2746 Russian Chemical Bulletin, International Edition, Vol. 54, No. 12, pp. 2746—2751, December, 2005

Effect of acid on the quantum yield of photodissociation of 9-(4-azidophenyl)acridine

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The quantum yield of photodissociation of 9-(4-azidophenyl)acridine (**1**) is equal to 0.82, and that of its protonated form **2** is $6.9 \cdot 10^{-3}$. The observed quantum yield of the system can smoothly be controlled in these limits varying the acidity of the medium. According to quantum chemical data, reactivity difference between neutral azide **1** and cation **2** is caused by the fact that in the lowest singlet-excited state (S_1) of azide **1** the antibonding σ^*_{NN} molecular orbital is occupied, while this orbital remains unoccupied in the excited state of cation **2**.

Key words: aromatic azide, photodissociation, quantum chemical calculations, acridine, photoreduction.

Aromatic azides are photochemically active and therefore widely used in science and technology. The key parameter of this activity is the quantum yield (φ) of azide photodissociation. The photodissociation of arylazides upon direct excitation in the long-wavelength absorption band (LWAB) was found[1—3] to occur in the lowest singlet-excited state (S_1). In this case, the quantum yield is determined as

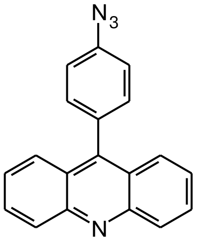
$$\varphi = k_r/(k_r + k_f + k_{ic} + k_{isc} + k_d), \quad (1)$$

where k_r is the rate constant for dissociation of the azido group in the S_1 state; k_f, k_{ic}, and k_{isc} are the rate constants for emission (fluorescence), internal conversion, and intersystem crossing, respectively; and k_d characterizes all other possible processes of deactivation of the excited state (energy transfer, other reactions, *etc*.). Depending on the azide structure, the φ value can vary by several orders of magnitude. In this respect arylazides are grouped into photoactive azides ($\varphi > 0.1$) and photoinert azides ($\varphi < 0.01$).[4] It is also known[5] that irradiation of azides with light at different wavelengths, accompanied by filling different electron-excited states (S_1, S_2, ..., S_n), can lead to variation of the quantum yield of azide photodissociation due to the change in the rate constant ratio in the denominator in formula (1) for these states. At the same time, the excitation of arylazide in the LWAB (occupation of the S_1 state) is usually characterized by a constant quantum yield determined by the molecular structure and virtually independent of the photolysis conditions.

At present, the problem of control of the photochemical properties of photosensitive compounds becomes topical due to the development of various photocontrolled molecular devices. Therefore, the search for systems with smoothly variable (over a wide range) photoactivity is of special interest.

In the present work, we describe for the first time an aromatic azide-based system, whose photoactivity, *i.e.*, the observed quantum yield (φ_{obs}), can be varied by two orders of magnitude by varying the acidity of the medium (for preliminary communication, see Ref. 6).

9-(4-Azidophenyl)acridine (**1**) was chosen as an object of studies. The quantum yield of photodissociation of azide **1** upon quaternization at the endocyclic nitrogen atom decreases[7] from 0.88 to 0.0038. We assumed that the main reason for activity loss of the *N*-methylated cation is the positive charge of the acridine moiety, and the protonation of azide **1** to compound **2** would result in a similar effect. Since the degree of protonation depends on the acid concentration, the photoactivity of azide **1** can be controlled changing the acidity of the medium.



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Experimental

9-(4-Azidophenyl)acridine (**1**) was synthesized following a described procedure.[7] The melting point (188 °C) and the IR spectrum agree with the published data.[7] Phenylacridine (**3**) was prepared by a known method.[8] Its melting point (184 °C) and the IR spectrum are consistent with the literature data.[9]

Ethanol (rectified, highest purity grade) was distilled prior to use.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2655—2660, December, 2005.

1066-5285/05/5412-2746 © 2005 Springer Science+Business Media, Inc.

A DRSh-500 mercury lamp was used as a light source; the 365-nm spectral line was separated by a set of the UFS-6 and BS-7 light filters. Photochemical studies were carried out at room temperature in air-saturated solutions in ethanol acidified with concentrated HCl to a necessary acid concentration. Solutions with azide concentrations of $(0.8-1.2) \cdot 10^{-5}$ mol L^{-1} and quartz cells with the optical path length $l = 1$ cm were used; the light intensity was $(4.5-5) \cdot 10^{-9}$ Einstein cm^{-2} s^{-1} (measured by a PP-1 cavity detector). The molar absorption coefficient of azide **1** at the irradiation wavelength was $\varepsilon_1 = 7720$ L mol^{-1} cm^{-1} (*cf.* 11 400 L mol^{-1} cm^{-1} for acridine **3**). Electronic absorption spectra were recorded on a Specord M-40 instrument.

Quantum chemical calculations were performed by the PM3 method using the MOPAC-93 program.[10] It has been shown previously[11] by comparison with the results of *ab initio* calculations that this method can be used to describe the photodissociation of the azido group in aromatic azides.

Results and Discussion

The spectrum of azide **1** exhibits characteristic vibrationally resolved absorption bands of the acridine moiety at $\lambda = 350-400$ nm (Fig. 1, curve *1*) and an intense band at $\lambda = 254$ nm (not shown in Fig. 1). Acridine compounds are known[12] to be prone to formation of aggregates, which is manifested as the appearance of new absorption bands with an increase in the concentration. Our study of solutions of azide **1** in the concentration range up to $5.82 \cdot 10^{-4}$ mol L^{-1} revealed retention of the spectral shape and a linear dependence between the absorbance and the azide concentration, which indicates no aggregation.

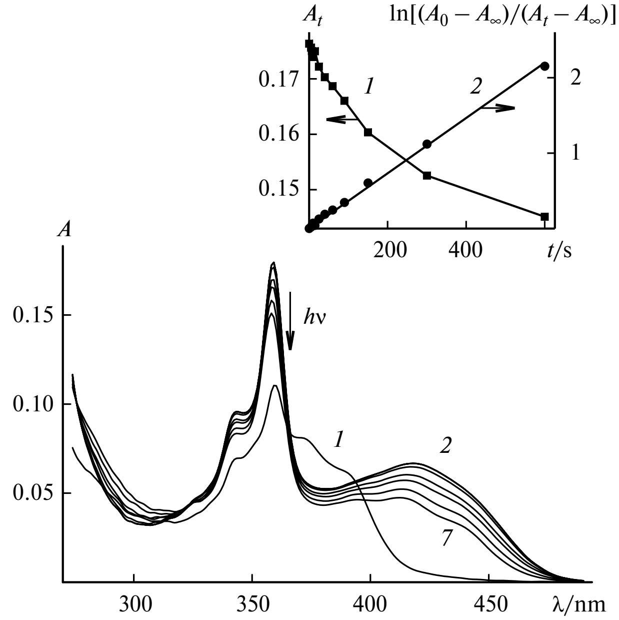


Fig. 1. Absorption spectrum of a $9.5 \cdot 10^{-6}$ *M* solution of 9-(4-azidophenyl)acridine (**1**) in the absence (*1*) and in the presence of 0.0219 *M* HCl (*2*). Spectral changes upon irradiation of the solution for 25 (*3*), 90 (*4*), 150 (*5*), 300 (*6*), and 600 s (*7*); light intensity $4.88 \cdot 10^{-9}$ Einstein cm^{-2} s^{-1}. The results of studying the kinetics of the change in the absorbance at 360 nm are presented in the inset: experimental data (*1*) and their anamorphosis in the coordinates of Eq. (3) (*2*).

Acidification of the reaction mixture (see Fig. 1, curve *2*) results in disappearance of the absorption band of the neutral azide and appearance of a long-wavelength absorption band with a maximum at $\lambda = 417$ nm. This band is characteristic of the chromophoric system of the acridine moiety protonated or alkylated at the endocyclic nitrogen atom.[7,13,14] The ratio between the absorbance of the solution (*A*), acidity constant of azide pK_a, and the pH value of the solution is given by the equation

$$pK_a = pH + \log[(A_1 - A)/(A - A_2)],$$

where A_1 and A_2 are respectively the absorbances of the basic (**1**) and protonated (**2**) forms of the azide at the same concentration. The curve of spectrophotometric titration of the azide at 254 nm in the region of the absorption maximum of the basic form is shown in Fig. 2. The measured pK_a value was 3.5±0.2. According to published data, the model compound containing no azido group, 9-phenylacridine (**3**), has a value of pK_a 4.8 in water[15] and 3.88 in 50% alcohol.[16] Thus, introduction of the azido group with a positive inductive effect into the molecule of compound **3** decreases the basicity of the acridine moiety.

Spectra *2—7* in Fig. 1 show the changes in the absorbance upon irradiation of the reaction mixture. Two photochemical reactions occur concurrently in the studied range of acid concentrations, *viz.*, the decomposition of azide **1** and its protonated form **2** with the quantum yields φ_1 and φ_2, respectively (Scheme 1).

The kinetics of decomposition of each component is given by

$$dC_i/dt = -\varphi_i I_i / l,$$

where C_i is the concentration of the component (mol L^{-1}), I_i is the intensity of the light absorbed by this compo-

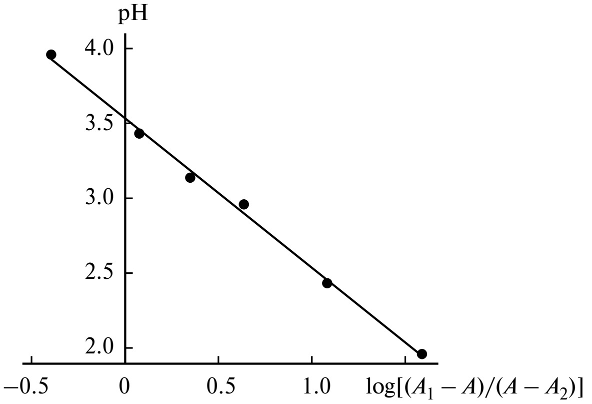


Fig. 2. Spectrophotometric titration curve of 9-(4-azidophenyl)acridine (**1**) $(2.7 \cdot 10^{-5}$ mol $L^{-1})$ at 254 nm in the logarithmic coordinates.

nent (Einstein $cm^{-2} s^{-1}$), and l is the optical path length (1 cm).

For an optically thin layer at the irradiation wavelength (365 nm, $A_{365} < 0.1$) one has

$$I_i = 2.3\varepsilon_i C_i l I_0,$$

where ε_i is the absorption coefficient (L mol^{-1} cm^{-1}) of the component at the irradiation wavelength (365 nm), and I_0 is the incident light intensity. In this case, the overall rate of the change in the azide concentration is

$$dC_1/dt + dC_2/dt = -2.3I_0(\varepsilon_1\varphi_1C_1 + \varepsilon_2\varphi_2C_2). \qquad (2)$$

One should take into account that the concentrations of the free (nonprotonated) azide C_1 and its protonated form C_2 are related to each other through the acidity constant K_a. In addition, the equilibrium between the free and protonated azide, which exists in the ground state (S_0) is not shifted as azide is consuming under steady-state photolysis conditions, because the rate of azide decomposition under the light intensities used is several orders of magnitude lower than the equilibration rate. With allowance for these conditions, Eq. (2) can be integrated analytically

$$\ln[(A_0 - A_\infty)/(A_t - A_\infty)] = 2.3\varepsilon_1\varphi_{obs}I_0t, \qquad (3)$$

where A_0, A_∞, and A_t are the initial, final, and current (at the instant t) absorbances of the reaction mixture at the observation wavelength. The observed quantum yield is

$$\varphi_{obs} = \beta\varphi_2 + (\varphi_1 - \beta\varphi_2)/(1 + \beta[HCl]/K_a), \qquad (4)$$

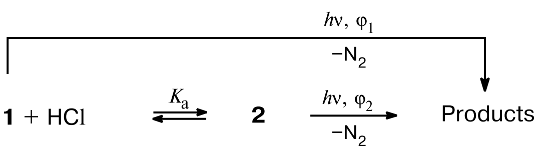
where $\beta = \varepsilon_2/\varepsilon_1 = 1.09$ is the ratio of the molar absorption coefficients of protonated and neutral azides at the wavelength of irradiation (365 nm).

The kinetics of the change in the absorbance at 360 nm and its anamorphosis in the semilogarithmic coordinates of Eq. (3) are shown in the inset in Fig. 1. The observed quantum yields of photodissociation of azide **1** at different HCl concentrations (EtOH, measurement error ±20%), which were calculated from the kinetic curves, are given below.

[HCl] • 100 /mol L^{-1}	φ_{obs} • 100	[HCl] • 100 /mol L^{-1}	φ_{obs} • 100
0	82	1.38	4.7
0.063	32	1.52	4.2
0.211	18	2.19	3.7
0.302	14	3.7	2.8
0.64	8.8	6.25	2.0
1.36	4.6	9.95	1.5

As the acid concentration increases to 0.1 mol L^{-1}, the φ_{obs} value decreases by more than 50 times. According to Eq. (4), the limiting value, lim(φ_{obs}), under the condition [HCl] → ∞ is determined by the product $\beta\varphi_2$. From experimental data on the dependence of the observed quantum yield on the inverse acid concentration it was found that lim(φ_{obs}) = $\beta\varphi_2$ = 0.0075. Using the β value (1.09) known from spectral data, the quantum yield of photodissociation of protonated azide **2** was calculated to be φ_2 = 0.0069. This value is two orders of magnitude lower than for neutral azide **1**, being of the same order of magnitude as the quantum yield of photodissociation of the *N*-methylated cation.[7]

Scheme 1



Taking into account the obtained φ_1 and $\beta\varphi_2$ values, Eq. (4) can be linearized

$$(\varphi_1 - \beta\varphi_2)/(\varphi_{obs} - \beta\varphi_2) = 1 + (\beta/K_a)[HCl]. \qquad (5)$$

Experimental data with the correlation coefficient 0.997 can be linearized in the coordinates of Eq. (5), as shown in Fig. 3, where $\varphi_1 - \beta\varphi_2 = 0.8125$. The acidity constant calculated from the slope of the straight line, $K_a = 1.03 \cdot 10^{-3}$ mol L^{-1}, is similar to the value measured during spectrophotometric titration.

Using experimental data, one can estimate the dissociation rate constant of the azido group in the excited state of azide **1** by comparing the rate constants for two competitive reactions, namely, dissociation and protonation.

The major contribution to the observed quantum yield is made by the dissociation of neutral azide **1** (see the above-presented data). As mentioned above, aromatic azides are photodissociated during direct excitation into the lowest singlet-excited state S_1. At the same time, it is known[14,17] that the basicity of the acridine moiety in the S_1 state increases by several orders of magnitude. Azide **1**

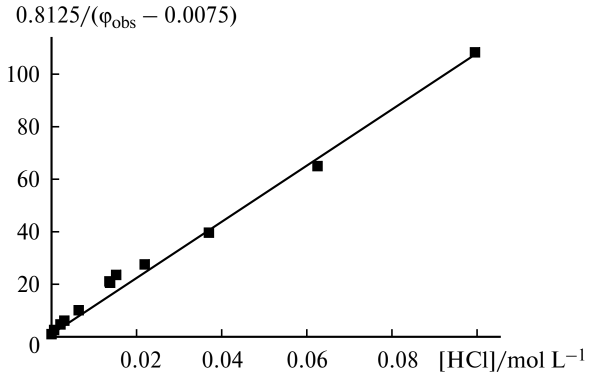


Fig. 3. Observed quantum yield of photodissociation of 9-(4-azidophenyl)acridine (**1**) plotted *vs.* acid concentration in the coordinates of Eq. (5); the correlation coefficient is 0.997.

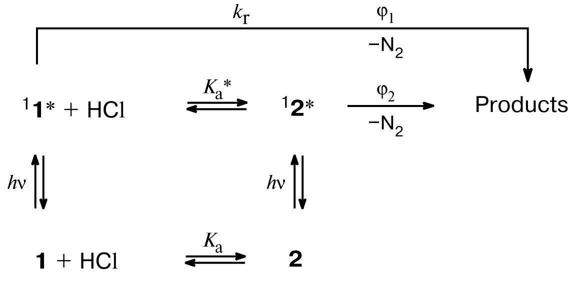
also exhibits a substantial increase in the basicity. Based on the spectral data, we calculated the pK_a* value for the singlet-excited azide **1** using the Förster method[18]:

$$pK_a^* = pK_a - (\nu_2 - \nu_1)/(2.3RT), \qquad (6)$$

where ν_1 and ν_2 are the LWAB energies (frequencies) of the azide and its protonated form (27840 and 24000 cm^{-1}, respectively). We obtained pK_a* = 11.6 by formula (6). Therefore, the relative content of the protonated form in the excited state increases substantially compared to the ground state, while the relative content of the nonprotonated form decreases under equilibrium conditions. For instance, using the acidity constants for the S_0 and S_1 states of azide **1**, we can calculate that the content of the nonprotonated form under equilibrium conditions is 33.4% in the S_0 state and lower than $4 \cdot 10^{-7}$% in the S_1 state at [HCl] = $6.3 \cdot 10^{-4}$ mol L^{-1}. Thus, if the excited state had time to achieve the acid-base equilibrium, the observed quantum yield of photodissociation would be determined by the decomposition of the protonated form only, being more than an order of magnitude lower than the experimentally determined value (0.32) at a given acid concentration.

Possible processes involving singlet-excited azide (^{1}**1***) and its protonated form (^{1}**2***) are shown in more detail in Scheme 2. Since ^{1}**1*** and ^{1}**2*** are not equilibrated, it is clear that the dissociation rate of the azido group exceeds the protonation rate of the acridine moiety. Assuming that protonation is always a diffusion-limited reaction with the reaction rate constant $k_{dif} \approx 10^{10}$ L mol^{-1} s^{-1} and using the maximum studied acid concentration [HCl] ~0.1 mol L^{-1} (see above), we have the lowest limit for the dissociation rate constant of the azido group in the lowest singlet-excited state S_1 of azide **1**: $k_r > 10^9$ s^{-1}. The experimentally measured k_r values for phenylazide and 2,4,6-tribromophenylazide are 10^{10} and $6 \cdot 10^{10}$ s^{-1}, respectively,[2] and the estimates obtained for 4-dimethylaminophenylazide[1] and 4-acetylphenylazide[3] are $k_r > 1.7 \cdot 10^{11}$ and $3 \cdot 10^{10}$ s^{-1}, respectively. In all cases, the azido group in photoactive azides dissociates in the picosecond time scale, which provides an explaination for high quantum yields of dissociation of these azides, namely, possible competitive processes occur at a lower rate (k_r in Eq. (1) predominates).

Scheme 2



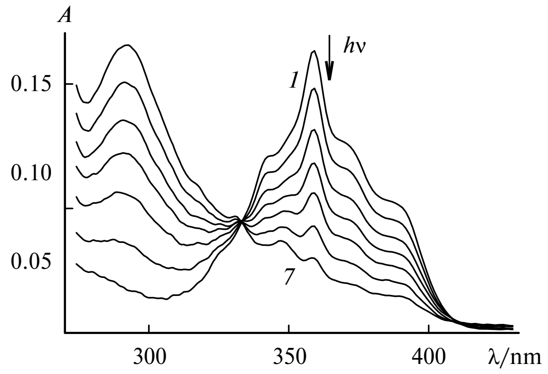


Fig. 4. Spectra of a $7.1 \cdot 10^{-6}$ *M* solution of 9-phenylacridine (**3**): initial solution (*1*), upon irradiation for 180 (*2*), 420 (*3*), 660 (*4*), 900 (*5*), 1260 (*6*), and 1800 s (*7*); light intensity $4.11 \cdot 10^{-9}$ Einstein cm^{-2} s^{-1}.

One of such competitive processes can be the photochemical reduction of the acridine moiety that occurs in proton-donor solvents.[19] To determine a possible contribution of this reaction to the observed spectral changes and the quantum yield, we carried out model experiments with a compound containing no azido group, namely, 9-phenylacridine (**3**). The spectral changes during the photolysis of **3** are shown in Fig. 4. The time interval and the character of these changes differ significantly from those for azide **1**, namely, the intensities of the absorption bands of the acridine moiety in the λ = 340—400 nm region (see Fig. 4, curve *1*) with a maximum at 359 nm and of the short-wavelength UV band with a maximum at 254 nm gradually decrease during photolysis. In addition, a new intense absorption band characteristic of the 9,10-dihydroacridine derivative, *viz*., acridan, appears at λ = 280—310 nm with a maximum at 293 nm (see Fig. 4, curve *7*). The quantum yield of photoreduction was 0.008. The protonation of phenylacridine **3** almost completely inhibits the photoreduction: the change in the absorbance of the solution in the presence of 0.1 *M* HCl was less than 1% within the same irradiation time interval. Thus, in the studied time interval, the photochemical behavior of both the neutral and protonated forms of azide **1** is determined by the photodissociation of the azido group.

On going from azide **1** to its cation **2** the quantum yield of photodissociation decreases by more than two orders of magnitude. The difference in the photochemical activity of these two azides can be explained taking into account the results of quantum chemical studies of the dissociation of aromatic azides in the ground and lowest excited states.[4,11] Regardless of photoactivity, all azides were shown to have similar ground-state geometric parameters. However, the structures of the photoactive and photoinert azides in the excited state differ dramatically.

Table 1. Parameters* of 9-(4-azidophenyl)acridine (**1**) and its cation **2** calculated by the PM3 method

Azide	State	r/Å	p	Angle N—N—N /deg	Z_{N_2}/e
1	S_0	1.27	1.35	169.5	0.39
	S_1	1.34	1.06	137.1	−0.05
2	S_0	1.28	1.29	169.6	0.45
	S_1	1.36	1.10	168.1	0.57

* The N—N_2 bond length(r), order of this bond (p), N—N—N bond angle, and the Mulliken effective charge on the N_2 group (Z_{N_2}) in the ground (S_0) and lowest singlet-excited (S_1) states are presented. Cation **2** was calculated without counterion.

The structural parameters of the azido group in azide **1** and its cation **2** calculated by the PM3 method are given in Table 1. In the ground state S_0 the azido groups of both molecules are quasi-linear (N—N—N angle is ~170°) with the N—N_2 bond length equal to 1.27—1.28 Å and a total charge on the terminal N_2 group of ~0.4 e. However, the lowest singlet-excited state S_1 of molecule **1** exhibits changes characteristic[4] of photoactive azides, namely, elongation of the N—N_2 bond and a decrease in the N—N—N bond angle, the order of the N—N_2 bond, and the positive charge on the terminal N_2 group (the leaving nitrogen atom is neutral). At the same time, the bond angle in cation **2** remains almost unchanged and the positive charge on the N_2 group is retained.

This distinction is related to the fact that in the S_1 state of azide **1** the σ^*_{NN}-molecular orbital (MO) (Fig. 5, *a*) with the antibonding character with respect to the N—N_2 bond is occupied. Occupation of this orbital is a prerequisite for the dissociation of this bond. In the S_1 state of cation **2** the π-MO bond localized on the acridine moiety is occupied (see Fig. 5, *b*) and the σ^*_{NN}-MO remains unoccupied. The difference in structures of the lowest singlet-excited state of two azides under study explains the difference in their photochemical properties.

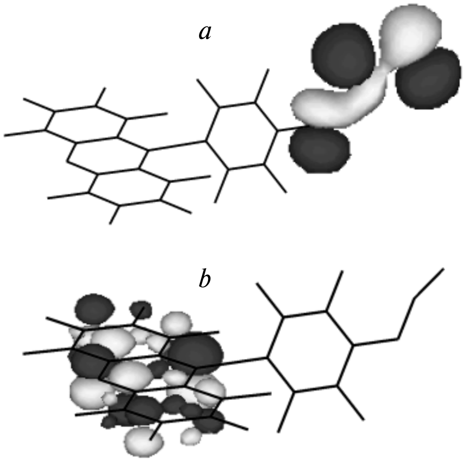


Fig. 5. Structure of the highest singly occupied MO in the S_1 state of 9-(4-azidophenyl)acridine (**1**) (*a*) and its protonated cation **2** (*b*) (counterion is not shown).

Thus, the dependence of the observed quantum yield of photodissociation of aromatic azide on the acidity of the medium was found for the first time for azide **1**. It is shown that the quantum yield of azido group photodissociation decreases by more than two orders of magnitude after an azide molecule gains a positive charge (protonation). The difference in the photochemical properties of azide and its cation can be explained by different structures of the azido group in the lowest singlet-excited state S_1, which is determined, in turn, by different types of the MO occupied in this state.

In conclusion it should be noted that the acidity of the medium can be varied using "photoacids," *i.e.*, substances that liberate a proton upon photoirradiation due to a sharp increase in the acidity constant in the excited state.[17,20] Being combined together, for instance, in a supramolecular system, the photoacid and acid-controlled photoactive azide produce a new photocontrolled photosensitive system. Provided that the absorption spectra of azide and photoacid are different, selective excitation of each component would induce a response of the system, which differs from the response to simultaneous excitation of both components. This creates prerequisites for using such compounds in molecularly organized data recording and processing systems.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 03-03-32116).

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Received November 4, 2004