Photochemistry of 2-azido-4,6-dichloro-*s*-triazine: matrix isolation of a strained cyclic carbodiimide containing four nitrogen atoms in a seven-membered ring

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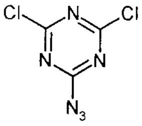
2-Azido-4,6-dichloro-*s*-triazine 1, matrix-isolated in Ar at 10 K, yields triplet nitrene 2 and the strained cyclic carbodiimide 3 upon photolysis.

The photochemistry of phenyl azides has been a controversial topic for a long time.[1,2] The generally accepted pathway includes primary formation of an open-shell singlet nitrene[3,4] followed by intersystem crossing (ISC) to the ground-state triplet nitrene and/or cycloaddition to a neighbouring C=C double bond in the arene system. The efficiency of the latter reaction depends on factors such as temperature and substitution. It yields didehydroazepines *via* intermediary azirines.[5] Heteroaromatic aryl azides have also been studied in some detail.[6] For instance, 2-pyridylnitrene **4**, generated from 2-azidopyridine or the isomeric tetrazolopyridine, yields didehydro-1,3-diazepine **5** (a cyclic carbodiimide) upon photolysis in an Ar matrix.[7] A variety of heteroaromatic aryl nitrenes could be characterized by EPR,[8] and in some instances also by IR spectroscopy.[6]



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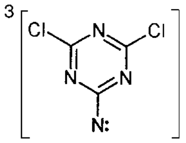

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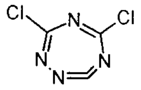

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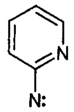

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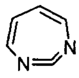

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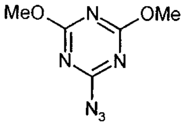
The products isolated following thermolysis[9] or photolysis[10] of azido-*s*-triazines in solution exclusively arise from reactions of the triplet or singlet nitrenes. Thus, thermolysis of 2-azido-4,6-dimethoxy-1,3,5-triazine **6** in cyclohexane yielded the C–H insertion product **7** and the aminotriazine **8**.[9] The formation of **8** is likely due to a reaction of the ground-state triplet nitrene, while **7** is probably formed through the S_1 state of the nitrene. Surprisingly, no products ascribable to reactions of a didehydrotetrazepine (*e.g.* **9**) have been reported. Their absence could be due to a lack of stability, or it could reflect an increased barrier for cycloaddition towards a nitrogen atom. Here we present our recent results on the photolysis of matrix-isolated 2-azido-4,6-dichloro-*s*-triazine **1** which are different from the ones described for **6**.

The matrix isolation set-up used in these experiments has been described elsewhere.[11] Argon was chosen as the matrix material. During deposition, the cold window (KBr or sapphire) was kept at 30 K, otherwise the temperature of the matrix was held at 10 K. Azide **1**[12] was sublimed at 10 °C/10^{-6} mbar. In experiments using UV–VIS detection, it was photolysed by the output of a 75 W Xe arc lamp coupled to a monochromator. The irradiation wavelength selected was 320 nm. In the case of IR detection, the output of a mercury low-pressure lamp (λ = 254 nm) was used. Brief irradiation (8 min) under these conditions led to the disappearance of the IR bands of **1** and to the formation of new bands at $\tilde{\nu}$ = 1951.2, 1550.0, 1467.6, 1446.4, 1254.5, 1246.8, 1110.2 and 1050.0 cm^{-1} along with some weaker bands below 900 cm^{-1} and around 2100 cm^{-1}. Upon extended irradiation with λ = 254 nm, these bands disappeared again, while the new absorptions at $\tilde{\nu}$ = 2271.2, 2214.2, 2112.9 and 2094.4 cm^{-1} were indicative of nitrile and possibly isonitrile and/or cumulene functionalities in the final product mixture.[13] Long-wavelength irradiation (λ > 420 nm) of the primary photoproducts led to a decrease in intensity of some bands ($\tilde{\nu}$ = 1467.6, 1446.4, 1254.5, 1246.8, 848.7, 787.9 and 580 0 cm^{-1}), while the intensity of other bands ($\tilde{\nu}$ = 1951.2, 1550.0, 1110.2, 1050.0 and 814.4 cm^{-1}) increased. Thus, the experimental findings are consistent with two compounds (these can be interconverted by long-wavelength photolysis) being predominantly formed during the initial stages of photolysis, which yield other, presumably ring-opened products, upon extension of 254 nm photolysis. In the UV–VIS, the product primarily formed showed absorption maxima at λ = 330 and 356 nm and a broad band between 380 and 490 nm with vibrational fine structure. Irradiation into this band (λ > 420 nm, Hg high pressure lamp with cut-off filter) led to the disappearance of the primary photoproduct and to the formation of a secondary photoproduct with λ_{max} = 328 and 352 nm (Fig. 1). Consistent with the results obtained using IR spectroscopy, this secondary photochemistry proved to be at least partially reversible. Photolysis of the product mixture thus obtained using λ = 320 nm again led to the formation of the spectrum with λ_{max} = 330, 356 and 380–490 nm, albeit with slightly reduced intensity. A likely explanation for this behaviour is formation of secondary (ring-opened) photoproducts, which do not show pronounced long-wavelength absorptions.



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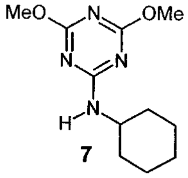

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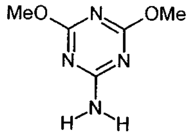

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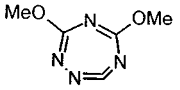

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The vibrational spectra of triplet nitrene **2** and dehydrotetrazepine **3** were calculated using density functional theory (B3LYP with a 6-31G* basis, unscaled).[14] The comparison with

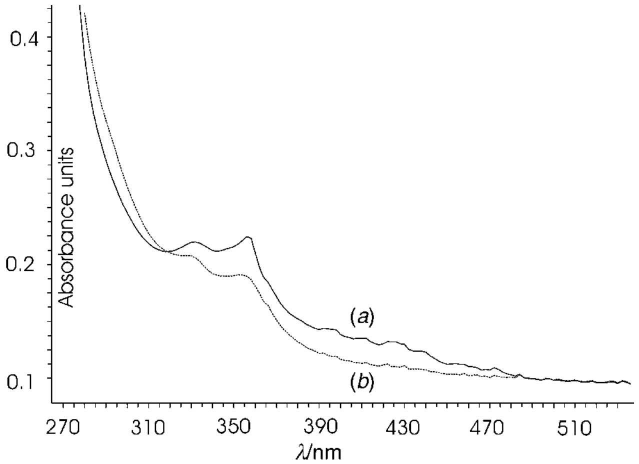

Fig. 1 (*a*) UV–VIS spectrum obtained after photolysis (3 h, λ = 320 nm) of **1** in Ar, 10 K. (*b*) UV–VIS spectrum obtained by photolyzing the same sample subsequently with λ = 475–620 nm, 2 h.

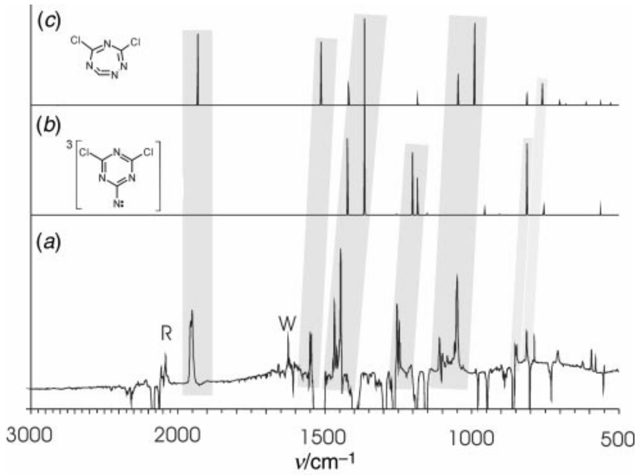

Fig. 2 (*a*) Difference IR spectrum obtained by subtracting the spectrum of **1** (Ar, 10 K) from the spectrum obtained after 8 min photolysis (λ = 254 nm). The bands pointing downward belong to **1**. Bands pointing upward are assigned to **2** and **3**, with the exception of the bands labelled W (water) and R (ring-opened secondary photoproduct). (*b*) Calculated IR spectrum (UB3LYP 6-31G*) of triplet nitrene **2**. (*c*) Calculated IR spectrum of **3** (B3LYP 6-31G*). The correlation with the experimental spectrum is highlighted by grey shading. The intensity of the band at $\tilde{\nu}$ = 1446.4 cm^{-1} is *ca.* 0.2 absorbance units.

the experimental data shows **2** and **3** to be indeed formed as primary products (Fig. 2).[15] This assignment is also consistent with the UV–VIS data, as the characteristics of the product initially formed upon photolysis at 320 nm (λ_{max} = 330 and 356 nm, broad band between 380 and 490 nm) are in line with the expected behavior of a triplet nitrene.[2]

The UV–VIS-spectrum attributed to **3** (λ_{max} = 328 and 352 nm) is very similar to a spectrum obtained by Yamada *et al.*[16] in a glassy EPA matrix at 77 K that was assigned to arise from triplet 4,6-dimethoxy-*s*-triazinyl nitrene. It thus appears likely that the product observed by them has to be reassigned to didehydrotetrazepine **9** or to its trapping products.[17]

The observation of didehydrotetrazepine **3** upon photolysis of azide **1** in an argon matrix could indicate that tetrazepines may actually be formed in the solution photochemistry of triazinyl azides. Experiments directed towards the isolation of derivatives of these heterocycles therefore may prove useful and are in progress.

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12 *Synthesis* of **1**: The preparation given before (C. V. Hart, *J. Am. Chem. Soc.*, 1928, **50**, 1928) gave only mixtures of products that could not be separated by crystallization, and the melting point stated to be 85 °C is most likely incorrect. The following method was successful: To a solution of cyanuric chloride (3.000 g, 16.27 mmol) in acetone (20 ml) in a small separation funnel, a solution of NaN_3 (1.000 g, 15.38 mmol) in water (10 ml) was added and the mixture shaken for 5 min. The organic phase was then separated and allowed to evaporate at room temperature. The crystals were chromatographed (silica gel, CH_2Cl_2–light petroleum = 1:1) to give pure **1** (1.13 g, 5.92 mmol, 36%) as a colorless powder, mp 59.5–61 °C; δ_H(300 MHz, $CDCl_3$) no signal; δ_C(75.5 MHz, $CDCl_3$) 171.39, 172.60; *m/z* (FAB) 190.99 (100, M + H$^+$); $\tilde{\nu}_{max}$/cm^{-1} (Ar, 10 K) 2168.9 (s), 1531.0 (vs), 1512.0 (vs), 1396.8 (s), 1295.8 (s), 1268.0 (s), 1187.6 (m), 1159.9 (m), 947.9 (w), 857.2 (m), 803.8 (w), 730.5 (vw).
13 The characterization of these final products is in progress; results will be published at a later time.
14 GAUSSIAN 98 software was used in the calculations.
15 *Selected data* for **2**: $\tilde{\nu}_{max}$/cm^{-1} (Ar, 10 K) 1467.6 (s), 1446.4 (vs), 1254.5 (s), 1246.8 (m), 852.9 (w), 848.7 (w), 787.9 (m), 580.0 (w). For **3**: $\tilde{\nu}_{max}$/cm^{-1} (Ar, 10 K) 1957.0 (vs), 1951.2 (vs), 1550.0 (m), 1546.2 (m), 1110.2 (m), 1050.0 (vs), 814.4. An N=C=N stretching band at $\tilde{\nu}$ = 1957.0 cm^{-1} for **3** is in the range expected for such a compound. For comparison, simple open-chain *N*-dialkylamino substituted carbodiimides absorb at ν = 2090 cm^{-1} (ref. 18). The decrease in frequency in **3** reflects the decrease in bond energy induced by strain. A similar trend has been observed in the case of other cyclic carbodiimides (ref. 6).
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17 There is a complete lack of absorption beyond λ = 420 nm in the spectra given by Yamada *et al.* However, a broad band would be expected for a triplet nitrene. In an EPA matrix, trapping of the didehydrotetrazepine by EtOH has to be considered.
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