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Photodissociation of 4-azidopyridine and 4-azidoquinoline in neutral and cationic forms

Mikhayl F. Budyka*, Natalya V. Biktimirova, Tatyana N. Gavrishova,
Olga D. Laukhina, Denis B. Zemtsov

Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Russia

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Abstract

The quantum yields of azido group photodissociation were determined for 4-azidopyridine and 4-azidoquinoline and their protonated and methylated derivatives at endocyclic nitrogen atoms. The dissociation yields are 0.49–0.83 (in MeCN) for neutral azides and decrease to 0.22–0.37 for the positively charged derivatives. The semiempirical and nonempirical quantum-chemical calculations were performed to interpret experimental data. For all azides studied, in the ground (S_0) state, the calculations predict rather large positive charge at two terminal nitrogen atoms of the azido group. In the lowest excited singlet (S_1) state, the antibonding σ^*_{NN} molecular orbital is filled that results in relatively high quantum yields of photodissociation ($\varphi > 0.1$) for all azides. The decrease of quantum yields on going from neutral to charged azides appears to be connected with increasing barrier for electron density transfer from positively charged aromatic nucleus to azido group.

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Keywords: Aromatic azide; Photodissociation; Quantum yield; Quantum-chemical calculations; Charge effect

1. Introduction

The photochemistry of aromatic azides receives continuous attention because of their useful applications in heterocyclic syntheses, photoresist techniques and photoaffinity labeling [1–4]. The key reaction in all cases is the photoinduced N–N bond dissociation with formation of nitrene (Eq. (1)), and main parameter of this reaction is the photodissociation quantum yield (φ):

$$RN{-}N_2 \xrightarrow[\varphi]{h\nu} RN + N_2 \qquad (1)$$

Recently we have found that quantum yield of azido group photodissociation reduces by two orders of magnitude (from 0.82 to 0.0069) on going from 9-(4′-azidophenyl)acridine (APA) to its protonated at endocyclic nitrogen atom cation [5]. The two-order reduction of quantum yield has been also observed on going from APA to *N*-methylated cation [6]. In both cases, insertion of positive charge into heteroaromatic azide molecule has led to a drastic change in the azide photoreactivity.

Examination of the ‘structure–reactivity’ relationship in the series of aromatic azides reveals a general interesting regularity in their photochemical properties: neutral azides decompose under light irradiation with high quantum yields ($\varphi > 0.1$), whereas for positively charged azides the φ values drop below 0.01 [7–10]. Based on the value of photodissociation quantum yield, aromatic azides can be divided into two types, photoactive ($\varphi > 0.1$) and photoinert ($\varphi < 0.01$) azides, respectively.

All photoinert azides are charged and most of them are heterocyclic cations. It seems reasonable to assume that insertion of positive charge into azide molecule gives rise to the loss of photosensitivity. This assumption is based on the results of quantum-chemical investigations of electronic structure of aromatic azides in the ground and lowest excited states [10,11]. In the ground (S_0) state, two terminal nitrogen atoms

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* Corresponding author. Tel.: +7 96 517 1903; fax: +7 96 514 3244.
E-mail address: budyka@icp.ac.ru (M.F. Budyka).

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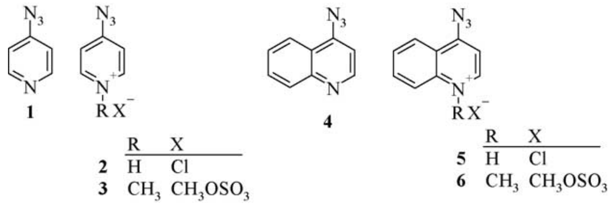
of the azido group possess rather large positive charge (up to 0.5*e*). During dissociation, this charge should be neutralized by electron density transfer from aromatic nucleus, since detaching nitrogen molecule is uncharged. Really, upon excitation from the S_0 to S_1 state, the structure of azido group in photoactive azides changes appreciably that results in the above electron density transfer and facilitates the dissociation reaction [11]. On the contrary, the structure of azido group in photoinert azides does not practically change, and terminal nitrogen atoms remain positively charged. Positive charge at aromatic nucleus appears to create a barrier for the electron density transfer from the nucleus to azido group that hinders subsequent cleavage of the $N–N_2$ bond.

On the other hand, all charged azides are dye derivatives, i.e. large molecules with three and more aromatic nuclei. Therefore, there is another possible explanation of the difference between photoactive and photoinert azides: in a large molecule, the enhanced internal conversion from the S_1 to S_0 state with following vibrational relaxation results in fast deactivation of reactive excited state and thus decreases quantum yield of the reaction. The similar effect is observed in luminophores, where fluorescence quantum yield decreases with increasing rate constant of competing internal conversion (non-radiative transition). Good luminophores have to be planar and rigid in order to reduce non-radiative transitions [12].

To disclose the effect of positive charge on photochemical properties of aromatic azides depending on the size of azide molecule, in the present paper, we studied experimentally and theoretically two azides, 4-azidopyridine and 4-azidoquinoline, and their derivatives. These heteroaromatic azides are convenient model compounds for the study of positive charge effect, since they can be easily transformed from the neutral to positively charged form by protonation or alkylation at endocyclic nitrogen atoms, the size of molecules being practically unchanged upon protonation.

The quantum yield of azido group photodissociation was measured for 4-azidopyridine (**1**), its hydrochloride (**2**), and 1-methyl-4-azidopyridinium methylsulphate (**3**), as well for 4-azidoquinoline (**4**), its hydrochloride (**5**), and 1-methyl-4-azidoquinolinium methylsulphate (**6**) (see Scheme 1). Moreover, the structure of azides was calculated in the ground (S_0) and lowest excited singlet (S_1) state, the quantum-chemical data were used for interpretation of the experimental results.

It should be noted that photochemical properties of isomeric azidopyridines and azidoquinolines and their derivatives have been studied earlier [13–16], main attention being paid to identification of various reaction products, whereas quantum yield of azide decomposition has been measured for **1** only, $\varphi = 0.75$ [17].



Scheme 1.

2. Experimental

4-Azidopyridine (**1**) and 1-methyl-4-azidopyridinium methylsulphate (**3**) were synthesized by known procedures [18]. 4-Azidoquinoline (**4**) and 1-methyl-4-azidoquinolinium methylsulphate (**6**) were prepared according to the reported methods [19,20]. Azidopyridinium hydrochloride (**2**) and azidoquinolinium hydrochloride (**5**) were obtained in situ by addition of conc. HCl to the solutions of **1** and **4**, respectively; the content of unprotonated azides in the reaction mixture was less than 0.1% of the total azide concentration.

The absorption spectra were recorded on a Specord M-40 spectrophotometer, using a 1 cm quartz cuvette. Air-saturated azide solutions were irradiated by low pressure (254 nm) or high pressure (313 nm) Hg lamps equipped with appropriate glass filters, light intensity was 7×10^{-10} to 9×10^{-10} Einstein $cm^{-2}\,s^{-1}$ at 254 nm, and 2.5×10^{-9} to 3×10^{-9} Einstein $cm^{-2}\,s^{-1}$ at 313 nm; 1×10^{-5} to 3×10^{-5} M azide concentrations were used.

Absorption coefficients (in $M^{-1}\,cm^{-1}$) of azides at irradiation wavelengths are as follows: at 254 nm: 13,200 and 9110 in EtOH for azides **1**, **2**, and 9720, 8840, 6320 in MeCN for azides **1**, **2**, **3**, respectively, at 313 nm: 7170, 14,200, 13,200 in MeCN for azides **4**, **5**, **6**, respectively.

Quantum-chemical calculations were performed using semiempirical method PM3 [21], program package MOPAC 93. The structures of compounds in the ground and lowest excited singlet states were calculated with full optimization of the geometrical parameters and using configuration interaction (CI = 2) for the excited states. It should be noted that PM3 method, as has been shown in previous investigations by comparison with results of the higher level ab initio calculations, describes correctly the photodissociation of azido group [11]. Ab initio and density functional theory (DFT) calculations were performed using the GAUSSIAN 94 program package [22] on supercomputer RM600 at the computer center of IPCP RAS.

3. Results and discussion

The electronic absorption spectra of 4-azidopyridine, 4-azidoquinoline and their hydrochlorides in acetonitrile are shown in Fig. 1. Azido group as a chromophore (in hydrazoic acid and alkyl azides) possesses a long-wave absorption band in the region of 250–320 nm arising from $n \to \pi^*$ transition [23,24]. This transition is forbidden and therefore is of very low intensity ($\varepsilon \sim 20\,M^{-1}\,cm^{-1}$). For the studied heteroaromatic azides, this band is masked by the two-order more intense $n–\pi^*$ bands of heteroaromatic nuclei and, also,

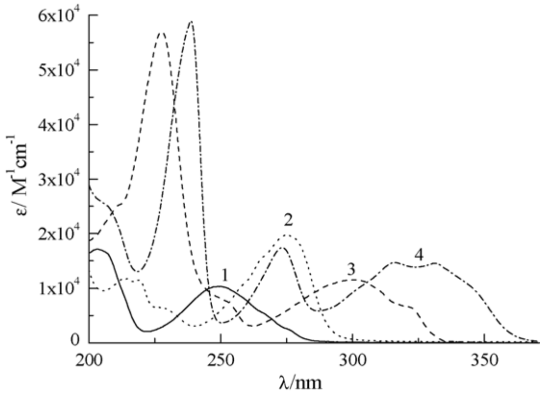


Fig. 1. The electronic absorption spectra in MeCN: (1) 4-azidopyridine (**1**), (2) 4-azidopyridinium hydrochloride (**2**), (3) 4-azidoquinoline (**4**), (4) 4-azidoquinolinium hydrochloride (**5**).

in azidoquinoline, by the π–π* band of quinoline nucleus [25,26].

Upon protonation, the long-wave absorption bands of azidoazines increase in intensity by 1.5–2-fold and are shifted to red from 249 to 275 nm and from 299 to 316–331 nm in 4-azidopyridine and 4-azidoquinoline, respectively (Fig. 1). This behavior resembles that of corresponding amino-derivatives of pyridine and quinoline [27].

Azido group in hydrazoic acid is known to be protonated in superacid solutions with formation of aminodiazonium ion, $H_2N{-}N_2^+$; in the gas-phase protonation, the iminodiazenium ion, $HNNNH^+$, can be also formed [28]. The protonation of azidopyridine and azidoquinoline takes place definitely at endocyclic (“azine”) nitrogen atom; the spectra of protonated azidoazines coincide with those of *N*-methylated ones.

During irradiation at long-wave absorption bands, all azides rapidly decomposed. As an example, Fig. 2 shows spectral changes observed upon irradiation of 1-methyl-4-azidoquinolinium methylsulphate (**6**). Simultaneously with the decay of the absorption bands of **6** at 238, 273, 314 and 331 nm, new bands at 229, 252 and 300 (shoulder) nm appeared, which can be presumably ascribed to reaction products of nitrene and rearranged intermediates with the solvent and with oxygen. The absorbance decay of **6** at irradiation wavelength (313 nm) was found to be first order over four orders of magnitude (see inset in Fig. 2).

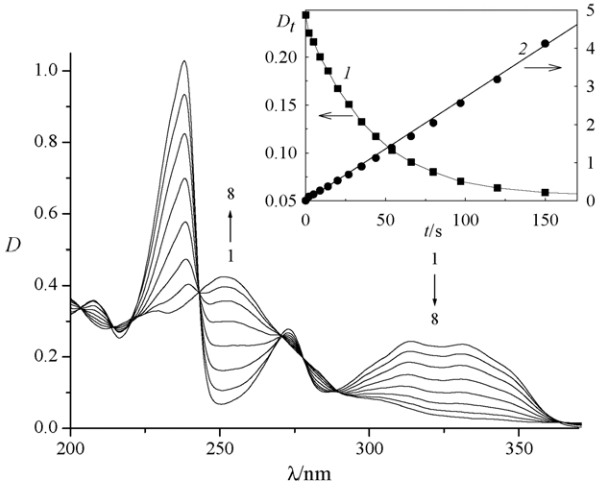


Fig. 2. Spectral changes upon irradiation (313 nm, Hg lamp) of 1.85×10^{-5} M solution of 1-methyl-4-azidoquinolinium methylsulphate (**6**) in MeCN, irradiation time (s), (1)–(8): 0, 5, 14, 27, 44, 66, 97, 210; light intensity 2.7×10^{-9} Einstein $cm^{-2}\,s^{-1}$. Inset: (1) absorbance decay at 313 nm and (2) semilogarithmic anamorphosis of the kinetic curve.

The photodissociation quantum yields of the heteroaromatic azides were calculated from kinetic curves according to formula (2):

$$\ln\left[\frac{D_0 - D_\infty}{D_t - D_\infty}\right] = 2.3\,\varepsilon\varphi I_0 t, \qquad (2)$$

where D_0, D_∞ and D_t are the initial and final optical densities of the reaction mixture and optical density at time *t*, respectively, ε an absorption coefficient of azide ($M^{-1}\,cm^{-1}$) at irradiation wavelength, I_0 an intensity of incident light (Einstein $cm^{-2}\,s^{-1}$), and *t* the reaction time (s). The φ values obtained are shown in Table 1. It is seen that insertion of positive charge into azide molecule results in decrease of the φ value; for example, quantum yield decreases from 0.83 to 0.22 (in MeCN) on going from 4-azidopyridine (**1**) to hydrochloride (**2**). A somewhat less decrease of the φ value is observed upon protonation of azidopyridine in ethanol and upon protonation or alkylation of azidoquinoline. And it should be noted that in all cases, the charged azides remain photoactive ($\varphi > 0.1$). Thus, photochemical properties of derivatives of 4-azidopyridine and 4-azidoquinoline differ appreciably from those of 9-(4′-azidophenyl)acridine, where insertion of positive charge resulted in two-order decrease of quantum yield (see above).

To explain the effects observed, the structures of azides in the ground (S_0) and lowest excited singlet (S_1) states were calculated by different quantum-chemical methods; the data obtained are shown in Table 2. One can see that in comparison with ab initio and DFT methods, PM3 overestimates the charge at terminal nitrogen atoms; nevertheless, all methods predict positive charge in the ground state even in the neutral azides. And all methods predict essential increase of charge upon protonation, for example, in cation **2** as compared with

Table 1
Dissociation quantum yields (φ) for 4-azidopyridine and 4-azidoquinoline and derivatives (irradiation by Hg arc lamp, 254 nm for azides **1**, **2**, **3**, and 313 nm for azides **4**, **5**, **6**, error ±20%)

Azide	solvent	φ
1	MeCN	0.83
1	MeCN/EtOH (1:1)	0.40
1	EtOH	0.35
2	EtOH	0.23
2	MeCN	0.22
3	MeCN	0.27
4	MeCN	0.49
5	MeCN	0.37
6	MeCN	0.36

Table 2
Selected optimized parameters for heterocyclic azides in the ground (S_0) and lowest excited singlet (S_1) states: $N—N_2$ bond length (r) and bond order (p), NNN valence angle (θ_{NNN}) and Mulliken charge (Z_N) on the terminal group N_2 (cations **2**, **3**, **5**, and **6** were calculated without counterions)

Azide	State	r (Å)	p	θ_{NNN} (°)	Z_N (e)	Method
1	S_0	1.27	1.35	169.5	0.40	PM3
		1.24	1.24	174.2	0.27	HF/6-31G*
		1.25	1.28	172.4	0.22	MP2/6-31G
		1.24	1.36	172.3	0.21	B3LYP/6-31G*
	S_1	1.35	1.02	133.4	−0.03	PM3
2	S_0	1.30	1.18	168.8	0.55	PM3
		1.27	1.08	172.1	0.39	HF/6-31G*
		1.26	1.25	170.4	0.34	B3LYP/6-31G*
	S_1	1.41	0.87	128.1	0.09	PM3
3	S_0	1.30	1.19	168.4	0.54	PM3
	S_1	1.40	0.88	129.3	0.08	PM3
4	S_0	1.27	1.34	169.3	0.41	PM3
	S_1	1.35	1.08	137.9	−0.05	PM3
5	S_0	1.30	1.19	168.6	0.55	PM3
	S_1	1.42	0.89	134.4	0.07	PM3
6	S_0	1.30	1.19	168.7	0.54	PM3
	S_1	1.41	0.92	134.9	0.07	PM3

azide **1** charge increases from 0.40 (0.21) to 0.55 (0.34), PM3 (B3LYP/6-31G*) data.

In the lowest excited singlet state, the $N–N_2$ bond is elongated by about 0.1 Å, the NNN valence angle is reduced by about 35°, and the charge at terminal nitrogen atoms decreases by about 0.45e (Table 2). These changes are defined by the nature of molecular orbital (MO) that is filled in the S_1 state. In the case of photoactive azides, this is an orbital of definite structure, namely, σ^*_{NN}-MO, which is localized on the azido group and is antibonding in respect to the $N–N_2$ bond [11]. As an example, Fig. 3 shows the structure of the frontier molecular orbitals for 4-azidoquinoline (**4**) and 4-azidoquinolinium ion (**5**): the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) for the S_0 state, the lowest semioccupied MO (LSOMO) and the highest semioccupied MO (HSOMO) for the S_1 state. In the both azides, in the ground state both HOMO and LUMO are π-type MOs localized mainly on the quinoline nucleus with some contribution by the atomic orbitals of azido group; in the S_0 state, the σ^*_{NN}-MO is LUMO + 1 in neutral azide **4** and LUMO + 2 in cation **5**. However, upon excitation to the S_1 state, as a result of relaxation, the σ^*_{NN}-MO is occupied instead of LUMO in both the neutral and cationic compounds (Fig. 3). Depopulation of π-HOMO, which becomes LSOMO in the S_1 state, and population of σ^*_{NN}-MO, which becomes HSOMO, results in the above structural changes: electron density transfer from aromatic nucleus to azido group, bending of this group and weakening of the $N–N_2$ bond.

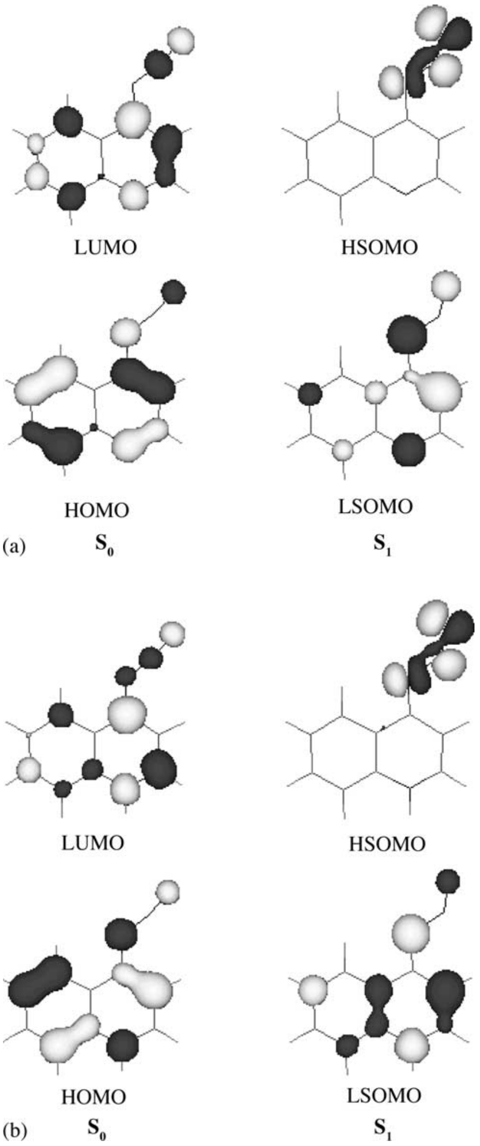


Fig. 3. Structure of the frontier molecular orbitals (MOs) for (a) 4-azidoquinoline (**4**) and (b) 4-azidoquinolinium ion (**5**): the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) in the S_0 state, and the lowest semioccupied MO (LSOMO) and the highest semioccupied MO (HSOMO) in the S_1 state.

Thus, the photoactivity of positively charged derivatives of 4-azidopyridine and 4-azidoquinoline ($\varphi > 0.1$) in contrast to the photoinertness of derivatives of 9-(4′-azidophenyl)acridine ($\varphi < 0.01$) is explained by the fact that in the first case, the antibonding σ^*_{NN}-MO is filled upon excitation, whereas in the latter case, the σ^*_{NN}-MO remains empty [5]. Nevertheless, protonation (alkylation) of azidoazines studied results in some decrease of quantum yield. Apparently, positive charge of aromatic nucleus increases the barrier of azido group dissociation reaction. The higher level ab initio or DFT scanning the S_1 potential energy surface should answer this question. Moreover, one should not exclude the possibility that in protonated (alkylated) azides, additional channel arises for dissipation of excitation energy.

The decrease of quantum yield for **1** on going from acetonitrile to ethanol (Table 1) can be explained as follows. Being comparatively strong organic base, pyridine nucleus is known to form hydrogen-bonded complexes with solvent molecules [29]. H-bond is strengthened in the S_1 state, since pyridine compounds become much more basic on excitation [30] (the basicity increase can reach 7–8 orders of magnitude); the limiting case is a full proton transfer. This gives rise to a positive charge increase on the endocyclic nitrogen atom and results in retardation of dissociation reaction. Consequently, the φ value for **1** decreases on going from MeCN to MeCN/EtOH mixture and further to EtOH, becoming closer to that for protonated azide **2** (Table 1).

4. Conclusion

Thus, experimental and theoretical results presented here, in combination with our earlier work, allow us to draw the following conclusion. The positive charge of aromatic nucleus influences the photochemical properties of aromatic azide, the effect depends on the size of azide molecule.

In small azides, with 1–2 aromatic nuclei, positive charge results in some decrease of azido group photodissociation quantum yield in comparison with the neutral analogue, quantum yield remaining rather high ($\varphi > 0.1$). The decrease appears to be connected with increasing barrier for electron density transfer from aromatic nucleus to azido group.

In large molecules, with 4 and more aromatic nuclei, positive charge leads to the loss of photoactivity, photodissociation quantum yield of charged azide decrease by 2 and more orders of magnitude ($\varphi < 0.01$) in comparison with the neutral photoactive analogue. In the photoinert azides, the antibonding σ^*_{NN}-MO remains empty in the lowest excited singlet (S_1) state, in contrast to the photoactive azides, where this orbital is filled in the S_1 state.

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