

2,3-Dihydroimidazol-2-ylidene[☆]

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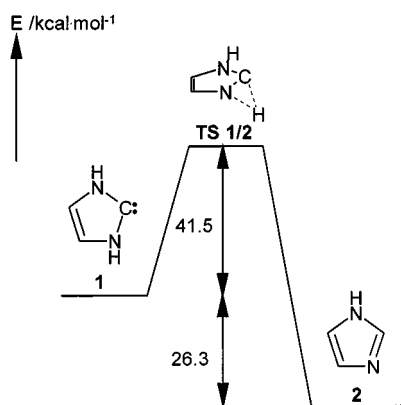
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Irradiation of imidazole-2-carboxylic acid (**3**) – matrix-isolated in argon at 10 K – with a wavelength of 254 nm leads to decarboxylation and the formation of a complex between 2,3-dihydroimidazol-2-ylidene and carbon dioxide (**1**·CO₂). Upon irradiation of 2,3-dihydroimidazol-2-ylidene (**1**) with

$\lambda = 254, 193,$ and 185 nm no imidazole can be detected. On the other hand flash vacuum pyrolysis of imidazole-2-carboxylic acid (**3**) produces imidazole and carbon dioxide. 2,3-Dihydroimidazol-2-ylidene (**1**) – the possible intermediate – cannot be trapped under these conditions.

In 1991 Arduengo and co-workers^[1] reported the isolation and characterization of the first stable carbene, 1,3-di(1-adamantyl)-2,3-dihydroimidazol-2-ylidene. Since that time many substituted nucleophilic carbenes have been prepared.^[2] The remarkable stability of 2,3-dihydroimidazol-2-ylidenes cannot be rationalized only by steric protection of the carbenic center, because 1,3-dimethyl-2,3-dihydroimidazol-2-ylidene is also a stable molecule. From ab initio studies it can be pointed out that cyclic electron delocalization is responsible for the extraordinary stability of 2,3-dihydroimidazol-2-ylidenes (**1**).^[3] Recently, Schwarz and co-workers^[4] were able to demonstrate that 2,3-dihydroimidazol-2-ylidene (**1**) is a stable molecule in the gas phase.

Scheme 1. Calculated reaction energies for the intramolecular 1,2-hydrogen shift of 2,3-dihydroimidazol-2-ylidene



Calculations

Although 2,3-dihydroimidazol-2-ylidene (**1**) is $26.3 \text{ kcal}\cdot\text{mol}^{-1}$ less stable than imidazole (**2**), the calculated energy barrier for the intramolecular hydrogen shift is very high ($41.5 \text{ kcal}\cdot\text{mol}^{-1}$) (Scheme 1).^[5] Because of the interaction of the nitrogen lone pairs with the empty p-orbital of the carbenic center, **1** should be a singlet carbene. The calculated singlet/triplet gap is $81.6 \text{ kcal}\cdot\text{mol}^{-1}$. The higher

thermodynamic stability of 2,3-dihydroimidazol-2-ylidene (**1**) over 2,3-dihydrothiazol-2-ylidene, which has recently been prepared both in the gas phase^[7] and in cryogenic matrices,^[8] is revealed by the calculated heats of hydrogenation of the carbene carbon atom (the calculated heat of hydrogenation for 2,3-dihydroimidazol-2-ylidene is $-12.0 \text{ kcal}\cdot\text{mol}^{-1}$ and for 2,3-dihydrothiazol-2-ylidene $-26.6 \text{ kcal}\cdot\text{mol}^{-1}$). It follows that 2,3-dihydroimidazol-2-ylidene (**1**) is thermodynamically more stable than 2,3-dihydrothiazol-2-ylidene.

As we have recently shown the decarboxylation of thiazole-2-carboxylic acid is an easy way to generate 2,3-dihydrothiazol-2-ylidene.^[8] Therefore we have chosen imidazole-2-carboxylic acid (**3**) as a precursor for our matrix isolation studies of **1**. In principle four rotamers of imidazole-2-carboxylic acid (**3**) are conceivable. The experimental spectrum of matrix-isolated imidazole-2-carboxylic acid (**3**) (Figure 1) is in very good agreement with the calculated spectrum of the most stable rotamer **3a**.

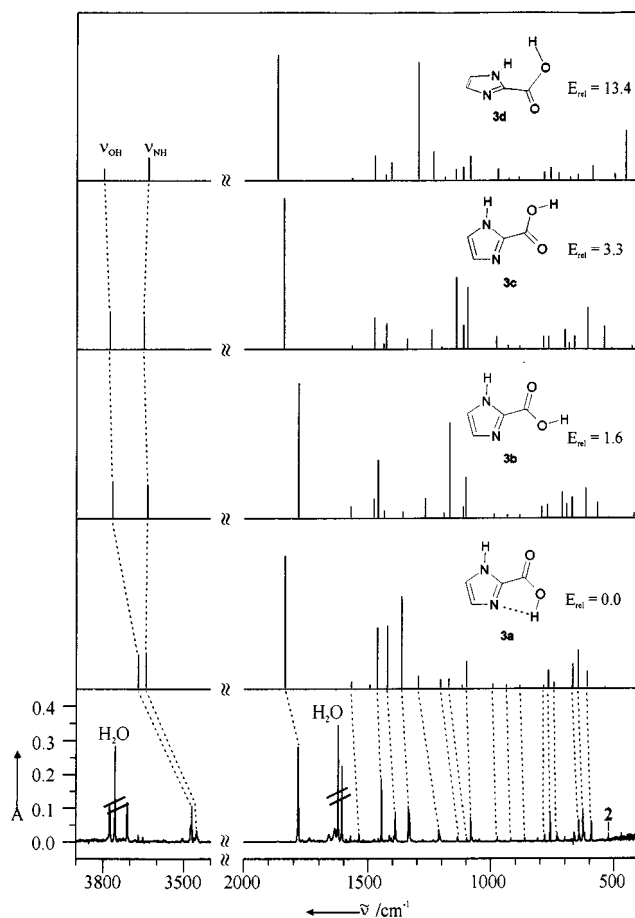
The calculated infrared spectra of **3b–3d** do not agree as well with the experimental infrared spectrum of matrix-isolated imidazole-2-carboxylic acid (**3**). Due to strong hydrogen bonds in solid imidazole-2-carboxylic acid (**3**) it is not possible to evaporate **3** without decarboxylation. Therefore in all our experimental spectra the signals of imidazole (**2**) and carbon dioxide are visible.

The calculated activation energy for the decarboxylation of **3a** is $20.8 \text{ kcal}\cdot\text{mol}^{-1}$ (Scheme 2).

Photofragmentation of Imidazole-2-carboxylic Acid (**3**)

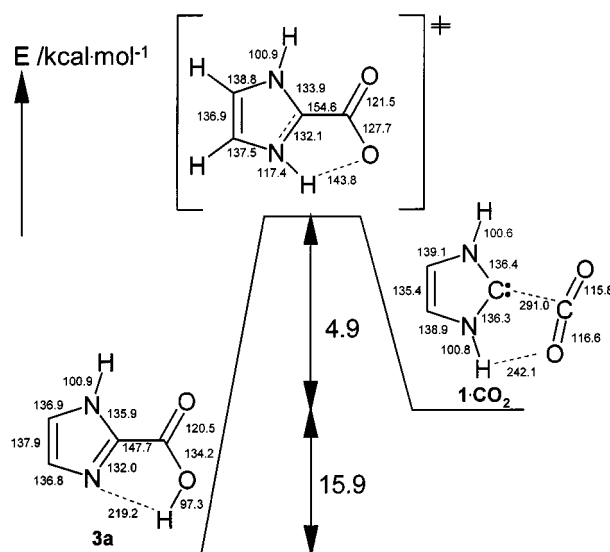
Shortly after the beginning of the irradiation of **3a** with a wavelength of $\lambda = 254 \text{ nm}$ the intensities of the signals of **3a** decreased, while a new signal arose at $\nu = 1738.1 \text{ cm}^{-1}$, which possibly is caused by rotamer **3b**. After 20 min of irradiation with $\lambda = 254 \text{ nm}$, the signals of imidazole-2-carboxylic acid (**3**) had completely disappeared. The new signals do not decrease upon further irradiation with $\lambda = 254 \text{ nm}$. In the region above 700 cm^{-1} they correspond very

Figure 1. Comparison of a section of the experimental spectrum of matrix-isolated imidazole-2-carboxylic acid (**3**) (argon, 10 K) with the calculated infrared spectra of rotamers **3a–3d**; relative energies of the four rotamers are given in kcal·mol⁻¹



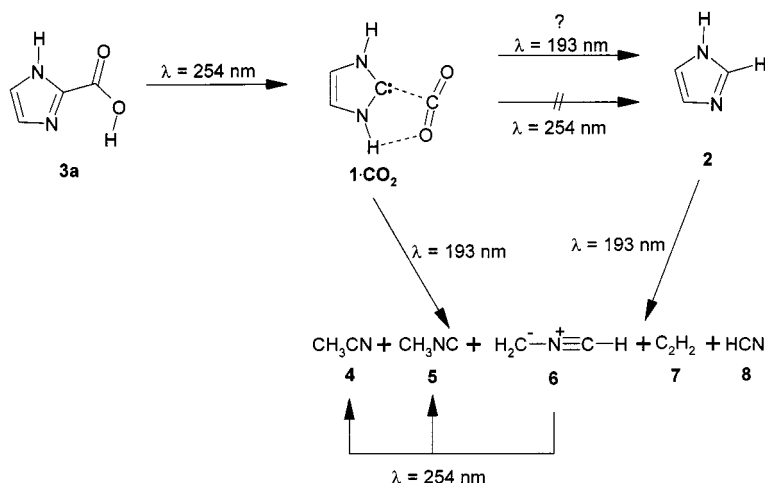
well with the calculated infrared spectrum of 2,3-dihydroimidazol-2-ylidene (**2**). Below 700 cm⁻¹ one additional signal, compared to the calculated infrared spectrum, at $\nu = 623.7$ cm⁻¹ is observed. In order to decide whether this signal belongs to 2,3-dihydroimidazol-2-ylidene (**1**) we also studied the photochemical decarboxylation of deuterated imidazole-2-carboxylic acid ([D₂]-**3**). Irradiation of [D₂]-**3a**

Scheme 2. Calculated reaction energies for the decarboxylation of **3a**; bond lengths are given in pm



with $\lambda \approx 254$ nm again produced, beside other signals, a band at $\nu = 623.7$ cm⁻¹. The absence of an isotopic shift and our experience with thiazole-2-carboxylic acid, which yields a complex between carbon dioxide and 2,3-dihydrothiazol-2-ylidene upon irradiation,^[8] led us to the conclusion that irradiation of imidazole-2-carboxylic acid (**3**) also results in the formation of a complex between 2,3-dihydroimidazol-2-ylidene (**1**) and carbon dioxide.

Quantum-mechanical calculations predict a complex between 2,3-dihydroimidazol-2-ylidene (**1**) and carbon dioxide, with a stabilization energy of 4.3 kcal·mol⁻¹ relative to its fragments. The comparison between the calculated infrared spectra of **1**·CO₂ and [D₂]-**1**·CO₂ reveals that there are only four signals showing no or a very small isotopic shift (Tables 1 and 2). They can all be assigned to vibrations of the carbon dioxide ligand. Due to the unsymmetrical arrangement of the carbon dioxide ligand and the bending vibration, which is degenerated in free carbon dioxide, splits into two distinct signals (calculated: 667.2 and 611.0 cm⁻¹)



and the symmetrical stretching vibration becomes infrared-active (calculated: 1365.8 cm^{-1}). The signals, which arise during the photolysis of imidazole-2-carboxylic acid (**3**), are in acceptable agreement with the calculated infrared spectrum of **1**·CO₂. In the presence of the carbon dioxide the high C_{2v} symmetry of 2,3-dihydroimidazol-2-ylidene (**1**) is disturbed, so the previously infrared-inactive ring bending vibrations of 2,3-dihydroimidazol-2-ylidene (**1**) below 700 cm^{-1} should now be detectable. Due to very low calculated intensities of these bending vibrations (Table 1) it is not possible to detect any of them in the experimental difference spectrum (Figure 2).

Table 1. Comparison of the calculated infrared spectrum for the carbon dioxide complex (**1**·CO₂) with the experimental (argon, 10 K) infrared spectrum after irradiation of imidazole-2-carboxylic acid (**3**) with $\lambda = 254\text{ nm}$; the five vibrations below 400 cm^{-1} are not listed; vibrations due to carbon dioxide are marked with an asterisk

No.	Sym.		$\tilde{\nu}_{\text{exp}} [\text{cm}^{-1}] (I_{\text{exp}})$	$\tilde{\nu}_{\text{calcd}} [\text{cm}^{-1}] (I_{\text{calcd}})$
v ₁	A'	v _{NH}	3510.7 (0.31)	3667.9 (0.31)
v ₂	A'	v _{NH}	3493.4 (0.37)	3649.4 (0.46)
v ₃	A'	v _{CH}	—	3281.7 (0.01)
v ₄	A'	v _{CH}	—	3260.3 (0.00)
v ₅	A'	v _{as, CO}	2332.1* (2.76)	2421.4* (2.99)
v ₆	A'	v _{C=C}	1581.0 (0.02)	1611.9 (0.04)
v ₇	A'	δ_{NH} (i.p.)	1410.7 (0.12)	1438.7 (0.27)
v ₈	A'	δ_{NH} (i.p.)	1376.9 (0.06)	1404.2 (0.03)
v ₉	A'	δ_{CHN}	1352.5 (0.02)	1384.3 (0.02)
v ₁₀	A'	v _{s, CO}	—	1365.8* (0.03)
v ₁₁	A'	δ_{NCN}	—	1211.7 (0.00)
v ₁₂	A'	δ_{CNC}	—	1176.6 (0.01)
v ₁₃	A'	δ_{NH} (i.p.)	1096.3 (0.06)	1121.5 (0.10)
v ₁₄	A'	δ_{CH} (i.p.)	1072.8 (0.03)	1090.2 (0.06)
v ₁₅	A'	δ_{CNC}	1028.9 (0.14)	1044.6 (0.15)
v ₁₆	A'	δ_{ring}	913.7 (0.02)	932.7 (0.02)
v ₁₇	A'	δ_{ring}	906.9 (0.03)	926.4 (0.04)
v ₂₂	A''	δ_{CH} (o.o.p.)	—	824.5 (0.00)
v ₂₃	A''	δ_{NH} (o.o.p.)	732.1 (1.00)	756.8 (1.00) ^[a]
v ₂₄	A''	$\delta_{\text{s, CH}}$ (o.o.p.)	—	706.5 (0.07)
v ₂₅	A''	δ_{NH} (o.o.p.)	—	685.2 (0.02)
v ₂₆	A''	δ_{OCO} (o.o.p.)	665.8* (0.06)	667.2* (0.10)
v ₂₇	A''	δ_{ring} (o.o.p.)	—	620.6 (0.00)
v ₁₈	A'	δ_{OCO} (i.p.)	623.7* (0.09)	611.0* (0.76)
v ₂₈	A''	δ_{ring} (o.o.p.)	579.4 (0.14)	592.7 (0.16)

^[a] Calculated absolute intensity: $185.9\text{ km}\cdot\text{mol}^{-1}$.

The calculated infrared spectrum of [D₂]-**1**·CO₂ is in very good agreement with the experimental difference spectrum of the photolysis of deuterated imidazole-2-carboxylic acid ([D₂]-**3**) (Figure 3, Table 2).

Isomerization of 2,3-dihydroimidazol-2-ylidene (**1**) to imidazole could not be detected during the irradiation with $\lambda = 254\text{ nm}$. Irradiation with a shorter wavelength ($\lambda = 193$ or 185 nm) results in the formation of acetylene (**7**), acetonitrile (**4**), methyl isocyanide (**5**), its ylidic tautomer **6**,^[9] and hydrocyanic acid (**8**). To decide whether these products arise from 2,3-dihydroimidazol-2-ylidene (**1**) or from its isomer imidazole (**2**), which is also present in the matrix (due to the decarboxylation during the evaporation process), we irradiated imidazole under the same conditions and found again the above-mentioned products. It is not clear whether 2,3-dihydroimidazol-2-ylidene (**1**) first isomerizes into imidazole (**2**) and **2** leads to the observed frag-

Figure 2. Comparison of the experimental difference spectrum (section from 1700 to 400 cm^{-1}) of the irradiation of imidazole-2-carboxylic acid (**3**) with $\lambda = 254\text{ nm}$ (the bands with negative values diminish, while those with positive values are formed upon irradiation) with the calculated infrared spectrum of **1**·CO₂; bands due to vibrations of the carbon dioxide ligand are marked with an asterisk

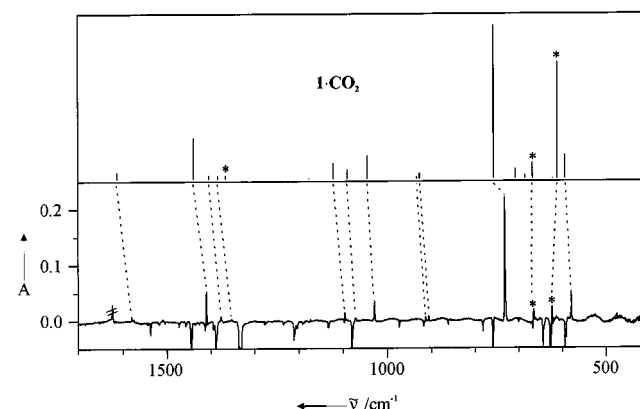
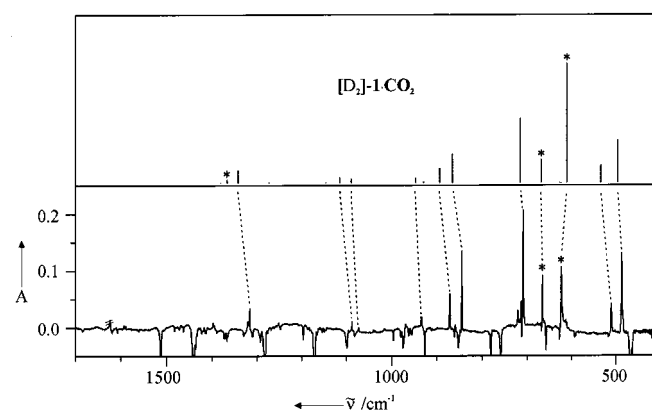


Figure 3. Comparison of the experimental difference spectrum (section from 1700 to 400 cm^{-1}) of the irradiation of deuterated imidazole-2-carboxylic acid ([D₂]-**3**) with $\lambda = 254\text{ nm}$ (the bands with negative values diminish, while those with positive values are formed upon irradiation) with the calculated infrared spectrum of [D₂]-**1**·CO₂; bands due to vibrations of the carbon dioxide ligand are marked with an asterisk



mentation products or 2,3-dihydroimidazol-2-ylidene (**1**) directly produces **5–8**.

In the case of 2,3-dihydrothiazol-2-ylidene annealing of the matrix at 60 K leads to the formation of thiazole.^[8] Annealing of a matrix which contains 2,3-dihydroimidazol-2-ylidene (**1**) at 60 K leads to the disappearance of the signals of 2,3-dihydroimidazol-2-ylidene (**1**). Afterwards only signals of imidazole (**2**) are present in the infrared spectrum. But due to the decarboxylation of imidazole-2-carboxylic acid (**3**) and formation of **2** during the evaporation process it is not possible to decide whether additional imidazole (**2**) is produced through an intramolecular hydrogen transfer of 2,3-dihydroimidazole (**1**) during the annealing process.

Pyrolysis of imidazole-2-carboxylic acid (**1**), performed at only 400°C , leads to nearly complete decarboxylation. The experimental spectrum of the trapped products showed only the signals of imidazole (**2**) and imidazole-2-carboxylic acid (**3**). The signals of 2,3-dihydroimidazol-2-ylidene (**1**) could not be found.

Table 2. Comparison of the calculated infrared spectrum for the carbon dioxide complex ($[D_2]-1\cdot CO_2$) with the experimental (argon, 10 K) infrared spectrum after irradiation of deuterated imidazole-2-carboxylic acid ($[D_2]-3$) with $\lambda = 254$ nm; the five vibrations below 400 cm^{-1} are not listed; vibrations due to carbon dioxide are marked with an asterisk

No.	Sym.		$\tilde{\nu}_{\text{exp}} [\text{cm}^{-1}] (I_{\text{exp}})$	$\tilde{\nu}_{\text{calcd}} [\text{cm}^{-1}] (I_{\text{calcd}})$
ν_1	A'	ν_{CH}	—	3281.8 (0.02)
ν_2	A'	ν_{CH}	—	3260.4 (0.00)
ν_3	A'	ν_{ND}	—	2694.6 (0.28)
ν_4	A'	ν_{ND}	2616.6 (1.61)	2679.6 (0.82)
ν_5	A'	$\nu_{as, CO}$	2332.1* (11.31)	2421.2* (7.24)
ν_6	A'	$\nu_{C=C}$	—	1585.8 (0.00)
ν_7	A'	$\delta_{CH} (\text{i.p.})$	—	1380.4 (0.01)
ν_8	A'	$\nu_{s, CO}$	—	1365.8* (0.06)
ν_9	A'	δ_{NCN}	1316.7 (0.44)	1341.5 (0.20)
ν_{10}	A'	ν_{CN}	—	1272.4 (0.02)
ν_{11}	A'	$\delta_{s, CH} (\text{i.p.})$	—	1145.9 (0.01)
ν_{12}	A'	$\delta_{as, CH} (\text{i.p.})$	1088.0 (0.09)	1114.6 (0.09)
ν_{13}	A'	δ_{CH}	1073.2 (0.06)	1089.3 (0.07)
ν_{14}	A'	δ_{CNC}	934.0 (0.14)	946.5 (0.08)
ν_{15}	A'	δ_{ring}	—	929.3 (0.02)
ν_{16}	A'	$\delta_{as, ND} (\text{i.p.})$	871.0 (0.41)	893.0 (0.23)
ν_{17}	A'	$\delta_{s, ND} (\text{i.p.})$	844.5 (0.74)	865.2 (0.45)
ν_{22}	A''	$\delta_{as, CH} (\text{o.o.p.})$	—	823.3 (0.00)
ν_{23}	A''	$\delta_{s, CH} (\text{o.o.p.})$	709.2 (1.00)	714.8 (1.00) ^[a]
ν_{24}	A''	$\delta_{OCO} (\text{o.o.p.})$	666.1* (0.58)	668.2* (0.37)
ν_{25}	A''	$\delta_{ring} (\text{o.o.p.})$	—	626.6 (0.00)
ν_{26}	A''	$\delta_{ring} (\text{o.o.p.})$	—	623.2 (0.00)
ν_{18}	A'	$\delta_{OCO} (\text{i.p.})$	623.7* (1.11)	610.9* (1.85)
ν_{27}	A''	$\delta_{ND} (\text{o.o.p.})$	510.3 (0.43)	532.9 (0.28)
ν_{28}	A''	$\delta_{ND} (\text{o.o.p.})$	485.8 (1.24)	494.9 (0.66)

^[a] Calculated absolute intensity: $76.9\text{ km}\cdot\text{mol}^{-1}$.

Experimental Section

Cryostat for Matrix Isolation: Displex closed-cycle refrigeration system CSA 202 from Air Products. — **Spectrometers:** IR: FT-IR spectrometer IFS 55 from Bruker, resolution 0.5 cm^{-1} — **Light**

Sources: Excimer laser LPX 105 MC from Lambda Physics, mercury high-pressure lamp HBO 200 from Osram, and mercury low-pressure spiral lamp from Gräntzel. — **Imidazole-2-carboxylic Acid (3)** was prepared according to the literature (see ref.^{[10]). — **$[D_2]$ -Imidazole-2-carboxylic Acid ($[D_2]-3$)** was prepared by recrystallization of imidazole-2-carboxylic acid (3) in D_2O .}

- ☆ Dedicated to Professor Gernot Boche on the occasion of his 60th birthday.
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