Photochemical & Photobiological Sciences

PAPER

Kinetics of photochemical reactions of biphotochromic compounds based on spironaphthopyran and enamine – conjugation effect

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A novel biphotochromic compound (BPC) with two photochromic fragments, namely spironaphthopyran and hydroxyazomethine, was synthesized and studied by nanosecond laser flash photolysis using the excitation wavelengths of 337, 430, 470 and 500 nm in methanol and toluene. The photoexcitation of BPC results in the formation of at least two colored transients. The first one is the merocyanine form B (the maximum in the absorption spectrum is near 600 nm and the lifetime is 0.1 and 0.05 s in methanol and toluene, respectively) due to the spiro–bond break followed by isomerization. The second one is the *trans*-keto form A^{Kt} (the maximum in the absorption spectra is near 480 nm and the lifetime is 0.1 and 5 ms in methanol and toluene, respectively) as a result of *cis*-enol or *cis*-keto tautomer transformations. The relative yields of B and A^{Kt} depends essentially on the wavelength of excitation. The form A^{Kt} is the key transient formed under excitation with the visible light, whereas its yield under excitation with UV light is comparable with that of B. The specific solvation by methanol molecules favors the spirocycle opening even under visible light excitation. The results obtained for novel BPC were compared with those for other BPC where the same fragments are combined in such a way that the form B is the major one under excitation with UV light whereas it virtually is not observed under visible light excitation. The difference in both BPC is discussed in terms of conjugation (π-coupling) between photochromic fragments.

1. Introduction

In recent years, bi- and multiphotochromic systems have been widely studied owing to their properties which can be attractive for practical purposes. One of their potential applications is the development of a new generation of materials for molecular electronics, such as molecular switching devices, molecular logic gates, *etc.*[1,2] The important features required for the design of such systems is a different photochemical behavior of the constituent elements implying the sensitivity to the wavelength of excitation and the molecular environment. There is a large diversity of structures described in the literature, using several switches connected through a variety of organic and inorganic structures.[3–12]

Nevertheless, effective multi-addressable and multi-active compounds remain a minority and the search for novel effective systems is an important task.

We have developed a synthetic route to a new type of biphotochromic compound on the basis of spironaphthoxazine linked to a substituted salicylideneaniline (SA).[13] The essential sensitivity to the excitation wavelength was detected for the triphotochromic compound of this series having the photochromic azobenzene substituent in the hydroxyazomethine fragment: only the merocyanine form was observed at the excitation by UV light, whereas three intermediates appeared after visible light excitation.[13]

In the present work, in order to proceed with our research further, we studied the spectral-kinetic properties of novel BPC composed of the naphthopyran and hydroxyazomethine (1,3-dihydro-8′-hydroxy-7′-(4-methylphenyliminomethyl-1,3,3-trimethylspiro[(2*H*)-indole-2,3′-[3*H*]-naphtho[2,1-*b*]pyran] (**1**) (Scheme 1, where 1A^E is (**1**) in the closed form of the spirocycle linked to the *cis*-enol form of the hydroxyazomethine fragment) in two solvents of different nature (toluene and methanol). The ns laser flash photolysis techniques with

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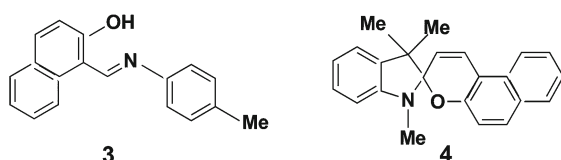*[b]N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Kosygina 4, Moscow 119991, Russia. E-mail: zaina@polymer.chph.ras.ru*
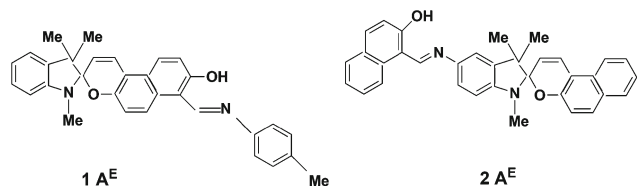
Scheme 1
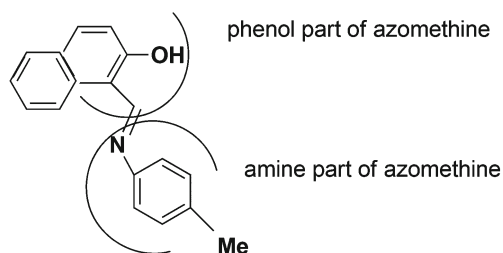
Scheme 2

Scheme 3

different wavelengths of excitation (337, 430, 470 and 500 nm) were used with the aim to vary the ratio between the intermediates (photoinduced isomeric species) of different nature.

The photochemical behavior of (1) is compared with that of the other BPC (2) – 1,3-dihydro-5-(2-hydroxy-1-naphthylmethylideneimino)-1,3,3-trimethylspiro[(2H)-indole-2,2'-(3H)-naphtho-[2,1-b]pyran] (Scheme 1, where 2A^E is (2) in the closed form of the spiro-cycle linked to the *cis*-enol form of the hydroxyazomethine fragment) studied earlier by us.[14,15]

The first structural difference between BPC (1) and (2) is that in (1) there is a conjugation between π-electronic systems of two photochromic fragments – spirocycle (naphthopyran) and hydroxyazomethine and in (2) the conjugation is expected to be between π-electronic systems of the indole and the hydroxyazomethine moieties. The second difference is that in (2) the indole fragment acts as the "aniline" part of the azomethine moiety whereas in (1) the naphthopyran fragment is a "phenol" type substituent (Scheme 2).

It was supposed that the comparison of the photochemical behavior of (1) and (2) can be useful to clarify the role of conjugation between different photochemical fragments in their selective photoexcitation. The compounds (3) and (4) (Scheme 3) were used as references representing the constituent fragments of the BPC (1) and (2).

2. Experimental

2.1. Materials

Toluene and methanol of spectroscopic grade and CDCl$_3$ were purchased from Aldrich and used as received. 1,3,3-Trimethyl-2-methylene-3H-indol purchased from Acros Organics was additionally purified by vacuum distillation. All other chemicals were reagent grade and used without additional purification.

2.2. Devices

The steady-state absorption spectra of solutions (using 10 mm quartz cells) were recorded in the UV and visible regions on a MultiSpec-1501 spectrophotometer.

The absorption spectra and kinetics of formation and decay of the intermediates were recorded in the time range ≥10 ns in the $400 \leq \lambda \leq 800$ nm spectral region by the nanosecond laser flash photolysis techniques with registration of electronic absorption.[13] A nitrogen laser (PRA LN 1000 with 1 ns pulse duration and a radiation wavelength of 337 nm, operating at ≤10 Hz), or a dye laser (PRA LN 102 with 0.5 ns pulse duration and a 430, 470 or 500 nm radiation wavelength) pumped by a nitrogen laser was used as an excitation source. The acquisition and averaging of kinetic curves were performed by the sequence of pulses followed at a repetition rate which was long enough to ensure the complete decay of the intermediates. The samples were sufficiently stable in the sense of photodegradation so that at least one hundred laser pulses can be used in experiments with a sample. The effect of molecular oxygen was found neither on the resistance of compounds nor on the decay kinetics of the intermediates. The data presented in this paper are average values obtained by processing at least ten kinetic curves under the same selected conditions. The absorbance at the excitation wavelength was adjusted to 10–40%. All measurements were carried out at ambient temperature.
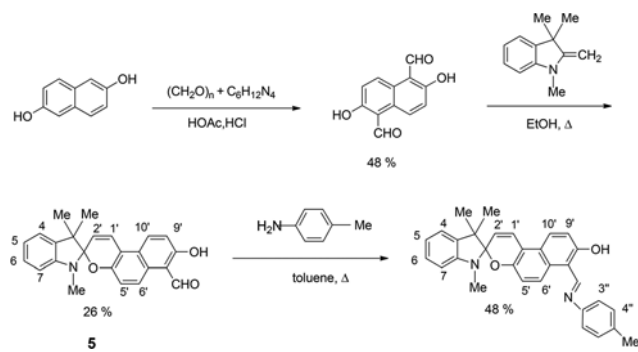
The ^{1}H NMR spectra were recorded using a Bruker WM 400 spectrometer, operating at 400 MHz, at 25 °C in CDCl$_3$. Elemental analyses were performed using an EuroVector analyzer Euro EA 3000.

2.3. Preparation of biphotochromic compounds

BPC (1) was synthesised according to Scheme 4. In short, we carried out the diformylation of the starting 2,6-dihydroxy-naphthalene by a modified Daff method,[16] and then 2,6-dihydroxy-1,5-naphthalenedicarboxaldehyde was condensed with 1 equivalent of 1,3,3-trimethyl-2-methylene-3H-indol giving 7'-formyl-8'-hydroxy-spironaphthopyran, which was condensed with *p*-toluidine. 1-(4-Methylphenyliminomethyl)-2-naphthol (3) was synthesized accordingly.[17]

BPC (2) was synthesized as described in ref. 18. The purity of the compounds was controlled by TLC, melting points, NMR (Bruker WM 400) and elemental analysis data.

1,3-Dihydro-7'-formyl-8'-hydroxy-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]naphtho[2,1-b][1,4]pyran] (5). The solution of 1,3,3-trimethyl-2-methylene-3H-indol (0.9 ml, 5 mmol) in 10 ml of

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Scheme 4

dry dioxane was added dropwise to a solution of 2,6-dihydroxy-1,5-naphthalenedicarboxaldehyde (4 g, 18.5 mmol) in 200 ml of dry dioxane and refluxed with stirring for 5.5 h. Then, the mixture was cooled to room temperature and the excessive dialdehyde was filtered off. The solvent was evaporated and the residue was separated from a concomitant dispiro-compound using column chromatography on SiO_2 with benzene as an eluent. The fractions with the desired product (R_f 0.6 in chloroform) were combined, the solvent was evaporated, and 5.37 g (26%) of a green precipitate, mp 240 °C (benzene), was obtained.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm), 1.22, 1.34 (both s, 3 H each, $C(CH_3)_2$); 2.75 (s, 3H, NCH_3); 5.88 (d, 1H, H(2′), $^3J_{1',2'}$ 10.5 Hz); 6.55 (d, 1 H, H(7), $^3J_{6,\,7}$ 7.9 Hz); 6.88 (t, 1 H, H(5), $^3J_{4,\,5} = {}^3J_{5,\,6}$ 7.4 Hz); 7.10 (d, 1 H, H(4), $^3J_{4,\,5}$ 7.4 Hz); 7.14 (d, 1 H, H (5′), $^3J_{5,\,6}$ 9.4 Hz); 7.20 (1H, H(6′)); 7.20 (1H, H(9′)); 7.54 (d, 1 H, H(1′) $^3J_{1',2'}$ 10.5 Hz); 8.15 (d 1H, H(10′), $^3J_{9',10'}$ 9.2 Hz); 8.25 (d, 1H, H(6′), $^3J_{5',6'}$ 9.4 Hz); 10.75 (s, 1H, C(O)H); 12.89 (s, 1H, OH).

Found: C, 77.53; H, 5.81; N, 3.88. $C_{24}H_{21}NO_3$ requires C, 77.61; H, 5.70; N, 3.77%.

1,3-Dihydro-8′-hydroxy 7′-(4-methylpheniliminomethyl)-1,3,3-trimethylspiro[2H-indole-2,3′-[3H]naphtho[2,1-b][1,4]pyran] (BPC 1). A solution of 95 mg (0.256 mmol) 1,3-dihydro-7′-formyl-8′-hydroxy-1,3,3-trimethylspiro[2H-indol-2,3′-[3H]naphtho-[2,1-b][1,4]pyran] (5) and 27.5 mg (0.256 mmol) of *p*-toluidine in 10 ml toluene was refluxed for 6 h. Then the mixture was cooled to room temperature and filtered. The solvent was evaporated and the residue was purified by preparative TLC on SiO_2 with a 19 : 1 benzene–acetone mixture as an eluent. The photochromic strip with R_f 0.7 was collected, the product desorbed by a 5 : 1 chloroform–acetone mixture, and the solvent was evaporated using a rotary evaporator to give 0.57 g (yield 48%) of an orange precipitate, mp 282 °C (benzene–acetone mixture).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.22, 1.34 (both s, 3 H, $C(CH_3)_2$); 2.40 (s, 3H, CH_3); 2.75 (s, 3H, NCH_3); 5.85 (d, 1H, H(2′), $^3J_{1',2'}$ 10.5 Hz); 6.54 (d, 1H, H(7), $^3J_{6,7}$ 7.7 Hz); 6.87 (t, 1H, H(5), $^3J_{4,5}$ 7.0 Hz, $J_{5,6}$ 7.4 Hz); 7.10 (d, 1H, H(4), $^3J_{4,5}$ 7.0 Hz); 7.18–7.22 (3H, H(6), H(9′), CHN); 7.25 (2H, H(2″)); 7.26 (2H, H(3″)); 7.04 (d, 1H, H(5′), $^3J_{5',6'}$ 9.3 Hz); 7.55 (d, 1H, H(1′), $^3J_{1',2'}$

10.5 Hz); 7.94 (d, 1H, H(10′), $^3J_{9',10'}$ 9.2 Hz); 8.09 (d, 1H, H(6′), $^3J_{5',6}$ 9.4 Hz); 9.32 (s, 1H, OH).

Found: C, 80.62; H, 6.34; N, 5.82. $C_{31}H_{28}N_2O_2$ requires C, 80.84; H, 6.13; N, 6.08%.

2.4. Abbreviations

The following symbols are used for marking the state of the components of BPC molecules. The capital letters A and B designate the initial closed and the final opened colored spirocycle fragment states, respectively. The upper case indexes E^c, E^t, K^c and K^t denote the *cis*- and *trans*-enol, *cis*-keto- and *trans*-keto states of the hydroxyazomethine fragment, respectively. The same abbreviations are used for the corresponding model compounds.

3. Results and discussion

3.1. Ground state absorption

The UV-vis absorption spectra of (**1**) and (**3**) in methanol and toluene are presented in Fig. 1. The model (**4**) in the A form absorbs in the UV region.[19] The absorption spectrum of (**3**) in toluene is characterized by the long-wavelength maximum at 380 nm and the relatively weak ones at 440 and 460 nm (Fig. 1, curve 4). It is well-known for anil-type compounds that their molecules may exist in E^c and K^c tautomeric forms (Scheme 5) depending on the molecular structure and the environmental conditions.[20–26] The E^c absorbs in near UV and it is usually more stable in aprotic solvents. The model (**3**) in toluene exists for the most part in E^c (maximum at 380 nm) although the presence of a small amount of K^c (maxima at 440 and 460 nm) is observed (approximately 10% if to assume the equality of the corresponding extinction coefficients).

The intensive absorption bands with a maxima at 440 and 460 nm are observed for (**3**) in methanol (Fig. 1, curve 3) indicating that (**3**) exists in methanol solution mainly in the K^c form (at least 70%). This difference between the absorption of (**3**) in toluene and methanol should be attributed to the specific solvation effect rather than to the polarity. Indeed the
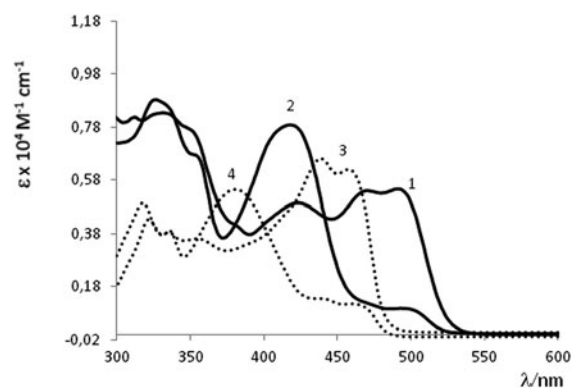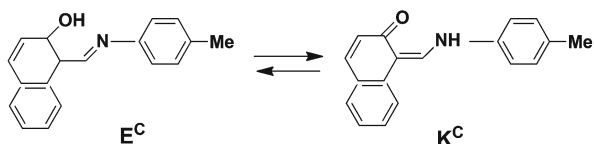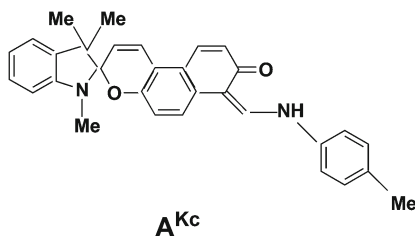

Fig. 1 UV-vis absorption spectra of PBC (**1**) (curves 1, 2) and model (**3**) (curves 3, 4) in toluene (curves 2, 4) and methanol (curves 1, 3) solutions.

Scheme 5 Tautomeric forms of *N*-naphthylsalicylideneimine molecules.

Scheme 6

Fig. 2 Visible absorption spectra of the intermediates produced by the 337 nm laser flash photolysis of (**3**) – (spectrum 1) and (**4**) – (spectrum 2) in methanol solution in 0.05 μs after the laser pulse.

Scheme 7 Photochromic process in spironaphthopyran (**4**).

absorption spectrum of (**3**) in acetonitrile is similar to that in toluene (the contribution of K^c is 20%).

The long-wavelength parts of the spectrum of (**1**) are considerably shifted to the longer wavelength with respect to that of the reference compound (**3**) in both solvents (Fig. 1, spectra 1 and 2). The absorption at 600 nm of the open B form was not observed, showing that (**1**) exists in the closed form A of spirocycle fragments in both solvents. The absorption of A^{Kc} (Scheme 6) in methanol (maxima at 470 and 490 nm) is pronounced as compared with that of A^{Ec} (maximum at 420 nm) (see Fig. 1, curve 1). The estimated contribution of A^{Kc} is at least 50%. The absorption of A^{Kc} (**1**) in toluene in the region ≥470 nm is relatively weak (see Fig. 1, curve 2, the estimated contribution of A^{Kc} is 10%). Very similar regularities were found for the solvent effect on the spectrum of BPC (**2**).[18] It is worthwhile mentioning that the arrangement and locations of the relevant bands in the spectra of both (**1**) and (**2**) resemble each other rather well. The equilibrium between *cis* and *trans* forms in the ground state was not found for both compounds on the basis of the UV-vis absorption spectra investigation as it is the case for the most of anil-type compounds.[20–22]

3.2. Intermediates of model compounds produced by excitation with UV and visible light

The spectra and kinetics of the intermediates obtained by the laser flash photolysis of the model compounds (**3**) and (**4**) representing the constituent fragments of BPC are required for the recognition of the BPC intermediate structure. It was shown earlier that the photoexcitation of (**4**) in methanol (Fig. 2, spectrum 2) and toluene by UV light (337 nm) produces in the time interval ≥10 ns the only one intermediate – merocyanine form B – (Scheme 7) with the absorption maximum at 560 and 550 nm and first order decay rate constant *k* = 14 and
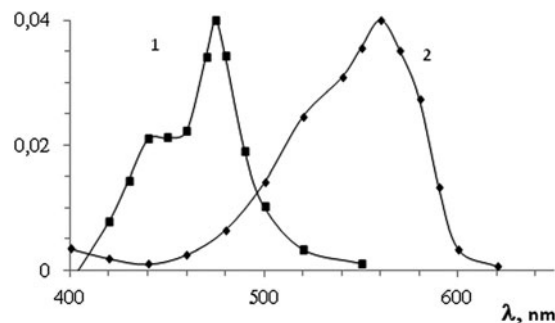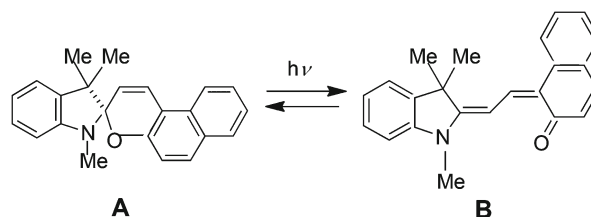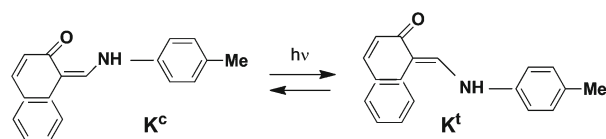
42 s^{-1} respectively.[18] Photoexcitation of (**4**) by the visible light has no result since it does not absorb at those wavelengths.[19]

The photoexcitation of (**3**) in both solvents with UV or visible light (except 500 nm where (**3**) practically does not absorb) results in the formation of a single intermediate with a characteristic absorption spectrum with a maxima at 450 and 480 nm in toluene and methanol (Fig. 2, spectrum 1), respectively.[18] Its decay kinetics is first order with the rate constants equal to 9.9×10^2 and 9.5×10^3 s^{-1} in toluene and methanol, respectively. We have identified this intermediate as *trans*-keto form K^t, which was formed due to the photoisomerization of K^c (Scheme 8) or proton transfer coupled with isomerization after the photoexcitation of E^c. The K^c decay is accelerated significantly in the hydrogen-bonding environment. Similar results were found for unsubstituted 1-(phenyliminomethyl)-2-naphthol[18] and *N*,*N*-bis-(salicylidene)-*p*-phenylenediamines[22] demonstrating that one and the same keto-tautomer is created either from the enol form *via* the excited state proton transfer coupled with isomerization or *via* the direct photoisomerization of the keto-form. The dynamics

Scheme 8 *cis*-Ketone to *trans*-ketone photoisomerization of model compound (**3**).

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of the K^t formation process is in the subpicosecond time scale as it is for spiro-compounds.[15,21,22,27–31]
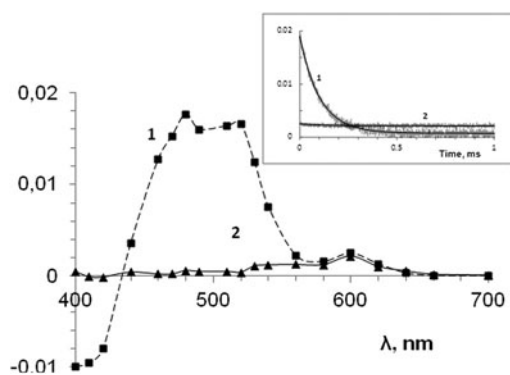
3.3. Intermediates of BPC (1) produced by excitation with UV and visible light in methanol

The photoexcitation of BPC (1) by visible light 500 nm (where only A^{Kc} absorbs) leads immediately after the laser pulse to the formation of two intermediates whose absorption spectra contain characteristic bands with maxima at 480, 520 and 600 nm (Fig. 3, spectrum 1). The intermediate with absorption at 480–520 nm is relatively short-lived (first order rate constant $(9.7 \times 10^3 \text{ s}^{-1})$ and very similar to that measured for model (3), whereas the one with absorption at 600 nm is long-lived (Fig. 3, spectrum 2, first order rate constant (11 s^{-1})) and very similar to that found for model (4).
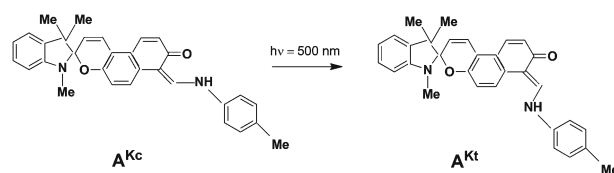
On the basis of flash-photolysis data for the model compounds (3) and (4), the relatively short lived intermediate can be identified as A^{Kt}. The long-lived one seems to be B^{Kc} since there is no visible change in absorption at $\lambda \leq 500$ nm. The form A^{Kt} is appeared as a result of ketone *cis–trans* photo-isomerization in the hydroxyazomethine fragment according to Scheme 9 and B^{Kc} arises *via* spiro-bond cleavage and corresponding isomerization according to Scheme 10. The yield of B^{Kc} was estimated to be 4% relative to that of A^{Kt} assuming that the ratio of the corresponding molar absorption coefficients of B and A^{Kt} at the maxima is 3.[17]

The same transients with the same yields were obtained under the photolysis with light 470 and 430 nm, where A^{Ec} also absorbs. Therefore, A^{Kt} is formed *via* the excited state proton transfer coupled with isomerization as well. The yield of A^{Kt} in comparison with that of Kt (3) was estimated to be 80%.
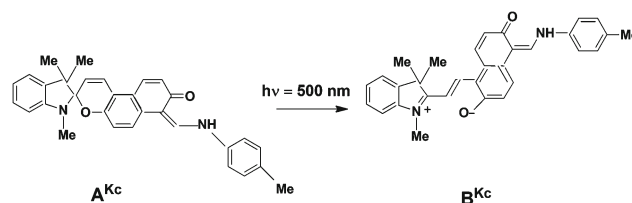
Laser photoexcitation of (1) by UV light (337 nm) yields the same two intermediates A^{Kt} and B^{Kc}, but the yield of merocyanine form B^{Kc} increases 2.5 times relative to that of A^{Kt}. The yields of A^{Kt} and B^{Kc} as compared with those of Kt (3) and

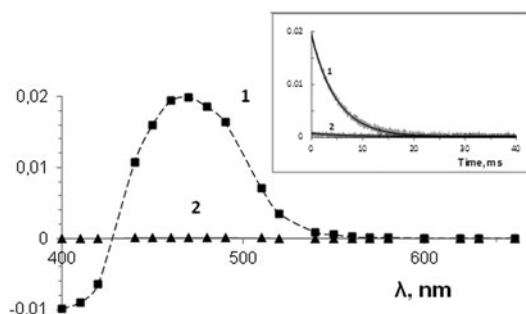**Scheme 9** Photochromic process in hydroxyazomethine fragment of BPC (1).

Scheme 10 Spiro-bond cleavage and formation of the merocyanine form B from A^{Kc} in BPC (1).

B (4) measured for the samples with the same absorption at 337 nm were estimated to be 60 and 2%, respectively.

The interconversion of A^{Kt} and B^{Kc} was not observed in the time interval studied. Therefore, two photoprocesses in BPC (1) – *cis–trans* isomerization of the azomethine fragment and merocyanine formation from spirocycle – occur simultaneously in the course of relaxation of singlet excited states.[15]

3.4. Intermediates of BPC (1) produced by excitation with UV and visible light in toluene

Pulse photoexcitation of (1) in toluene with visible light results in the formation of the only single isomer A^{Kt} with the absorption maximum at 470 nm (Fig. 4) and the first-order decay rate constant being $2.0 \times 10^2 \text{ s}^{-1}$. The yield of A^{Kt} in comparison with that of Kt (3) was estimated to be 80% as it is in methanol.

Fig. 3 Visible absorption spectra of the intermediates produced by the 500 nm laser flash photolysis of BPC (1) in methanol solution in 0.05 μs (spectrum 1) and 1 ms (spectrum 2) after the laser pulse. Insert – decay kinetics of the intermediates, observed at 480 nm (1) and 600 nm (2) under flash photolysis of (1) with 500 nm light in MeOH.

Fig. 4 Visible absorption spectra of the intermediates produced by the 500 nm laser flash photolysis of BPC (1) in toluene solution in 0.05 μs (1), and 30 ms after the laser pulse (2). Insert – decay kinetics of the intermediates, observed at 480 nm (1) and 600 nm (2) under laser flash photolysis of BPC (1) with 500 nm light in toluene.

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However, a small amount of B^{Ec} is observed (maximum at 580 nm, first-order decay rate constant 18 s^{-1}) under the UV light photoexcitation in addition to A^{Kt}. The estimated yield of B^{Kc} relative to that of A^{Kt} (assuming that the ratio of the corresponding molar absorption coefficients of B and A^{Kt} at the maxima is 3, ref. 17) was found to be 3%, that is three times smaller than that in methanol. The absorption spectrum of B^{Ec} (**1**) has a maximum which is slightly shifted to the long-wavelength region with respect to that of form B of the model compound (**4**).

3.5. The comparison between the photochemical behaviors of BPC (**1**) and (**2**)

Pulse photoexcitation of BPC (**2**) with the visible light in toluene as well as in methanol results in *cis–trans* isomerization of the azomethine fragment whereas the form B formation was not found at all.[18] The rise time of the precursor of *trans* isomers (corresponding nonrelaxed singlet excited states) was 0.2 ps.[15] Since the excitation with visible light corresponds to the electronic transitions localized in the hydroxynaphthalydeneimine moiety of (**2**), which is insufficiently coupled with the spiro fragment, then the spiro bond rupture is inefficient in the time interval of the localized singlet excited state relaxation. In the case of BPC (**1**), the more efficient corresponding coupling results in the formation of a small amount of form B even under visible light excitation. It is worthwhile mentioning that the hydrogen bond formation between (**1**) and methanol favors the spiro bond scission in (**1**) probably due to the decrease of the corresponding energy required and/or the retardation of hydroxyazomethine fragment isomerization.

On the one hand, photoexcitation of BPC (**2**) with UV light results in the formation of form B as a major product in both solvents.[18] The relatively poor coupling between spiro and hydroxynaphthalydeneimine parts of (**2**) ensures an opportunity of spiro bond break in the course of high singlet excited state relaxation (the rise time of the B precursor after UV excitation of (**2**) was 0.15 ps ref. 15) rather than it would be relaxed to the low-lying singlet excited states localized on the hydroxynaphthalydeneimine fragment. On the other hand, most parts of the high singlet excited states of (**1**) relax principally to the low-lying singlet excited states localized in the azomethine part of (**1**) due to the efficient coupling and the form B still remains the minor product even under UV excitation of (**1**).

4.   Conclusion

Our previous studies were directed towards the search for biphotochromic compounds whose photochemical behavior would be dependent on the wavelength of excitation light.[13,14] We had synthesized two series of BPCs, whose molecules combine the spirocycle and hydroxyazomethine fragments in different ways in order to modify the conjugation (π-coupling) between photochromic fragments. No excitation wavelength effect was observed in the first series of compounds with conjugation between the fragments, however, one compound from

the second series, namely BPC (**2**), demonstrated a pronounced excitation wavelength effect.[18] In order to gain insight into the effect of conjugation on the photochemistry of biphotochromic compounds, we have synthesized novel BPC (**1**) with the other type of the connection between spirocycle and hydroxyazomethine fragments. The coupling in compound (**1**) seems to be somewhat intermediate between those insensitive and considerably sensitive to the wavelength of excitation. The specific solvation effect was found. The hydrogen bonding with methanol molecules favors the spirocycle opening even under visible light excitation whereas it was not observed in toluene. However the spirocycle opening in (**1**) remains the minor pathway even under UV light excitation while the *cis–trans* photoisomerization coupled to the excited state intramolecular proton transfer in hydroxyazomethine fragment is the basic process.

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