= PHOTOCHEMISTRY =

# Study of Spectral and Kinetic Characteristics of Products of Photolysis of a Trifunctional Compound with Light of Different Wavelengths

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**Abstract**—Spectral and kinetic characteristics of intermediate products of photolysis of a novel phototrifunctional compound (PTC), whose molecule combines spironaphthoxazine, hydroxyazomethine, and azobenzene fragments, have been studied by microsecond flash photolysis with UV and visible light in toluene and methanol solutions. Three products of PTC photolysis have been detected. It has been found that the efficiency of the photoprocesses substantially depends on the solvent and the wavelength of excitation light.

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Works on design and study of the properties of photocontrolled hybrid photochromic systems are extensively developing at present. On the one hand, of interest are photochromic probes and labels, which permit, using light, monitoring the properties of a modified object [1]. On the other hand, such compounds are promising for creation, on their basis, of materials for molecular electronics: optical switches, logical devices, and others [2, 3].

For this purpose, we studied the dynamics of photoprocesses in a number of novel photobifunctional compounds (PBC), whose molecule includes two structurally different fragments, in which two different processes can occur under the action of light, for example, photoinduced ring opening, proton transfer process, and luminescence. We found using nanosecond flash photolysis that during photolysis of PBC, a few photoproducts are observed, which differ in the maximums of the absorption spectra and whose relative yields depend on the medium and the wavelength of excitation light [4–6]. One of the compounds studied is a model of two all-photonic logical devices [7].

To develop works on the photochemistry of hybrid multiaddressed compounds, we have synthesized a novel phototrifunctional compound (PTC), whose molecule combines three different structural fragments, in which photoprocesses different in nature can occur:



In spironaphthoxazine 1, being a constituent of the PTC molecule, a photochromic process occurs under the action of light, which includes photodissociation of the C-O spiro bond in the initial closed form A and subsequent cis-trans isomerization to form the colored merocyanine form B. The closed form A has an intense absorption band at 337 nm and does not practically absorb in the region of 400–500 nm [8]. Photoexcitation of 1 with UV light leads to the formation of the open merocyanine form B with  $\lambda_{\text{max}} \approx 600$  nm and a sufficiently high quantum yield (about 0.2) [8].



In salicylidenenaphthylamine 2, being the second constituent of the PTC molecule, analogous to well studied salicylideneanilines [9–13], under the action of light, conversion of the *cis*-enol form to the *trans*-keto form can occur as a result of electronically excited-state intramolecular proton transfer (ESIPT) conjugated with cis–trans isomerization:



An important property of salicylidenenaphthylamine 2 is that it occurs in the *cis*-enol form  $E^c$ ( $\lambda_{max} = 360$  nm) in toluene, whereas the presence of *cis*-ketone is noticeable ( $\lambda_{max} = 460$  nm) along with  $E^c$ in MeOH solution [14].



Azobenzene 3 was chosen as the third constituent of the PTC molecule, because in this fragment the occurrence of the process of trans-cis isomerization about the N=N bond, occurring reversibly and with a high quantum yield, was expected, which was well studied for azobenzenes [15-20]. The initial *trans*isomer has a broad absorption band with a maximum at about 350 nm, whereas the *cis*-isomer exhibits an absorption maximum at about 450 nm [15, 17]. The *cis*-isomer of 3, as a rule, is characterized by a long lifetime (with respect to the form B1).



In the PTC molecule, the three aforementioned fragments are combined in such a manner that conjugation exists between the  $\pi$ -electron systems of spironaphthoxazine, hydroxyazomethine, and azobenzene fragments in the ground state of the molecule.

Hence, in PTC we may expect the occurrence of all three described above photoisomerization processes of different nature, which lead to the formation of spectrally different photoproducts. This peculiarity of PTC can be useful regarding the possible application as molecular switches, especially upon realization of selective photoexcitation of various processes by variation of the exciting light wavelength and the medium.

## **EXPERIMENTAL**

To prepare solutions, methanol and toluene (UV spectroscopic grade) were used.

Absorption spectra in the UV and visible regions were measured on a MultiSpec-1501 spectrophotometer.

The absorption spectra and the formation and decay kinetics of the intermediate products were measured in the time range  $\geq 1 \ \mu$ s on a microsecond flash photolysis apparatus with registration of the electronic absorption [4]. Combinations of standard light filters for photolyzing flash lamps were used, which transmitted UV light with  $300 \leq \lambda \leq 370 \ nm$  or visible light with  $400 \leq \lambda \leq 500 \ nm$ . The data presented in this work are average values obtained as a result of analysis of at least ten kinetic curves under the indicated conditions. All measurements were carried out at room temperature. The <sup>1</sup>H NMR spectra were recorded on a Bruker WM-400 spectrometer in CDCl<sub>3</sub> at 25°C.

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## 1,3-Dihydro-8'-(2-hydroxy-5phenylazobenzylidenimino)-1,3,3-trimethylspiro[2Hindol-2,3'-[3H]naphtho[2,1-b][1,4]oxazine] (PTC)

To a hot solution of 1,3-dihydro-8'-amino-1,3,3trimethylspiro[2H-indol-2,3'-[3H]naphtho[2,1-b][1,4]oxazine] (0.5 g, 1.45 mmol), which was obtained according to the procedure described in [21], in absolute ethanol (20 ml), a hot solution of 5-phenylazosalicylic aldehyde (0.338 g, 1.49 mmol), which was synthesized according to [22], in absolute ethanol (15 ml) was added and refluxed for 2 h. Then, the mixture was cooled to room temperature, and the precipitate was filtered off and recrystallized from acetonitrile. Orange-red powder (0.4 g, 50%) with mp 225-227°C was obtained, whose purity was checked by elemental analysis, <sup>1</sup>H NMR spectrum, and thin-layer chromatography. Found: C, 76.11; H, 5.35; N, 12.76. Calculated for C<sub>35</sub>H<sub>29</sub>N<sub>5</sub>O<sub>2</sub>: C, 76.20; H, 5.30; N, 12.70.  $R_f = 0.52$  (with chloroform eluent and SiO<sub>2</sub> TLC plates (Merck)).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *J*/Hz), δ/ppm: 1.37, 1.38 (both s, 3 H each, C(CH<sub>3</sub>)<sub>2</sub>); 2.79 (s, 3H, NCH<sub>3</sub>); 6.60 (d, 1 H, H(7),  ${}^{3}J_{6, 7} = 7.8$ ); 6.93 (t, 1 H, H(5),  ${}^{3}J_{4, 5} = {}^{3}J_{5, 6} = 7.4$ ); 7.08 (d, 1 H, H(3"),  ${}^{3}J_{3", 4"} = 9.0$ ); 7.10 (d, 1 H, H(4),  ${}^{3}J_{4, 5} = 7.4$ ); 7.18 (d, 1 H, H(5),  ${}^{3}J_{5, 6} = 8.8$ ); 7.24 (dd, 1 H, H(6),  ${}^{3}J_{5, 6} = 8.8$ ,  ${}^{3}J_{6, 7} =$ 8.8); 7.47 (d, 1 H, H(4"),  ${}^{3}J_{4", 3"} = 9.1$ ); 7.53 (dd, 2 H, H(3""), H(5""),  ${}^{3}J_{2", 3"} = {}^{3}J_{3", 4"''} = 7.7$ ); 7.65 (d, 1 H, H(9'),  ${}^{3}J_{9,10'} = 8.9$ ,  ${}^{4}J_{7,9'} = 3.2$ ); 7.70 (d, 1 H, H(7'),  ${}^{4}J_{7,9'} = 3.2$ ); 7.72 (1 H, H(6'),  ${}^{3}J_{5',6'} = 8.9$ ); 7.79 (s, 1 H, H(2')); 7.90 (d, 2 H, H(2"), H(6"),  ${}^{3}J_{2", 3"} = {}^{3}J_{5", 6"} =$ 7.7); 8.06 (dd, 1 H, H(4"),  ${}^{3}J_{4", 3"} = 8.9$ ,  ${}^{4}J_{4", 6"} = 2.3$ ); 8.11 (1 H, H(6"),  ${}^{4}J_{4", 6"} = 2.3$ ); 8.64 (d, 1 H, H(10'),  ${}^{3}J_{9,10'} = 9.0$ ); 8.92 (s, 1H, H<sub>α</sub>). 14.08 (broadened s, 1 H, OH).

## **RESULTS AND DISCUSSION**

#### Absorption Spectra of PTC

It follows from the <sup>1</sup>H NMR spectra (see Experimental) that the compound of interest in a chloroform solution occurs in the closed form of the spirocyclic fragment with the enol form of the salicylidenimine fragment, that is,  $A^E$  (within the accuracy of the <sup>1</sup>H NMR method); only the enol form of the salicylidenimine fragment is also observed in a toluene solution of PTC, analogously to PBC studied earlier, including those containing such electron-withdrawing groups as a nitro group [4]. This is indicated by the presence in the <sup>1</sup>H NMR spectra of the signal of a hydroxy group bound to an aromatic core with  $\delta \approx 14$  ppm, whereas the signal of protons of an amino group (should be



**Fig. 1.** Absorption spectra of PTC  $(5 \times 10^{-5} \text{ mol } \text{L}^{-1})$  in (1) methanol and (2) toluene.

observed in the <sup>1</sup>H NMR spectrum of the keto isomer) bound to an aromatic core is located in the region of 2.5–5.0 ppm. The broadening of the OH-group signal at 14 ppm indicates the presence of an intramolecular hydrogen bond, that is, that the initial state of the PTC molecule in toluene is A<sup>E</sup>. Since it is known that the ground state of azobenzenes (and, hence, the corresponding fragment in the PTC molecule) is the transisomer (with respect to the N=N bond), the complete description of the initial state of the PTC molecule in toluene can be  $A_t^E$ . Here and below we use the following notation to describe the states of all three constituent fragments in the PTC molecule. The letters A and B denote the state of the spirocyclic fragment; the superscript and the subscript denote the states of the hydroxyazomethine and azobenzene fragments,

respectively. Unfortunately, it is impossible to determine, using the method of NMR spectroscopy, in which form these compounds occur in an alcoholic solution due to very low solubility of them in alcohols.

Figure 1 shows the electronic absorption spectra of PTC. Their long-wavelength edge is bathochromically shifted with respect to the spectra of the constituent fragments. The absorption spectrum of PTC in a toluene solution also indicates the existence of PTC in the  $A_t^E$  form, because the shoulder at about 470 nm characteristic of the *cis*-ketone is absent [6, 11].

The presence of a weak absorption band in the region of about 470 nm in the absorption spectrum of PTC in methanol indicates the noticeable presence, along with  $A_t^E$ , of the *cis*-keto form  $A_t^{Kc}$ . This is in accordance with the known fact that the azo group is an electron-withdrawing substituent with the strength being between NO and NO<sub>2</sub> groups [24] and, hence,

favors the shift of the thermal keto—enol equilibrium toward the *cis*-ketone.

## Intermediate Products of PTC Photolysis in Toluene

UV light flash photoexcitation of PTC in toluene solutions leads immediately after the flash to an appearance of the merocyanine form B of the fragment 1, which possesses a characteristic absorption spectrum with a maximum at about 600 nm (Fig. 2, spectrum *I*) [4, 5, 8]. The decay kinetics of the absorbance of the form B in the region of  $\lambda \ge 600$  nm is described by the first-order rate law with a rate constant of 0.56 s<sup>-1</sup>, which coincides with the data for the form B<sup>E</sup> of PBC studied in our earlier works [4, 5].

However, in the shorter wavelength region, a relatively weak absorbance of an intermediate with a much longer lifetime (with a first-order rate constant of  $0.036 \text{ s}^{-1}$ ) is observed after disappearance of the form

B. The absorption spectrum of this product is characterized by a band with a maximum at about 450 nm (Fig. 2, spectrum 2), which corresponds to absorbance of the *cis*-isomer of the fragment **3**.

In the case of visible light photolysis, the relative yield of the *cis*-isomer of the fragment **3** is significantly higher (Fig. 3). This intermediate product is formed within the time of a light flash, as well as B.

Hence, upon photolysis of PTC in toluene, at least two processes occur, (1) spiro cycle opening in the fragment 1 to form the deeply colored merocyanine form (Scheme 1) and (2) trans—cis isomerization of the azobenzene fragment 3 leading to the formation of the *cis*-photoisomer, which has a much longer lifetime and absorbs in the visible region (Scheme 2).

The relative yields of these intermediate products significantly depend on the wavelength of excitation light.



Scheme 2. *Trans–cis* isomerization in the PTC molecule.

Note that for PTC in toluene in the time range studied, the formation of photoproducts appearing as a result of

 $A_t^E$ 

ESIPT in the fragment **2** of the molecule, that is, relatively short-lived  $A_{t}^{Kt}$  (Scheme 3), is not observed.

A<sup>E</sup><sub>c</sub>



Fig. 2. Absorption spectra of the intermediate products obtained upon UV light flash photolysis of PTC in toluene (1) immediately and (2) within 10 s after a light flash.



Fig. 3. Absorption spectra of the intermediate products obtained upon visible light flash photolysis of PTC in toluene (1) immediately and (2) within 10 s after a light flash.



In analogous PBC and model compounds studied by us earlier, the corresponding lifetimes of the form  $A^{Kt}$  were no less than 10 µs [4, 5]. For PBC containing an NO<sub>2</sub> group in the SA fragment, the yield of the form with ESIPT drastically dropped as compared with other compounds, and in the case of PBC Br- and NO<sub>2</sub>-substituted in the SA fragment, the formation of the form  $A^{Kt}$  was not observed at all [4]. We may suppose that for PTC these forms are characterized by short lifetimes ( $\leq 1 \mu_s$ ).

## Intermediate Products of PTC Photolysis in MeOH

The initial state of PTC molecules in methanol is a predominance of the form  $A_t^E$  with a small amount of the form  $A_t^{Kc}$ .



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UV light flash photoexcitation of PTC in methanol solutions leads immediately after flash to the appearance of the only photoproduct, the merocyanine form of the fragment  $1 - B_t^E$ , which possesses a characteristic absorption spectrum with a maximum at about 600 nm [4, 5, 8]. The decay kinetics of the absorbance of the form  $B_t^E$  is described by the first-order equation with the rate constant of 0.48 s<sup>-1</sup>.

Upon visible light photolysis of PTC in methanol solutions, the formation of three photoproducts is observed. The shortest-lived photoproduct (with the decay rate constant of 24 s<sup>-1</sup>) is characterized by an absorption spectrum with a maximum in the long-wavelength region at about 650 nm and a noticeable absorbance in the region of 450-500 nm (Fig. 4, spectrum *I*). We observed earlier the analogous photoproduct upon photolysis in methanol solutions of analogous PBC containing only fragments **1** and **2** [4]. It was identified as the merocyanine form B of the fragment **1** bound to the *cis*-keto form of 2, that is,  $B_t^{Kc}$ . The analogous form is apparently formed also upon visible light photolysis of PTC from the form  $A_t^{Kc}$  in methanol solutions (Scheme 4).



**Scheme 4.** Spiro cycle opening process in  $A_t^{Kc}$  to form the merocyanine form.

Note that a source of  $B_t^{Kc}$  can be not only the closed form  $A_t^{Kc}$  present in methanol in a small amount, which can convert to  $B_t^{Kc}$  upon absorption of a light quantum. It is very probable that in PTC, analogously to PBC studied earlier [4],  $B_t^{Kc}$  also appears upon photoexcitation of the enol form of PTC. We may suppose that  $B_t^{Kc}$  is formed as a result of occurrence of phototropic processes being variation of thermodynamic relaxation of the common precursor of the B forms.

The second intermediate product is characterized by an absorption spectrum with a maximum at about 450 nm and the decay rate constant of  $0.89 \text{ s}^{-1}$  (Fig. 4, spectrum 2). We may suppose that this is the form of PTC with the *cis*-isomer of the fragment 3, namely,  $A_c^E$ , because all B forms absorb in much longer-wavelength spectral region.



**Fig. 4.** Absorption spectra of the intermediate products obtained upon visible light flash photolysis of PTC in methanol (1) immediately and within (2) 0.2 and (3) 2 s after a light flash.

The substantial increase in the rate constant of *cis trans* isomerization on passing from toluene to methanol (25 times) is due to solvation effects and is typical on passing to alcohols [25].

The third photoproduct, which has the longest lifetime, is completely analogous to that observed upon UV flash photoexcitation of PTC in methanol solutions and represents PTC with the merocyanine form B of the fragment **1**, in which no changes occur in other fragments, namely,  $B_t^E$  (Fig. 4, spectrum 2).

Hence, three processes occur upon photolysis of PTC in methanol: (1) spiro cycle opening in the fragment **1** to form the deeply colored merocyanine form, without changing configuration of other fragments; (2) trans–cis isomerization of the azobenzene fragment **3** leading to an appearance of the corresponding *cis*-isomer absorbing in the near visible region, without changing configuration of other fragments; (3) spiro cycle opening in PTC in the form  $A_t^{Kc}$  to form the deeply colored merocyanine form, but a portion of this product is possibly formed also as a result of parallel cis–trans isomerization with proton transfer in the fragment **2**.

The kinetic data obtained indicate that the forms  $B_t^E$ ,  $B_t^{Kc}$ , and  $A_c^E$  are not converted to one another, but return to the initial forms  $A_t^E$  and  $A_t^{Kc}$  during the course of the dark reaction. Hence, the photoprocesses observed, on the one hand, occur in parallel, but, on the other hand, the formation of the final form  $B_t^{Kc}$  in methanol can also involve the proton transfer process. The relative yields of these intermediate products substantially depend on the wavelength of excitation light.

## **CONCLUSIONS**

A photochromic phototrifunctional compound that is colored by the action of not only UV, but also visible light has been synthesized. The relationship among the efficiencies of the photoprocesses occurring in this compound substantially depends on the wavelength of excitation light. The initial and intermediate absorption spectra, as well as the kinetic behavior of the system, essentially depend on the solvent nature, which, along with the wavelength of photolyzing light, provides additional possibilities to control photochromism.

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