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Generation of quintet dinitrenes by the γ-radiolysis of crystalline 2,4,6-triazido-3,5-dicyanopyridine

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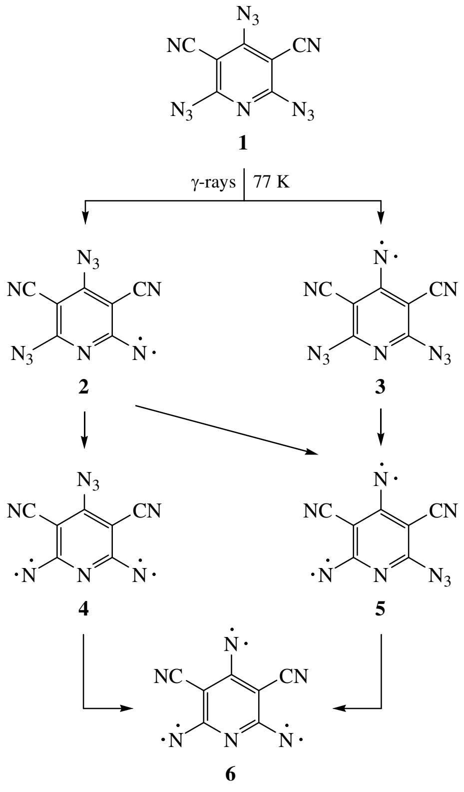
Quintet 4-azido-3,5-dicyanopyridyl-2,6-dinitrene and 6-azido-3,5-dicyanopyridyl-2,4-dinitrene can be successfully obtained using the γ-radiolysis of crystalline 2,4,6-triazido-3,5-dicyanopyridine at 77 K.

High-spin nitrenes are promising organic magnetic materials for molecular electronics.[1] These compounds are usually obtained by low-temperature solid-phase photolysis of aromatic azides, the aromatic ring of which is protected by appropriate substituents from undesirable intramolecular reactions with nitrenic centres.[2] Unfortunately, many substituents (*e.g.*, CF_3[3] or CN[4]) in aryl nitrenes do not protect them from photochemical rearrangements and this substantially cuts down the potential of photochemical synthesis of high-spin nitrenes. Thus, for instance, our previous attempts[5] to obtain high-spin nitrenes **4**, **5** and **6** by the photolysis of triazide **1** were unsuccessful.

In order to develop a method for generating photochemically unstable high-spin nitrenes, the γ-radiolysis of crystalline triazide **1** at 77 K was studied.

Although 2,4,6-triazidopyridines are high-energy compounds and readily decompose upon the action of UV light, X-ray, temperature or pressure, triazide **1**[†] showed unexpectedly high stability toward γ-rays. Only a very prolonged γ-irradiation of crystalline **1** in a vacuum[‡] at 77 K led to the appearance of two EPR signals at 3030 and 3346 G [Figure 1(*a*)], which are characteristic of quintet 2,4- and 2,6-dinitrenopyridines, respec-tively.[6] Similar EPR spectra with two characteristic signals of quintet 2,4-dinitreno-6-azido-3,5-dichloropyridine at 3009 G and of 2,6-dinitreno-4-azido-3,5-dichloropyridine at 3345 G have been recorded during the photolysis of 2,4,6-triazido-3,5-dichloropyridine **7** in frozen (77 K) solutions in 2-methyl-tetrahydrofuran.[7] Owing to the presence of chlorine atoms in the 3- and 5-positions of the pyridine ring, high-spin nitrenes were photochemically stable and available by photochemical synthesis.[5] The successful generation of quintet dinitrenes **4** and **5** from triazide **1** shows that light-sensitive high-spin nitrenes can be readily prepared by low-temperature γ-radiolysis of crystalline azides. This method is insensitive to transparency of the solid phase and allows the generation of high-spin nitrenes in the whole volume of a crystalline sample but not only on its surface.



Our kinetic studies of the initial stages of the γ-radiolysis of crystalline triazide **1** showed that radiation yields of quintet dinitrenes **4** and **5** are equal to 0.200 and 0.015 per 100 eV of the energy applied, respectively. Note that quintet dinitrenes **4** and **5** were also obtained in nearly the same radiation yields (0.130 and 0.017) on γ-irradiation of crystalline **1** in air[‡] at 77 K. This indicates that generation of high-spin nitrenes in azide crystals by γ-radiolysis is insensitive to air.

According to statistical considerations, quintet dinitrenes **4** to **5** should be formed in equal quantities. The much higher radiation yield of quintet **4** indicates that α-azido groups of triazide **1** on comparison with its γ-azido group are much more sensitive toward the action of γ-irradiation. The preferential decomposition of the α-azido groups has been observed in the

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[†] The synthesis of triazide **1** was described elsewhere.[11]

[‡] The γ-radiolysis was carried out with a Gammatok-100 setup (the dose rate of ^{60}Co γ-radiation was 1.5 kGy h^{-1}). An EPR tube made from signal-clear SK-4b glass was filled with 50 mg of polycrystalline triazide **1**, degassed under a high vacuum, sealed and exposed to γ-rays at 77 K. The reaction was monitored with an X-band EPR spectrometer ($\nu_0 =$ = 9.60006 GHz, working area from 0 to 4000 G). The radiation yields of dinitrenes were determined by the conventional technique from EPR spectra using a sample of the nitroxyl radical RNO containing a known number of spins. Studies on thermal stability of dinitrenes in host crystals involved the following operations: a sample subjected to radiolysis was warmed up to a particular temperature and then dropped again into liquid nitrogen and studied by EPR spectroscopy. Owing to this procedure, we were able to detect EPR signals of quintet dinitrenes, which obey Curie law and become indistinguishable at temperatures above 100 K.

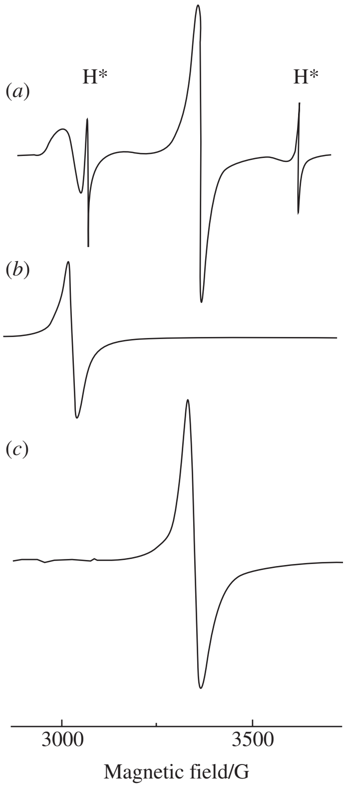

Figure 1 EPR spectrum from γ-radiolysis (77 K, 500 kGy, H* are signals of the hydrogen atoms from EPR tube) of (*a*) triazide **1**, simulated signals of the Y_2 transitions for quintet spin states with (*b*) $|D/hc| = 0.193$ cm^{-1}, $|E/hc| = 0.038$ cm^{-1} and (*c*) $|D/hc| = 0.210$ cm^{-1}, $|E/hc| = 0.056$ cm^{-1}.

photolysis of triazide **7**.[7] This gives the grounds to conclude that decomposition of azides upon both γ-ionization and photolysis occurs by a similar mechanism. Obviously, the first step of the γ-radiolysis of **1** involves the generation of triplet nitrenes **2** and **3**, EPR signals of which[5(*b*)] are observed at 7100 G and lie beyond the range of our EPR spectrometer. As in the case of the photolysis of **7**,[7] the absence of EPR signals around 2000 G after the γ-radiolysis of **1** indicated that septet trinitrene **6** is not formed under these reaction conditions. This can be related to either low stability of trinitrene **6** toward γ-irradiation or low probability of decomposition of all three azido groups in a molecule of **1** upon γ-radiolysis.

Our EPR studies of thermal stability of quintet dinitrenes **4** and **5** in host crystals of **1** showed[‡] that the intensities of EPR signals of both **4** and **5** remained constant on warming the crystals form 77 to 160 K and then gradually decayed, reaching a zero level at 230 K. A similar thermal stability has been observed in other quintet dinitrenes obtained by the photolysis of azide-containing organic crystals.[8]

In order to evaluate the magnetic properties of new quintet dinitrenes **4** and **5**, we simulated[§] their EPR spectra [Figure 1(*b*),(*c*)]. Recently,[9] it was found that the EPR signals of quintet dinitrenes at *ca*. 3000 G belong to Y_2 transitions that are typical of quintet dinitrenes, where the vector angles Θ between two nitrene C–N bonds is roughly 120–124°, as it is the case in quintet 2,4-dinitrenopyridines, the EPR spectra of which usually display only one strong signal of the Y_2 transitions around 3009 G.[6] By contrast, most quintet 2,6-dinitrenopyridines have $\Theta = 114$–115°, giving the strongest signals of the Y_2 transitions around 3345 G in EPR spectra.[10] As a rule, the ratio between the zero-field splitting parameters $|E|$ and $|D|$ for quintet dinitrenes of the first type is close to 1/5, while quintet dinitrenes of the second type have $|E|/|D| \approx 1/3$–$1/4$. Based on these data, we simulated signals of the Y_2 transitions of new quintet dinitrenes **4** and **5** using $g = 2.0023$ and $\nu_0 = 9.60006$ GHz. The simulation for quintet dinitrene **4** gave $|D/hc| = 0.210$ cm^{-1} and $|E/hc| = 0.056$ cm^{-1}, whereas the isomeric quintet dinitrene **5** has $|D/hc| = 0.193$ cm^{-1} and $|E/hc| = 0.038$ cm^{-1} [Figure 1(*b*),(*c*)]. According to these estimates, both dinitrenes **4** and **5** are characterised by a large W_{-2}/W_{+2} splitting ($W_{-2}/W_{+2} = 6|D| + 6|E|$)[9] and can be classified as strong molecular magnets.

In summary, we report a new method of generation of high-spin nitrenes using the γ-radiolysis of crystalline azides at 77 K. This method is insensitive to the transparency of solid phases and to the presence of air and allows the generation of photochemically unstable high-spin nitrenes. As an example, we report EPR spectra and the zero-field splitting parameters of quintet dinitrenes **4** and **5**, which cannot be obtained by low-temperature solid-phase photolysis of triazide **1**.

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[§] Simulations were accomplished using a non-empirical SIM ESR program[12] based on numerical diagonalizing the spin Hamiltonian matrices with parameters (microwave frequency ν_0, spin multiplicity S, g-value and fine-structure parameters D and E) and designed for simulating EPR spectra of randomly oriented in solid phase high-spin molecules.