ISSN 0018-1439, High Energy Chemistry, 2016, Vol. 50, No. 4, pp. 259–265. © Pleiades Publishing, Ltd., 2016. Original Russian Text © P.P. Levin, N.L. Zaichenko, A.S. Tatikolov, A.I. Shienok, L.S. Kol'tsova, I.M. Shcherbakova, O.Yu. Os'kina, I.R. Mardaleishvili, A.O. Ait, A.A. Berlin, 2016, published in Khimiya Vysokikh Energii, 2016, Vol. 50, No. 4, pp. 270–276.

=== PHOTOCHEMISTRY ====

Kinetics of Photochemical Reactions of a New Biphotochromic Compound upon Photolysis with Light of Different Wavelengths

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Abstract—Using the method of microsecond flash photolysis with UV and visible light, the spectral and kinetic characteristics of intermediate products of photolysis in toluene and methanol solutions of a new biphotochromic compound have been studied, in which two photochromic moieties, spironaphthoxazine and azomethine, are linked to each other in such a way that there is conjugation between π -electronic systems of the moieties in the ground state of the molecule. Two intermediate products have detected, whose relative efficiency of formation substantially depends on the solvent and the wavelength of excitation light.

Keywords: bichromophoric compound, spironaphthoxazine, azomethine, photochromism, merocyanine, photoinduced proton transfer, *cis–trans* isomerization, flash photolysis

DOI: 10.1134/S001814391604010X

The design of photocontrollable multiphotochromic systems, whose photochemical and photophysical behavior can be controlled by changing the wavelength of excitation light, and study of their properties are an active area of current research [1-7]. Such compounds are promising to create on their basis of a new generation of materials for molecular electronics: photocontrollable molecular switches, logic gates, molecular devices, etc.

In continuation of our works on the search for compounds with switchable properties [8–11], we synthesized and studied a new biphotochromic compound—1,3-dihydro-9'-hydroxy-10'-(4-meth-oxyphenyliminomethyl)-1,3,3-trimethylspiro[2*H*-indole-2,3'-[3*H*]naphtho[2,1-b][1,4]oxazine] (BPC-I), whose molecule combines two moieties of different nature, photochromic processes in which lead to spectrally distinguished products. In the synthesis of compound I, we used the developed by us earlier method of regioselective *ortho*-formylation of 9'-hydroxysubstituted spironaphthoxazine with the use of paraformaldehyde and the complex of magnesium dichloride with triethylamine [12], which led to the

formation of 10'-formyl derivative. Then condensation of 10'-formyl derivative with *p*-methoxyaniline was performed, whereby a compound was obtained in which two photochromic moieties, spironaphthoxazine and azomethine, were linked to each other in such a way that there was conjugation between the π -electronic systems of the spironaphthoxazine and hydroxyazomethine moieties in the ground state of the molecule, with the "phenolic" part of the hydroxyazomethine moiety being incorporated in the spironaphthoxazine moiety, unlike all compounds studied by us earlier [8–11].

In spironaphthoxazine II, as a part of the BPC-I molecule, a photochromic process occurs under the action of light, involving photodissociation of the C–O spiro bond in the closed form IIA (having an absorption band with $\lambda_{max} \sim 337$ nm, which practically does not absorb in the region of 400–500 nm) and *cis–trans* isomerization to form the colored merocyanine form IIB with an absorption maximum at 600 nm [11].



In *p*-methoxyanil of 2-hydroxy-1-naphthaldehyde III, which models the second photochromic moiety of the BPC-I molecule, under the action of light, transition from the *cis*-enol form to the *trans*-keto form can occur as a result of intramolecular proton transfer in the electronically excited state (excited state intramolecular proton transfer, ESIPT), followed by *cis*-*trans* isomerization [13–16]. Hence, for BPC-I, we may expect occurring the photoprocesses of different nature, which were described above, leading to the formation of spectrally distinguished photoproducts.

II A

EXPERIMENTAL

To prepare solutions, methanol and toluene of UV spectroscopic grade were used. Absorption spectra in the UV and visible regions were measured on a Multi-Spec-1501 spectrophotometer.

The absorption spectra and the kinetics of formation and decay of intermediate products were measured in the time range $\geq 10 \ \mu s$ on a microsecond flash photolysis apparatus with registration of electronic absorption [9]. Combinations of standard light filters for photolytic flash lamps permeable to UV light in the range of $300 \le \lambda \le 370$ nm or visible light in the range of $440 \le \lambda \le 520$ nm were used. The data of the work represent the average values obtained by the treatment for at least ten kinetic curves under these conditions [9].

II B

All measurements were carried out at room temperature. ¹H NMR spectra were recorded on a Bruker WM-400 spectrometer at 25°C in CDCl₃.

Calculation and optimization of the structures of molecules in the ground state were performed by the DFT method with the B3LYP functional in the 6-31G(d, p) basis.

Synthesis of BPC-I

1,3-Dihydro-9'-hydroxy-10'-formyl-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]naphto[2,1-b][1,4]oxazine] (43 mg, 0.115 mmol) and *p*-methoxyaniline (21 mg,

0.17 mmol) were dissolved in toluene (5 ml) in a roundbottom flask equipped with a reflux water condenser and refluxed for 1.5 h. The reaction was monitored by TLC in the system benzene–acetone 19 : 1. Then the cooled reaction mixture was evaporated. The product was isolated by preparative TLC in the system benzene–acetone 9 : 1. The photochromic fraction with $R_{\rm f} = 63$ was collected. It was desorbed from silica gel by the system benzene–acetone 5 : 1. 50 mg (0.104 mmol) of beige powder with mp 222–224°C was obtained with the yield of 91%.

¹H NMR (400 MHz, CDCl₃, *J*/Hz), δ /ppm: 1.37 (s, 3H, C(CH₃)); 1.38 (s, 3H, C(CH₃)); 2.79 (c, 3H, NCH₃); 3.85 (s, 3H, O(CH₃)); 6.59 (d, 1H, H(7), $J_{6,7} = 7.8$); 6.75 (d, 1H, H(5'), $J_{5,6} = 8.5$); 6.85 (d, 1H, H(8'), $J_{7,8'} = 9.0$); 6.90 (t, 1H, H(5), $J_{4,5} = 7.1$, $J_{5,6} = 7.4$); 7.00 (d, 2H, H(2''), $J_{2",3"} = 8.7$); 7.09 (d, 1H, H(4), $J_{4,5} = 7.1$); 7.23 (t, 1H, H(6), $J_{5,6} = 7.4$, $J_{6,7} = 7.8$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3''), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3''), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3''), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3''), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3''), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3''), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3''), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3''), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3''), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3'')), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3'')), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3'')), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3'')), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3'')), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3'')), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3'')), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3'')), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3'')), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3'')), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3'')), $J_{2",3"} = 8.7$); 7.26 (c, 1H, CHN); 7.35 (d, 2H, H(3'')), $J_{2",3"} = 8.7$); 7.27 (d, 2H, H(3'')), $J_{2",3"} = 8.7$); 7.28 (d, 2H, 2H, 2H); 7.28 (d, 2H, 2H); 7.28 (d, 2H, 2H); 7.28 (d, 2H); 7.28 (d,

8.7); 7.43 (d, 1H, H(6'), $J_{5',6'} = 8.5$); 7.59 (d, 1H, H(7'), $J_{7',8'} = 9.0$); 7.76 (s, 1H, H(2')); 10.72 (s, 1H, OH). Found, %: C, 73.42; H, 5.85; N, 8.18. Calculated, %: C, 75.45; H, 5.70; N, 8.80. C₃₀H₂₇N₃O₃.

RESULTS AND DISCUSSION

Absorption Spectra of BPC-I

The absorption spectrum of BPC-I in a toluene solution (Fig. 1) indicates its presence mainly in the form of A^{E} with a small amount of A^{Kc} , because a shoulder at about 470 nm characteristic of the *cis*-ketone is observed [17]. The presence of the intense absorption band at about 470 nm in the absorption spectrum of BPC-I in methanol indicates the predominance of the form A^{Kc} in this solvent.



Photolysis of Model Compound III

Model azomethine III in a MeOH solution is mainly present in the form of *cis*-ketone $\mathbf{K}_{\mathbf{c}} (\lambda_{\text{max}} = 440$ and 460 nm) and in toluene in the form of *cis*-enol $\mathbf{E}_{\mathbf{c}}$ $(\lambda_{\text{max}} = 390 \text{ nm})$ with a high content of $\mathbf{K}_{\mathbf{c}}$ [11]. In the wavelength region \geq 430 nm, mostly $\mathbf{K}_{\mathbf{c}}$ form absorbs, which provides a possibility of its selective photoexcitation with light of 430 or 470 nm. Flash photoexcitation of III in toluene and methanol solutions with UV and visible light at the absorption bands of the E_c and K_c tautomers leads to the formation of one intermediate product, K_t , with maximums in the absorption spectra at 450 and 480 nm in toluene and methanol, respectively [11, 18]:



The decay kinetics of \mathbf{K}_t obeys the one-exponential law with the rate constants of 7.1×10^2 and $2.0 \ 2.0 \times 10^4 \ s^{-1}$ in toluene and methanol, respectively.

Photolysis of I in Methanol

BPC-I in a methanol solution occurs mainly in the *cis*-keto form A^{Kc} .

Upon flash photoexcitation of A^{Kc} with visible light, the formation of two intermediate products with absorption maximums at 470 and 600 nm is observed, the ratio of their intensities = 5.5 : 1, and the rate constants of their one-exponential decay $\approx 5.0 \times 10^4$ and 0.86 s⁻¹, respectively (Fig. 2). By analogy with the hybrid compounds studied by us earlier [9–11] and the data for the model azomethine II, they were assigned to the forms A^{Kt} and B^{Kc} , respectively. Upon photolysis of I in methanol with visible light, photoexcitation occurs predominantly of A^{Kc} , which leads to *cis*-*trans* isomerization in the hydroxyazomethine moiety and the formation of A^{Kt} without breaking the spiro bond C-O:





But since the two photochromic moieties in the molecule are in conjugation, breaking of the spiro bond also occurs with a relatively low yield, and a merocyanine

form, likely $\mathbf{B}^{\mathbf{Kc}}$, appears as a result of successive *cis*-*trans* isomerizations:





Fig. 1. Absorption spectra of BPC-I in (1) toluene and (2) methanol and model II in (3) toluene and (4) methanol.

Upon excitation of I with UV light, the same two intermediate products are observed, but their ratio dramatically changes toward increasing the portion of the merocyanine form (the ratio of their intensities = 1.33:1).

This behavior of BPC-I differs very much from that of BPC-IV studied by us earlier [9], in which spironaphthoxazine and azomethine moieties were also combined with conjugation between them, but these moieties were differently combined into a molecule (the spironaphthoxazine moiety was the "amine" part of the hydroxyazomethine fragment).



Fig. 2. Absorption spectra of intermediate products arising upon photolysis with visible light of I in methanol, measured (1) immediately and (2) in 50 μ s after the flash.



In a series of BPC-IV with different substituents $(R_1 = R_2 = H; R_1 = R_2 = Cl; R_1 = H, R_2 = Br; R_1 = H, R_2 = NO_2; R_1 = R_2 = NO_2)$, under the conditions of laser photolysis, the formation of three isomeric forms was observed: A^{Kt} , B^E , and B^{Kc} , characterized by different absorption spectra and decay constants: for $A^{Kt} - \lambda_{max} \approx 500 \text{ nm}, k = 1 \times 10^4 - 1 \times 10^5 \text{ s}^{-1}$; for $B^E - \lambda_{max} \approx 600 \text{ nm}, k = 0.5 - 1.6 \text{ s}^{-1}$; for $B^{Kc} - \lambda_{max} \approx 620 \text{ nm}, k = 14 - 17 \text{ s}^{-1}$. A strong dependence of the ratio of these intermediates on the nature of the solvent and the substituents in the azomethine moiety was observed, whereas a dependence of the ratio of the



Fig. 3. Absorption spectra of intermediate products arising upon photolysis with visible light of I in toluene, measured (1) immediately and (2) in 30 ms after the flash.

photolysis products on the wavelength of exciting light was not observed at all.

Photolysis of I in Toluene

Molecules of I in a toluene solution exist mainly in the A^{Ec} form, but the portion of the keto-form A^{Kc} remains noticeable, in contrast to BPC-IV, for which it was not observed in toluene [9].

Flash photoexcitation of I in toluene solutions with visible light results in the formation of two isomers: A^{Kt} and a product with the open form **B** in the ratio of 7.6 : 1, which were characterized by the absorption maximums at 470 and 590 nm (Fig. 3). The decay kinetics of these isomers obeys the first order law with the rate constants of 1.0×10^2 and 23 s^{-1} , respectively. We believe that in this case the merocyanine form B^{Kc} is also formed:



This conclusion is confirmed by calculations and optimization of the isomeric forms of the molecules in the ground state, performed by the DFT method, which showed that in this case the difference of the energies of the ground states of the structures \mathbf{B}^{Kc} and \mathbf{B}^{Kt} is 0.443 eV, which is almost 20 times higher than the energy kT at 0°C, and the difference of the energies of the ground states of the structures \mathbf{B}^{E} and \mathbf{B}^{Kc} is 0.443 eV.

0.1562 eV, which is almost 7 times higher than the energy kT at 0°C. Hence, it follows from thermodynamic considerations that in successive *cis-trans* isomerizations, the only form \mathbf{B}^{Kc} will be observed. Note that the source of \mathbf{B}^{Kc} can be not only the closed form \mathbf{A}^{Kc} present in toluene in a small amount, which can be converted into \mathbf{B}^{Kc} upon absorption of a quantum of light. The relatively high quantum yield of \mathbf{B}^{Kc}



Fig. 4. Projection of the structure of A^{Kt} optimized by the DFT method for compound I.

apparently indicates that \mathbf{B}^{Kc} appears also upon photoexcitation of the enol form \mathbf{A}^{E} of compound I. We may assume that \mathbf{B}^{Kc} is formed as a result of prototropic processes being a kind of thermodynamic relaxation of a common precursor of the forms **B**.

It is noteworthy that unlike the case of model compound III and BPC-IV studied earlier (the rate constant of about $4 \times 10^3 \text{ s}^{-1}$) [9], the A^{Kt} form of I has a very long lifetime (about 15 ms). The most likely reason for this fact is the stabilizing effect of the intramolecular hydrogen bond between the oxazine nitrogen atom and hydrogen of the NH group of the azomethine moiety (Fig. 4). The distance between covalently unbound H and N atoms in $A^{Kt} = 1.70$ Å, which in its value is close to analogous distances in six-membered cycles in $\mathbf{A}^{\mathbf{Kc}}$ (1.62 Å) and $\mathbf{A}^{\mathbf{E}}$ (1.57 Å), in which a hydrogen bond is known to exist, in contrast to the structure $\mathbf{B}^{\mathbf{Kt}}$ (1.95 Å), in which, according to the data on optimization of the structure of the molecule, there is no hydrogen bond due to a constrained non-planar structure.





Fig. 5. Absorption spectra of intermediate products arising upon photolysis with UV light of I in toluene, measured (*1*) immediately and (*2*) in 30 ms after the flash.

This stabilizing effect is not observed in methanol because of the interaction of molecules of I with the solvent.

The same two isomeric products are observed upon photolysis of I with UV light, but with the ratio of their signals of 2.13 : 1 (Fig. 5). The kinetic parameters of these processes coincide with the analogous values obtained upon photolysis with visible light.

In summary, the photolysis of I in both toluene and methanol leads to the formation of two intermediate products differing in absorption as a result of competitive photochromic processes: opening of the spiro cycle, ESIPT, and conversion of cis-ketone to transketone. The ratio of these products strongly depends on the nature of the solvent and the wavelength of exciting light. In particular, the portion of the merocyanine form increases about four times upon photolysis with UV light compared with that upon photolysis with visible light in toluene solution. The formation of the merocyanine form upon excitation with visible light is likely due to existence of conjugation between the photochromic moieties. The intramolecular hydrogen bond between the oxazine N atom and the proton of the NH group of the azomethine moiety leads to a very strong increase in the lifetime of the form A^{Kt} in toluene.

ACKNOWLEDGMENTS

This work was supported by the Russian Academy of Sciences under Presidium program no. 8 and by the Russian Foundation for Basic Research, project no. 13-03-00396a.

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Translated by A. Tatikolov