Photochemistry of Matrix-Isolated 4-Diazo-4*H*-imidazole: IR-Spectroscopic Identification of 4*H*-Imidazol-4-ylidene

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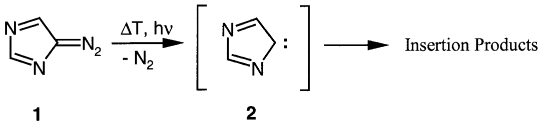
Irradiation of 4-diazo-4*H*-imidazole (**1**) in an argon matrix at 10 K at a wavelength of $\lambda = 313$ nm leads to rapid loss of nitrogen and the formation of 4*H*-imidazol-4-ylidene (**2**). Upon photoexcitation of 4*H*-imidazol-4-ylidene (**2**) at wavelengths longer than 570 nm, the ring-opened carbene **S-6** can be detected. **S-6** can be photochemically converted ($\lambda > 310$ nm) to 2-cyano-2*H*-azirene (**5**). In CO-doped argon matrices, **2** is trapped and 4*H*-imidazol-4-ylidene ketene (**7**) can be observed.

Introduction

Only a few investigations into the chemistry of 4*H*-imidazol-4-ylidene (**2**) have been carried out. Shechter and Amick have studied the chemical behavior of 4-diazo-4*H*-imidazole (**1**) in solution.[1] They found that the thermal or photochemical decomposition of **1** in the presence of benzene derivatives or cyclohexane leads to C−H insertion products of carbene **2**.



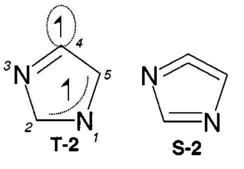
The fact that no kinetic isotope effect was observed when using mixtures of benzene and deuterated benzene led the authors to conclude that **2** is a highly electrophilic singlet carbene, which preferentially attacks the π electrons of benzene in the rate-determining step and not the C−H bonds. EPR experiments, carried out in methanol at 77 K, showed no EPR signal upon irradiation of **1**, indicating that **2** probably has a singlet ground state.[1]

Results and Discussion

Calculations

Ab initio studies performed by Pasto at the MP2 level of theory using a standard 6-31G(d) basis set predicted a triplet ground state for 4*H*-imidazol-4-ylidene (**2**), this lying just 0.4 kcal mol^{-1} below the first excited singlet state.[2] According to Pasto, the observed reactivity of **2** may be explained in terms of the co-existence of both species in solution. However, more recent calculations by Whitehead et al. at the HF level of theory using a standard 6-31G(d) basis set gave a larger T/S gap, with the triplet state ($^3A''$) lying 34.7 kcal mol^{-1} below the first excited singlet state ($^1A'$).[3] Since our aim of identifying matrix-isolated **2** had to be based on the comparison of a calculated with the experimental matrix IR spectra, we performed several additional calculations[4] at the B3LYP level of theory using a standard 6-311+G(d,p) basis set. Our own result is that the ground state of 4*H*-imidazol-4-ylidene (**2**) is a triplet state situated 10.7 kcal mol^{-1} below the singlet state. As far as perturbation theory methods are concerned, specifically MP4 single-point calculations [MP4SDTQ(fc)/6-311+G(d,p)//B3LYP/6-311+G(d,p)], the ground state is also predicted to be a triplet state ($\Delta E_{S-T} = +19.7$ kcal mol^{-1}).

The calculated structures of **S-2** and **T-2** merit some comment. The triplet state **T-2** is predicted to have C_s symmetry (Figure 1). The N(3)−C(4) bond length [C(4) is the carbenic center] is very short and indicates the presence of a double bond between these two centers. The C(4)−C(5) bond length is rather long and corresponds to a C−C single bond between these atoms. The calculated Mulliken spin densities (Figure 1) clearly indicate that the two unpaired electrons are not both localized at the carbenic center. One of the two electrons is located at the carbenic center, while the other is delocalized over the C(2)N(1)C(5) segment, which corresponds to a nitrogen analogue of an allyl radical.



Like singlet 2*H*-imidazol-2-ylidene, which we have described recently,[5] singlet 4*H*-imidazol-4-ylidene (**S-2**) shows an unusual C_s-symmetric structure, which cannot be adequately described using normal valence formulae (Figure 1). A remarkable feature is the short N(3)−C(4) bond length, which is comparable to the length of a C=N double bond. The C(5)−C(4) bond length corresponds to that of a C=C double bond. The C(5)−N(1) bond is longer, while

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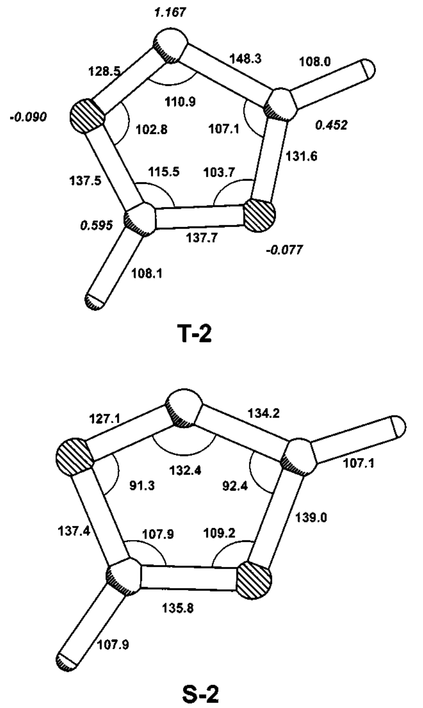
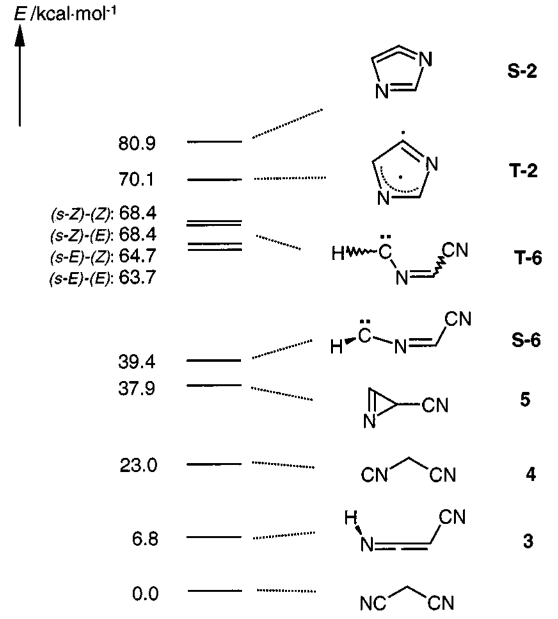


Figure 1. Calculated [B3LYP/6-311+G(d,p)] distances [pm] and bond angles [°] of triplet and singlet 4*H*-imidazol-4-ylidene (**T-2**, **S-2**), together with Mulliken spin densities for **T-2** (italics)

N(1)−C(2) is shorter than in **T-2**. The calculated structure of **S-2** can best be rationalized in terms of the presence of a cumulenic unit between the atoms N(3), C(4), and C(5). This result is also supported by the calculated N(3)−C(4)−C(5) bond angle (132.4°).

$C_3H_2N_2$ Energy Hypersurface

Numerous isomers of the elemental composition $C_3H_2N_2$ are conceivable. A few of them have been calculated within the scope of this study (Scheme 1). The species relevant to the experiments discussed below are the carbenes **2** and **6**, ketenimine **3**, azirene **5**, and isonitrile **4**.

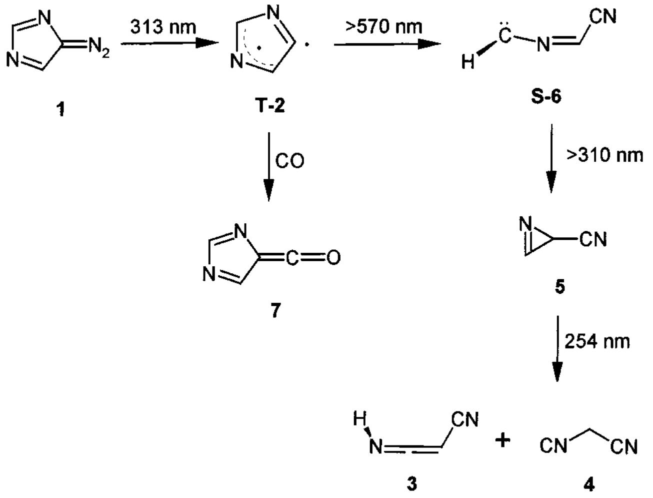


Scheme 1. Relative energies [B3LYP/6-311+G(d,p)] of selected $C_3H_2N_2$ isomers; ZPEs are included

Matrix-Isolation Experiments

Photolysis of 4-Diazo-4*H*-imidazole (1) in Argon Matrices

The matrix UV spectrum of **1** shows one strong absorption at λ_{max} = 296 nm. In spite of the fact that **1** is a yellow crystalline compound, no absorption can be detected in the visible region of the spectrum.



Irradiation of **1** with light of wavelength λ = 313 nm leads to a rapid decrease in the intensity of the IR signals of **1**, while numerous new bands arise. Especially noteworthy is the appearance of a new, unusually broad absorption at $\tilde{\nu}$ = 1980.9/1973.2 cm^{-1} and a double band at $\tilde{\nu}$ = 730.7/713.2 cm^{-1}. The IR spectrum after irradiation of **1** is rather complicated. Nevertheless, the absorptions due to **2** can be assigned by subsequent irradiation at λ > 570 nm. This secondary irradiation of the photoproducts of **1** results in a rapid decrease in the intensity of several signals, but the bands at $\tilde{\nu}$ = 1980.9/1973.2 cm^{-1} and 730.7/713.2 cm^{-1} (attributable to **S-6**, see below) intensify (Figure 2). It is noteworthy that this secondary photoreaction also takes place upon irradiation with light of wavelengths longer than 700 nm. Recapture of the evolved nitrogen molecule, as was observed in the case of 2*H*-imidazol-2-ylidene[5] under similar conditions, could not be detected. Comparison of those IR bands that decrease upon secondary irradiation at λ > 570 nm with the calculated IR spectra of singlet and triplet 4*H*-imidazol-4-ylidene (**S-2** and **T-2**) reveals a very good agreement only with the calculated spectrum for the triplet species **T-2** (Figure 2, Table 1).

Tertiary irradiation of the remaining products in the matrix with light of wavelengths longer than 310 nm leads to a decrease in the intensities of the broad signal at $\tilde{\nu}$ = 1980.9/1973.2 cm^{-1} and the double band at $\tilde{\nu}$ = 730.7/713.2 cm^{-1}. We assign these bands to the ring-opened carbene **S-6**. Comparison of the calculated IR spectra of **S-6** and **T-6** with the observed absorption after the photolysis of **T-2** at λ > 570 nm shows good agreement only for the singlet spe-

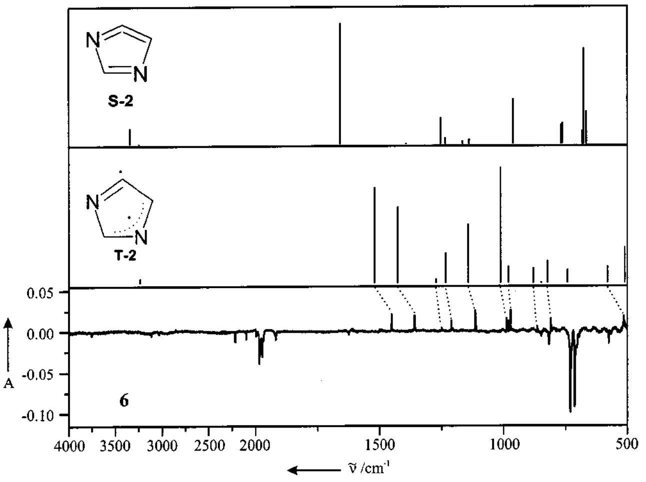


Figure 2. Comparison of the experimental (argon, 10 K; bottom section) with the calculated [B3LYP/6-311+G(d,p)] IR spectrum of **T-2** (middle section) and **S-2** (top section); the experimental spectrum is a difference spectrum of the reaction **T-2** → **S-6** upon irradiation with light of λ > 570 nm; IR bands with positive values diminish, while those with negative values intensify during the irradiation

Table 1. Comparison of the calculated [B3LYP/6-311+G(d,p)] IR spectrum of 4*H*-imidazol-4-ylidene (**T-2** and **S-2**) with the experimental (argon, 10 K) IR absorptions of **T-2** (derived from the disappearance of the bands upon irradiation of **T-2** at λ > 570 nm)

No.	Sym.		$\tilde{\nu}_{exp}$ [cm^{-1}] (I_{exp})[b]	**T-2** $\tilde{\nu}_{calcd.}$ [cm^{-1}] (I_{rel})	**S-2**[a] $\tilde{\nu}_{calcd.}$ [cm^{-1}] (I_{rel})
ν_1	A′	ν_{CH}	–	3242.8 (0.00)	3345.0 (0.13)
ν_2	A′	ν_{CH}	–	3232.0 (0.04)	3241.0 (0.00)
ν_3	A′	$\nu_{NC:} + \delta_{CH}$	1452.0 (s)	1520.6 (0.83)	1658.2 (1.00)[c]
ν_4	A′	$\nu_{NC} + \delta_{CH}$	1358.9 (s)	1426.6 (0.66)	1392.6 (0.01)
ν_5	A′	$\delta_{CH,as}$	1250.6 (w)	1273.5 (0.04)	1254.9 (0.22)
ν_6	A′	$\delta_{CH,s}$	1210.3 (m)	1233.2 (0.26)	1234.4 (0.05)
ν_7	A′	δ_{NCN}	1114.0 (s)	1142.6 (0.51)	1165.5 (0.03)
ν_8	A′	$\nu_{NC} + \delta_{CH}$	988.6/ 981.1 (s)	1012.9 (1.00)[d]	1139.5 (0.04)
ν_9	A′	$\nu_{C-C:}$	971.9 (m)	979.9 (0.15)	961.7 (0.37)
ν_{10}	A′	δ_{NCN}	864.1 (w)	880.8 (0.13)	767.8 (0.16)
ν_{12}	A"	δ_{CH}	–	847.7 (0.01)	764.0 (0.17)
ν_{13}	A"	δ_{CH}	810.0 (m)	822.6 (0.19)	682.5 (0.11)
ν_{11}	A′	δ_{CCN}	–	741.2 (0.12)	677.4 (0.79)
ν_{14}	A"	δ_{ring}	516.1 (m)	580.1 (0.14)	666.2 (0.27)
ν_{15}	A"	$\delta_{CH} + \delta_{ring}$	–	511.2 (0.31)	100.2 (0.01)

[a] Numbering, symmetries, and approximate descriptions are not suitable for the vibrations of **S-2**. – [b] vs = very strong, s = strong, m = medium, w = weak. – [c] Calculated absolute intensity: 132.3 km·mol^{-1}.[d] Calculated absolute intensity: 67.5 km·mol^{-1}.

cies **S-6** (Figure 3, Table 2). The broadness of the bands is discussed in the context of annealing experiments (see below). The product of the tertiary irradiation is 2-cyano-2*H*-azirene (**5**). The experimental band positions (negative values in Figure 3) are in satisfactory accordance with those in the calculated spectrum (Table 3).

The matrix UV spectrum recorded after the photolysis of **1** shows only one absorption at $\lambda_{max} = 277$ nm. After the secondary photolysis with light of wavelengths longer than 570 nm, this absorption intensifies still further. Therefore, this electronic transition cannot be due to 4*H*-imidazol-4-ylidene (**T-2**), but can only be attributed to **S-6**. After the disappearance of **S-6** (irradiation at λ > 310 nm), the matrix UV spectrum shows only one absorption at $\lambda_{max} = 257$ nm, which can be assigned to 2-cyano-2*H*-azirene (**5**). The growth of this band is accompanied by a concomitant decrease in the UV absorption at 277 nm, which gives a second indication that this band can be attributed to carbene **S-6**.

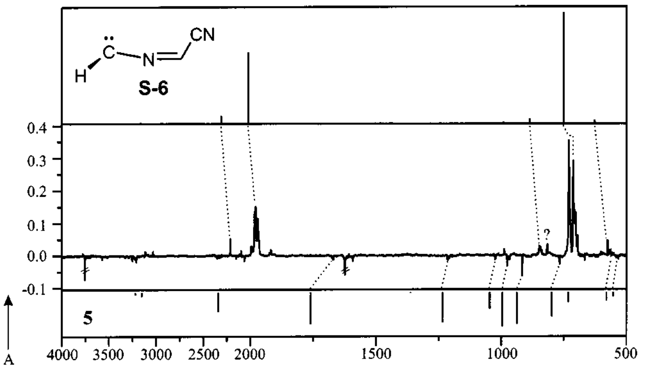


Figure 3. Comparison of the experimental (argon, 10 K; middle section) with the calculated [B3LYP/6-311+G(d,p)] IR spectra of **5** (bottom section) and **S-6** (top section); the experimental spectrum is a difference spectrum of the reaction **S-6** → **5** upon irradiation with light of λ > 310 nm; IR bands with positive values diminish, while those with negative values intensify during the irradiation

Table 2. Comparison of the calculated [B3LYP/6-311+G(d,p)] IR spectrum of the ring-opened carbene **S-6** with the experimental (argon, nitrogen, 10 K) IR absorptions of **S-6** (derived from the disappearance of the bands upon irradiation of **S-6** at λ > 310 nm)

No.		$\tilde{\nu}_{exp}$ [cm^{-1}] (I_{exp})	$\tilde{\nu}_{calcd}$ [cm^{-1}] (I_{rel})
ν_1	ν_{CH}	–	3194.8 (0.01)
ν_2	ν_{CH}	–	3165.5 (0.01)
ν_3	ν_{CN}	Ar: 2216.1 (w) N_2: 2216.3	2311.4 (0.07)
ν_4	ν_{NC}	Ar: 1980.9/1973.2 (s) N_2: 1985.0/1975.4 (s)	2027.6 (0.64)
ν_5	$\delta_{:CH}$	–	1430.8 (0.00)
ν_6	δ_{CH}	–	1224.0 (0.00)
ν_7	$\delta_{NCC} + \nu_{CC}$	–	991.9 (0.01)
ν_8	$\delta_{CH} + \delta_{:CH}$	Ar: 848.8.0 (w) N_2: 847.3 (w)	886.2 (0.04)
ν_9	$\delta_{:CH}$	Ar: 730.7/713.2 (vs) N_2: 735.7/713.9 (vs)	751.5 (1.00)[a]
ν_{10}	$\delta_{:CH}$	Ar: 575.5 (w) N_2: 576.3 (w)	628.7 (0.03)
ν_{11}	$\delta_{CCN} + \delta_{CNC}$	–	625.4 (0.01)
ν_{12}	δ_{NCCNC}	Ar: 442.8 (m) N_2: 449.3 (m)	458.2 (0.06)
ν_{13}	$\delta_{CH} + \delta_{:CH}$	–	377.6 (0.03)
ν_{14}	δ_{CCN}	–	364.7 (0.01)
ν_{15}	δ_{CNC}	–	155.2 (0.00)

[a] Calculated absolute intensity: 132.3 km·mol^{-1}.

Irradiation of 2-cyano-2*H*-azirene (**5**) with light of wavelength λ = 254 nm leads to a decrease in the intensity of the IR absorptions of **5**, while two new, very intense signals arise at $\tilde{\nu}$ = 2154.6 and 2066.6 cm^{-1}, respectively. The signal at $\tilde{\nu}$ = 2154.6 cm^{-1} is probably due to the presence of an isocyano group ($\nu_{N=C:}$). This absorption can most likely be assigned to isocyanoacetonitrile (**4**), although other signals of **4** could not be detected. Following our studies on

Table 3. Comparison of the calculated [B3LYP/6-311+G(d,p)] IR spectrum of 2-cyano-2*H*-azirene (**5**) with the experimental (argon, nitrogen, 10 K) IR absorptions of **5** (derived from the disappearance of the bands upon irradiation of **S-5** at $\lambda = 254$ nm)

No.		$\tilde{\nu}_{exp}$ [cm^{-1}] (I_{exp})	$\tilde{\nu}_{calcd}$ [cm^{-1}] (I_{rel})
ν_1	$\nu_{=CH}$	–	3220.8 (0.06)
ν_2	ν_{CH}	–	3152.1 (0.11)
ν_3	$\nu_{C\equiv N}$	–	2341.8 (0.56)
ν_4	$\nu_{C=N}$	Ar: 1676.2 (m) N_2: 1671.5 (m)	1760.3 (0.92)
ν_5	δ_{CH}	–	1362.4 (0.02)
ν_6	$\delta_{=CH} + \nu_{C-C}$	Ar: 1214.2 (m) N_2: 1209.4 (m)	1235.1 (0.87)
ν_7	$\delta_{=CH}$	Ar: 1025.1 (w) N_2: 1028.1 (w)	1046.4 (0.48)
ν_8	δ_{CH}	Ar: 977.1 (m) N_2: 980.7 (m)	995.9 (1.00)[a]
ν_9	$\delta_{=CH} + \delta_{CH}$	Ar: 917.7 (s) N_2: 919.4 (s)	938.0 (0.92)
ν_{10}	$\delta_{=CH}$	Ar: 768.0 (m) N_2: 750.7 (m)	799.0 (0.71)
ν_{11}	δ_{ring}	Ar: 708.4 (w) N_2: –	732.3 (0.29)
ν_{12}	$\delta_{CCN} + \delta_{CH}$	Ar: 561.3 (vw) N_2: 562.8 (vw)	579.6 (0.24)
ν_{13}	δ_{CCN}	Ar: 533.9 (vw) N_2: 535.1 (vw)	552.9 (0.12)
ν_{14}	δ_{ring}	–	242.8 (0.43)
ν_{15}	$\delta_{C\equiv N}$	–	221.3 (0.18)

[a] Calculated absolute intensity: 23.3 km·mol^{-1}.

N-cyano-1*H*-azirene,[5] it is obvious that the IR absorption at $\tilde{\nu} = 2066.6$ cm^{-1} has to be attributed to a ketenimine (ν_{NCC}). A signal at $\tilde{\nu} = 2234.7$ cm^{-1} (cyano group) can also be observed. These data indicate the presence of ketenimine **3** (Figure 4, Table 4). The formation of both products **3** and **4** can be rationalized in terms of cleavage of the saturated C−C or C−N ring bond in azirene **5** accompanied by a hydrogen shift.

Annealing Experiments in Argon Matrices

The IR absorption of carbene **S-6** at $\tilde{\nu} = 1980.9/1973.2$ cm^{-1} is extremely broadened in comparison with the CN stretching vibration at $\tilde{\nu} = 2216.8$ cm^{-1}. The most intense signal, which according to our calculations should be observed at $\tilde{\nu} = 751$ cm^{-1} (δ_{CH}), is split into two broad signals at $\tilde{\nu} = 730.7$ and 713.2 cm^{-1}, respectively. Annealing of the matrix should lead to the escape of the nitrogen molecule from the matrix cage and result in a change in the appearance of the IR absorptions of **S-6**. Indeed, warming of the matrix to 30 K leads to a reduction in the broadening of the band at $\tilde{\nu} = 1980.9$ cm^{-1} and to the disappearance of the signal at $\tilde{\nu} = 1973.2$ cm^{-1}. The large splitting of the double band at $\tilde{\nu} = 730.7/713.2$ cm^{-1} is reduced to a band at $\tilde{\nu} = 706.3/703.7$ cm^{-1}. This remaining doublet probably arises because of different matrix sites. The aforementioned spectral changes that occur upon warming can be rationalized in terms of the formation of donor−acceptor complexes between the evolved nitrogen molecule, which is present in the same matrix cage, and the carbenic center of **S-6**. This behavior is in accordance with our observations concerning 2*H*-imidazol-2-ylidene.[5] The ab initio calculations also show that the LUMO of **S-6** has a significantly large coefficient at the carbenic carbon atom, which allows for easy complexation with electron-donating partners.

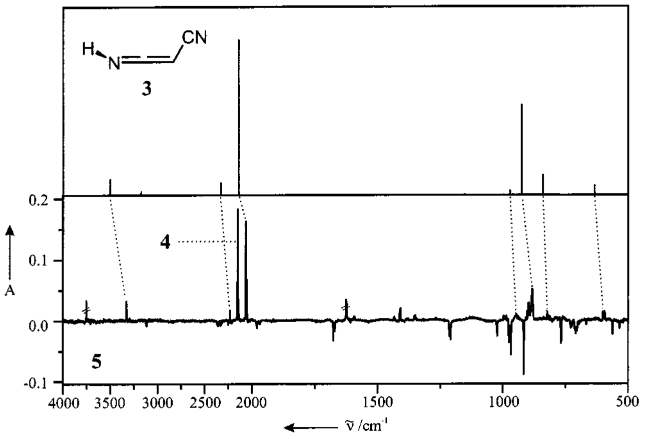


Figure 4. Comparison of the experimental (argon, 10 K; bottom section) with the calculated [B3LYP/6-311+G(d,p)] IR spectrum of **3** (top section); the experimental spectrum is a difference spectrum of the reaction $\mathbf{5} \rightarrow \mathbf{3} + \mathbf{4}$ upon irradiation with light of $\lambda = 254$ nm; IR bands with negative values diminish, while those with positive values intensify during the irradiation

Table 4. Comparison of the calculated [B3LYP/6-311+G(d,p)] IR spectrum of 2-cyanoketenimine (**3**) with the experimental (argon, 10 K) IR absorptions of **3** (derived from the appearance of the bands upon irradiation of **5** at $\lambda = 254$ nm)

No.		$\tilde{\nu}_{exp}$[cm^{-1}] (I_{exp})	$\tilde{\nu}_{calcd}$[cm^{-1}] (I_{rel})
ν_1	ν_{NH}	3331.6 (w)	3500.5 (0.10)
ν_2	ν_{CH}	–	3173.4 (0.03)
ν_3	ν_{CN}	2238.9 (w)	2329.6 (0.08)
ν_4	ν_{CCN}	2070.4 (vs)	2140.3 (1.00)[a]
ν_5	$\delta_{CH} + \delta_{CCC}$	–	1401.6 (0.00)
ν_6	δ_{CH}	–	1152.9 (0.01)
ν_7	$\delta_{CCC} + \nu_{CN}$	950.5 (vw)	971.8 (0.03)
ν_8	δ_{NH}	890.7 (s)	925.6 (0.58)
ν_9	$\delta_{CH/NH}$	830.9 (vw)	840.8 (0.13)
ν_{10}	δ_{CCC}	–	639.0 (0.00)
ν_{11}	$\delta_{NH} + \delta_{CH}$	598.0 (vw)	634.1 (0.06)
ν_{12}	δ_{NCCCN}	–	459.4 (0.05)
ν_{13}	δ_{NCCCN}	–	413.5 (0.00)
ν_{14}	$\delta_{CCN} + \delta_{CH/NH}$	–	373.0 (0.05)
ν_{15}	δ_{CCC}	–	149.4 (0.01)

[a] Calculated absolute intensity: 579.4 km·mol^{-1}.

Photolysis of 4-Diazo-4H-imidazole (1) in Nitrogen Matrices

It is noteworthy that 4*H*-imidazol-4-ylidene (**T-2**) cannot be observed in nitrogen matrices. After the photolysis of **1** at $\lambda = 313$ nm, only ring-opened carbene **S-6** and 2-cyano-2*H*-azirene (**5**) can be detected in the matrix IR spectrum. The initially formed 4*H*-imidazol-4-ylidene (**2**) most probably recaptures the nitrogen molecule with immediate reversion to 4-diazo-4*H*-imidazole (**1**). Under these conditions, the steady-state concentration of **2** is too low for its observation in the matrix IR spectrum.

Photolysis of 4-Diazo-4H-imidazole (1) in Argon Matrices Doped with CO

The photolysis of **1** in CO-doped argon matrices (5% v/v) with light of $\lambda = 313$ nm leads to rapid decomposition

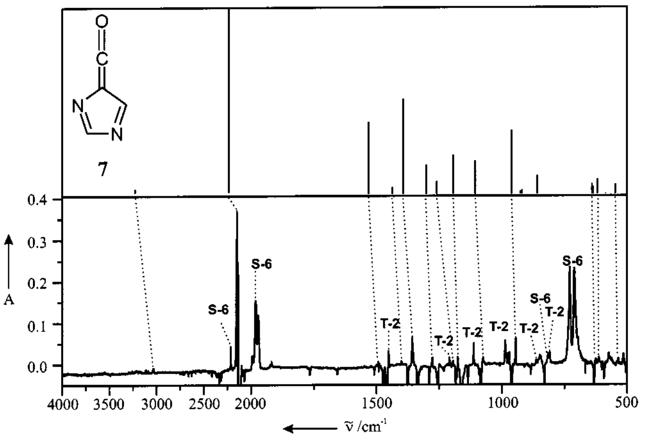


Figure 5. Comparison of the experimental (argon with 5% v/v CO, 10 K) difference spectrum after 10 min irradiation of **1** at $\lambda = 313$ nm (bottom section) and the calculated [B3LYP/6-311+G(d,p)] IR spectrum of **7** (top section); IR bands with negative values diminish, while those with positive values intensify during the irradiation

of **1** and, besides the absorptions of the usual photoproducts [4*H*-imidazol-2-ylidene (**T-2**) and carbene **S-6**], several new IR bands can be identified. The most characteristic band appears at $\tilde{\nu} = 2152.7$ cm^{-1}, which can best be accounted for by the formation of ketene **7** (Figure 5, Table 5).

Table 5. Comparison of the calculated [B3LYP/6-311+G(d,p)] IR spectrum of the 4*H*-imidazol-4-ylidene ketene (**7**) with the experimental (argon, 10 K) IR absorptions of **7**

No.	Sym.		$\tilde{\nu}_{exp}$[cm^{-1}] (I_{exp})	$\tilde{\nu}_{calcd}$[cm^{-1}] (I_{rel})
ν_1	A′	ν_{CH}	3036.1 (vw)	3227.7 (0.02)
ν_2	A′	ν_{CH}	–	3223.7 (0.01)
ν_3	A′	ν_{CCO}	2152.7 (vs)	2235.6 (12.47)
ν_4	A′	$\nu_{CH} + \nu_{C=N}$	1493.5 (m)	1531.4 (0.76)
ν_5	A′	$\nu_{C=C}$	1402.0 (vw)	1436.7 (0.07)
ν_6	A′	$\delta_{CH} + \nu_{C=N}$	1359.0 (m)	1393.5 (1.00)[a]
ν_7	A′	$\delta_{CH} + \delta_{ring}$	1278.3 (w)	1302.0 (0.31)
ν_8	A′	δ_{CH}	1197.5 (vw)	1260.2 (0.13)
ν_9	A′	$\nu_{NCN} + \delta_{CH}$	1177.8 (w)	1194.3 (0.41)
ν_{10}	A′	$\nu_{N-C} + \delta_{CH}$	1077.3 (w)	1106.0 (0.35)
ν_{11}	A′	δ_{ring} (*i.p.*)	946.4 (m)	961.0 (0.67)
ν_{12}	A′	$\nu_{CN} + \delta_{CH}$	–	925.5 (0.03)
ν_{16}	A"	δ_{CH} (*o.o.p.*)	–	919.5 (0.04)
ν_{17}	A"	δ_{CH} (*o.o.p.*)	–	858.4 (0.20)
ν_{18}	A"	δ_{ring} (*o.o.p.*)	627.1 (vw)	640.3 (0.11)
ν_{13}	A′	δ_{CCO} (*i.p.*)	–	636.0 (0.08)
ν_{19}	A"	δ_{ring} (*o.o.p.*)	616.3 (vw)	618.8 (0.16)
ν_{14}	A′	δ_{ring} (*i.p.*)	–	585.5 (0.00)
ν_{20}	A"	δ_{CCO} (*o.o.p.*)	537.4 (vw)	546.9 (0.10)
ν_{15}	A′	δ_{ring} (*i.p.*)	–	160.2 (0.02)
ν_{21}	A"	δ_{ring} (*o.o.p.*)	–	137.0 (0.00)

[a] Calculated absolute intensity: 72.4 km·mol^{-1}.

Conclusion

In its triplet ground state, 4*H*-imidazol-4-ylidene (**2**) possesses an unusual structure, which can best be described by formula **T-2**. It is possible to use the matrix IR spectrum to determine its multiplicity. **T-2** is a highly reactive carbene, as demonstrated by the addition of carbon monoxide to yield 2*H*-imidazol-2-ylidene ketene (**7**). With light of wavelengths longer than 570 nm, a photochemically induced rearrangement of **T-2** to the ring-opened carbene **S-6** occurs, which can be transformed into 2-cyano-2*H*-azirene (**5**) by subsequent irradiation at $\lambda > 310$ nm. Upon irradiation at $\lambda = 254$ nm, **5** yields 2-cyanoketenimine (**3**) and isocyanoacetonitrile (**4**).

Experimental Section

Matrix-Isolation Spectroscopy: Cryostat: Displex closed-cycle refrigeration system HC-2 from APD. – Spectrometers: IR: Bruker IFS 55 FT-IR spectrometer, resolution 0.7 cm^{-1}; UV: Hewlett Packard HP 8453 diode-array spectrophotometer (190–1100 nm, 1 diode nm^{-1}). – Light Sources: Osram HBO 200 high-pressure mercury lamp with monochromator or cut-off filters and Gräntzel low-pressure spiral mercury lamp.

4-Diazo-4*H*-imidazole (1): Prepared according to ref.[6] Compound **1** was used for the matrix-isolation experiments without further purification. Matrix-isolated samples were prepared by sublimation of **1** at 0 °C and deposition on a CsI window at 10 K together with a large excess of inert gas.

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