Selective photolysis of the azido groups in 2,4-diazidopyridines

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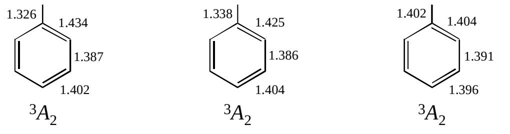
Selective photolysis of the α-azido group in 2,4-diazidopyridines has been determined by EPR spectroscopy and theoretically treated in terms of non-adiabatic photodissociation processes.

The selective photochemical cleavage of chemical bonds in organic compounds is a very important problem in chemistry.[1] In continuation of our research on selective derivatization of the azide groups in aromatic polyazides,[2] an EPR study of the primary products formed in the photolysis of 2,4- and 2,6-diazidopyridines has been performed, the results of which are described here.

Azides **1a**–**e**, **3a**,**b**, **5a**–**e** and **8a**,**b** were irradiated in degassed, frozen solutions of 2-methyltetrahydrofuran at $\lambda > 300$ nm for 5 min at 77 K.[†] Upon irradiation all samples became blue and displayed X-band EPR spectra typical[3–6] of triplet nitrene signals in the region of 6870–7100 G (Table 1). In order to differentiate the isomeric triplet pyridylnitrenes on the basis of their EPR characteristics, published data[3–5] on the related EPR spectra were considered. In addition, PM3 computations[‡] for a series of heteroarylnitrenes were carried out. Contrary to the case of *para*-substituted phenylnitrenes,[3,6] the zero-field splitting (zfs) *D*-values of heteroarylnitrenes correlate fairly well, although non-linearly, with electron-withdrawing properties of the heteroaryl substituents and with computed C–N bond lengths (Table 2). The adequacy of the PM3 computations is supported by an excellent fit of the geometrical parameters for triplet phenylnitrene calculated by this and CASSCF(8,8)/6-31G*[8] methods (Figure 1).

Using the correlation between the *D*-values and the PM3 C–N bond lengths for triplet heteroarylnitrenes, the EPR spectra of the primary products formed by photolysis of azides **1a**–**e**, **3a**,**b**, **5a**–**e** and **8a**,**b** were analysed. As can be seen in Table 1, among nitrenes **2a**–**e** (generated from **1a**–**e**), nitrenes **2b**–**d** have the same *D*-values and C–N bond lengths, whereas **2a** and **2e** have lower *D*-values and shorter C–N bonds. An explanation of these effects comes from an analysis of the structures of **2a**–**e**. The structures of **2b**–**d** are better described by the resonance form **I**, those of **2a**,**e**, by form **II**. The former has shorter C(5)–Cl and longer C(6)–NHAr bonds. The low *D*-value for **4a**, formed by photolysis of **3a**, is presumably associated with the presence of a strong electron-donating aziridine substituent at the pyridine ring of this nitrene. In comparison with **4a**, dicyano derivative **4b** has a higher *D*-value and longer C–N bond, due to the stronger electron-withdrawing character of the pyridine ring and the inability of a nitrene unit to conjugate with the *para*-chlorine atom.



SCF PM3 CASSCF(8,8)/6-31G* MCSCF(8,8)/3-21G

Figure 1 The molecular geometry parameters of triplet phenylnitrene, computed by the SCF PM3, CASSCF(8,8)/6-31G*[8] and MCSCF(8,8)/3-21G[9] methods.

Table 1 The line positions, *D*-values and computed C–N bond lengths of nitrenes **2a**–**e**, **4a**,**b**, **6a**–**e**, **7a**–**e**, **9a**,**b** and **10a**,**b**.

Nitrene	Field/G	$\|D\,hc^{-1}\|$/cm^{-1}	C–N/Å
2a	7008	1.026	1.3291
2b	7045	1.040	1.3297
2c	7045	1.040	1.3297
2d	7105	1.063	—
2e	6911	0.989	1.3282
4a	6877	0.976	1.3282
4b	7020	1.031	1.3299
6a	6877	0.976	—
6b	6877	0.976	1.3260
6c	6877	0.976	1.3260
6d	6877	0.976	—
6e	6899	0.983	—
7a	7059	1.046	—
7b	—[a]	—	1.3264
7c	6989	1.019	1.3264
7d	6990	1.018	—
7e	—[a]	—	—
9a	7040	1.038	1.3290
9b	7105	1.062	1.3293
10a	—	—	1.3277
10b	—	—	1.3278

[a] Shoulder.

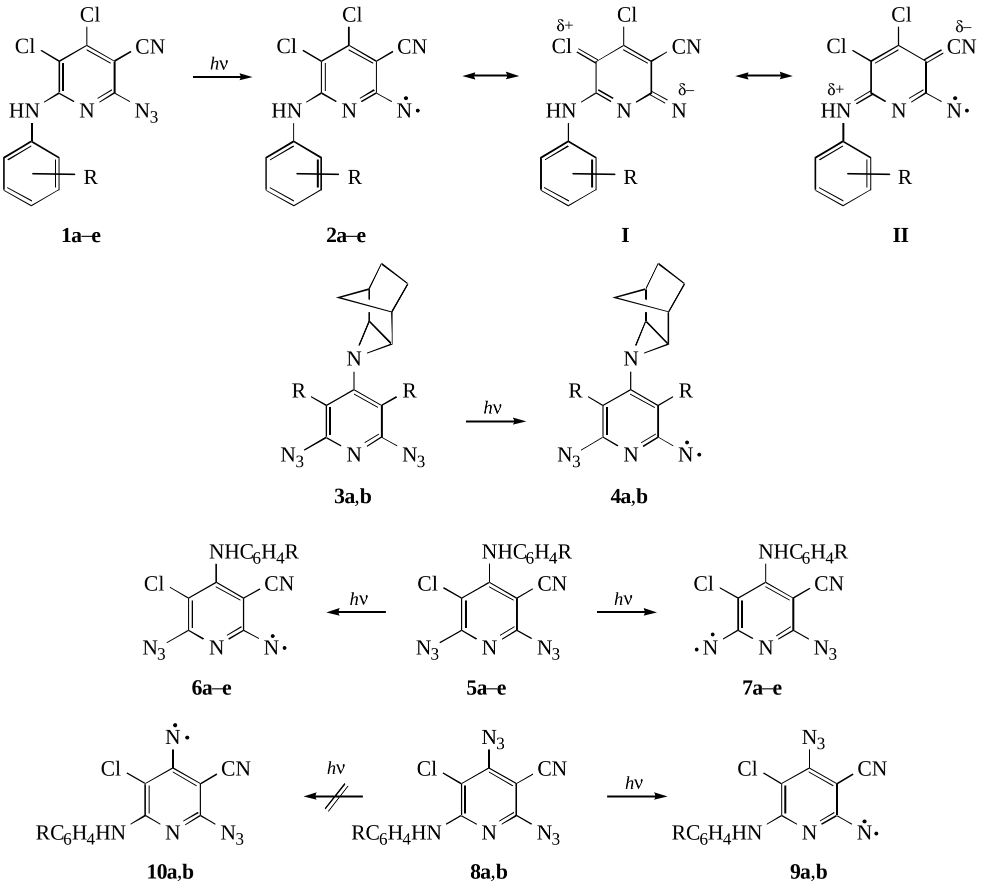
The photolysis of **5a**–**d** led to EPR spectra with two triplet nitrene signals. By analogy with **4a**,**b**, the low-field signals were assigned to nitrenes **6a**–**e** bearing the chlorine atom at the *para*-position to the nitrene unit, whereas the high-field signals were assigned to nitrenes **7a**–**e**. This assignment is supported by shorter C–N bond lengths in **6a**–**e**, comparing with those for **7a**–**e** (Table 1). The effect is quite small, but reasonably consistent. The nitrene peaks from photolysis of **5b**,**e** showed shoulders, but were insufficiently resolved to distinguish two different nitrene signals. The small effect of substituents in the ArNH moieties on the *D*-value of **6a**–**e** and **7a**–**e** is likely explained by a weak conjugation of these moieties with the pyridine ring. The C(5)–C(4)–N–C(1′) torsion angles in **6a**–**e** and **7a**–**e** are about 122°, while the related angles in **2a**–**e** are about 20°. In contrast to **5a**–**e**, diazides **8a**,**b** upon irradiation displayed in the EPR spectra only one triplet nitrene, the line position of which was almost the same as that for nitrenes **2b**–**d**. An answer to the question of which nitrenes, 2-nitreno **9a**,**b** or/and 4-nitreno **10a**,**b**, give the EPR signals in the experiment, was suggested by an analysis of the C–N bond lengths in **9a**,**b** and **10a**,**b**. The substantial difference in these bonds for **9a**,**b** and **10a**,**b** (Table 1) suggests that signals of these isomers should not coincide in the EPR spectra. Nitrenes **9a**,**b** match better to the spectral line positions observed.

Table 2 The *D*-values and computed C–N bond lengths of nitrenes.

Nitrene	$\|D\,hc^{-1}\|$/cm^{-1}	C–N/Å	Reference
Py-3-N	1.005	1.3248	3
Py-2-N	1.051	1.3308	4
5-Trifluoromethylpyridyl-2-nitrene	1.087	1.3315	5
3,5-Bis(trifluoromethyl)pyridyl-2-nitrene	1.108	1.3333	5
Diazidocyanurylnitrene	1.44	1.3571	7

[†] The synthesis of azides **1a**–**e**, **2a**,**b**, **3a**,**b** and **4a**–**e** was described elsewhere.[13] The photolysis and EPR measurements were described previously.[14]

[‡] The structures of azides, triplet nitrenes and excited states were calculated with the full optimization of geometrical parameters using the PM3 method (UHF, SCF level).[15]



1, **2**, **5**–**7**: **a** R = *p*-OMe
b R = *p*-Me
c R = H
d R = *p*-Br
e R = *m*-NO_2

3, **4**: **a** R = Cl
b R = CN

8–**10**: **a** R = *p*-Me
b R = *p*-Br

Both the C–N bond lengths and the *D*-values for **9a**,**b** are almost equal to those for 2-nitreno species **2b**–**d**, which have similar nitrene peak positions and *D*-values.

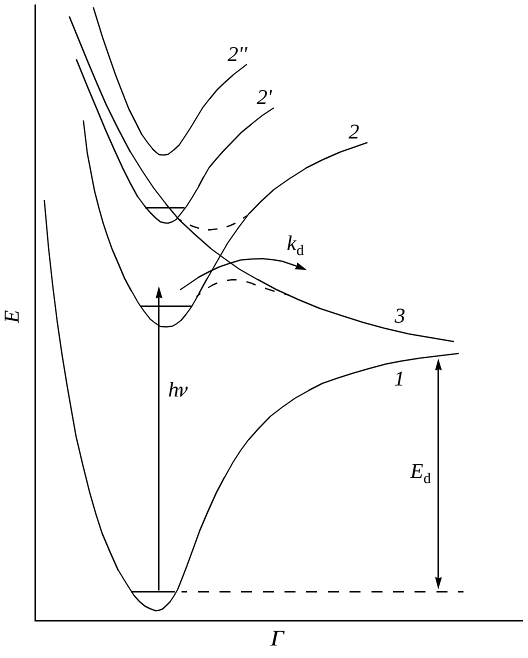
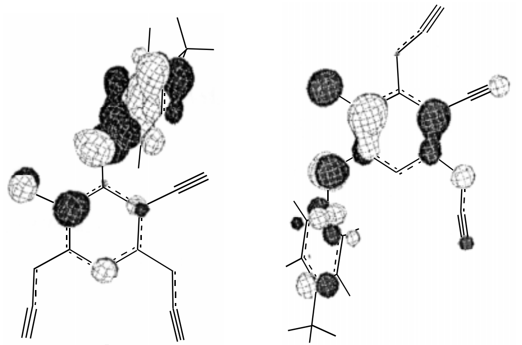


Figure 2 Schematic diagram of the electronic terms for non-adiabatic dissociation (*1*, *2*, *2'* and *2''* are electronic terms for the ground and excited states, respectively; *3* is the repulsive term; E_d is the energy of dissociation; k_d is the dissociation rate constant).

The selective photolysis of the α-azido group in **8a**,**b** can be rationalised from an analysis of the energies for two different excited T_0 states of **8a**,**b** (α-T_0 and γ-T_0 states for dissociation of the α- and γ-azido group, respectively). The photodissociation of chemical bonds in the molecules occurs as a result of energy transfer from the potentials of the excited states (curves *2* and *2'* in Figure 2) onto the potential of the repulsive term (curve *3*).[10] The higher the energy of the excited states, the higher the probability that surfaces *2* or *2'* will be crossed by surface *3*. As has been recently shown,[11] the most prominent feature of the azides in their excited T_0 state is the considerable bending of the azido group (from about 170° in the ground state to about 128° in the T_0 state) and a dramatic fall in the activation energy of N–N_2 bond dissociation (from about 35 to 2 kcal mol^{-1}, respectively).

The computational distortion of the α- or γ-azido group in **8a**,**b** to 135° followed by the PM3 geometry optimization of the molecules in the T_0 state allowed us to determine the energies of the α-T_0 and γ-T_0 states of **8a**,**b**. The energy of the former state was found to be higher by 4 kcal mol^{-1}. This finding supports the idea that the α-excited states (T_0, S_1, T_1, *etc.*)[11] of **8a**,**b**, indeed, lie more closely to the reaction coordinate, so that photodissociation of the α-azido groups in these compounds should be[1,10] the preferable process. Note that the PM3 computation of the T_0 state for **8a** without preliminary bending of one of the azido groups was found to yield the α-T_0 state by preference.

Another interesting finding is the substantial difference in the orbital density distribution between the α- and γ-azido groups in the HOMO of **8a**,**b** (Figure 3). Assuming that the loss of stronger bonding interactions in the molecules leads to the formation of the less stable intermediates,[12] the presence of a higher bonding orbital density at the N_α and N_β atoms[11] of the α-azido group in the HOMO of **8a**,**b** explains fairly well the higher



5b **8a**

Figure 3 The orbital density distribution in the HOMO of **5b** and **8a**. The higher bonding orbital density at the N_α atom of the α-azido group in the HOMO of **8a** indicates that α-excited states (T_0, S_1, T_1, *etc*.) of **8a**,**b** should lie more closely to the reaction coordinate.

energies for the α-T_0 state of these molecules. Figure 3 also demonstrates that the azido groups in the HOMO of **5b** are equal (have almost no orbital density at the N_α atoms). Thus, it is no surprise that the energies of the α- and α′-T_0 states for **5b** were also computed to be equal, and the photolysis of this diazide led to formation of both isomers **6b** and **7b**. It seems reasonable to assume that selective photolysis of the azido groups in polyazides can be possible only for those compounds in which the azido groups significantly differ in the HOMO orbital density distribution. Conversely, the computational modelling of the bonding orbital density will be helpful to predict the relative photolability of azido groups in aromatic polyazides.

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