

A new nitrene to carbene rearrangement upon photolysis of 4-amino-2,6-diazido-3,6-dichloropyridine

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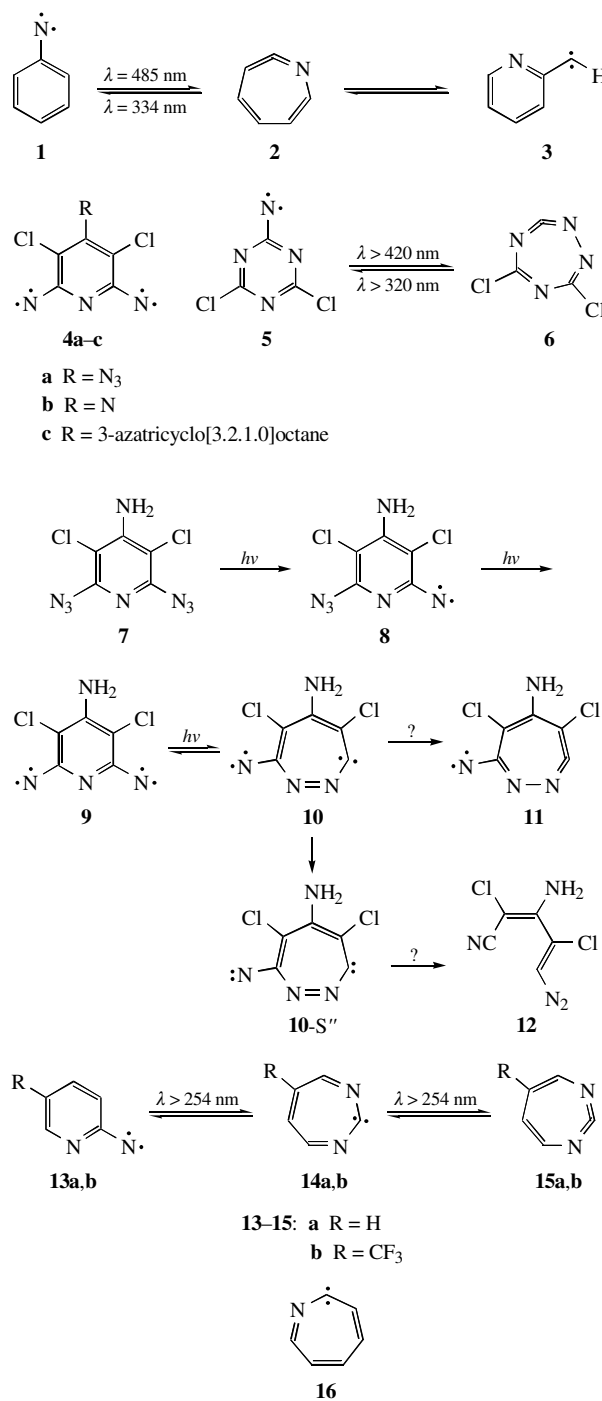
A novel rearrangement of quintet 2,6-dinitrenopyridine to 3-nitreno-1,2-diazacycloheptatrienylidene was discovered by EPR spectroscopy during the photolysis of 4-amino-2,6-diazido-3,5-dichloropyridine in a cryogenic matrix at 77 K.

Despite years of scrutiny,¹ the complete picture of the photochemistry of aromatic azides has only recently begun to unfold. Beyond offering mechanistic novelty, these compounds are widely used as photoresists in microelectronics^{1,2} and as photoaffinity labelling reagents in biochemistry.³ Early IR⁴ and EPR⁵ investigations revealed that triplet phenylnitrene **1** (formed on irradiation of phenyl azide in cryogenic matrices) readily isomerises into azacycloheptatetraene **2** and pyridylcarbene **3**. This reaction can be suppressed by introduction of two *ortho* substituents to the nitrene unit of **1**.⁶ Much less is known on the stability of polysubstituted α -heteroarylnitrenes. Thus, it was found⁷ that pyridyl-2,6-dinitrenes **4a–c** or their nitrenozide precursors are thermally and photochemically stable in cryogenic matrices and do not undergo isomerization involving intramolecular insertions of nitrenes into heterocyclic rings. On the other hand, a recently⁸ discovered rearrangement of **5** into **6** has demonstrated that such intramolecular reactions are in principle possible. Assuming that photochemical rearrangements of polysubstituted 2,6-dinitrenopyridines might yield new spin-carrying species with distinctive EPR spectral characteristics, encouraged us to obtain the EPR spectra of open-shell products formed on irradiation of diazide **7** in cryogenic matrices at 77 K.

The irradiation of diazide **7**[†] in a degassed frozen 2-methyl-tetrahydrofuran (MTHF) solution for 5 min with a xenon arc lamp (Pyrex filtered, > 300 nm) at 77 K led to the appearance of an EPR spectrum displaying strong signals at 463, 3356, 5310, 6788 and 7039 G (Figure 1). Based on the results of an eigen-field simulation¹⁰ [Figure 1(a)], the signals at 463 and 3356 G can be assigned to quintet dinitrene **9** with the zero field splitting (zfs) parameters $|D/hc| = 0.247 \text{ cm}^{-1}$ and $|E/hc| = 0.052 \text{ cm}^{-1}$. The zfs parameters deduced for **9** are very close to those reported for quintet dinitrene **4c**.^{7(c)} The presence of three strong signals at 5310, 6788 and 7039 G in the spectrum indicates the formation of new open-shell products in the photolysis of **7**, species which were not observed previously upon irradiation of related polysubstituted 2,6-diazidopyridines.[‡] By analogy with triplet nitrene¹¹ and carbene spectra,¹² the signals at 6788 and 7039 G can be assigned to two different triplet nitrene species, while

[†] The synthesis of diazide **7** is described elsewhere.⁹

[‡] Weak signals of triplet carbenes were also observed previously in the EPR spectra of **4a,c**.^{7(b),(c)} That time we were unable to assign these signals. FTIR studies of the photolysis of dicyano derivatives of **4a,c** in argon at 7 K revealed that these dinitrenes mostly undergo the opening of the pyridine ring to form presumably intermediates of the **12**-type (appearance of new strong absorption at 2090 cm^{-1} and disappearance of bands of the pyridine ring).^{7(a)} The PM3 geometry optimization of closed-shell singlet configurations of **10-S''** yielded the structure of **12**. The energies of open-shell **10**-singlet and **11** lie 23.2 and 24.4 kcal mol^{-1} (PM3) above the energy of quintet **9**, while the energy of **12** (formed from **10-S''**) lies 4.1 kcal mol^{-1} below the energy of quintet **9**. The EPR observations of weak carbene signals^{7(b),(c)} along with the absence of the IR absorptions of $\text{N}=\text{C}=\text{C}$ bonds of structures **11**^{7(a)} during the photolysis of **4a–c** are consistent with the results of these computations. Both experimental and computational data indicate that further transformations of quintet pyridyl-2,6-dinitrenes involve the intermediate formation of carbenes and opening of the pyridine rings rather than rearrangements of quintet 2,6-dinitrenes into structures **11**.



the signal at 5310 G can be attributed to a single triplet carbene unit. The formation of all of the triplet species produced during the photolysis of **7** can readily be explained by a reaction scheme, which includes the rearrangement of quintet dinitrene **9** to carbenonitrene **10**.[‡] Similar rearrangements leading to 1,3-diazacycloheptatrienylienes **14a** ($|D/hc| = 0.425 \text{ cm}^{-1}$ and $|E/hc| = 0.0222 \text{ cm}^{-1}$)^{13(a)} and **14b** ($|D/hc| = 0.450 \text{ cm}^{-1}$ and $|E/hc| = 0.0059 \text{ cm}^{-1}$)^{13(b)} were detected previously in the photolysis of azides **13a,b**. Unlike precursors **13a,b**, diazide **7** has chlorine atoms at 3- and 5-positions of the pyridine ring; therefore, the ring expansion of **9** to **10** (such as that of **5** to **6**) has precedent. According to the theory,¹⁴ the spin-carrying units of carbenonitrene **10** should be isolated from mutual ferromagnetic exchange interactions and give rise to EPR signals of isolated triplet nitrene and carbene units. The close similarity between the D -parameters of **14a,b** and **10** ($|D/hc| = 0.462 \text{ cm}^{-1}$) supports the proposed formation of carbenonitrene **10**. The signal at 6788 G can be assigned to triplet nitrene **8** ($|D/hc| = 0.98 \text{ cm}^{-1}$, $|E/hc| = 0.002 \text{ cm}^{-1}$), while the high-field signal at 7039 G can be attributed to an isolated nitrene unit of **10** ($|D/hc| = 1.08 \text{ cm}^{-1}$, $|E/hc| = 0.002 \text{ cm}^{-1}$). This is in good agreement with the previously studied azatricyclo[3.2.1.0]octane-substituted derivative of **8** ($|D/hc| = 0.976 \text{ cm}^{-1}$).¹¹ This assignment is consistent with data from ref. 15 which demonstrate that vinyl nitrenes have substantially larger D -values than aromatic nitrenes.

Previous attempts^{16,17} to explain the formation of seven-membered cyclic carbenes (CCs) and azacycloheptatetraenes (AHTs) upon the photolysis of aryl azides as a sequence of thermal transformations of singlet nitrenes into AHTs and the latter into CCs are in conflict with direct observations of photochemical interconversions of triplet nitrenes **1** and **5**, on the one hand, and **2** and **6**, on the other hand.^{4(b),8} Strong arguments in favour of the photochemical rearrangements of triplet nitrenes in AHTs come also from an analysis of the trapping of AHTs with dimethylamine during the photolysis of *para*-substituted phenyl azides (Table 1).¹⁶ Despite almost equal stability of all 5-substituted AHTs relative to the parent triplet nitrenes,[§] the yields of 3*H*-azepines (products of AHTs with dimethylamine) vary drastically. On the other hand, a nice correlation between the D -values of triplet nitrenes[¶] and the yields of 3*H*-azepines indicates that the triplet units of nitrenes are the reactive centres in rearrangements of nitrenes into AHTs. Table 1 shows that the strengthening of electronic interactions between substituents and triplet units (this can be seen as a decrease in D -values for donor-substituted nitrenes and as an increase in D -values for acceptor-substituted nitrenes)^{15,18} increases the stability of nitrenes to the level at which they only undergo thermal self-dimerization to form corresponding azobenzenes in high yields. An analysis of the D -values of triplet nitrenes is also instructive for prediction of photochemical reactivity of pyridyl nitrenes.[¶] Thus, it has been shown^{7(b),11} that many substituted 2-nitrenopyridines with zfs

Table 1 D -values of *para*-substituted phenyl nitrenes and the yields of azobenzenes and 3*H*-azepines from the photolysis of relevant phenyl azides.

Nitrene	$ D/hc / \text{cm}^{-1}$	Azobenzene ^b (%)	3 <i>H</i> -Azepine ^c (%)
PhN	0.999	15	80
<i>p</i> -MeOC ₆ H ₄ N	0.936	80	27
<i>p</i> -Me ₂ NC ₆ H ₄ N	0.896	92	0
<i>p</i> -ClC ₆ H ₄ N	0.951	80	100
<i>p</i> -BrC ₆ H ₄ N	0.911	80	71
<i>p</i> -IC ₆ H ₄ N	0.871	96	34
<i>p</i> -NCC ₆ H ₄ N	0.951	74	68
<i>p</i> -O ₂ NC ₆ H ₄ N	0.964	73	< 3

^a D -values from ref. 18. ^bPhotolysis in neat cyclohexane.¹⁶ ^cPhotolysis in a mixture of cyclohexane and dimethylamine.¹⁶

[§] According to our PM3 calculations, the energies of all 5-substituted derivatives of **2** (Table 1) lie 22–24 kcal mol^{−1} above the energies of the respective triplet nitrenes. The energy gap between **1** and **2** evaluated by CASSCF(8,8)/6-31G* computations is equal to 21.2 kcal mol^{−1}.¹⁷ The structures of all open- and closed-shell singlet, triplet and quintet molecules under consideration were calculated with the full geometry optimization parameters using the PM3 method (RHF or UHF, SCF level).²⁰

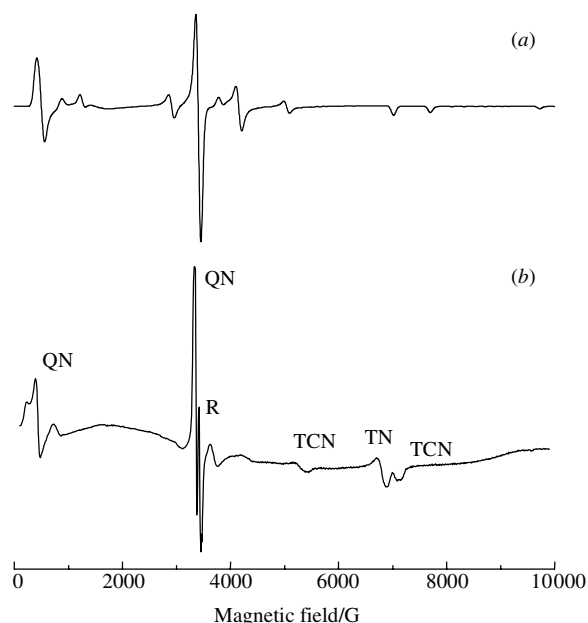


Figure 1 (a) Simulated¹⁰ EPR spectrum for a randomly oriented system **9** with $S = 2$, $|D/hc| = 0.247 \text{ cm}^{-1}$ and $|E/hc| = 0.052 \text{ cm}^{-1}$; (b) EPR spectrum from the photolysis of diazide **7** ($\nu_0 = 9.607 \text{ GHz}$) at 77 K in a 2-methyl-tetrahydrofuran glass. The peaks TN, QN, TCN and R correspond to triplet nitrene **8**, quintet dinitrene **9**, triplet carbenonitrene **10** and a radical impurity from MTHF, respectively.

parameters of $|D/hc| = 0.976\text{--}1.040 \text{ cm}^{-1}$ are very stable upon irradiation at $\lambda > 300 \text{ nm}$. By contrast, nitrenes **13a** ($|D/hc| = 1.051 \text{ cm}^{-1}$)^{13(a)} and **13b** ($|D/hc| = 1.087 \text{ cm}^{-1}$)^{13(b)} readily rearrange into **15a,b** on photolysis in cryogenic matrices.¹³ These results are consistent with our observations^{7(a)–(c)} that 2-nitrenopyridines with $|D/hc| = 1.051\text{--}1.22 \text{ cm}^{-1}$ are very photolabile and almost completely decompose to some diamagnetic products even at 7 K.[‡] On the ground of these observations, we assume that **10** can only arise from **9** rather than due to initial rearrangement of **8** ($|D/hc| = 0.98 \text{ cm}^{-1}$) into a cyclic azidocarbene followed by deazetation of the latter to **10**.

The intense EPR signals of **10** evidence for relatively high photochemical stability of this intermediate. According to the theory,^{12(a)} the larger the energy gap between the ground and highest-spin states of radicals, the higher the stability. Using CASSCF(8,8)/6-31G* computations, it has been shown¹⁷ that the triplet–singlet energy gaps in carbenes **14a** and **16** are 2.6 and 1.4 kcal mol^{−1}, respectively. Almost the same $\Delta E(\text{T–S})$ values (2.2 kcal mol^{−1} for **14a** and 1.3 kcal mol^{−1} for **16**) were obtained by PM3 computations.[§] Despite this quite small difference in the triplet–singlet gaps of **14a** and **16**, the former carbene has a sufficiently long lifetime to be observable by EPR spectroscopy.^{13(a)} The PM3 computations indicate that carbenonitrene **10** has the singlet ground state, which lies 1.2 and 10.4 kcal mol^{−1} below its triplet and quintet states, respectively. Obviously, the observable EPR signals of triplet carbene and extra-nitrene upon photolysis of **7** belong to thermally populated triplet spins of **10**. Thus, many 4,4'-dinitrostilbenes also display intense EPR signals of triplets in cryogenic matrices at 77 K despite the singlet ground

[¶] Depending on the electronic properties of substituents, all substituted phenyl nitrenes are divided into several groups.¹⁸ Within each of these groups, the chemical properties of nitrenes correlate well with D -values (Table 1). The electronic properties of nitrene centres in pyridyl-2-nitrenes are less sensitive to individual effects of substituents and mostly depend on the total electron-deficiency of the pyridine ring.¹¹ Owing to this, a good correlation between the chemical properties and D -values of 2-nitrenopyridines is observed within all series of these compounds. The correlation between D -values and the chemical behaviour of cyano- and nitro-substituted phenyl nitrenes (Table 1) resembles that observed for pyridyl-2-nitrenes. The drastically differing reactivities of cyano- and nitro-substituted phenyl nitrenes, despite a small difference in their D -values (0.013 cm^{−1}), demonstrate that even small changes in spin densities on nitrene centres dramatically affected the reactivities of such species.

states of these species.¹⁹ The rather large singlet–quintet energy gap of carbenonitrene **10** suggests that this species is even more photochemically stable than triplet carbenes **14a,b**.

To our knowledge, the rearrangement of **9** into **10** is the first chemical reaction discovered for quintet dinitrenes. The high reactivity of **9** can be rationalised by an analysis of the *D*-values of this ($|D/hc| = 0.247 \text{ cm}^{-1}$) and two other parent **4a** ($|D/hc| = 0.283 \text{ cm}^{-1}$)^{7(b)} and **4c** ($|D/hc| = 0.257 \text{ cm}^{-1}$)^{7(c)} quintet dinitrenes. The smallest *D*-value for **9** indicates that exchange interactions between unpaired electrons of two nitrene units in **9** are the weakest.¹⁵ This is also supported by the results of PM3 computations, which show that the molecule of **9** has the longest N=C=N–C–N distance between two nitrene units and the shortest C(4)–N, C(2)–C(3) and C(6)–C(5) bonds. Obviously, the weakening of conjugation between the nitrene units and the pyridine ring in quintet pyridyl-2,6-dinitrenes, as in the case of triplet pyridyl-2-nitrenes, favours the localization of spin density on the nitrene centres, thus increasing their reactivity. As has been noted earlier, the border between ‘stable’ and ‘reactive’ triplet pyridyl-2-nitrenes lies in the region of nitrenes with $|D/hc| = 1.04\text{--}1.05 \text{ cm}^{-1}$. Judging on results of the photolysis of **4a**, **4c** and **9**, a similar border between ‘stable’ and ‘reactive’ quintet pyridyl-2,6-dinitrenes lies in the region of nitrenes with $|D/hc| = 0.25\text{--}0.26 \text{ cm}^{-1}$. Taking into account small magnitudes of the *D*-parameters of quintet dinitrenes, it is reasonable to assume that even very small changes in the *D*-values of quintet pyridyl-2,6-dinitrenes (much smaller than in the case of triplet nitrenes)¹¹ evidence for essential changes in the reactivities of such species.

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