

# Electronic absorption spectra of quintet and septet pyridylnitrenes

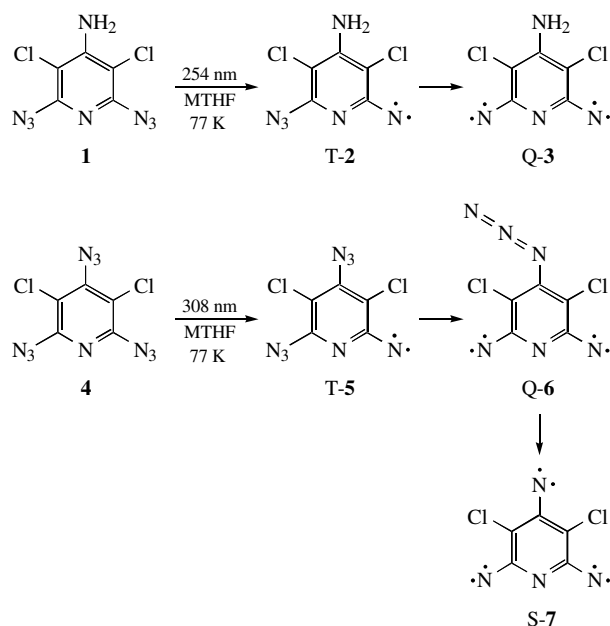
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First electronic absorption spectra of quintet and septet nitrenes were recorded during the photolysis of 4-amino-2,6-diaza-3,5-dichloropyridine and 2,4,6-triazido-3,5-dichloropyridine in frozen solution matrices at 77 K.

In the last decade, much attention has been focused on explorations of high-spin nitrenes, which are promising magnetic materials for electronics.<sup>1</sup> Dozens of quintet dinitrenes<sup>2</sup> and several septet trinitrenes<sup>3</sup> have now been characterised by EPR spectroscopy and some of them, using FTIR spectroscopy.<sup>4</sup> However, all attempts<sup>5</sup> to study the electronic absorption spectra of such species were unsuccessful. Many precursors of high-spin nitrenes eliminated nitrogen and rearranged into low-spin side products at the early stages of photolysis. As a result, most quintet and septet nitrenes were formed in quantities insufficient for UV-VIS detection. Recent FTIR studies have demonstrated that the photolysis of 4-amino-2,6-diaza-3,5-dichloropyridine **1** and 2,4,6-triazido-3,5-dichloropyridine **4** in cryogenic matrices yields only triplet, quintet and septet nitrenes, which are photochemically stable and do not rearrange into low-spin products.<sup>4</sup> This provided an opportunity to investigate the UV-VIS characteristics of quintet and septet nitrenes for the first time. In this work, we report the electronic absorption spectra of quintet and septet nitrenes formed during the photolysis of diazide **1** and triazide **4** in frozen solution matrices at 77 K.



The irradiation of diazide **1**<sup>†</sup> in a degassed 2-methyltetrahydrofuran (MTHF) solution at 77 K for 30 s with light at  $\lambda = 254$  nm led to the appearance of new absorption bands with maxima at 342, 356, 492 and 524 nm (Figure 1). Due to these spectral changes, the solution turned a bright purple colour. The UV-VIS spectrum is typical of triplet arylnitrenes.<sup>6</sup> Weak and broad absorptions of triplet arylnitrenes in the region from

480 to 560 nm can be analysed. The main component involves promotion of an electron in an orbital concentrated in the aromatic ring to an  $n_x$  ( $3b_1$ ) orbital of the nitrene centre, while a minor contribution involves electron promotion from an  $n_x$  ( $3b_1$ ) orbital to the aromatic ring.<sup>7</sup> Due to the absorption of triplet arylnitrenes in the region 480–560 nm, frozen solutions of such species usually have a purple colour.<sup>6</sup> Thus, it is reasonable to assume that a carrier of the UV-VIS spectrum recorded after brief irradiation of **1** is triplet nitrene T-2. Previous EPR studies<sup>2(g)</sup> have shown that T-2 has zero-field splitting  $D$ - and  $E$ -parameters of  $|D/hc| = 0.98$  cm<sup>-1</sup> and  $|E/hc| = 0.00$  cm<sup>-1</sup>.

Further irradiation led to the gradual disappearance of absorption bands at 492 and 524 nm and to the appearance of two new strong and broad absorption bands with maxima at 375 and 638 nm (Figure 1). During these spectral changes, the solution changed its colour from purple to bluish-green. The strong absorption band extending from 550 to 700 nm with a maximum at 638 nm, which was not observed before<sup>5,6</sup> during the photolysis of azides, indicates the formation of new open-shell species with an extended polyradical system. A reasonable assumption for the carrier of this band is quintet dinitrene Q-3, which is formed in this matrix as found by EPR spectroscopy ( $|D/hc| = 0.247$  cm<sup>-1</sup>,  $|E/hc| = 0.052$  cm<sup>-1</sup>).<sup>2(g)</sup> Note that the formation of greenish solutions was earlier observed on generation of singlet dinitrenes in their excited quintet states.<sup>8</sup> According to our EPR studies and UB3LYP/6-31G\* calculations,<sup>2(e),3(a)</sup> dinitrenes formed on the photolysis of 2,6-diaza-3,5-dichloropyridines have quintet ground spin-states lying 12–15 kcal mol<sup>-1</sup> below their  $T_0$  excited triplet states.

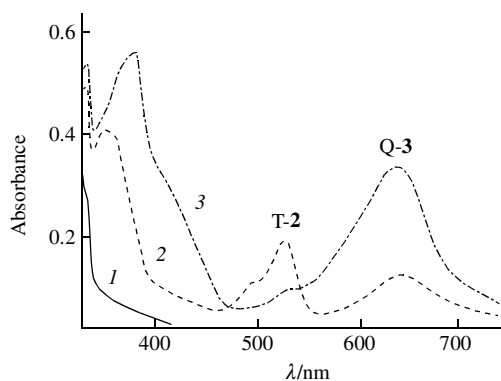
The finding that quintet dinitrenes absorb light at ~640 nm simplified the analysis of the UV-VIS spectrum of the photolysis products of triazide **4**.<sup>†</sup> The irradiation of **4** in a degassed frozen MTHF solution for 0.5 min with monochromatic light at 308 nm led to the appearance of two strong and very broad absorption bands with maxima at 499 and 527 nm, which are attributable to triplet nitrene T-5 (Figure 2). The predominant formation of this nitrene on the photolysis of **4** was found previously by EPR spectroscopy.<sup>2(f)</sup> As expected, the sample was bright purple at this stage of the photolysis. Further irradiation led to gradual disappearance of the absorption bands at

**Table 1** Ground-state spin multiplicities ( $S$ ), zero-field splitting  $D$ -parameters ( $|D/hc|$ ), UB3LYP/6-31G\* calculated the lowest excited/ground state energy gaps ( $\Delta E_{\text{ExG}}$ ) and spin populations ( $q_N$ ) on the nitrene units, and the longest wavelength absorption bands ( $\lambda_{\text{max}}$ ) of nitrenes T-2, T-5, Q-3, Q-6 and S-7.

Nitrene	$S$	$ D/hc /\text{cm}^{-1}$	$\Delta E_{\text{ExG}}/\text{cm}^{-1}$	$q_N$	$\lambda_{\text{max}}/\text{cm}^{-1}$
T-2	1	0.98 <sup>a</sup>	7500 <sup>c</sup>	1.6079	19100 <sup>e</sup>
T-5	1	0.96 <sup>b</sup>	7400 <sup>c</sup>	1.5928	19000 <sup>e</sup>
Q-3	2	0.247 <sup>a</sup>	4200 <sup>d</sup>	1.6583 (2-N/6-N)	15700
Q-6	2	0.283 <sup>b</sup>	4500 <sup>d</sup>	1.6440 (2-N)	16100
				1.6535 (6-N)	
S-7	3	0.100 <sup>b</sup>	2500 <sup>b</sup>	1.6463 (2-N/6-N)	14100
				1.5823 (4-N)	

<sup>a</sup>From ref. 2(g). <sup>b</sup>From ref. 3(a). <sup>c</sup>Experimentally determined  $\Delta E_{\text{ST}}$  for phenylnitrene is 6300±700 cm<sup>-1</sup> (see ref. 12). <sup>d</sup>UB3LYP/6-31G\* calculated  $\Delta E_{\text{TQ}}$  for unsubstituted 2,6-dinitrenopyridine is 5000 cm<sup>-1</sup> [see ref. 3(a)]. <sup>e</sup>DZ+d CISD+Q calculated  $\Delta E_{\text{ST}}$  and adiabatic  $T_0$ – $T_1$  transition for phenylnitrene are 6200 and 18600 cm<sup>-1</sup>, respectively [see ref. 7(a)].

<sup>†</sup> The syntheses of diazide **1** and triazide **4** are described elsewhere.<sup>10,11</sup> The photolysis of the samples and the recording of UV-VIS spectra were performed in a quartz cryostat with plane-parallel windows containing liquid nitrogen. Prior being frozen to an optical glass, solutions of **1** ( $3 \times 10^{-3}$  M) or **4** ( $3 \times 10^{-3}$  M) in dry MTHF were purged with Ar for 5 min. Ray-o-Net 254 and 308 nm lamps were used as light sources. UV-VIS spectra were recorded with a Lambda 6 UV-VIS spectrophotometer.



**Figure 1** UV-VIS spectra from the photolysis ( $\lambda = 254$  nm, 77 K, MTHF) of diazide **1** after (1) 0, (2) 30 and (3) 270 s of irradiation.

499 and 527 nm and to the appearance of three new weak and broad absorption bands with maxima at 576, 620 and 709 nm (Figure 2). The solution changed its colour from purple to slightly greenish and then became almost colourless in the course of the photolysis. Two bands with maxima at 576 and 620 nm can be assigned to quintet dinitrene **Q-6**, which is the major product of the photolysis of **4** with light at  $\lambda < 313$  nm.<sup>2(f)</sup> The fact that the UV-VIS spectrum of quintet **Q-6** displays two absorption bands can tentatively be explained by the non-equivalence of nitrene units in this quintet because of the azido group at the 4-position of the pyridine ring. Thus, for instance, UB3LYP/6-31G\* calculations show that two nitrene units in **6** significantly differ in spin populations (Table 1). A new very weak and broad absorption band extending from 680 to 740 nm with a maximum at 709 nm is evidence for the formation of an open-shell species with an even more extended polyradical system than that in quintet dinitrenes. A reasonable candidate for the carrier of this band is septet trinitrene **S-7**, the formation of which in the reaction was previously proved by FTIR<sup>4</sup> and EPR spectroscopy ( $|D/hc| = 0.100$  cm<sup>-1</sup>,  $|E/hc| = 0.0005$  cm<sup>-1</sup>).<sup>3(a)</sup> According to kinetic FTIR studies,<sup>4</sup> this septet trinitrene is always formed in the matrix substantially contaminated with **Q-6**, which is more photochemically stable. This probably explains why all our attempts to record a clean UV-VIS spectrum of **S-7** without bands of **Q-6** were unsuccessful. Longer (> 5 min) irradiation gradually destroyed the UV-VIS spectra of both **Q-6** and **S-7**.

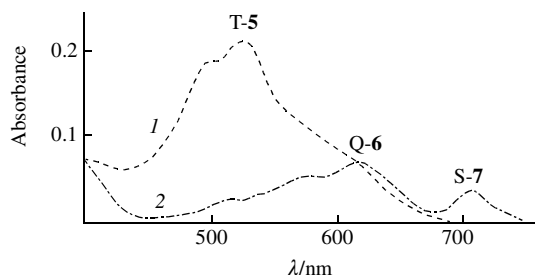
To the best of our knowledge, the UV-VIS spectra of **Q-3**, **Q-6** and **S-7** are the first electronic absorption spectra of organic compounds that have quintet and septet ground spin-states. The results show that an increase in the ground-state spin multiplicity of nitrenes by 1 is accompanied by a bathochromic shift of the longest wavelength absorption band in the UV-VIS spectra of nitrenes by ~100 nm. This trend nicely correlates with a decrease in both the  $D$ -values of nitrenes and the energy gaps between the high-spin ground and the lowest excited states of nitrenes going from triplets to septets (Table 1). The smaller the  $D$ -values of nitrenes, the weaker the stabilising exchange interactions between spins<sup>9</sup> and, as a result, the lower the stability of the nitrenes. Due to weaker exchange interactions of spins in quintet and septet nitrenes, these species require less

excitation energy. An increase in the photochemical activity in parallel with an increase in the ground-state spin multiplicity of nitrenes should be taken into account when designing the photochemical preparation of high-spin nitrenes. Thus, brief irradiation of diazides at  $\lambda = 300$ –350 nm followed by irradiation of the resulting products with light at  $\lambda = 450$ –550 nm can be recommended for more efficient generation of photochemically low-stable quintet dinitrenes. The generation of septet trinitrenes from quintet azidodinitrenes is better performed with light of  $\lambda = 500$ –670 nm, which can destroy only triplet and quintet nitrenes.

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**Figure 2** UV-VIS spectra from the photolysis ( $\lambda = 308$  nm, 77 K, MTHF) of triazide **4** after (1) 30 and (2) 240 s of irradiation.

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