Synthesis and kinetics of photochemical reactions of novel bifunctional salicylideneiminospironaphthoxazines

N. L. Zaichenko,[a] P. P. Levin,[b] I. R. Mardaleishvili,[a] A. I. Shienok,[a] L. S. Kol´tsova,[a] O. Yu. Os´kina,[a] and A. S. Tatikolov[b]*

[a]*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 ul. Kosygina, 119991 Moscow, Russian Federation. Fax: +7 (495) 137 8284. E-mail: zaina@polymer.chph.ras.ru*

[b]*N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 4 ul. Kosygina, 119991 Moscow, Russian Federation. Fax: +7 (495) 137 4101. E-mail: levinp@sky.chph.ras.ru*

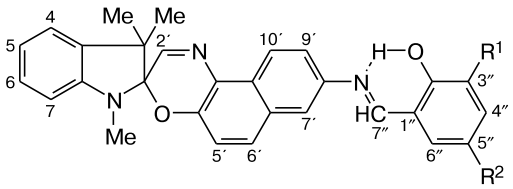
A series of novel photochemically bifunctional compounds was synthesized. Their molecules combine the photochromic spironaphthoxazine fragment with a salicylideneimine fragment containing various substituents. The latter can undergo intramolecular proton transfer in the electron-excited state. Photolysis products of three types, namely, open merocyanine forms having an enol or *cis*-keto form of the salicylideneimine moiety and a *trans*-keto form with the closed spiro fragment, were detected using pulse photolysis technique in toluene and methanol solutions. The spectral kinetic characteristics of the photoproducts were studied, and their quantum yields were measured. The effects of substituents in the salicylideneimine fragment and the solvent nature were discussed.

Key words: synthesis, photobifunctional compounds, photochromism, spironaphthoxazine, proton transfer, pulse photolysis, NMR spectroscopy.

Photochromic compounds experiencing reversible phototransformations, which are accompanied by changes in color and other properties, attract considerable attention because they can be used in diverse areas. These are the creation of automated photomodulators,[1] detecting media for optical memory,[2,3] molecular logical devices,[4,5] protein activity photoswitchers,[6] and others.

Hybrid molecules containing different fragments, each of which can undergo photochemical transformations mainly related to ring opening,[7—9] have recently been synthesized in order to extend the functional properties of photochromic compounds. In the photobifunctional compounds developed by us, the hybrid molecules contain two functionally different fragments in which light can induce two different photoprocesses, for example, photocyclization or ring photo-opening, proton transfer, luminescence, charge transfer, *etc.*

For the purpose to investigate photochemistry of bifunctional compounds,[10,11] namely, to study the effects of substituents and medium on the efficiency of formation of various products and their decay, we synthesized for the first time a series of new bifunctional compounds **1**—**5**, whose molecules include the salicylideneimine fragment with various substituents in addition to the spironaphthoxazine fragment.



1—5

$R^1 = R^2 = H$ (**1**); $R^1 = R^2 = Cl$ (**2**); $R^1 = H$, $R^2 = Br$ (**3**); $R^1 = H$, $R^2 = NO_2$ (**4**); $R^1 = Br$, $R^2 = NO_2$ (**5**)

The photochromic process including the photodissociation of the $O—C_{spiro}$ bond in initial closed form **A** to form intermediate *cis*-cisoid isomer **X** followed by *cis*—*trans*-isomerization to colored merocyanine form **B** occurs in spironaphthoxazines upon irradiation. It has earlier[12] been found by femtosecond laser absorption spectroscopy that *cis*-cisoid isomer **X** is formed in spironaphthoxazines within ~300 fs, whereas colored form **B** is produced within 16 ps.

It is known[13—17] that salicylideneanilines (SA) exist in solution in two tautomeric forms: *cis*-ketone and *cis*-enol. The ratio of these tautomers depends on the temperature, solvent, and nature of substituents in SA. The enol form predominates in nonpolar solvents at room temperature, whereas the presence of the *cis*-keto form is observed in

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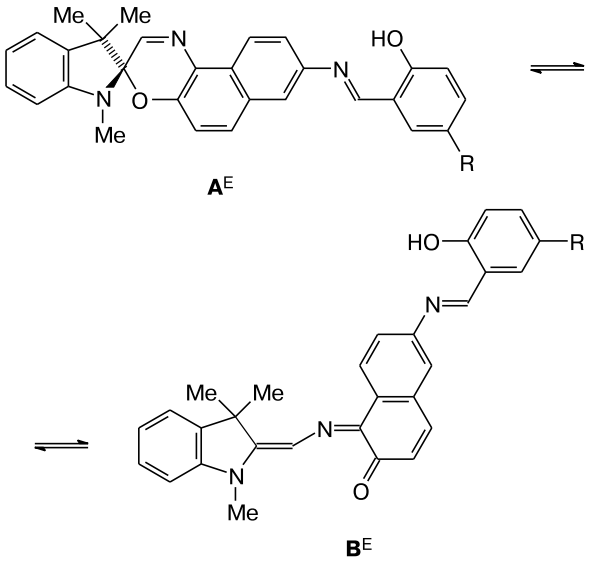
polar hydroxyl-containing solvents (such as alcohols). The introduction of electron-withdrawing substituents into the aniline part of the SA molecule shifts equilibrium to the enol form in any solvent,[15] whereas the same substituents introduced into the phenol part of the SA molecules give an opposite effect.[13]

Photoirradiation of SA can induce reversible photochemical transformations, namely, transition from the enol to keto form due to excited state intramolecular proton transfer (ESIPT). The primary ESIPT process occurs within the time less than 80 fs to form intermediate forms, which are further transformed into the relatively stable *trans*-isomer ($\mathbf{A}^{Kt}$) through rotation of the fragments of the molecule about the C(1″)—C(7) bond within ~11 ps (see Refs 14 and 18). The quantum yield of the *trans*-keto form for 2-hydroxynaphthylidene-1′-naphthylamine in methylcyclohexane[17] and *N*,*N*′-bis(salicylidene)-*p*-phenylenediamine in acetonitrile[16] is ~30%. It should be mentioned that upon photoexcitation the *cis*-keto form is not transformed into the *trans*-keto form.[13]

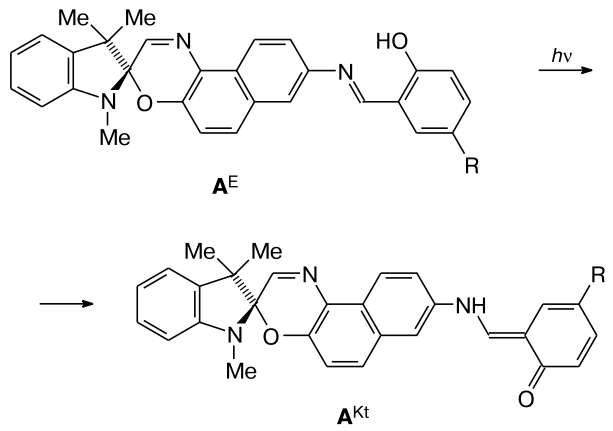
For photochemically bifunctional compounds (PBC) **1**—**5** studied in this work one can expect the both described above processes to occur: the photochromic process with O—C_{spiro} bond cleavage followed by *cis*—*trans*-isomerization in the spironaphthoxazine fragment of the molecule (Scheme 1) and ESIPT in the salicylideneimine fragment (Scheme 2).

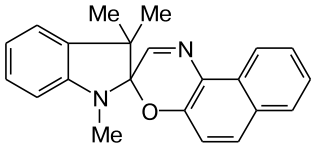
The absorption spectra and decay kinetics of products of the two described above processes that occur in the PBC molecules, namely, in open form **B**, whose formation completes the photochromic process in the spironaphthoxazine fragment, and *trans*-keto form $\mathbf{A}^{Kt}$ appeared due to the ESIPT in the salicylideneimine fragment and its isomerization, were studied by nano- and microsecond pulse photolysis technique. Unsubstiuted spironaphthoxazine **6** was also studied as a model for comparison.

Scheme 1



Scheme 2





6

The ^{1}H NMR spectra (see Experimental) show that in chloroform all compounds under study exist in enol form $\mathbf{A}^{E}$ (within the accuracy of the NMR method), and the single enol form is observed in toluene for unsubstituted PBC **1** and PBC **4** containing strong withdrawing substituents. This is indicated by the ^{1}H NMR signal at $\delta \approx 9.3$—14 from the OH group attached to the aromatic ring, whereas the signal of protons of the amino group (which should be observed in the ^{1}H NMR spectrum of the keto isomer) attached to the aromatic ring lies at δ 2.5—5.0 (Ref. 19). The state of the substituent in position 2″ of the salicylideneimine fragment is indicated by the chemical shift of the adjacent H(3″) proton. In the case of the enol form, the electron-releasing OH group should exert the upfield shift of the signal of the H(3″) proton compared to the signals of other proton of the aromatic ring. In the case of the keto isomer, the keto group, being itself a electron-withdrawing substituent, should produce a downfield shift for this signal. The observed upfield (relatively to other aromatic protons) shift of the signal of the H(3″) proton unambiguously indicates the electron-donor character of the adjacent group and, hence, that the compounds exist in enol form $\mathbf{A}^{E}$. Unfortunately, NMR spectroscopy does not allow one to establish the form of these compounds in an ethanolic solution because of too low solubility of the latter in alcohols.

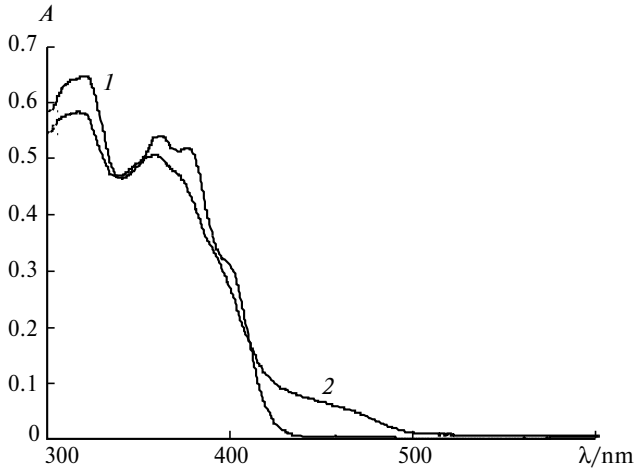


Fig. 1. Absorption spectra of compound **4** in toluene (*1*) and MeOH (*2*) ($C = 5.6 \cdot 10^{-5}$ mol L^{-1}, $l = 0.5$ cm).

The absorption spectra of compound **4** in toluene and MeOH are shown in Fig. 1. The absorption spectra of other PBC in the region of wavelengths shorter than 400 nm resemble the spectrum of compound **4** and have absorption band maxima at 320—370 nm. The exception is the most informative (from the viewpoint of existence of the *cis*-keto form) longwave-length part of the spectrum, because this is the region that allows one to judge about keto—enol equilibrium in the salicylideneaniline fragment of the molecule. It is known[13–17] that in the absorption spectra of SA the absorption band with a maximum at 370 nm corresponds to the enol form and that with a maximum at 450 nm belongs to the *cis*-keto form. Almost no band at 450 nm is observed in the absorption spectra of the PBC studied in toluene solutions. This band is noticeable only in the spectra of nitro-containing compounds **4** and **5** in MeOH, whereas it is nearly absent from the spectra of other PBC in MeOH. Thus, in alcoholic solutions the compounds studied mainly exist in enol form $\mathbf{A}^{E}$, whereas the fraction of *cis*-keto form $\mathbf{A}^{Kc}$ grows with an increase in the acceptor properties of the substituents in the SA fragment of the molecule, but it is relatively low even for the compounds containing nitro groups.

Pulse photoexcitation of model compound **6** in toluene and methanol solutions in the time interval ≥10 ns produces the only photoreaction product: merocyanine form **B** possessing the characteristic absorption spectrum with a maximum at ~600 nm. The decay kinetics for form **B** obeys a monoexponential law. The obtained decay rate constants of form **B** ($k_{\mathbf{B}}$) for compound **6** coincide with known published data[20] (Table 1).

Pulse photoexcitation of the PBC in toluene in the time interval ≥10 ns produces two photoproducts (the exception is compound **5**). A short-living product (which is not observed in the case of compound **5**) also appears in addition to the relatively long-living merocyanine form **B** with $\lambda_{max} = 600$ nm analogous to form **B** for compound **6**. The spectrum of the short-living product with $\lambda_{max} = 500$ nm corresponds to the known absorption spectra[16,17] of *trans*-keto form $\mathbf{A}^{Kt}$.

The quantum yield of form **B** ($\varphi_{\mathbf{B}}$) for PBC **1** is substantially lower than that for compound **6** because of the efficient competition with ESIPT (Table 2). The quantum yield of form $\mathbf{A}^{Kt}$ for PBC **1** is somewhat lower than $\varphi_{\mathbf{B}}$. It should be mentioned that the total quantum yield of two colored forms ($\varphi_{\mathbf{A}^{Kt}} + \varphi_{\mathbf{B}}$) for **1** is close to $\varphi_{\mathbf{B}}$ for model compound **6** (see Table 2).

The introduction of halogen atoms into the phenyl ring of the salicylideneimine fragment (compounds **2** and **3**) exerts almost no effect on the yield of forms **B** and $\mathbf{A}^{Kt}$ in toluene, whereas the introduction of the nitro group (compounds **4** and **5**) increases the total yield of form **B** due to its stabilization. In this case, the yield of $\mathbf{A}^{Kt}$ decreases sharply (see Table 2). It is known[20] that the introduction of electronegative substituents into the naphthalene fragment of compound **6** increases the quantum yield of form **B** due to its stabilization. On the contrary, electronegative substituents in the phenyl ring of SA prevent the formation of the "twisted" keto state or the charge-transfer state, which is the precursor of $\mathbf{A}^{Kt}$ (see Ref. 21).

Table 1. Rate constants for decay of the colored forms

Compound	**B**			$\mathbf{A}^{Kt}$			
	Toluene	MeOH		Toluene		MeOH	
	$k_{\mathbf{B}^E}$	$k_{\mathbf{B}^E}$	$k_{\mathbf{B}^K}$	$k_{1,\mathbf{A}^{Kt}}$	$k_{2,\mathbf{A}^{Kt}} \cdot 10^9$	$k_{1,\mathbf{A}^{Kt}}$	$k_{q,\mathbf{A}^{Kt}} \cdot 10^9$
	s^{-1}			$/s^{-1}$	/L mol^{-1} s^{-1}	$/s^{-1}$	/L mol^{-1} s^{-1}
1	1.6	0.54	15	4000	3.5	8800	0.04
2	0.57	0.38	16	1000	1.5	28000	0.36
3	1.2	0.54	17	3500	1.8	14000	0.31
4	0.74	0.78	16	520	0.98	93000	0.87
5	0.51	0.58	14	—	—	—	—
6	0.54	0.67	—	—	—	—	—

Table 2. Quantum yields (φ) of the colored forms

Compound	**B**			$\mathbf{A}^{Kt}$		Total yield of colored forms	
	Toluene	MeOH		Toluene	MeOH	Toluene	MeOH
	$\varphi_{\mathbf{B}^E}$	$\varphi_{\mathbf{B}^E}$	$\varphi_{\mathbf{B}^K}$	$\varphi_{\mathbf{A}^{Kt}}$	$\varphi_{\mathbf{A}^{Kt}}$	$\varphi_{\mathbf{B}^E} + \varphi_{\mathbf{A}^{Kt}}$	$\varphi_{\mathbf{B}^E} + \varphi_{\mathbf{B}^K} + \varphi_{\mathbf{A}^{Kt}}$
1	0.076	0.040	0.025	0.10	0.12	0.18	0.18
2	0.071	0.0063	0.040	0.096	0.082	0.17	0.13
3	0.076	0.0097	0.055	0.11	0.097	0.19	0.16
4	0.28	0.0076	0.068	0.021	0.013	0.3	0.09
5	0.28	0.0029	0.051	—	—	0.28	0.054
6	0.23	0.19	—	—	—	0.23	0.19

The decay kinetics of form **B** in the case of PBC **1** obeys a monoexponential law (Fig. 2), and the $k_{\mathbf{B}}$ value for form **B** of compound **1** (see Table 1) is appreciably higher than the corresponding value for model compound **6**, which can be due to the weak electron-donor character of the salicylideneimine substituent in the spironaphthoxazine fragment.[20]

The introduction of electronegative substituents into the salicylideneimine fragment elongates the lifetime (decreases the decay rate constants) of form **B** in toluene solutions, indicating a decrease in the electron-donor properties of this fragment.

The lifetime of form $\mathbf{A}^{Kt}$ in toluene is substantially (by three orders of magnitude) shorter than that of form **B**. The lifetimes about 1 ms are typical of the colored forms of salicylideneanilines and related compounds in both solutions and crystalline state.[22–24] The decay kinetics of $\mathbf{A}^{Kt}$ (Fig. 3) obeys a law of the mixed first and second orders, because two processes occur: *cis—trans*-isomerization followed by intramolecular backward proton transfer and bimolecular proton exchange between $\mathbf{A}^{Kt}$, which finally results (with some probability depending, most likely, on the ratio of acid-base properties of the fragments containing the N and O atoms) in the formation of the *trans*-enol forms. The corresponding rate constants of the first and second order ($k_{1,\mathbf{A}^{Kt}}$ and $k_{2,\mathbf{A}^{Kt}}$) are listed in Table 1 (the $k_{2,\mathbf{A}^{Kt}}$ value was calculated from the experimental $k_{2,\mathbf{A}^{Kt}}/\varepsilon l$ values, where l is the optical path length equal to 1 mm, and ε is the molar absorption coefficient of $\mathbf{A}^{Kt}$ accepted to be $1.5 \cdot 10^4$ L mol^{-1} cm^{-1} at the band maximum about 500 nm).[25] The $k_{2,\mathbf{A}^{Kt}}$ value for **1** is close to the rate constant of a diffusionally controlled reaction ($k_d = 8RT/3\eta \approx 1 \cdot 10^{10}$ L mol^{-1} cm^{-1}, where η is viscosity), as should be expected for the proton exchange reaction. The introduction of electronegative substituents into the salicylideneimine fragment is accompanied by a decrease in the decay rate constants for $\mathbf{A}^{Kt}$ *via* both routes due to the stabilization of the proton-transferred forms.

The pulse photoexcitation of PBC **1** in methanol in the time interval ≥10 ns produces three photoproducts with λ_{max} = 500, 600, and 620 nm (Fig. 4). A considerably shorter-living merocyanine form $\mathbf{B}^{Kc}$ (the corresponding rate constants $k_{\mathbf{B}E}$ and $k_{\mathbf{B}K}$ are given in Table 1) is observed in addition to long-living form **B** analogous in spectral kinetic characteristics to form **B** in toluene with λ_{max} = 600 nm (merocyanine form with the enol salicylideneimine fragment $\mathbf{B}^E$). This $\mathbf{B}^{Kc}$ form has a substantially broader absorption spectrum shifted to the long-

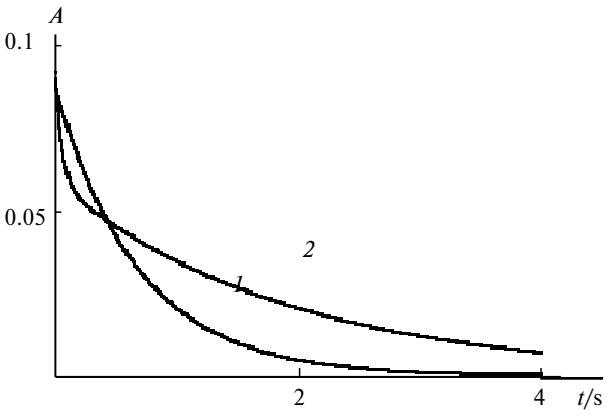


Fig. 2. Decay kinetics of the intermediate products detected at 600 nm under the conditions of laser pulse photolysis of compound **1** ($1 \cdot 10^{-4}$ mol L^{-1}) in toluene (*1*) and MeOH (*2*).

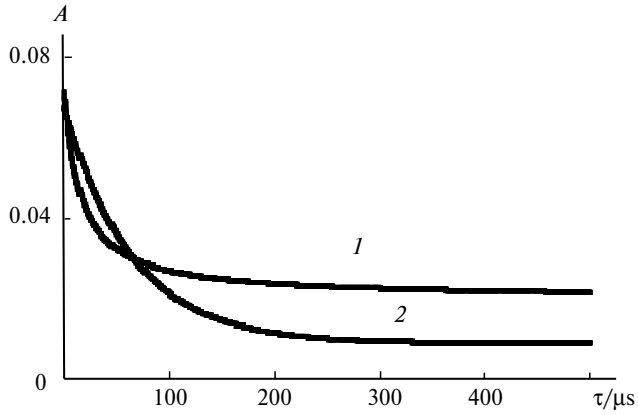


Fig. 3. Decay kinetics of the intermediate products detected at 500 nm under the conditions of laser pulse photolysis of compound **1** ($1 \cdot 10^{-5}$ mol L^{-1}) in toluene (*1*) and MeOH (*2*).

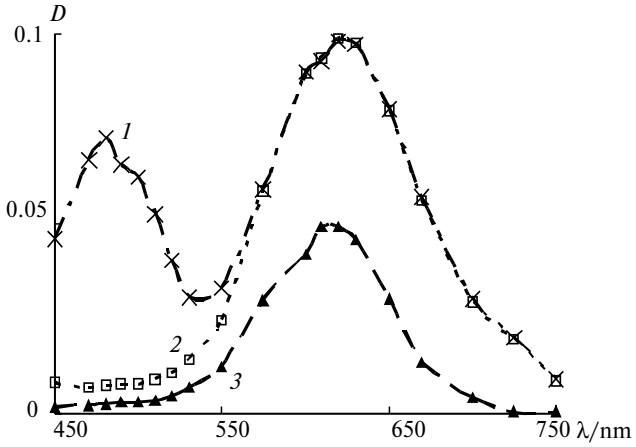


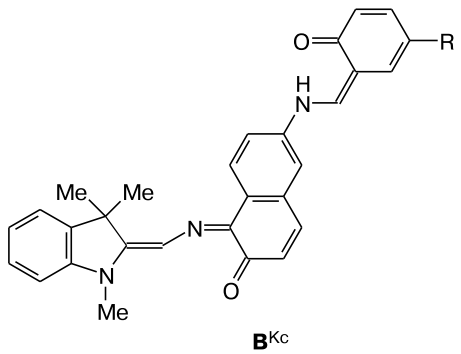
Fig. 4. Absorption spectra of the intermediate products obtained by the laser pulse photolysis of PBC **1** in methanol ($1 \cdot 10^{-4}$ mol L^{-1}) 0.5 μs (*1*), 0.5 ms (*2*), and 0.5 s (*3*) after a laser pulse.

wavelength region with λ_{max} = 620 nm. It should be mentioned that two open forms decay independently of each other.

The quantum yields of two forms **B** ($\varphi_{\mathbf{B}^E}$ and $\varphi_{\mathbf{B}^K}$) calculated on the basis of assumption about equality of the corresponding molar absorption coefficients are given in Table 2. The total quantum yield of two forms **B** in the case of PBC **1** in methanol is close to $\varphi_{\mathbf{B}}$ in toluene, as the total quantum yield of photocoloring (see Table 2).

Unlike the process in toluene, in methanol the introduction of electronegative substituents into the salicylideneimine fragment exerts a weak effect on the total yield of merocyanine form **B** ($\varphi_{\mathbf{B}^E} + \varphi_{\mathbf{B}^K}$). However, in this case, the yield of $\mathbf{B}^E$ drops sharply and that of $\mathbf{B}^{Kc}$ increases. Unlike the kinetic behavior of $\mathbf{B}^E$ in toluene, in methanol the introduction of electronegative substituents into the salicylideneimine fragment weakly affects the decay kinetics of the both forms of **B**.

It seems hardly probable that two forms of **B** are two different isomers of open form **B**, which differ only by the conformation of the merocyanine fragment.[26] Relatively high decay rate constant indicates that for $\mathbf{B}^{Kc}$ with λ_{max} = 620 nm the salicylideneimine fragment has pronounced electron-donor properties. This fact and



$\mathbf{B}^{Kc}$

the sharp increase in the quantum yield of $\mathbf{B}^{Kc}$ upon the introduction of electronegative substituents into the salicylideneimine fragment suggest that in $\mathbf{B}^{Kc}$ salicylideneimine fragment exists as *cis*-ketone or in the zwitterionic form.

Another argument in favor of the aforesaid is the fact that the absorption spectrum of $\mathbf{B}^{Kc}$ contains bands in the region of 450 nm characteristic of the absorption of the *cis*-keto form of SA,[14–17] which is not observed in the absorption spectra of $\mathbf{B}^E$.

It should be mentioned that the source of $\mathbf{B}^{Kc}$ can be not only closed form $\mathbf{A}^{Kc}$, which exists in a minor amount in methanol and can transform into $\mathbf{B}^{Kc}$ upon the absorption of a photon. The relatively high quantum yield of $\mathbf{B}^{Kc}$ even for PBC **2** and **3**, which exist in a methanolic solution exclusively in the enol form, indicates, most likely, that $\mathbf{B}^{Kc}$ is also formed due to the photoexcitation of the enol form of the PBC. It can be assumed that $\mathbf{B}^{Kc}$ is formed due to phototropic processes, being a variety of thermodynamic relaxation of the common precursor of forms **B**. Therefore, the total yield of two forms **B** is almost independent of substituents.

The signal at λ_{max} = 500 nm in methanol, as in the case of the solution in toluene, was ascribed to form $\mathbf{A}^{Kt}$. In both methanol and toluene solutions, the yield of form $\mathbf{A}^{Kt}$ decreases for the compounds with the electronegative substituents in the salicylideneimine fragment (compounds **2**—**5**). As in toluene, the electronegative substituents in the phenyl ring of SA prevent the formation of the "twisted" keto state or the charge-transfer state,[21] which is the precursor of $\mathbf{A}^{Kt}$.

The decay kinetics of $\mathbf{A}^{Kt}$ in methanol obeys a first-order law with the rate constant that depends linearly on the concentration of the PBC due to two processes: intramolecular backward proton transfer and bimolecular proton exchange between $\mathbf{A}^{Kt}$ and molecules of the initial form, which finally results in the formation of the starting PBC. The corresponding rate constants of the first and second order ($k_{1,\mathbf{A}^{Kt}}$ and $k_{q,\mathbf{A}^{Kt}}$) are listed in Table 1 (the $k_{q,\mathbf{A}^{Kt}}$ value was calculated from the slope of the corresponding linear dependences). The $k_{q,\mathbf{A}^{Kt}}$ value is by two orders of magnitude lower than the rate constant of the diffusionally controlled reaction ($\sim 1 \cdot 10^{10}$ L mol^{-1} s^{-1} in methanol).

The compounds with the electronegative substituents exhibit acceleration of the both channels of $\mathbf{A}^{Kt}$ decay rather than retardation as in toluene, which is explained, most likely, by an increase in lability of the corresponding protons.

The obtained kinetic data indicate unambiguously that forms $\mathbf{A}^{Kt}$, $\mathbf{B}^E$, and $\mathbf{B}^{Kc}$ are not transformed into each other but return to the initial form $\mathbf{A}^E$ during the dark reaction. Thus, two photoprocesses, *viz.*, ring opening in the spironaphthoxazine fragment and proton transfer in the salicylideneimine fragment, occur, on the one hand,

independently of each other, but on the other hand, in methanol the formation of the final form **B** can also include the proton transfer process. It was shown that the solvent exerts the decisive influence on the number of observed photoproducts, kinetics, and mechanism of their transformation into the initial forms of the PBC. The substituents in the salicylideneimine fragment of the PBC molecules affect the ratio of the photoreaction routes, but this effect is weaker than that of the solvent.

Experimental

The ^{1}H NMR spectra were recorded on a Bruker WM-400 spectrometer at 25 °C.

The UV-Vis absorption spectra were recorded on Specord UV-Vis and MultiSpec-1501 spectrophotometers.

The absorption spectra and the kinetics of formation and decay of intermediate products in concentrated solutions ($\geq 1 \cdot 10^{-4}$ mol L^{-1}) were measured on a nanosecond laser photolysis technique with detection of electronic absorption.[27,28] A nitrogen laser operating in the frequency mode of 10 Hz was used as the excitation source (PRA LN 1000, pulse duration 1 ns, radiation wavelength 337 nm). Accumulation and averaging of kinetic curves (16—128 laser pulses per each curve) were carried out using a UF.258 high-performance analog-to-digital converter (Sweden) attached to a personal computer based on the Pentium 4 processor. Depending on the duration of the process, each kinetic curve contained from 4096 to 16 384 points remote at the distance from 4 to 400 ns. The data presented in the work are average values obtained by the processing of at least 10 kinetic curves for the indicated conditions. The absorption spectra and the decay kinetics of intermediate products in dilute solutions ($\leq 1 \cdot 10^{-5}$ mol L^{-1}) were also detected on a microsecond pulse photolysis setup with detection of electronic absorption.[29]

Solutions of PBC with the same absorbance ($D = 1$) at the exciting light wavelength with $\lambda = 337$ nm were used in determination of the quantum yield of photoproducts. The $\varphi_{\mathbf{B}}$ values were measured by comparing with model compound **6** assuming that the molar absorption coefficients of the corresponding forms **B** are equal and $\varphi_{\mathbf{V}} = 0.23$ and 0.19 for compound **6** in toluene and MeOH (see Ref. 20), respectively.

The $\varphi_{\mathbf{A}^{Kt}}$ values were measured by comparing the absorption of $\mathbf{A}^{Kt}$ at the absorption maximum at 500 nm with allowance for the absorption of **B** at this wavelength with the absorption of **B** at the band maximum at 600 nm, and it was assumed that the ratio of the corresponding molar absorption coefficients of **B** and $\mathbf{A}^{Kt}$ at the maximum is 3 (see Refs 25 and 30).

8′-Amino-1,3,3-trimethylspiro[2*H*-indole-2,3′-[3*H*]naphtho-[2,1-*b*][1,4]oxazine] (**7**), which is the starting compound for the synthesis of bifunctional compounds, was obtained according to an earlier described procedure.[31]

8′-(2-Hydroxybenzylideneimino)-1,3,3-trimethyl-1,3-dihydrospiro[2*H*-indole-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (1). A solution of compound **7** (0.373 g, 1.0 mmol) and salicylaldehyde (0.12 g, 1.0 mmol) in a mixture of toluene (30 mL) and ethanol (20 mL) was refluxed for 2 h with the Dean—Stark receiver slowly distilling off ~40 mL of the solvent. Then toluene (20 mL) was added, and ~20 mL of the solvent was distilled off during 1 h. The residue was evaporated on a rotary evaporator and purified by chromatography on a column packed with silica gel (45—70 μm (Aldrich), benzene with gradual addition of 0.5, 1, 2, 5, and 10% acetone as eluent). The fractions containing the yellow-orange Schiff base with R_f 0.66 (chloroform—acetone (19 : 1) mixture) were collected, evaporated on a rotary evaporator, and crystallized from a benzene—hexane (3 : 1) mixture. Lemon-yellow crystals with m.p. 171—174 °C were obtained in a yield of 0.16 g (32%). Found (%): C, 77.81; H, 5.44; N, 9.39. $C_{29}H_{25}N_3O_2$. Calculated (%): C, 77.83; H, 5.63; N, 9.39. ^{1}H NMR ($CDCl_3$), δ: 1.38, 1.39 (both s, 3 H each, CMe_2); 2.79 (s, 3 H, NMe); 6.61 (d, 1 H, H(7), $^3J_{6,7} = 7.8$ Hz); 6.92 (t, 1 H, H(5), $^3J_{4,5} = {}^3J_{5,6} = 7.3$ Hz); 6.98 (td, 1 H, H(4″), $^3J_{3″,4″} = {}^3J_{4″,5″} = 7.5$ Hz, $^4J_{4″,6″} = 1.8$ Hz); 7.06 (d, 2 H, H(5′), H(6′), $^3J_{5′,6′} = 8.8$ Hz); 7.11 (d, 1 H, H(4), $^3J_{4,5} = 7.3$ Hz); 7.25 (ddd, 1 H, H(6), $^3J_{5,6} = 7.3$ Hz, $^3J_{6,7} = 7.8$ Hz, $^4J_{4,6} = 1.0$ Hz); 7.40 (ddd, 1 H, H(5″), $^3J_{4″,5″} = 7.5$ Hz, $^3J_{5″,6″} = 8.9$ Hz, $^4J_{3″,5″} = 1.3$ Hz); 7.44 (dd, 1 H, H(3″), $^3J_{3″,4″} = 7.5$ Hz, $^4J_{3″,5″} = 1.3$ Hz); 7.60 (dd, 1 H, H(9′), $^3J_{9′,10′} = 8.9$ Hz, $^4J_{7′,9′} = 2.0$ Hz); 7.65 (d, 1 H, H(7′) $^4J_{7′,9′} = 2.0$ Hz); 7.67 (d, 1 H, H(6″), $^4J_{4″,6″} = 1.8$ Hz); 7.79 (s, 1 H, H(2′)); 8.62 (d, 1 H, H(10′), $^3J_{9′,10′} = 8.9$ Hz); 8.79 (s, 1 H, H(7″)); 13.5 (br.s, 1 H, OH′). ^{1}H NMR (toluene-d_8), δ: 1.09, 1.24 (both s, 3 H each, CMe_2); 2.46 (s, 3 H, NMe); 6.31 (d, 1 H, H(7), $^3J_{6,7} = 7.8$ Hz); 6.73 (ddd, 1 H, H(5), $^3J_{4,5} = 7.5$ Hz, $^3J_{5,6} = 7.2$ Hz, $^4J_{5,7} = 1.0$ Hz); 6.72 (d, 1 H, H(5′), $^3J_{5′,6′} = 8.8$ Hz); 6.83 (ddd, 1 H, H(6), $^3J_{5,6} = 7.2$ Hz, $^3J_{6,7} = 7.8$ Hz, $^4J_{4,6} = 2.0$ Hz); 6.86 (dd, 1 H, H(4), $^3J_{4,5} = 7.5$ Hz, $^4J_{4,6} = 2.5$ Hz); 6.97 (dd, 1 H, H(3″), $^3J_{3″,4″} = 7.5$ Hz, $^4J_{3″,5″} = 1.4$ Hz); 7.01—7.11 (m, 3 H, H(4″), H(5″), H(6″)); 7.22 (d, 1 H, H(7′), $^4J_{7′,9′} = 2.2$ Hz); 7.25 (dd, 1 H, H(9′), $^3J_{9′,10′} = 8.9$ Hz, $^4J_{7′,9′} = 2.2$ Hz); 7.26 (d, 2 H, H(6′), $^3J_{5′,6′} = 8.8$ Hz); 7.61 (s, 1 H, H(2′)); 8.16 (s, 1 H, H(7″)); 8.93 (d, 1 H, H(10′), $^3J_{9′,10′} = 8.9$ Hz); 13.61 (s, 1 H, OH).

8′-(2-Hydroxy-3,5-dichlorobenzylideneimino)-1,3,3-trimethyl-1,3-dihydrospiro[2*H*-indole-2,3′-[3*H*]naphtho[2,1-*b*][1,4]-oxazine] (2). A mixture of compound **7** (0.17 g, 0.49 mmol) and 3,5-dichlorosalicylaldehyde (0.1 g, 0.53 mmol) in anhydrous toluene (40 mL) was refluxed for 3 h slowly distilling off 30—35 mL of toluene. The remained amount of the solvent was distilled off on a rotary evaporator. The residue was chromatographed on a column packed with silica gel (45—70 μm (Aldrich), benzene as eluent). The fractions with R_f 0.77 (chloroform—acetone (18 : 1) mixture) were collected, the eluent was evaporated on a rotary evaporator, and the residue was recrystallized from a benzene—hexane (3 : 1) mixture. Compound **4** (0.1 g, 27%) was obtained as orange crystals with m.p. 229—230 °C. Found (%): C, 67.27; H, 4.53; Cl, 13.94; N, 7.91. $C_{29}H_{23}Cl_2N_3O_2$. Calculated (%): C, 67.45; H, 4.49; Cl, 13.73; N, 8.14. ^{1}H NMR ($CDCl_3$), δ: 1.37, 1.38 (both s, each 3 H, CMe_2); 2.78 (s, 3 H, NMe); 6.60 (d, 1 H, H(7), $^3J_{6,7} = 7.8$ Hz); 6.92 (dd, 1 H, H(5), $^3J_{4,5} = 7.1$ Hz, $^3J_{5,6} = 7.4$ Hz); 7.09 (d, 1 H, H(5′), $^3J_{5′,6′} = 8.9$ Hz); 7.10 (d, 1 H, H(4), $^3J_{4,5} = 7.1$ Hz); 7.24 (dd, 1 H, H(6), $^3J_{5,6} = 7.4$ Hz, $^3J_{6,7} = 7.8$ Hz); 7.36 (d, 1 H, H(6″), $^4J_{4″,6″} = 2.4$ Hz); 7.47 (d, 1 H, H(4″), $^4J_{4″,6″} = 2.4$ Hz); 7.60 (dd, 1 H, H(9′), $^3J_{9′,10′} = 9.0$ Hz, $^4J_{7′,9′} = 1.8$ Hz); 7.67 (d, 1 H, H(7′), $^4J_{7′,9′} = 1.8$ Hz); 7.70 (d, 1 H, H(6′), $^3J_{5′,6′} = 8.9$ Hz); 7.78 (s, 1 H, H(2′)); 8.63 (d, 1 H, H(10′), $^3J_{9′,10′} = 9.0$ Hz); 8.73 (s, 1 H, H(7″)); 14.0 (br.s, 1 H, OH).

8′-(5-Bromo-2-hydroxybenzylideneimino)-1,3,3-trimethyl-1,3-dihydrospiro[2*H*-indole-2,3′-[3*H*]naphtho[2,1-*b*][1,4]-oxazine] (3). A solution of compound **7** (0.114 g, 0.33 mmol) and 5-bromosalicylaldehyde (0.067 g, 0.33 mmol) in a mixture

of toluene (20 mL) and ethanol (10 mL) was refluxed for 2 h with the Dean—Stark receiver slowly distilling ~20 mL of the solvent. Then toluene (20 mL) was added, and ~20 mL of the solvent was distilled off for 2 h. The residue was evaporated on a rotary evaporator and purified by chromatography on a column packed with silica gel (45—70 μm (Aldrich), benzene with the gradual addition of 0.5, 1, 2, 5, and 10% acetone as eluent). The fractions containing the yellow-orange Schiff base were collected, evaporated on a rotary evaporator, and crystallized from a benzene—hexane (3 : 1) mixture. Yellow-orange crystals with m.p. 210—215 °C were obtained (0.06 g, 35%), R_f 0.67 (chloroform—acetone, 19 : 1). Found (%): C, 66.41; H, 4.92; N, 7.49. $C_{29}H_{24}BrN_3O_2$. Calculated (%): C, 66.17; H, 4.60; N, 7.98. ^{1}H NMR ($CDCl_3$), δ: 1.37, 1.38 (both s, 3 H each, CMe_2); 2.78 (s, 3 H, NMe); 6.59 (d, 1 H, H(7), $^3J_{6,7}$ = 7.7 Hz); 6.91 (t, 1 H, H(5), $^3J_{4,5}$ = $^3J_{5,6}$ = 7.3 Hz); 6.95 (d, 1 H, H(5′), $^3J_{5',6'}$ = 8.8 Hz); 7.06 (d, 1 H, H(6′), $^3J_{5',6'}$ = 8.8 Hz); 7.10 (dd, 1 H, H(4), $^3J_{4,5}$ = 7.3 Hz, $^4J_{4,6}$ = 1.2 Hz); 7.22 (td, 1 H, H(6), $^3J_{5,6}$ = $^3J_{6,7}$ = 7.3 Hz, $^4J_{4,6}$ = 1.2 Hz); 7.45 (dd, 1 H, H(4″), $^3J_{3'',4''}$ = 8.9 Hz, $^4J_{4'',6''}$ = 2.5 Hz); 7.56 (d, 1 H, H(6″), $^4J_{4'',6''}$ = 2.5 Hz); 7.59 (dd, 1 H, H(9′), $^3J_{9',10'}$ = 8.0 Hz, $^4J_{7',9'}$ = 2.0 Hz); 7.64 (d, 1 H, H(7′), $^4J_{7',9'}$ = 2.0 Hz); 7.69 (d, 1 H, H(3″), $^3J_{3'',4''}$ = 8.9 Hz); 7.78 (s, 1 H, H(2′)); 8.62 (d, 1 H, H(10′), $^3J_{9',10'}$ = 8.0 Hz); 8.71 (s, 1 H, H(7″)); 14.2 (br.s, 1 H, OH).

8′-(2-Hydroxy-5-nitrobenzylideneimino)-1,3,3-trimethyl-1,3-dihydrospiro[2*H*-indole-2,3′-[3*H*]naphtho[2,1-*b*][1,4]-oxazine] (4). A solution of compound **7** (0.2 g, 0.58 mmol) and 5-nitrosalicylaldehyde (0.11 g, 0.66 mmol) in a mixture of toluene (15 mL) and ethanol (15 mL) was refluxed for 2 h slowly distilling off the solvent (20 mL) with the Dean—Stark receiver. Then toluene (20 mL) was added, and the solvent was again distilled off slowly for 2 h. After the solvent was completely removed on a rotary evaporator, the precipitate was refluxed in petroleum ether and then filtered off. The precipitate was chromatographed on a column with silica gel (35—70 μm, Aldrich), eluting first with benzene and then with a benzene—acetone (100 : 1) mixture. Orange fractions with R_f 0.60 (chloroform—acetone (18 : 1) mixture) were collected, the eluent was evaporated on a rotary evaporator, and the residue was recrystallized from benzene and washed with petroleum ether. Orange crystals with m.p. 236—238 °C were obtained (0.09 g, 30%). Found (%): C, 70.50; H, 4.95; N, 11.31. $C_{29}H_{24}N_4O_4$. Calculated (%): C, 70.72; H, 4.91; N, 11.38. ^{1}H NMR ($CDCl_3$), δ: 1.37, 1.38 (both s, 3 H each, CMe_2); 2.79 (s, 3 H, NMe); 6.60 (d, 1 H, H(7), $^3J_{6,7}$ = 7.7 Hz); 6.92 (t, 1 H, H(5), $^3J_{4,5}$ = $^3J_{5,6}$ = 7.3 Hz); 7.09 (dd, 1 H, H(4), $^3J_{4,5}$ = 7.4 Hz, $^4J_{4,6}$ = 1.1 Hz); 7.10 (d, 1 H, H(5′)); 7.11 (m, 1 H, H(3″)); 7.24 (ddd, 1 H, H(6), $^3J_{5,6}$ = 7.3 Hz, $^3J_{6,7}$ = 7.7 Hz, $^4J_{4,6}$ = 1.1 Hz); 7.63 (dd, 1 H, H(9′), $^3J_{9',10'}$ = 8.7 Hz, $^4J_{7',9'}$ = 2.0 Hz); 7.70 (d, 1 H, H(7′), $^4J_{7',9'}$ = 2.0 Hz); 7.71 (d, 1 H, H(6′)); 7.79 (s, 1 H, H(2′)); 8.28 (dd, 1 H, H(4″), $^3J_{3'',4''}$ = 8.9 Hz, $^4J_{4'',6''}$ = 1.9 Hz); 8.44 (d, 1 H, H(6″), $^4J_{4'',6''}$ = 1.9 Hz); 8.65 (d, 1 H, H(10′)), $^3J_{9',10'}$ = 8.7 Hz); 8.88 (s, 1 H, H(7″)); 14.7 (br.s, 1 H, OH). ^{1}H NMR (toluene-d_8) δ: 1.10, 1.24 (both s, 3 H each, CMe_2); 2.47 (s, 3 H, NMe); 6.32 (d, 1 H, H(7), $^3J_{6,7}$ = 7.8); 6.68 (d, 1 H, H(3″), $^3J_{3'',4''}$ = 9.0 Hz); 6.77 (d, 1 H, H(5′), $^3J_{5',6'}$ = 8.8 Hz); 6.84 (m, 1 H, H(5), $^3J_{5,6}$ = 7.3 Hz); 6.86 (m, 1 H, H(4)); 6.99 (d, 1 H, H(7′), $^4J_{7',9'}$ = 2.2 Hz); 7.10 (ddd, 1 H, H(6), $^3J_{5,6}$ = 6.7 Hz, $^3J_{6,7}$ = 7.8 Hz, $^4J_{4,6}$ = 2.0 Hz); 7.21 (dd, 1 H, H(9′), $^3J_{9',10'}$ = 8.8 Hz, $^4J_{7',9'}$ = 2.2 Hz); 7.30 (d, 1 H, H(6′), $^3J_{5',6'}$ = 8.8 Hz); 7.63 (s, 1 H, H(2)); 7.71 (s, 1 H, H(7″)); 7.80 (d, 1 H, H(6″), $^4J_{4'',6''}$ = 2.8 Hz); 7.83 (dd, 1 H, H(4″), $^3J_{3'',4''}$ = 9.0 Hz, $^4J_{4'',6''}$ = 2.8 Hz); 14.0 (s, 1 H, OH).

8′-(3-Bromo-2-hydroxy-5-nitrobenzylideneimino)-1,3,3-trimethyl-1,3-dihydrospiro[2*H*-indole-2,3′-[3*H*]naphtho-[2,1-*b*][1,4]oxazine] (5). A solution of compound **7** (0.12 g, 0.35 mmol) and 3-bromo-5-nitrosalicylaldehyde (0.09 g, 0.37 mmol) in a mixture of toluene (15 mL) and ethanol (15 mL) was refluxed for 2 h slowing distilling off 20 mL of the solvent with the Dean—Stark receiver. Then toluene (20 mL) was added, and the solvent was again distilled off slowly for 2 h. After the solvent was completely removed on a rotary evaporator, the precipitate was refluxed in benzene and filtered off. Compound **5** (0.11 g, 55%) was obtained as a brick-red powder with m.p. 247—248 °C, R_f 0.79 (chloroform—acetone (18 : 1) mixture). Found (%): C, 59.07; H, 4.00; N, 9.34. $C_{29}H_{23}BrN_4O_4 \cdot H_2O$. Calculated (%): C, 59.09; H, 4.28; N, 9.58. ^{1}H NMR ($CDCl_3$), δ: 1.37, 1.39 (both s, 3 H each, CMe_2); 2.78 (s, 3 H, NMe); 6.60 (d, 1 H, H(7), $^3J_{6,7}$ = 7.7 Hz); 6.93 (dd, 1 H, H(5), $^3J_{4,5}$ = 7.1 Hz, $^3J_{5,6}$ = 7.7 Hz); 7.10 (d, 1 H, H(4), $^3J_{4,5}$ = 7.1 Hz); 7.11 (d, 1 H, H(5′), $^3J_{5',6'}$ = 8.9 Hz); 7.24 (t, 1 H, H(6), $^3J_{5,6}$ = $^3J_{6,7}$ = 7.7 Hz); 7.65 (dd, 1 H, H(9′), $^3J_{9',10'}$ = 9.0 Hz, $^4J_{7',9'}$ = 2.0 Hz); 7.72 (d, 1 H, H(6′), $^3J_{5',6'}$ = 8.9 Hz); 7.76 (d, 1 H, H(7′), $^4J_{7',9'}$ = 2.0 Hz); 7.79 (s, 1 H, H(2′)); 8.40 (d, 1 H, H(4″), $^4J_{4'',6''}$ = 2.6 Hz); 8.59 (dd, 1 H, H(6″), $^4J_{4'',6''}$ = 2.6 Hz); 8.69 (d, 1 H, H(10′), $^3J_{9',10'}$ = 9.0 Hz); 8.85 (s, 1 H, H(7″)); 14.5 (br.s, 1 H, OH).

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References

1. V. A. Barachevskii, *Zh. Nauchn. Prikl. Fotografii* [*Journal of Scientific and Applied Photography*], 1998, **43**, 79 (in Russian).
2. G. Berkovic, V. Krongauz, V. Weiss, *Chem. Rev.*, 2000, **100**, 1741.
3. M. Irie, *Chem. Rev.*, 2000, **100**, 1685.
4. M. Figoli, G. H. Mehl, *Angew. Chem., Int. Ed.*, 2005, **44**, 5048.
5. G. J. Brown, A. P. De Silva, S. Pagliari, *Chem. Commun.*, 2002, 2461.
6. S. Kobatake, M. Irie, *Tetrahedron*, 2003, **59**, 8359.
7. B. Z. Chen, M. Z Wang, Q. F. Luo, H. Tian, *Synth. Met.*, 2003, **137**, 985.
8. A. J. Myles, T. J. Wigglesworth, N. R. Branda, *Adv. Mater.*, 2003, 745.
9. K. Yagi, M. Irie, *Chem. Lett.*, 2003, **32**, 848.
10. A. I. Shienok, N. L. Zaichenko, L. S. Kol′tsova, V. S. Marevtsev, *Izv. Akad. Nauk*, *Ser. Khim.*, 2003, 2169 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 2294].
11. A. K. Frolov, F. E. Gostev, I. V. Shelaev, A. I. Shienok, N. L. Zaichenko, L. S. Kol′tsova, V. A. Barachevskii, O. M. Sarkisov, *Khim. Fiz.* [*Chemical Physics*], 2007, **26**, 1021 (in Russian).
12. S. A. Antipin, A. N. Petrukhin, F. E. Gostev, V. S. Marevtsev, A. A. Titov, V. A. Barachevskii, Yu. P. Strokach, O. M. Sarkisov, *Khim. Fiz.* [*Chemical Physics*], 2002, **21**, 10 (in Russian).

13. R. S. Becker, W. F. Richey, *J. Am. Chem. Soc.*, 1967, **89**, 1298.
14. M. Z. Zgierski, A. Grabowska, *J. Chem. Phys.*, 2000, **112**, 6329.
15. W. V. F. Fabian, L. Antonov, D. Nedeltcheva, F. S. Kamounah, P. J. Taylor, *J. Phys. Chem. A*, 2004, **108**, 7603.
16. M. Ziotek, J. Kubicki, R. Naskrecki, A. Grabowska, *J. Chem. Phys.*, 2006, **124**, 124518.
17. P. Fita, E. Lusina, Cz. Radzewicz, A. Grabowska, *J. Chem. Phys.*, 2006, **125**, 184508.
18. F. E Gostev, A. N. Petrukhin, A. A. Titov, V. A. Nadtochenko, O. M. Sarkisov, A. V. Metelitsa, V. I. Minkin, *Khim. Fiz.* [*Chemical Physics*], 2004, **23**, 3 (in Russian).
19. *Tables of Spectral Data for Structure Determination of Organic Compounds*, Ed. W. Fresenius, J. F. K. Huber, E. Pungor, G. A. Rechnitz, W. Simon, Th. S. West, Springer-Verlag, Berlin—Heidelberg—New York—London—Paris—Tokio—Hong Kong, 1989, 426 pp.
20. V. Lokshin, A. Sama, A. V. Metelitsa, *Usp. Khim.*, 2002, **71**, 1015 [*Russ. Chem. Rev.*, 2002, **71** (Engl. Transl.)].
21. V. Vargas C., *J. Phys. Chem. A*, 2004, **108**, 281.
22. J. S. Stephan, A. Mordzinski, C. Rios Rodriguez, K. H. Grellmann, *Chem. Phys. Lett.*, 1994, **229**, 541.
23. A. Grabowska, K. Kownacki, J. Karpiuk, S. Dobrin, L. Kaczmarek, *Chem. Phys. Lett.*, 1997, **267**, 132.
24. F. Bayrakceken, P. C. Sevinc, *Spectrochim. Acta A: Mol. Biomol. Spectrosc.*, 2007, **66**, 184.
25. G. O. Dudek, E. P. Dudek, *J. Am. Chem. Soc.*, 1966, **88**, 2407.
26. R. N. Christie, C. K. Agyako, K. Mitchell, *Dyes and Pigments*, 1995, **29**, 241.
27. P. P. Levin, N. B. Sul´timova, O. N. Chaikovskaya, *Izv. Akad. Nauk*, *Ser. Khim.*, 2005, 1391 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 1433].
28. N. B. Sul´timova, P. P. Levin, O. N. Chaikovskaya, *Izv. Akad. Nauk*, *Ser. Khim.*, 2005, 1397 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 1439].
29. A. S. Tatikolov, S. M. B. Costa, *J. Photochem. Photobiol. A: Chem.*, 2001, **140**, 147.
30. J.-L. Pozzo, A. Samat, R. Guglielmetti, D. De Keukeleire, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1327.
31. V. Yu. Nedoshivin, N. L. Zaichenko, N. N. Glagolev, V. S. Marevtsev, *Izv. Akad. Nauk*, *Ser. Khim.*, 1996, 1243 [*Russ. Chem. Bull.*, 1996, **45**, 1182 (Engl. Transl.)].

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