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

Sergei V. Chapyshev*[a] and Paul R. Serwinski[b]

[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 096 515 3588; e-mail: chap@icp.ac.ru*
[b] *Department of Chemistry, University of Massachusetts, Amherst, MA 01003–4510, USA. Fax: +1 413 545 4490; e-mail: serwinsk@chem.umass.edu*

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 IR[4] and EPR[5] 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 found[7] that pyridyl-2,6-dinitrenes **4a–c** or their nitrenoazide 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 recently[8] 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-methyltetrahydrofuran (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 eigenfield simulation[10] [Figure 1(a)], the signals at 463 and 3356 G can be assigned to quintet dinitrene **9** with the zero field splitting (zfs) parameters $|D/hc| = 0.247$ cm^{-1} and $|E/hc| = 0.052$ 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 nitrene[11] 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 N=C=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**.
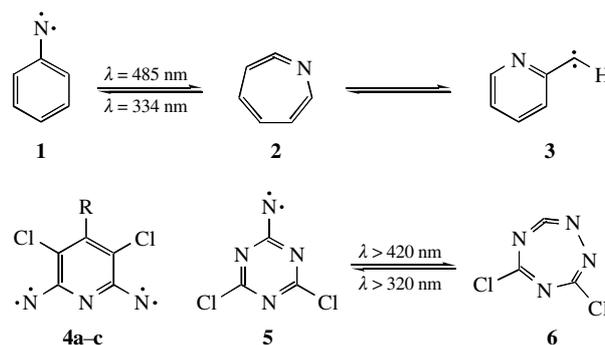
a R = N$_3$
b R = N
c R = 3-azatricyclo[3.2.1.0]octane
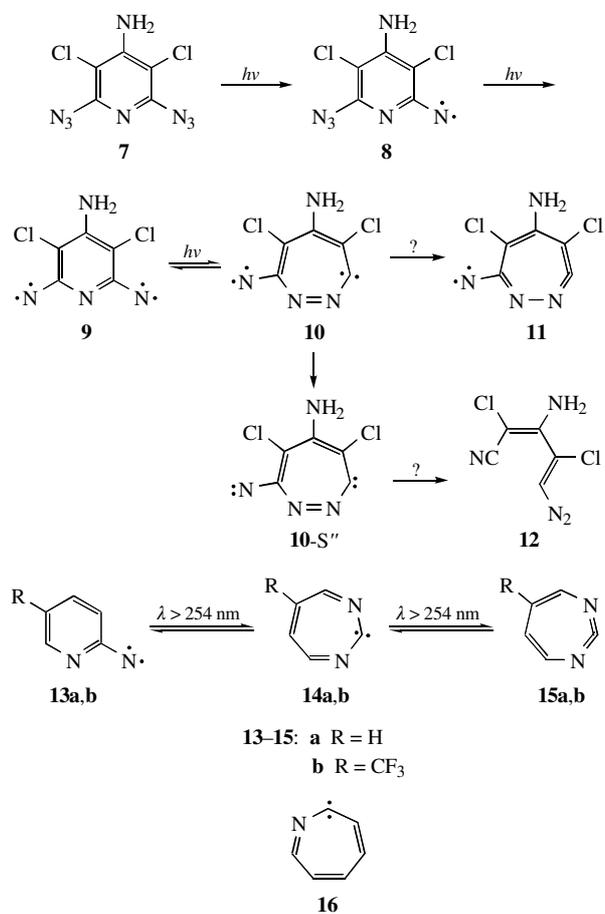
13–15: a R = H
b R = CF$_3$

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-diazacycloheptatrienylidenes **14a** ($|D/hc|$ = 0.425 cm^{-1} and $|E/hc|$ = 0.0222 cm^{-1})[13(a)] and **14b** ($|D/hc|$ = 0.450 cm^{-1} and $|E/hc|$ = = 0.0059 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 carbeno-nitrene **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 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 cm^{-1}, $|E/hc|$ = 0.002 cm^{-1}), while the high-field signal at 7039 G can be attributed to an isolated nitrene unit of **10** ($|D/hc|$ = 1.08 cm^{-1}, $|E/hc|$ = 0.002 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 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 pyridylnitrenes.¶ Thus, it has been shown[7(b),11] that many substituted 2-nitrenopyridines with zfs

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

Nitrene	$|D/hc|^a$/cm^{-1}	Azobenzene^b (%)	3*H*-Azepine^c (%)
PhN	0.999	15	80
p-MeOC$_6$H$_4$N	0.936	80	27
p-Me$_2$NC$_6$H$_4$N	0.896	92	0
p-ClC$_6$H$_4$N	0.951	80	100
p-BrC$_6$H$_4$N	0.911	80	71
p-IC$_6$H$_4$N	0.871	96	34
p-NCC$_6$H$_4$N	0.951	74	68
p-O$_2$NC$_6$H$_4$N	0.964	73	< 3

^{a}*D*-values from ref. 18. ^{b}Photolysis in neat cyclohexane.[16] ^{c}Photolysis 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]
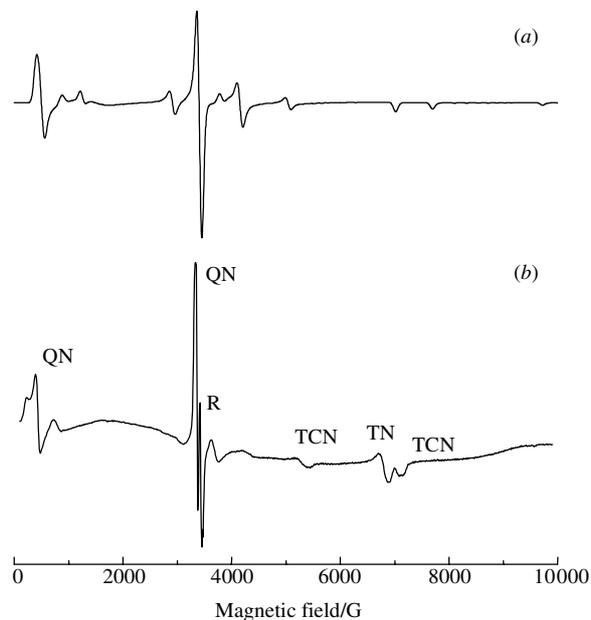

Figure 1 (*a*) Simulated[10] EPR spectrum for a randomly oriented system **9** with S = 2, $|D/hc|$ = 0.247 cm^{-1} and $|E/hc|$ = 0.052 cm^{-1}; (*b*) EPR spectrum from the photolysis of diazide **7** (v_0 = 9.607 GHz) at 77 K in an 2-methyltetrahydrofuran glass. The peaks TN, QN, TCN and R correspond to triplet nitrene **8**, quintet dinitrene **9**, triplet carbenonitrene **10** and a radical impurity from MTHF, respectively.

parameters of $|D/hc|$ = 0.976–1.040 cm^{-1} are very stable upon irradiation at λ > 300 nm. By contrast, nitrenes **13a** ($|D/hc|$ = = 1.051 cm^{-1})[13(a)] and **13b** ($|D/hc|$ = 1.087 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-nitreno-pyridines with $|D/hc|$ = 1.051–1.22 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 cm^{-1}) into a cyclic azidocarbene followed by deazation 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 shown[17] that the triplet–singlet energy gaps in carbenes **14a** and **16** are 2.6 and 1.4 kcal mol^{-1}, respectively. Almost the same ΔE(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′-dinitrenostilbenes 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 phenylnitrenes 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 phenylnitrenes (Table 1) resembles that observed for pyridyl-2-nitrenes. The drastically differing reactivities of cyano- and nitro-substituted phenylnitrenes, 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 ($|D/hc| = 0.247$ cm^{-1}) and two other parent **4a** ($|D/hc| = 0.283$ cm^{-1})[7(b)] and **4c** ($|D/hc| = 0.257$ 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 $|D/hc| = 1.04$–1.05 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 $|D/hc| = 0.25$–0.26 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)¶ evidence for essential changes in the reactivities of such species.

References

1 (*a*) P. A. S. Smith, in *Azides and Nitrenes, Reactivity and Utility*, ed. E. F. V. Scriven, Academic Press, New York, 1984, ch. 3; (*b*) E. F. V. Scriven and K. Turnbull, *Chem. Rev.*, 1988, **88**, 297; (*c*) G. B. Schuster and M. S. Platz, *Adv. Photochem.*, 1992, **17**, 69.

2 (*a*) D. S. Breslow, in *Azides and Nitrenes, Reactivity and Utility*, ed. E. F. V. Scriven, Academic Press, New York, 1984, ch. 10; (*b*) E. W. Meijer, S. Nijhuis and F. C. B. M. van Vroonboven, *J. Am. Chem. Soc.*, 1988, **110**, 7209.

3 (*a*) H. Bayley and J. V. Staros, in *Azides and Nitrenes, Reactivity and Utility*, ed. E. F. V. Scriven, Academic Press, New York, 1984, ch. 9; (*b*) S. A. Fleming, *Tetrahedron*, 1995, **51**, 12479.

4 (*a*) O. L. Chapman and J. P. LeRoux, *J. Am. Chem. Soc.*, 1978, **100**, 282; (*b*) J. C. Hayes and R. S. Sheridan, *J. Am. Chem. Soc.*, 1990, **112**, 5879.

5 O. L. Chapman, R. S. Sheridan and J. P. LeRoux, *J. Am. Chem. Soc.*, 1978, **100**, 6245.

6 (*a*) I. R. Dunkin and P. C. P. Thomson, *J. Chem. Soc., Chem. Commun.*, 1982, 1192; (*b*) I. R. Dunkin, T. Donnelly and T. S. Lockhart, *Tetrahedron Lett.*, 1985, **26**, 359.

7 (*a*) S. V. Chapyshev, A. Kuhn, M. Wong and C. Wentrup, *J. Am. Chem. Soc.*, 2000, **122**, 1572; (*b*) S. V. Chapyshev, R. Walton, J. A. Sanborn and P. M. Lahti, *J. Am. Chem. Soc.*, 2000, **122**, 1580; (*c*) S. V. Chapyshev, R. Walton and P. M. Lahti, *Mendeleev Commun.*, 2000, 114; (*d*) S. V. Chapyshev, R. Walton and P. M. Lahti, *Mendeleev Commun.*, 2000, 187.

8 G. Bucher, F. Siegler and J. J. Wolff, *J. Chem. Soc., Chem. Commun.*, 1999, 2113.

9 S. V. Chapyshev and M. S. Platz, *Mendeleev Commun.*, 2001, 56.

10 (*a*) Y. Teki, I. Fujita, T. Takui, T. Kinoshita and K. Itoh, *J. Am. Chem. Soc.*, 1994, **116**, 11499; (*b*) K. Sato, *PhD Thesis*, Osaka City University, 1994.

11 S. V. Chapyshev, R. Walton and P. M. Lahti, *Mendeleev Commun.*, 2000, 7.

12 (*a*) W. Sander, G. Bucher and S. Wierlacher, *Chem. Rev.*, 1993, **93**, 1583; (*b*) S. V. Chapyshev, R. Walton and P. M. Lahti, *Mendeleev Commun.*, 2000, 138.

13 (*a*) C. Wentrup, M. Kuzaj and H. Luerssen, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 480; (*b*) R. A. Evans, M. Wong and C. Wentrup, *J. Am. Chem. Soc.*, 1996, **118**, 4009.

14 S. Nimura and A. Yabe, in *Magnetic Properties of Organic Materials*, ed. P. M. Lahti, Marcel Dekker, New York, 1999, ch. 7.

15 E. Wasserman, *Prog. Phys. Org. Chem.*, 1971, **8**, 319.

16 Y.-Z. Li, J. P. Kirby, M. W. George, M. Poliakoff and G. B. Schuster, *J. Am. Chem. Soc.*, 1988, **110**, 8092.

17 W. L. Karney and W. T. Borden, *J. Am. Chem. Soc.*, 1997, **119**, 1378.

18 J. H. Hall, J. M. Fargher and M. R. Gisler, *J. Am. Chem. Soc.*, 1978, **100**, 2029.

19 M. Minato and P. M. Lahti, *J. Am. Chem. Soc.*, 1997, **119**, 2187.

20 (*a*) J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 221; (*b*) *Spartan, version 4.0*, Wavefunction, Inc., USA, 1995.