FULL PAPER

2H-Imidazol-2-ylidene: New Insights from a Matrix-Spectroscopic Study

Günther Maier* and Jörg Endres[a]

Abstract: Irradiation of 2-diazo-2H-imidazole (**1**) in a matrix at 10 K with a wavelength of $\lambda = 313$ nm leads to the rapid loss of nitrogen and the formation of 2H-imidazol-2-ylidene (**2**). Upon photoexcitation of 2H-imidazol-2-ylidene (**2**) with wavelengths longer than 570 nm, 1-cyano-1H-azirene (**5**) can be detected, which can be effectively converted into N-cyanoketenimine (**4**) by irradiation with a wavelength of $\lambda = 254$ nm. Irradiation of 2-diazo-2H-imidazole (**1**) in a xenon matrix generates the complex **2**·Xe between 2H-imidazol-2-ylidene and the matrix material. In CO-doped argon matrices the trapping product 2H-imidazol-2-ylideneketene (**7**) can be observed. On the other hand, flash vacuum pyrolysis of **1** yields only imidazole. 2H-Imidazol-2-ylidene (**2**) cannot be trapped under thermal conditions.

Keywords: carbenes · heterocycles · matrix isolation · photochemistry · quantum-chemical calculations

Introduction

Azacyclopentadienylidenes (azolylidenes) represent an interesting class of reactive intermediates. Several substituted azolylidenes have been generated by the thermolysis and photolysis of the corresponding diazo compounds, and their chemical properties have been studied.[1] Additionally, several theoretical studies on azolylidenes have been published.[2]

Trapping experiments of 2H-imidazol-2-ylidene (**2**), generated by thermolysis or photolysis of 2-diazo-2H-imidazole (**1**), with benzene derivatives yielded only C−H insertion products, such as **3** (Scheme 1). A [2+1] cycloaddition
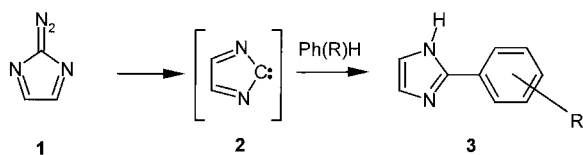
Scheme 1. Photolysis or thermolysis of 2-diazo-2H-imidazole (**1**) and subsequent trapping with benzene derivatives.

resulting in a norcaradiene-type compound could not be detected.[1b] 2H-Imidazol-2-ylidene (**2**) was regarded as a highly reactive carbene with a strong singlet diradical character with a very electrophilic carbon atom.[1b]

Matrix-isolation spectroscopy is a very useful tool for the investigation of reactive intermediates, especially of carbenes, which can be generated through photolysis from the corre-

[a] Prof. Dr. G. Maier, Dipl.-Chem. J. Endres
    Institut für Organische Chemie der Justus-Liebig-Universität Giessen
    Heinrich-Buff-Ring 58, D-35392 Giessen (Germany)
    Fax: (+49) 641-99-34309

sponding diazo compounds.[3] As a continuation of our studies of 2,3-dihydroimidazol-2-ylidene,[4] we decided to use the same technique in order to obtain a deeper insight into the peculiar electronic properties of imidazol-2-ylidene (**2**).

Results and Discussion

Calculations: The question of the electronic ground state of carbene **2** is of major interest. Calculations (two configuration SCF calculations, (TC)SCF/6-31G(d)) performed by Olivella and co-workers indicate that the electronic ground state of **2** is a triplet state ($^3B_1$) lying 12.9 kcal mol^{-1} below the first singlet state ($^1A'$). This singlet state shows a nonplanar folded structure.[2a] Calculations carried out by Pasto (MP2/6-31G(d)//HF/6-31G(d)) revealed that the electronic ground state of **2** should be a singlet state, with a planar C_{2v} geometry. The triplet state, which also possesses a C_{2v} geometry, was calculated to be 9.0 kcal mol^{-1} above the singlet state.[2b] More recent calculations have been published by Whitehead and co-workers in 1997; however, they used only semiempirical and ab initio methods at the HF/6-31G(d,p) level.[2c]

Since the published calculations differ with regard to the ground state of 2H-imidazol-2-ylidene (**2**), and because our work is based on the comparison of the calculated with the experimental matrix IR spectra, we have performed several additional calculations at the Hartree–Fock, BLYP, B3LYP, and the MP2 levels of theory with a standard 6-311 + G(d,p) basis set to describe the ground-state multiplicity, the geometry, and the vibrational spectrum of **2**.[5]

Hartree–Fock (HF) calculations (HF/6-311 + G(d,p)) predict a triplet ground state ($^3B_1$), which lies 33.3 kcal mol^{-1}

beneath the singlet state. The hybrid Density Functional Theory (DFT) Hartree–Fock method B3LYP (B3LYP/6-311 + G(d,p)) predicts a singlet–triplet gap of 1.7 kcal mol^{-1} that favors the triplet state. The DFT method BLYP (BLYP/6-311 + G(d,p)) shows a singlet–triplet gap (ΔE_{S-T}) of -1.8 kcal mol^{-1} that favors the singlet state.

As far as perturbation theory methods are concerned, MP4 single point calculations (MP4SDTQ(fc)/6-311 + G(d,p)// B3LYP/6-311 + G(d,p)) also indicate a remarkable stabilization of the singlet state ($\Delta E_{S-T} = -7.2$ kcal mol^{-1}).[6]

In all the theoretical studies the calculated geometry of the singlet state of 2H-imidazol-2-ylidene (S-2) is very similar (Figure 1). All methods, except BLYP, predict a planar C_{2v}
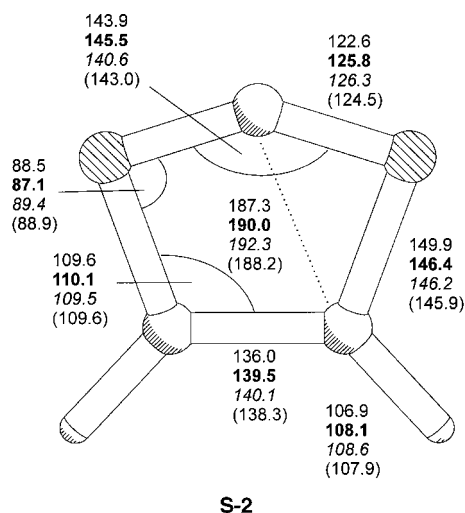

S-2

Figure 1. Calculated (6-311 + G(d,p) basis set) distances [pm] and bond angles [°] of singlet 2H-imidazol-2-ylidene (S-2) [HF values, B3LYP values (bold), BLYP values (italic), and MP2 values (in parentheses)].

symmetry. The calculated geometry of S-2 is rather astonishing: the wide NCN angle, the very short N–C2 bond length (numbering as in 2H-1,3-diazole), and the very small C-N-C bond angle are conspicuous. The short distances between the carbenic carbon atom and the carbon atoms in the backbone (C4 and C5) are also noteworthy. These calculated geometrical features indicate that S-2 is a rather interesting molecule which cannot be easily described by normal valence formulas. The calculated bond lengths in the NCN framework suggest the presence of a cumulenic unit. On the other hand, the situation is quite different from that of an open-chain carbodiimide structure. The two bonds between the nitrogen atoms and the carbon atoms, C4 and C5 cannot be perpendicular but are forced into an eclipsed orientation by the rigid structure of the five-membered ring. As a result of the widened angle of the NCN segment one observes a shortening of the bond distances between the carbenic carbon atom and the olefinic backbone carbon atoms. In other words: S-2 should be regarded as a strained cumulene rather than a normal carbene.

Only the DFT method BLYP predicts a nonplanar C_s symmetry for S-2. The carbenic carbon atom C2 is twisted out of the plane which is defined by all other atoms. The C2-N-C4-C5 torsion angle is 5.3°.

The geometries of the triplet state of 2, calculated at the HF, BLYP, and B3LYP levels of theory, agree quite well. All three methods predict a C_{2v} geometry for T-2 (Figure 2). The calculated structure can best be described as a triplet carbene in which one of the
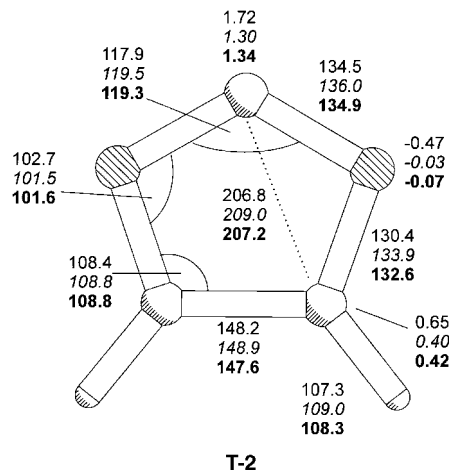

T-2

Figure 2. Calculated (6-311 + G(d,p) basis set) distances [pm], bond angles [°], and Mulliken spin densities of triplet 2H-imidazol-2-ylidene (T-2) [HF values, BLYP values (italic), and B3LYP values (bold)].

two electrons is delocalized into the C=N double bonds. The calculated Mulliken spin densities support this interpretation.

At the MP2 level of theory the triplet state of 2H-imidazol-2-ylidene (T-2) is still a planar molecule; however, the C_{2v} symmetry is disturbed. A planar molecule with C_s symmetry is predicted and all the bonds lengths are different. The calculated distances and bond angles of T-2 at this level of theory describe more a triplet allylic diradical than a normal triplet carbene. This interpretation is also supported by the corresponding calculated Mulliken spin densities.

C$_3$H$_2$N$_2$ energy hypersurface: Numerous isomers of the composition C$_3$H$_2$N$_2$ are conceivable, and a few of them have been calculated within the scope of this work (Figure 3). The species relevant for the experiments discussed below are the carbenes 2 and 6, as well as ketenimine 4 and azirene 5.

Photolysis of 2-diazo-2H-imidazole (1) in argon matrices: The matrix UV spectrum of 2-diazo-2H-imidazole (1) shows only one absorption at $\lambda \approx 310$ nm. In spite of the yellow color of 1, an absorption in the visible region could not be detected in the matrix UV spectrum.

Photolysis of 1 with light of the wavelength $\lambda = 313$ nm initiated a rapid decrease in the IR absorptions of 1. Some of the new IR absorptions which resulted are significantly broader than others. Remarkable are two new absorptions at $\tilde{\nu} = 1684.7$ and 1707.3 cm^{-1}, which agree very well with the strongest calculated IR absorption of singlet 2H-imidazol-2-ylidene (S-2) ($\tilde{\nu} = 1797$ cm^{-1}) (Figure 4, Table 1).
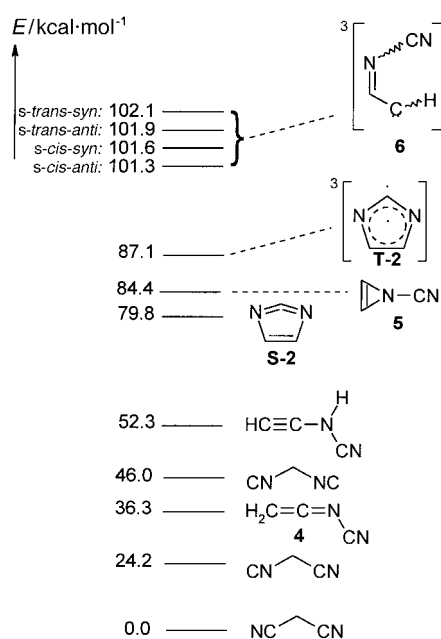
Figure 3. Relative energies (MP4SDTQ(fc)/6-311 + G(d,p)//B3LYP/6-311 + G(d,p), zero-point vibrational energy not included) of selected $C_3H_2N_2$ isomers.

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

No.	Sym.		$\tilde{\nu}_{exp}$ [cm^{-1}] (I_{exp})[a]	**S-2** $\tilde{\nu}_{calcd}$ [cm^{-1}] (I_{calcd})	**T-2**[b] $\tilde{\nu}_{calcd}$ [cm^{-1}] (I_{calcd})
ν_1	A_1	$\nu_{s, CH}$	–	3259.8 (0.00)	3213.9 (0.09)
ν_{11}	B_2	$\nu_{as, CH}$	–	3240.1 (0.01)	3201.1 (0.00)
ν_{12}	B_2	$\nu_{as, NCN}$	1707.3/1684.7 (vs)	1797.2 (1.00)[c]	1453.5 (0.49)
ν_2	A_1	$\nu_{C=C}$	–	1454.0 (0.05)	1409.8 (0.25)
ν_3	A_1	$\nu_{NC} + \delta_{CCN}$	–	1321.7 (0.01)	1289.6 (0.67)
ν_{13}	B_2	$\delta_{as, CH}$ (i.p.)	1207.3/1196.7 (m)	1222.1 (0.17)	1196.6 (0.67)
ν_4	A_1	$\delta_{s, CH}$ (i.p.)	1077.8 (w)	1093.4 (0.06)	1178.2 (0.43)
ν_{14}	B_2	$\nu_{as, CN}$	–	1000.7 (0.00)	984.8 (1.00)[d]
ν_5	A_1	$\nu_{s, CN}$	979.2/967.7 (s)	995.0 (0.26)	978.0 (0.01)
ν_7	A_2	$\delta_{as, CH}$ (o.o.p.)	–	792.2 (0)	881.5 (0.00)
ν_6	A_1	δ_{NCN}	718.1 (m)	740.6 (0.18)	866.3 (0)
ν_{15}	B_2	δ_{ring} (i.p.)	–	717.8 (0.02)	783.3 (0.07)
ν_9	B_1	δ_{ring} (o.o.p.)	672.9/670.0 (s)	704.1 (0.21)	777.0 (0.45)
ν_8	A_2	δ_{ring} (o.o.p.)	–	584.4 (0)	676.0 (0.00)
ν_{10}	B_1	δ_{ring} (o.o.p.)	–	235.2 (0.12)	548.0 (0)

[a] vs = Very strong, s = strong, m = medium, w = weak; i.p. = in-plane, o.o.p. = out-of-plane. [b] Numbering, symmetry, and approximate description are not suitable for the vibrations of **T-2**. [c] Calculated absolute intensity: 263.8 km mol^{-1}. [d] Calculated absolute intensity: 79.6 km mol^{-1}.

CIS calculations (CIS/6-311 + G(d,p)//B3LYP/6-311 + G(d,p)) of carbene **S-2** predict an electronic transition at $\lambda = 401$ nm ($f = 0.0001$). However, the matrix UV spectrum did not show any absorptions after the photolysis of 2-diazo-2H-imidazole (**1**).

On the other hand, secondary irradiation after the photolysis ($\lambda = 313$ nm) of **1** (formation of **2**) with light of wavelengths greater than 570 nm resulted in a rapid decrease of the broadened IR bands. The comparison of these bands with the calculated IR spectra of triplet and singlet 2H-imidazol-2-ylidene (**2**) shows a very good agreement only for the singlet state (Figure 4, Table 1). It is noteworthy that irradiation of **2** with $\lambda > 570$ nm or $\lambda > 700$ nm produces remarkable amounts
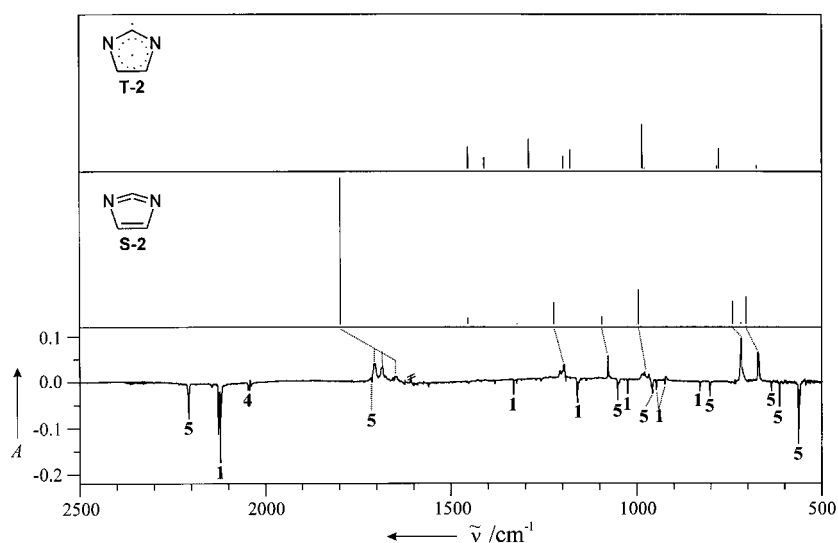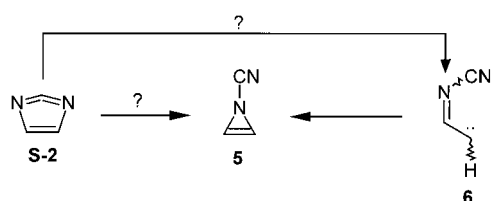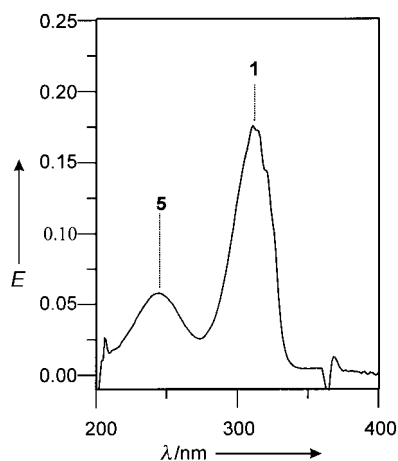
of **1** (recapture of N$_2$) and several other IR absorptions (Figure 4).

Identification of N-cyano-1H-azirene (5): It is well known that 3H-pyrazolylidenes readily isomerize to the corresponding 2H-azirenes.[7] In analogy, it is possible that photoexcitation of **2** results in the formation of a 1H-azirene (**5**), either directly or via the intermediate iminocarbene **6** (Scheme 2).
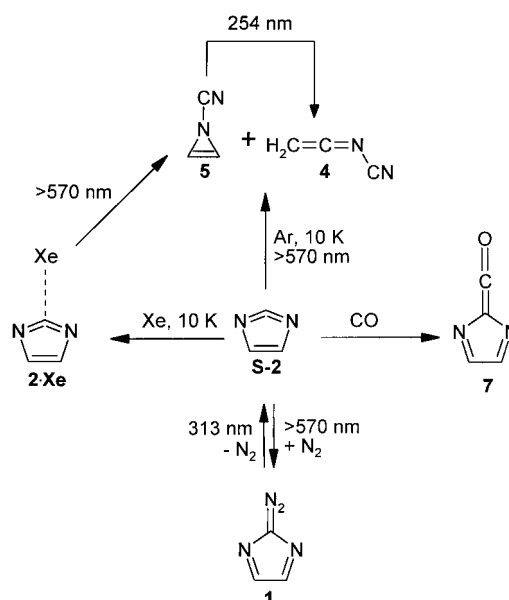
Regitz and co-workers showed that the photolysis of alkoxy-substituted α-diazoimines yields α-iminocarbenes of type **6** (alkoxy group at the imino carbon atom), which can be identified by trapping with a solvent molecule or by observation of the transformation products, namely the corresponding ketenimines or 2-alkoxy-1H-azirenes (detected by matrix IR spectroscopy).[8]

In our matrix experiments we found that after the disappearance of the IR bands of 2H-imidazol-2-ylidene (**2**) by irradiation ($\lambda > 570$ nm), which initiates a partial backreaction to **1**, the recorded matrix UV spectrum shows, as well as the strong absorption of 2-diazo-2H-imidazole (**1**), an additional absorption at $\lambda = 244$ nm (Figure 5). CIS calculations (CIS/6-311 + G(d,p)//B3LYP/6-311 + G(d,p)) of N-cyano-1H-azirene (**5**) predict an absorption at $\lambda = 208$ nm ($f = 0.084$), which can be assigned to the observed UV band at $\lambda = 244$ nm (Figure 5).

Figure 4. Comparison of a section ($\tilde{\nu} = 2500 - 500$ cm^{-1}) of the experimental (Ar, 10 K; bottom) with the calculated (B3LYP/6-311 + G(d,p)) IR spectrum of **S-2** (middle) and **T-2** (top). The experimental spectrum is a difference spectrum of the reaction **2** → **1** + **4** + **5** upon irradiation with light ($\lambda > 570$ nm). IR bands with positive values diminish, while those with negative values are formed during irradiation.

Scheme 2. Possible pathways to 1H-azirene (**5**) by the photoexcitation of **2**.

Figure 5. Matrix UV spectrum (Ar, 10 K) after the secondary photolysis ($\lambda > 570$ nm) of **2**.

Scheme 3. Photoreactions of **2** and its derivatives.

Obviously, the nitrogen molecule, which is evolved during the photolysis of **1**, forms a complex with **2**, which can explain the unusual halfwidth of the observed IR bands of **2**. Irradiation of **1** ($\lambda = 313$ nm) at 30 K instead of 10 K was performed in order to allow the split-off nitrogen molecule to leave the matrix cage. This led to IR bands of **2** with a much smaller halfwidth.

The main IR band of **2** (calcd: $\tilde{v} = 1797$ cm^{-1}) in the experimental spectrum is split into two distinct bands at $\tilde{v} = 1685$ and 1707 cm^{-1}. This effect can be explained by Fermi resonance between the combination signal of v_6 and v_{14} and the fundamental vibration v_{12}.

Photolysis of 2-diazo-2H-imidazole (1) in nitrogen matrices: Irradiation of **1** ($\lambda = 313$ nm) in nitrogen matrices led to a

Subsequent irradiation ($\lambda = 254$ nm) results in a rapid decrease of some of the IR bands which were present after the irradiation of **2** with $\lambda > 570$ nm. These diminishing IR bands can be assigned to N-cyano-1H-azirene (**5**, Figure 6, Table 2). The resulting photoproduct shows two very strong absorptions at $\tilde{v} = 2049$ and 734 cm^{-1}, respectively, indicating the formation of a ketenimine. The calculated IR spectrum of N-cyanoketenimine (**4**) and the experimental matrix IR spectrum are in very good agreement (Figure 6, Table 3).

Annealing experiments in argon matrices: 2-Diazo-2H-imidazole (**1**) was photolyzed with $\lambda = 313$ nm until there were no longer even traces of **1**, but only **2**, **4**, and **5** were observed in the IR spectrum. The matrix was then annealed at 25 K for 30 min. The surprising result was a nearly complete backreaction of **2** to **1** (Figure 7). Diffusion processes in argon matrices can normally be observed at temperatures above 30 K. In the present case the photochemically generated **2** recaptures the nitrogen which is in the same matrix cage. In order to exclude any photoexcitation by normal daylight, the annealing experiments were carried out in complete darkness.
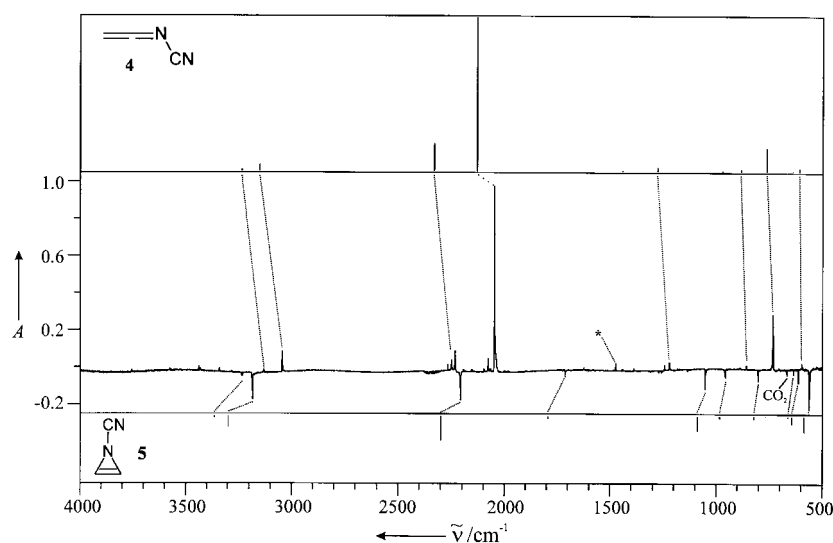

Figure 6. Comparison of the experimental (Ar, 10 K; middle) with the calculated (B3LYP/6-311 + G(d,p)) IR spectrum of **5** (bottom) and **4** (top). The experimental spectrum is a difference spectrum of the reaction **5** → **4** upon irradiation ($\lambda = 254$ nm). IR bands with negative values diminish, while those with positive values are formed during irradiation ($* = 2 \times v_7$).

Table 2. Comparison of the calculated (B3LYP/6-311 + G(d,p)) IR spectrum of *N*-cyano-1*H*-azirene (**5**) with the experimental (Ar, N$_2$, 10 K) absorptions of **5** (derived from the disappearance of **5** upon irradiation with $\lambda = 254$ nm).

No.	Sym.		$\tilde{\nu}_{exp}$ [cm^{-1}] (I_{exp})[a]	$\tilde{\nu}_{calcd}$ [cm^{-1}] (I_{calcd})
ν_1	A′	$\nu_{s, CH}$	Ar: 3235.1 (w)	3364.0 (0.07)
			N$_2$: 3233.6 (w)	
ν_{10}	A″	$\nu_{as, CH}$	Ar: 3185.7/3183.1 (s)	3297.7 (0.46)
			N$_2$: 3183.7/3181.6 (s)	
ν_2	A′	ν_{CN}	Ar: 2207.4 (s)	2300.0 (1.00)[b]
			N$_2$: 2217.6/2207.4 (vs)	
ν_3	A′	$\nu_{C=C}$	Ar: 1712.6 (w)	1792.0 (0.10)
			N$_2$: 1714.1 (w)	
ν_4	A′	ν_{N-C}	Ar: 1051.8 (m)	1088.5 (0.60)
			N$_2$: 1049.0 (s)	
ν_5	A′	$\delta_{s, CH}$ (i.p.)	Ar: 960.0 (w)	985.6 (0.06)
			N$_2$: 961.8 (w)	
ν_{11}	A″	$\delta_{as, CH}$ (i.p.)	Ar: 958.0 (w)	982.6 (0.10)
			N$_2$: –	
ν_6	A′	$\nu_{N-C} + \delta_{s, CH}$ (i.p.)	Ar: 803.2 (w)	822.2 (0.10)
			N$_2$: 803.2 (w)	
ν_{12}	A″	$\delta_{as, CH}$ (o.o.p.)	–	765.8 (0.01)
ν_{13}	A″	δ_{NCN}	Ar: 636.7 (vw)	661.6 (0.05)
			N$_2$: 635.0 (w)	
ν_7	A′	$\delta_{NCN} + \delta_{s, CH}$ (o.o.p.)	Ar: 613.6 (m)	643.2 (0.31)
			N$_2$: 618.8 (w)	
ν_8	A′	$\delta_{NCN} + \delta_{s, CH}$ (o.o.p.)	Ar: 562.8 (m)	585.0 (0.62)
			N$_2$: 580.7/571.3 (m)	
ν_{14}	A″	δ_{ring}	Ar: –	475.0 (0.00)
			N$_2$: –	
ν_{15}	A″	δ_{ring}	–	232.5 (0.02)
ν_9	A′	δ_{ring}	–	226.5 (0.11)

[a] vs = Very strong, s = strong, m = medium, w = weak. [b] Calculated absolute intensity: 99.9 km mol^{-1}.

Table 3. Comparison of the calculated (B3LYP/6-311 + G(d,p)) IR spectrum of *N*-cyanoketenimine (**4**) with the experimental (Ar, N$_2$, 10 K) absorptions of **5** (derived from the appearance of **4** upon irradiation of **5** with $\lambda = 254$ nm).

No.	Sym.		$\tilde{\nu}_{exp}$ [cm^{-1}] (I_{exp})[a]	$\tilde{\nu}_{calcd}$ [cm^{-1}] (I_{calcd})
ν_{11}	A″	$\nu_{as, CH}$	Ar: 3136.4 (vw)	3234.5 (0.01)
			N$_2$: 3123.3 (vw)	
ν_1	A′	$\nu_{s, CH}$	Ar: 3044.7 (w)	3149.0 (0.04)
			N$_2$: 3035.4 (w)	
ν_2	A′	ν_{CN}	Ar: 2267.0/2249.7/2232.8 (m)	2330.3 (0.18)
			N$_2$: 2253.8/2235.9 (m)	
ν_3	A′	ν_{CCN}	Ar: 2048.9 (vs)	2128.7 (1.00)[b]
			N$_2$: 2041.8 (vs)	
ν_4	A′	δ_{CH_2}	–	1441.1 (0.01)
ν_5	A′	CH$_2$ rock + δ_{CNC}	Ar: 1222.0 (vw)	1276.8 (0.03)
			N$_2$: 1221.6 (w)	
ν_{12}	A″	CH$_2$ rock	–	971.5 (0.00)
ν_6	A′	$\nu_{CN} + \delta_{CNC}$	Ar: 857.9 (vw)	882.9 (0.02)
			N$_2$: 862.5 (vw)	
ν_7	A′	ω_{CH_2}	Ar: 733.5 (m)	761.1 (0.15)
			N$_2$: 749.9/747.3 (m)	
ν_{13}	A″	$\omega_{CH_2} + \delta_{NCN}$	–	638.8 (0.00)
ν_8	A′	$\delta_{NCN} + \delta_{CCN}$	Ar: 596.3 (vw)	606.9 (0.02)
			N$_2$: 601.4 (vw)	
ν_9	A′	$\delta_{NCN} + \delta_{CCN}$	–	465.0 (0.01)
ν_{14}	A″	CH$_2$ def. + δ_{CCN}	–	404.1 (0.00)
ν_{15}	A″	CH$_2$ def.	–	316.7 (0.01)
ν_{10}	A′	δ_{CCN}	–	145.2 (0.00)

[a] vs = Very strong, s = strong, m = medium, w = weak, vw = very weak. [b] Calculated absolute intensity: 614.6 km mol^{-1}.

decomposition of the precursor which was four times slower. However, no traces of **2** were detected. The photolysis gave only *N*-cyano-1*H*-azirene (**5**) and *N*-cyanoketenimine (**4**) as

observable products (Figure 8, Tables 2 and 3). The observed photochemistry of **5** in nitrogen matrices (irradiation with $\lambda = 254$ nm and conversion into **4**) is the same as in argon matrices. Obviously, 2*H*-imidazol-2-ylidene (**2**) attacks a nitrogen molecule from the matrix material during the irradiation with $\lambda = 313$ nm, and the steady-state concentration of **2** remains too low for detection. The reaction with nitrogen is typical for very reactive carbenes, such as methylene.[9]

The use of ^{15}N-labeled nitrogen as the matrix material revealed that after a very short irradiation time ($\lambda = 313$ nm, < 2 min), additional IR bands were observed, which can be assigned to [^{15}N$_2$]-2-diazo-2*H*-imidazole ([^{15}N$_2$]**1**). This experiment proves that **2** readily recaptures nitrogen from the matrix material.

Photolysis of 2-diazo-2*H*-imidazole (1) in xenon matrices: Irradiation ($\lambda = 313$ nm) of **1** in xenon matrices led to several new IR bands, from which one at $\tilde{\nu} \approx 707$ cm^{-1} shows an unusual broadness. After irradiation with $\lambda > 570$ nm this IR band decreased, as did some other IR bands (Figure 9, Table 4). The products of the secondary photochemical conversion with $\lambda > 570$ nm are the same as those in an argon matrix (*N*-cyano-1*H*-azirene (**5**) and *N*-cyanoketenimine (**4**)).

Evidently, the species of the primary photolysis of **1** in a xenon matrix is also 2*H*-imidazol-2-ylidene (**2**). Our experiments carried out in an argon matrix show a pair of bands for **2** at $\tilde{\nu} = 1685$ and 1707 cm^{-1} (Table 1) which cannot be observed in a xenon matrix. However, a pair of bands can be observed at $\tilde{\nu} = 1496.1$ and 1520.5 cm^{-1} (Table 4). The experiments in an argon matrix clearly show that **2** readily undergoes complexation with electron donors, such as nitrogen, which leads to the broadening of the IR bands. The calculations show that the LUMO of **2** has a significantly large coefficient at the carbenic carbon atom, which allows the facile formation of a donor–acceptor complex with electron-donating atoms or molecules, such as xenon or nitrogen. It has recently been shown that xenon also forms complexes with electron acceptors, such as C$_2$[10] or difluorvinylidene.[11]

Our calculations strongly indicate the formation of the complex **2**·Xe. The calculated stabilization energy for this 1:1 complex is −3.3 kcal mol^{-1} (B3LYP/LANL2DZ, Figure 10).[12] It is noteworthy that the N-C-N angle becomes smaller through the complexation with xenon. This effect causes a significant shift of the N-C-N stretching vibration from ≈ 1707 cm^{-1} (**2**) to ≈ 1520 cm^{-1}
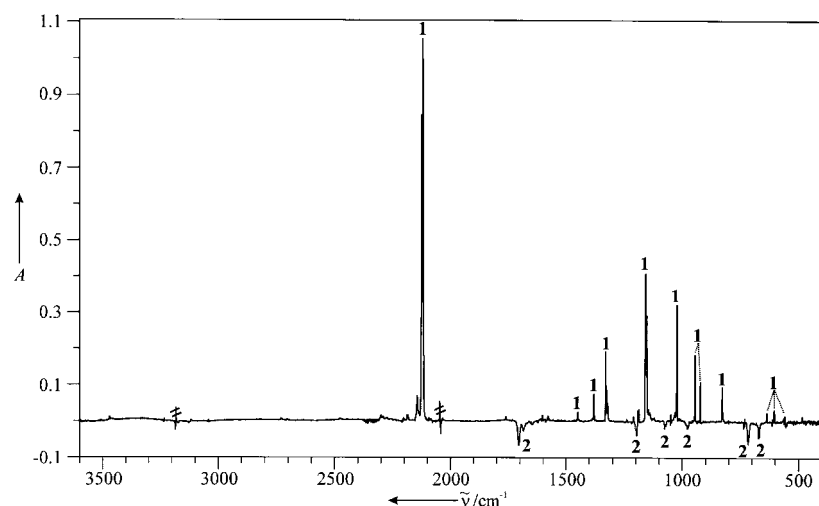
Figure 7. Experimental (Ar, 10 K) difference spectrum after annealing the matrix (15 min, 25 K). IR bands with negative values diminish, while those with positive values are formed during the annealing process.
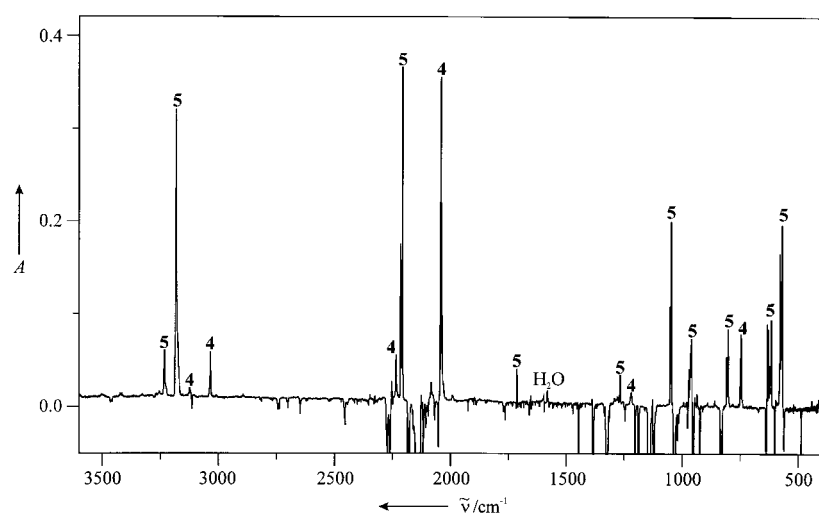

Figure 8. Experimental (nitrogen, 10 K) difference spectrum after irradiation ($\lambda = 313$ nm, 10 min) of **1**. IR bands with negative values diminish, while those with positive values are formed during irradiation.
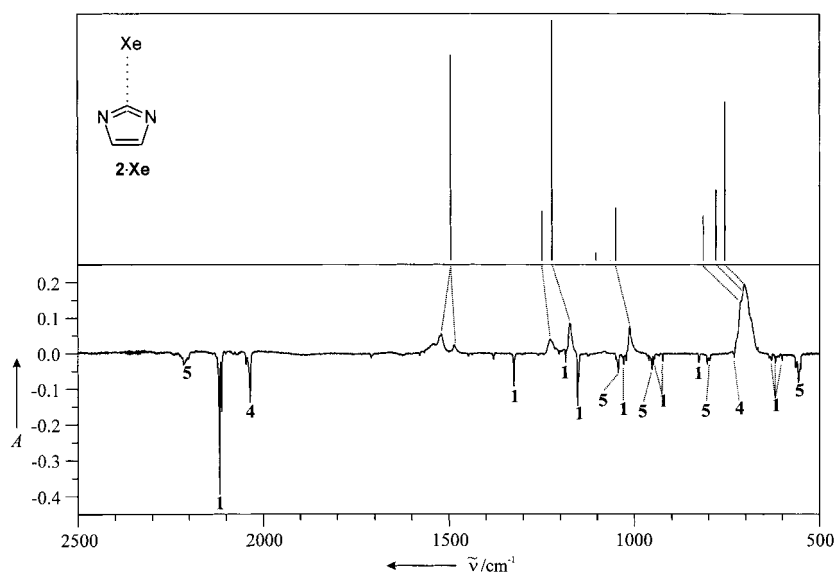

Figure 9. Comparison of a section ($\nu = 2500 – 500$ cm^{-1}) of the experimental (xenon, 10 K; bottom) with the calculated (B3LYP/LANL2DZ) IR spectrum of **2** · Xe (top). The experimental spectrum is a difference spectrum of the photoreaction **2** → **1** + **4** + **5** upon irradiation ($\lambda > 570$ nm). IR bands with positive values diminish, while those with negative values are formed during irradiation.

(**2** · Xe). The calculated IR spectrum for the complex **2** · Xe is in acceptable agreement with the observed IR spectrum of **2** in a xenon matrix (Figure 9, Table 4). The broad IR absorption at $\tilde{\nu} \approx 707$ cm^{-1} is the result of an overlap of three bands, which are broadened, like all the other observed IR transitions. This leads to the observed unusual shape.

The identification of xenon complex **2** · Xe is reminiscent of the stable halonium ylides of 4,5-dicyano-2*H*-imidazol-2-ylidene, formed by the reaction of the corresponding diazo compound with C$_6$H$_5$X (X = Cl, Br, I),[13] and of the same type of ylides which result from acceptor-substituted diazocyclopentadienes.[14, 15]

Photolysis of 2-diazo-2*H*-imidazole (1) in argon matrices doped with CO: As we mentioned above, 2*H*-imidazol-2-ylidene (**2**) has a low-lying LUMO. Therefore, **2** readily reacts with electron donors so that it should be possible to trap **2** with CO to form ketene **7**.

The photolysis ($\lambda = 313$ nm) of **1** in CO-doped argon matrices (5 vol %) led to the rapid decomposition of **1**. In addition to the absorptions of the usual photoproducts (2*H*-imidazol-2-ylidene (**2**), *N*-cyano-1*H*-azirene (**5**), and *N*-cyanoketenimine (**4**)) several new IR bands could be registered. The most characteristic one is an IR absorption $\tilde{\nu} = 2156.0$ cm^{-1}, which can best be explained by the formation of ketene **7** (Figure 11, Table 5).

Flash vacuum pyrolysis of 2-diazo-2*H*-imidazole (1): Complete thermal deazotization of **1** was achieved at 700 °C. The main product trapped on the matrix window cooled to 10 K was imidazole. Obviously, under the conditions used two hydrogen atoms are captured by **2**.

Table 4. Comparison of the calculated (B3LYP/LANL2DZ) IR spectrum of the 2*H*-imidazol-2-ylidene-xenon complex (**2** · Xe) with the experimental (Xe, 10 K) IR absorptions of **2** · Xe.

No.	Sym.		$\tilde{v}_{exp}$ [cm^{-1}] $(I_{exp})^{[a]}$	$\tilde{v}_{calcd}$ [cm^{-1}] (I_{calcd})
v_1	A$_1$	$v_{s, CH}$	–	3324.3 (0.02)
v_{13}	B$_2$	$v_{as, CH}$	–	3296.1 (0.00)
v_{14}	B$_2$	v_{NCN}	1520.5/1496.1 (w)	1493.8 (0.86)
v_2	A$_1$	v_{CC}	–	1416.1 (0.00)
v_{15}	B$_2$	$\delta_{as, CH}$ (i.p.)	1228.1 (w)	1248.7 (0.21)
v_3	A$_1$	$\delta_{NCN} + v_{NC}$	1173.3 (m)	1221.3 (1.00)$^{[b]}$
v_4	A$_1$	$\delta_{as, CH}$ (i.p.) $+ v_{CN}$	–	1102.3 (0.03)
v_{16}	B$_2$	$v_{as, CN}$	–	1064.7 (0.00)
v_5	A$_1$	$\delta_{s, CH}$ (i.p.)	952.5 (m)	1049.5 (0.22)
v_8	A$_2$	$\delta_{as, CH}$ (o.o.p.)	–	840.4 (0)
v_{17}	B$_2$	δ_{ring} (i.p.)	707 (vs, br)	814.2 (0.19)
v_{10}	B$_1$	$\delta_{s, CH}$ (o.o.p.)	707 (vs, br)	779.3 (0.30)
v_6	A$_1$	δ_{NCN}	707 (vs, br)	755.8 (0.66)
v_9	A$_2$	δ_{ring} (o.o.p.)	–	597.7 (0)
v_{11}	B$_1$	δ_{ring} (o.o.p.)	–	336.3 (0.02)
v_{18}	B$_2$	$\delta_{Xe-ring}$ (o.o.p.)	–	155.0 (0.00)
v_{12}	B$_1$	$\delta_{Xe-ring}$ (o.o.p)	–	117.3 (0.01)
v_7	A$_1$	$v_{Xe-ring}$	–	100.5 (0.07)

[a] vs = Very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad. [b] Calculated absolute intensity: 301.9 km mol^{-1}.

Conclusions

The singlet ground state of 2*H*-imidazol-2-ylidene (**2**) possesses an unusual structure, which can best be represented by formula **S-2**. It is possible to use the matrix IR spectrum to determine its multiplicity. **S-2** is a highly reactive electrophile, as demonstrated, firstly, by the thermal addition of nitrogen at 25 K to give **1**, secondly, by the addition of carbon monoxide to yield 2*H*-imidazol-2-ylideneketene (**7**), and thirdly, by the formation of the complex **2** · Xe in xenon matrices. Irradiation ($\lambda > 570$ nm) of **2** in the presence of a nitrogen molecule in the same matrix cage also results in the recapture of nitrogen. Parallel to this reaction, a photochemically induced rearrangement of **S-2** to *N*-cyano-1*H*-azirene (**5**) occurs, which can be transformed into *N*-cyanoketenimine (**4**) by subsequent irradiation ($\lambda = 254$ nm).

Experimental Section

Matrix isolation spectroscopy: Cryostat: displex closed cycle refrigeration system HC-2 from APD. Spectrometers: IR: FT-IR spectrometer IFS 55 from Bruker, resolution 0.7 cm^{-1}; diode array spectrometer HP 8453 from Hewlett–Packard (190–1100 nm, 1 diode nm^{-1}). Light sources: Mercury high-pressure lamp HBO 200 from Osram with monochromator or cutoff filters and a mercury low-pressure spiral lamp from Gräntzel.

2-Diazo-2*H*-imidazole (1): Prepared according to the literature procedure.[16] Imidazole **1** was used for the matrix-isolation experiments without further purification. Matrix-isolated samples were prepared by sublimation of **1** at −30 °C and deposition on a CsI window at 10 K together with a large excess of inert gas.

Figure 10. Calculated (B3LYP/LANL2DZ) distances [pm] and bond angles [°] of **2** · Xe (values of **S-2** at the same level of theory in parentheses).

Flash vacuum pyrolysis: Imidazole **1** was evaporated from a trap at −30 °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 10 K immediately after leaving the hot zone.

[1] a) U. G. Kang, H. Shechter, *J. Am. Chem. Soc.* **1978**, *100*, 651–652; b) N. Bru, J. Vilarrasa, *Chem. Lett.* **1980**, 1489–1492; c) T. J. Amick, H. Shechter, *Tetrahedron Lett.* **1986**, *27*, 901–904.

[2] a) J. Farràs, S. Olivella, A. Solé, J. Vilarrasa, *J. Phys. Chem.* **1991**, *95*, 10623–10630; b) D. J. Pasto, *Heteroatom Chem.* **1992**, 1–9; c) C. I. Williams, M. A. Whitehead, B. J. Jean-Claude, *J. Mol. Struct. (Theochem)* **1997**, *389*, 13–25.

[3] For a recent review on carbenes in matrices, see: W. Sander, G. Bucher, S. Wierlacher, *Chem. Rev.* **1993**, *93*, 1583–1621.
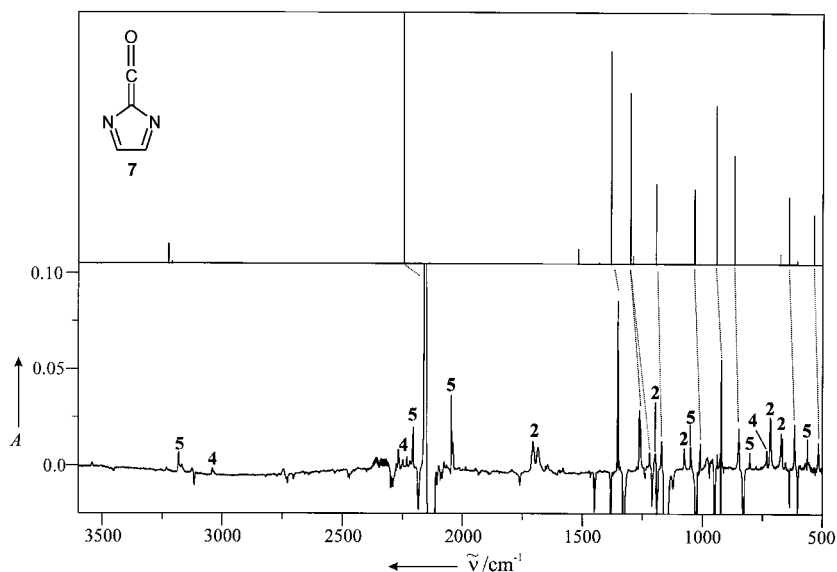
Figure 11. Comparison of the experimental (Ar with 5 vol% CO, 10 K) difference spectrum after 2 min irradiation of **1** with $\lambda = 313$ nm (bottom) and the calculated (B3LYP/6-311 + G(d,p)) IR spectrum of **7** (top). IR bands with negative values diminish, while those with positive values are formed during the irradiation.
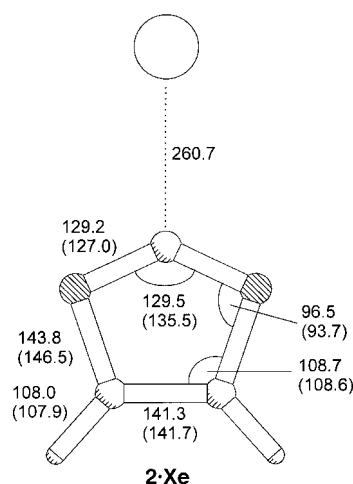
Table 5. Comparison of the calculated (B3LYP/6-311 + G(d,p)) IR spectrum of the 2*H*-imidazol-2-ylidene-ketene (**7**) with the experimental (Ar, 10 K) observed IR absorptions of **7**.

No.	Sym.		$\tilde{\nu}_{exp}$ [cm^{-1}] (I_{exp})[a]	$\tilde{\nu}_{calcd}$ [cm^{-1}] (I_{calcd})
ν_1	A′	$\nu_{s, CH}$	–	3223.2 (0.10)
ν_3	A′	$\nu_{as, CH}$	–	3208.1 (0.02)
ν_3	A′	ν_{CCO}	2156.0 (vs)	2244.4 (17.60)
ν_4	A′	$\nu_{as, NC}$	–	1516.3 (0.08)
ν_5	A′	$\nu_{CC} + \nu_{s, NC}$	–	1429.8 (0.01)
ν_6	A′	$\delta_{s, CH}$ (i.p.)	1352.4 (m)	1379.2 (1.00)[b]
ν_7	A′	$\nu_{s, NC} + \nu_{CC}$	1264.9 (m)	1300.2 (0.81)
ν_8	A′	$\delta_{NCN} + \delta_{as, CH}$ (i.p.)	1220.8 (w)	1288.7 (0.04)
ν_9	A′	$\delta_{as, CH}$ (i.p.) + δ_{NCN}	1171.7 (w)	1192.5 (0.38)
ν_{10}	A′	ν_{CC}	1009.7 (w)	1033.7 (0.36)
ν_{11}	A′	δ_{NCN}	921.5 (m)	941.3 (0.75)
ν_{12}	A′	δ_{CCN}	–	940.6 (0.20)
ν_{16}	A″	$\delta_{as, CH}$ (o.o.p.)	–	918.0 (0.00)
ν_{17}	A″	$\delta_{s, CH}$ (o.o.p.)	848.9 (m)	867.0 (0.52)
ν_{18}	A″	δ_{ring}	–	675.0 (0.05)
ν_{13}	A′	δ_{CCO} (i.p.)	617.1 (m)	639.6 (0.32)
ν_{19}	A″	δ_{ring}	–	625.7 (0.00)
ν_{14}	A′	δ_{NCN}	–	605.2 (0.02)
ν_{20}	A″	δ_{CCO} (o.o.p.)	517.3 (w)	534.9 (0.24)
ν_{15}	A′	δ_{ring}	–	163.4 (0.00)
ν_{21}	A″	δ_{ring}	–	152.2 (0.05)

[a] vs = Very strong, s = strong, m = medium, w = weak, vw = very weak. [b] Calculated absolute intensity: 72.4 km mol^{-1}.

[4] G. Maier, J. Endres, *Eur. J. Org. Chem.* **1998**, 1517–1520.
[5] All calculations were performed with the Gaussian programme package: Gaussian 94, Revision D.3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Pittsburgh, PA, **1995**.

[6] All stated energies, except for MP4 single point calculations, include the zero-point vibrational energies.
[7] W. L. Magee, H. Shechter, *J. Am. Chem. Soc.* **1977**, *99*, 633–634.
[8] M. Regitz, B. Arnold, D. Danion, H. Schubert, G. Fusser, *Bull. Soc. Chim. Belg.* **1981**, *90*, 615–631.
[9] a) C. B. Moore, G. C. Pimentel, *J. Chem. Phys.* **1964**, *41*, 3504–3509; b) G. Maier, H. P. Reisenauer, *Angew. Chem.* **1986**, *98*, 829–831; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 819–822.
[10] G. Maier, C. Lautz, *Eur. J. Org. Chem.* **1998**, 769–776.
[11] C. Kötting, W. Sander, J. Breidung, W. Thiel, M. Senzlober, H. Bürger, *J. Am. Chem. Soc.* **1998**, *120*, 219–220.
[12] The basis set used for the calculation of the complex **2**·Xe (LANL2DZ) leads to a large deviation of the calculated structure of **2** compared to the calculations performed with a 6-311 + G(d,p) basis set (e.g. the N-C-N angle varies from 135.5° for the LANL2DZ basis set to 145.5° for the 6-311 + G(d,p) basis set).
[13] W. A. Sheppard, O. W. Webster, *J. Am. Chem. Soc.* **1973**, *95*, 2695–2697.
[14] E. P. Janulis, Jr., A. J. Arduengo, III, *J. Am. Chem. Soc.* **1983**, *105*, 3563–3567.
[15] K. Friedrich, H.-J. Gallmeier, H.-G. Fritz, *J. Prakt. Chem.* **1994**, *336*, 145–149.
[16] W. L. Magee, C. B. Rao, J. Glinka, H. Hui, T. J. Amick, D. Fiscus, S. Kakodkar, M. Nair, H. Shechter, *J. Org. Chem.* **1987**, *52*, 5538–5548.