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Effect of spin density on the photochemical stability of aromatic nitrenes

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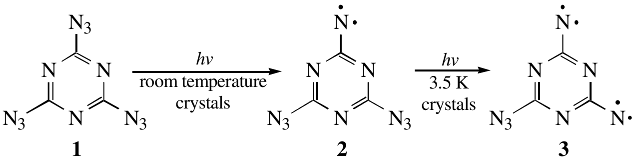
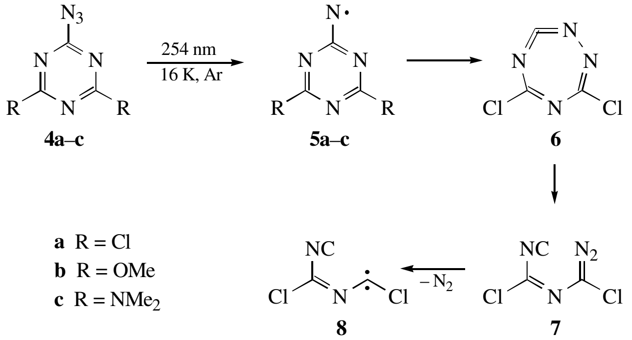
FTIR studies and UB3LYP/6-31G* calculations showed that triplet nitreno-1,3,5-triazines with zero-field splitting D-parameters of $|D/hc| > 1.40$ cm^{-1} and spin populations on the nitrene centres of $\rho_N > 1.77$ are photochemically very stable and do not rearrange into ring-expanded products on photolysis in cryogenic matrices.

In the last decade, much attention has been focused on explorations of high-spin nitrenes, which are promising magnetic materials for electronics.[1] These compounds result from the sequential photodecomposition of azido groups in aromatic oligoazides. They can be obtained in high yields only if intermediate nitrenoazides do not rearrange into low-spin by-products at the early stages of photolysis.[2] Meanwhile, factors controlling the photochemical stability of aromatic nitrenes remained unclear. Thus, EPR studies[3] have shown that the photolysis of triazide **1** in crystals yields triplet nitrene **2**, which is stable at room temperature. Weak EPR signals of quintet dinitrene **3** were detected only during the photolysis of **1** at 3.5 K.[4] These data indicated that undesirable photochemical rearrangements of nitrenes into low-spin products most likely occur at the stage of generation of quintet **3**, while triplet **2** is a fairly stable nitrene. On the other hand, recent FTIR studies[5] of the photolysis of azide **4a** in solid argon showed that triplet **5a** readily rearranges into **6**. On this basis, an assumption was made that all triplet nitrenes with an *s*-triazine skeleton are photochemically unstable and rearrange into ring-expanded products.[5] Here, FTIR studies of the photolysis of azides **4a–c** in solid argon are considered, showing the remarkable stabilizing effect of high spin density on the photochemical stability of aromatic nitrenes.

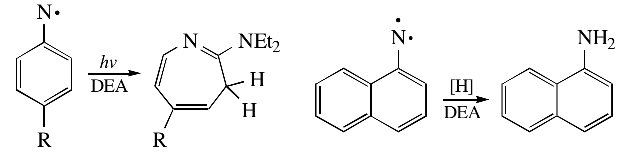
The irradiation of azides **4a–c**† in argon matrices (16 K) with light at $\lambda = 254$ nm led to the disappearance of the IR bands of the starting azides and to the formation of new bands. The photolysis of azide **4a** occurred in accordance with the published mechanism[5] to give triplet nitrene **5a** (bands at $\nu = 1467$, 1446, 1254, 1245, 988, 852, 788 and 580 cm^{-1}), cyclic carbodiimide **6** (bands at $\nu = 1951$, 1546, 1110, 1049, 813, 668 and 624 cm^{-1}) and ring-opened photoproducts arising from **6** (bands at $\nu = 2263$, 2210, 2092, 2087, 1084 and 708 cm^{-1}). Previous attempts to identify these ring-opened products were unsuccessful.[5] The UB3LYP/6-31G* calculations suggest that photochemical ring opening in **6** most likely involves the intermediate formation of diazo compound **7** and triplet carbene **8** (Figure 1). Thus, two characteristic bands at 2087 and 708 cm^{-1} in the IR spectrum recorded after irradiation of **4a** for 10 min fit best to compound **7**, which gives strong IR bands at 2078 (566 km mol^{-1}) and 704 cm^{-1} (130 km mol^{-1}). Relatively low intensities of these bands in experimental spectra indicate that **7** is photochemically labile and decomposes to form presumably triplet carbene **8**. According to calculations, the IR spectrum of **8** has four strong bands at 2082 (158 km mol^{-1}), 1620 (205 km mol^{-1}), 1113 (209 km mol^{-1}) and 701 cm^{-1} (240 km mol^{-1}), which overlap with the IR bands of **6**, **7** and water. Longer (> 1 h) irradiation of the matrix led to a decrease in the IR band intensities of **5a**, **6** and **7** and to an increase in the intensities of bands at 2263 and 2210 cm^{-1}, which are attributable to the products of further photochemical degradation of triplet **8**.

Contrary to azide **4a**, the photolysis of azides **4b,c** in argon matrices gave only triplet nitrenes **5b,c** (Figure 2). The IR bands of triplet **5b** appeared at $\nu = 1525$, 1518, 1452, 1403, 1353, 1284, 1242, 1182, 1110, 1093, 941, 808, 708 and 597 cm^{-1}, while those of triplet **5c**, at $\nu = 1555$, 1483, 1416, 1185, 1149,

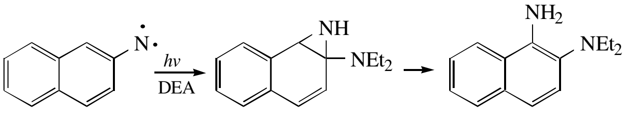

1 **2** **3**

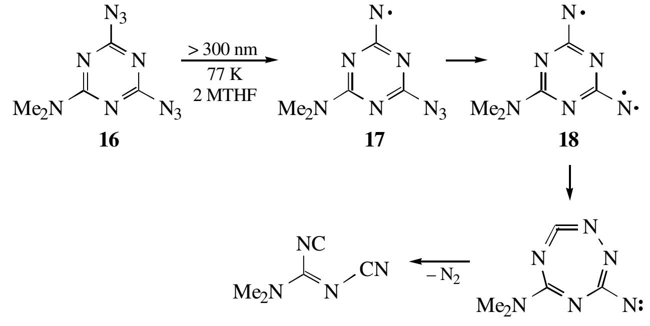

4a–c **5a–c** **6** **7** **8**

a R = Cl
b R = OMe
c R = NMe$_2$


9a–c **10a**, 0% **10b**, 27% **10c**, 80% **11** **12**, 80%

a R = NMe$_2$
b R = OMe
c R = H


13 **14** **15**, 94%


16 **17** **18** **19** **20**

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† The syntheses of azides **4a–c** and **16** were described elsewhere.[10,11]

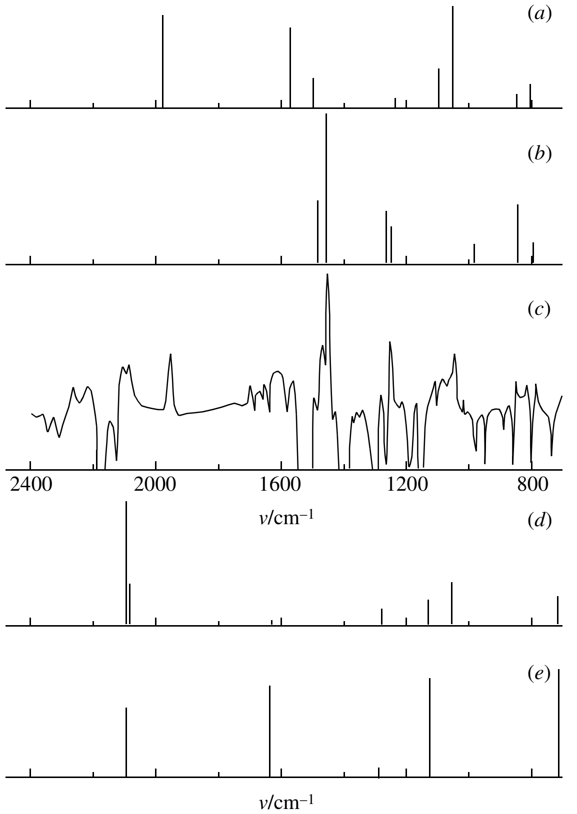

Figure 1 (*a*) B3LYP/6-31G* calculated IR spectrum of **6**. (*b*) UB3LYP/6-31G* calculated IR spectrum of **5a**. (*c*) Difference IR spectrum from the photolysis (10 min, $\lambda = 254$ nm) of **4a** in Ar, 16 K. (*d*) B3LYP/6-31G* calculated IR spectrum of **7**. (*e*) B3LYP/6-31G* calculated IR spectrum of triplet **8**.

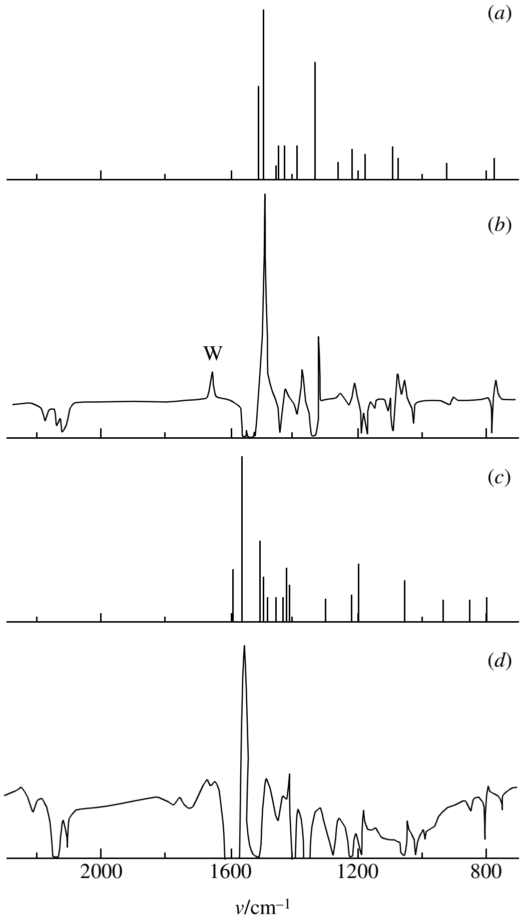

Figure 2 (*a*) UB3LYP/6-31G* calculated IR spectrum of **5b**. (*b*) Difference IR spectrum from the photolysis (50 min, $\lambda = 254$ nm) of **4b** in Ar, 16 K. W denotes the IR bands of molecular water. (*c*) UB3LYP/6-31G* calculated IR spectrum of **5c**. (*d*) Difference IR spectrum from the photolysis (20 min, $\lambda = 254$ nm) of **4c** in Ar, 16 K.

930 and 787 cm^{-1}. Both **5b** and **5c** were photochemically very stable and did not undergo further transformations on irradiation with light at $\lambda = 254$, 308 or > 420 nm. These observations are consistent with published data,[6] according to which only the corresponding amines are the final products of the photolysis of **4b**,**c** in solutions.

Previously,[7] it was found that aromatic nitrenes, such as triplet **9a** and **11**, are also photochemically very stable and do not form rearrangement products. In this work, nitrenes **9a** and **11** were found to have very small *D* values and low spin populations on nitrene centres (Table 1). On comparison with **9a** and **11**, their close derivatives **9b**,**c** and **13** have higher values of *D* and spin populations on the nitrene centres and are more photochemically reactive to form rearrangement products **10b**,**c** and **15** during the photolysis.[7] Within the series of triplets **9a–c**,[7(*a*)] the higher the spin populations on the nitrene centres, the higher the photochemical reactivity of triplet arylnitrenes (Table 1). Obviously, the border between photochemically reactive and inert arylnitrenes **9a–c** lies through nitrenes with *D* values of ~0.90 cm^{-1} and spin populations of ~1.55 on the nitrene centres. Our study of triplet **5a–c** for the first time proves the existence of a similar border between photochemically reactive and inert arylnitrenes at very high spin populations on the nitrene centres.[‡] Based on the data in Table 1, it is reasonable to assume that such a border for nitreno-s-triazines lies through nitrenes with *D* values of ~1.40 cm^{-1} and spin populations of ~1.76 on the nitrene centres. This border provides a clue to the photochemical behaviour of triplet **2** and quintet **3**. Thus, the UB3LYP/6-31G* calculations[§] show that triplet **2** is characterised by a very high spin population (1.7728) on the nitrene centre; therefore, it should be photochemically stable. By contrast, relatively low spin populations (1.7396 and 1.7447) on nitrene units of quintet **3** suggest that this species is even more photolabile than triplet **5a** ($\rho_N = 1.7549$). Another example

Table 1 Yields of rearrangement products (RP), zero-field splitting *D* parameters and UB3LYP/6-31G* calculated spin populations (ρ_N) on the nitrene units of triplet nitrenes **2**, **5a–c**, **9a–c**, **11**, **13**, **17** and quintet dinitrenes **3** and **18**.

Nitrene	RP (%)	|*D*/*hc*|/cm^{-1}	ρ_N
2	—	1.402[a]	1.7728
3	—	0.280[a]	1.7396 (2-N) 1.7447 (4-N)
5a	yes	1.377[b]	1.7549
5b	0	1.427[b]	1.7791
5c	0	1.465[b]	1.7930
9a	0[c]	0.896[d]	1.5432
9b	27[c]	0.936[d]	1.5750
9c	80[c]	0.999[d]	1.6001
11	0[e]	0.789[f]	1.4900
13	94[e]	1.008[f]	1.5619
17	—	1.480[g]	1.7800
18	—	—	1.7584

[a]From ref. 4. [b]From ref. 12. [c]From ref. 7(*a*). [d]From ref. 13. [e]From ref. 7(*b*). [f]From ref. 14. [g]$|E/hc| = 0.0031$ cm^{-1}.

[‡] According to recent EPR studies,[12] the geometries of nitrene centres with very high or very low spin populations substantially differ from the geometry of nitrene centres of typical triplet nitrenes. Obviously, this effect is responsible for the high photochemical stability of triplet **5b**,**c** and **9a**, in the molecules of which the quasi-sp^2 hybridization of the nitrene centres disfavours the promotion of electron from orbitals concentrated on the aromatic ring to singly occupied quasi-*p* orbitals of nitrene units. Thus, for instance, very long C–N bonds[12] in the molecules of triplets **5b**,**c** indicate the antibonding interactions between two *p*-electrons, which should postpone the promotion of another electron to the nitrene centres of **5b**,**c**.

[§] All the test molecules were calculated with the full optimization of geometry parameters using the Gaussian-94 program (Revision D.4).

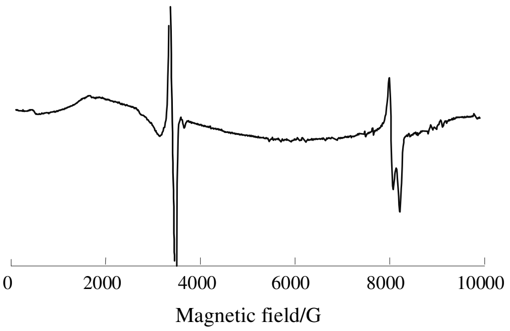

Figure 3 EPR spectrum from the photolysis of diazide **16** (ν_0 = 9.605 GHz, H_0 at 3400 G) with light at $\lambda > 300$ nm for 5 min in 2MTHF at 77 K.

of this series is quintet dinitrene **18**. The EPR studies of the photolysis of diazide **16**† in a degassed 2-methyltetrahydrofuran (2MTHF) solution frozen at 77 K with light at $\lambda > 300$ nm allowed only the detection of triplet **17** (Figure 3). The very high spin population (1.7800) on the nitrene unit of **17** is consistent with the high photochemical stability of this nitrene. On the other hand, relatively low spin populations (1.7584) on nitrene units of quintet **18** suggest that this dinitrene is photochemically very labile and readily rearranges into low-spin products (presumably into **20** *via* **19**).

The current strategy of constructing organometallic ferrimagnets is based on the use of pyridylcarbenes as organic magnetic components.[1,8] Having low spin populations on carbenic centres, arylcarbenes are photochemically stable and do not rearrange into ring-expanded products.[9] However, because of relatively low spin populations on carbenic centres, the complexes of pyridylcarbenes with paramagnetic metals are characterised by moderate exchange interactions between magnetic sites.[1,8] The finding that triplets **5b**,**c** are photochemically stable despite very high spin populations on their nitrene units can be of practical interest for constructing new nitrene-based organometallic ferrimagnets.

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