Absolute intensity 66 km mol^{-1}

The IR spectrum of **8** (Figure 4) is dominated by the very strong CN stretching band of the isocyano group at 1860 cm^{-1}. This rather low wavenumber (cf. methyl isocyanide: 2160 cm^{-1}) indicates weakening of the C=N bond by conjugation with the empty p orbital of the carbene C atom. The CH stretching vibration occurs at 2834 cm^{-1}, which is also unusually low. For example, the corresponding band of triplet **6** lies about 400 cm^{-1}, and that of methane about 200 cm^{-1} higher. The second intense IR band (1173 cm^{-1}) can be described as the CN single-bond vibration. The HCN-bending vibration leads to a very weak band at 1080 cm^{-1}, which is shifted to 904 cm^{-1} upon deuteration. The remaining two fundamental vibrations, both CNC bending motions, are calculated to absorb below 400 cm^{-1} as very weak bands. For both reasons we have not yet been able to observe them. Two main conclusions may be drawn from the experimental IR data in comparison with the calculations: First, isocyanocarbene (**8**) has a singlet ground state. Second, **8** is a well-behaved strongly bent molecule. Both findings are in contrast to those found for **6**, which has a triplet ground state and is quasilinear.

A similar contrast for compounds **6** and **8** is also found in their electronic spectra. Compound **6** exhibts only absorptions in the UV range between 340 and 240 nm (Figure 2a), while **8** shows a very weak absorption in the near infrared (1100–600 nm, $\lambda_{max} = 855$ nm) with a distinct vibrational fine structure (vibrational progression ca. 520 cm^{-1}, not visible in a nitrogen matrix), together with a second, much stronger band system between 311 and 270 nm, which shows two vibrational series (ca. 1950 and ca. 400 cm^{-1}), and a third absorption band between 240 and 200 nm ($\lambda_{max} = 218$ nm; Figure 2b).

Azacyclopropenylidene (9): A third C_2HN isomer, namely, azacyclopropenylidene (**9**), was obtained upon irradiation of **8** with light correponding either to the UV band around 300 nm (313 nm, high-pressure mercury lamp/monochromator) or to the near IR absorption band ($\lambda > 700$ nm, high-pressure mercury lamp/cutoff filter). The latter wavelength range gave the cleanest result, in that the band of **8** completely vanished and no back reaction to **6** took place. When 313 nm light was used, a mixture of all three isomers **6**, **8**, and **9** was obtained.

The identity of **9** follows from its IR spectrum. All six fundamental bands of the parent and the deuterated isotopomers are observed and compare very well to the theoretical data obtained from a B3LYP/6-311++G** calculation on the singlet species (Figure 5, Tables 9 and 10). The detection of the UV/Vis bands of **9** was more difficult, because they are much weaker than those of **6** and **8** and partially overlap with them. With the help of difference spectra at various stages of photolyses with high and low concentrations of **9**, it can be shown that **9** has a broad structureless absorption between 300 and 240 nm ($\lambda_{max} = 264$ nm; Figure 2c). Another, even weaker band should be present between ca. 350 and 450 nm. We were not able to detect this band directly, but its existence follows indirectly from the observation that irradiation of **9** with light of this wavelength range leads to a quick and clean rearrangement to **6**, thus closing the circle of the photochemical interconversions of the three C_2HN isomers.

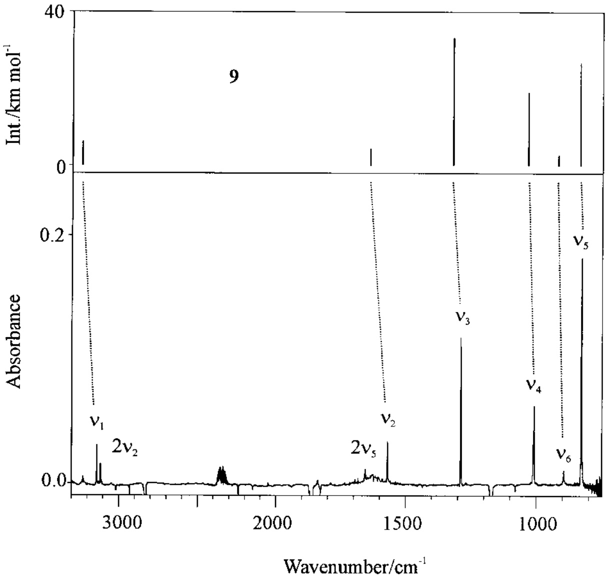


Figure 5. Comparison of the experimental (Ar, N_2, 12 K) and calculated (B3LYP/6-311++G**, harmonic approximation) IR spectrum of azacyclopropenylidene (**9**). Top: Calculated spectrum of singlet **9**. Bottom: Difference spectrum of the photoreaction **8**→**9** ($\lambda > 700$ nm, 4 h).

Table 9. Azacyclopropenylidene (**9**). Experimentally observed IR bands (cm^{-1}; Ar and N_2 matrix, 12 K; peak areas relative to the strongest band in parentheses) and calculated harmonic vibrational transitions (B3LYP/6-311++G**).

exptl (Ar)	exptl (N_2)	calcd	approx. description	sym	
3140.2(22)[a]	3154.4	3238(17)	C–H str.	a′	ν_1
3118.2(9)[a]	3126.1	–	–	a′	$2\nu_2$
1655.7(5)	1683.1	–	–	a′	$2\nu_5$
1571.0(11)	1573.3	1640(13)	C=N str.	a′	ν_2
1290.5(61)	1289.6	1321(100)[b]	C–C str. + HCC bend	a′	ν_3
1009.2(42)	1018.2	1034(57)	C–N str. + HCC bend	a′	ν_4
895.7(8)	903.2	918(68)	H–CC oop bend	a″	ν_6
828.6(100)	843.1	835(80)	HCN bend + C–N str.	a′	ν_5

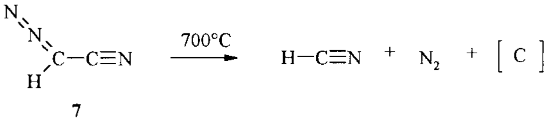
[a] Perturbation by Fermi-resonance. [b] Absolute intensity 33 km mol^{-1}

Table 10. Deuteroazacyclopropenylidene ([D]**9**). Experimentally observed IR bands (cm^{-1}; Ar and N_2 matrix, 12 K; peak areas relative to the strongest band in parentheses) and calculated harmonic vibrational transitions (B3LYP/6-311++G**).

exptl (Ar)	exptl (N_2)	calcd	approx. description	sym	
2365.8(15)	2376.3	2426(14)	C–D str.	a′	ν_1
1532.1(13)	1533.3	1591(10)	C=N str.	a′	ν_2
1331.9(4)	–	–	–	a′	$2\nu_5$
1290.3(6)	–	–	–	–	–
1268.5(100)	1268.9	1297(100)[a]	C–C str. + DCC bend	a′	ν_3
957.9(65)	964.5	981(46)	C–N str. + C–C str.	a′	ν_4
829.3(8)[b]	843.1[b]	728(<1)	DCC oop bend	a″	ν_6
668.2(73)	677.5	670(39)	DCN ip bend	a′	ν_5

[a] Absolute intensity 32 km mol^{-1}. [b] Assignement uncertain.

Flash vacuum thermolysis of diazoacetonitrile (7): Diazoacetonitrile (**7**) was evaporated from a trap at −40 °C and passed through a quartz tube (i.d. 10 mm, length of heated zone 50 mm) at 700 °C. The reaction products were matrix isolated with a large excess of argon at 12 K immediately after leaving the hot zone. During the pyrolysis the quartz tube became blackened with graphite. The IR spectrum of the pyrolysate showed only small bands of **7** and very strong absorptions of hydrogen cyanide, but no signals of **6**. Probably **6** is formed in the first step by elimination of N_2 from **7** and subsequently decomposes on the hot surface of the quartz tube to give HCN and graphite (Scheme 4).



$$N_2CH{-}C{\equiv}N \xrightarrow{700°C} H{-}C{\equiv}N + N_2 + [C]$$

7

Scheme 4. Thermolysis of **7**.

Conclusions

Cyanocarbene (**6**) and isocyanocarbene (**8**) are peculiar isomers in that they differ in their multiplicity and therefore in their chemical behavior. Compound **6** has a triplet ground state and is a quasilinear molecule. It reacts with carbon monoxide under irradiation to form cyanoketene (**5**). In contrast, **8** is a singlet molecule with a rigid structure and is inert towards carbon monoxide. These differences are reflected in the diverging geometries and spectroscopic (IR, UV) properties of **6** and **8**. It is even possible to use the IR spectra to determine the multiplicity of these species. The third C_2HN isomer, azacyclopropylidene (**9**), is not the transition state in the nitrile/isonitrile rearrangement **6**$\rightarrow$**8**, but a real energy minimum.

Experimental Section

Matrix isolation spectroscopy: Cryostat: displex closed cycle refrigerator system CSW 202, Air Products, with CsI (IR spectra) or BaF_2 windows (UV/Vis and IR spectra). Spectrometers: diode array spectrometer: Hewlett-Packard HP8453 (190–1100 nm, 1 diode nm^{-1}); FTIR spectrometers: Bruker IFS85 (4000–220 cm^{-1}) and IFS55 (7500–400 cm^{-1}). Light sources: superhigh-pressure mercury lamps (Osram HBO 200) with monochromator (Bausch & Lomb) or cutoff filters; low-pressure mercury lamps (Gräntzel), excimer laser (Lambda Physik) LPX 105 with ArF (193 nm).

4,8-Dihydrobenzo[1,2-d:4,5-d′]bis[1,2,3]triazol-4,8-dione (**3**): Hexaaminobenzene,[19] freshly synthesized from triaminotrinitrobenzene (4.0 g, 15.5 mmol),[20] was dissolved in degassed water (15 mL) and degassed acetic acid (6 mL). $NaNO_3$ (3.44 g, 49.8 mmol) in degassed water (5.5 mL) was added to the dark blue solution at 0 °C in one portion. The reaction mixture was warmed to 50 °C over 30 min, then cooled to room temperature. The brown precipitate was separated and extracted with 2 N ammonia. The resulting solution was acidified with concentrated HCl to give a pale brown precipitate. The first fraction (0.5 g) was contaminated with about 15 % benzotristriazole; the second fraction (0.59 g) was pure **3** and was used for the matrix-isolation experiments without further purification.

Diazoacetonitrile (**7**) **and deuterodiazoacetonitrile** ([D]**7**): Aminoacetonitrile hydrochloride (2.3 g, 25 mmol) was dissolved in water, and the solution was cooled to 0 °C and introduced into a separating funnel together with CH_2Cl_2 (3 mL). An equimolar amount of $NaNO_2$, (1.7 g, 25 mmol) in water was added in small portions with shaking. The bright yellow organic layer was separated, and the aqueous phase extracted a second time. The combined organic layers were dried over Na_2SO_4. The solvent was removed completely in vacuo at -40 °C to give bright yellow **7**, which was crystalline at -40 °C and an oil at room temperature. The compound was used for matrix-isolation experiments without further purification. Solutions of diazoacetonitrile in CH_2Cl_2 are stable for more than a week; the pure compound is stable for several days at -30 °C. For deuteration, a solution of **7** in CH_2Cl_2 was stirred with D_2O (made slightly alkaline by K_2CO_3) for about a minute and worked up as described above. **Caution**: Solvent-free diazoacetonitrile may explode even at low temperatures.

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