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Chemical Physics 323 (2006) 490–500
Chemical Physics
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Photochemistry of phenanthroline-containing spirooxazines in a low-temperature methanol matrix

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Received 19 April 2005; accepted 18 October 2005
Available online 15 November 2005

Abstract

Both stationary and laser flash photolysis were applied to study the photochemistry of a closed A-form of phenanthroline-containing spirooxazines in a methanol matrix (77 K). One of spirooxazines was nonsubstituted (SPO1) and the second one (SPO2) had a long alkyl substituent, n-$C_{16}H_{33}$, in the indoline part of the molecule. For SPO1, excitation of the A-form causes absorption of the B-form (600 nm) during the action of a laser pulse. Kinetics of a further increase in the concentration of B-form is determined by the inhomogeneity of a rigid matrix and is described by a set of exponents with characteristic times from hundreds of nanoseconds to tens of milliseconds. Absorption of the B-form is accompanied by absorption in the region of 400–750 nm, which belongs to X-isomer (an intermediate form of spirooxazine). The disappearance of X-isomer was described by a set of exponential functions with the characteristic times similar to those typical of the B-form appearance. For SPO1, only the B-form is accumulated during the stationary photolysis (X-isomer is completely transformed into the B-form). For SPO2, a range of characteristic times moves toward long times so that the X-isomer absorption is observed even upon stationary photolysis. Thus, a long X-isomer lifetime indicates that the B-form originates from the ground state of this intermediate. The existence of a long substituent substantially increases the time of X → B transformation in a frozen matrix. The appearance of a narrow absorption band at 600 nm immediately after the laser pulse was assigned to the formation of only one of the possible isomers of B-form upon X → B transformation.

Keywords: Phenanthroline-containing spirooxazines; Photochemistry of closed A-form; Frozen matrix; Laser flash photolysis; X-isomer

1. Introduction

Spirooxazines are the class of photochromic compounds that are of greatest practical utility. As compared with the structurally similar spiropyrans, spirooxazines exhibit a high stability to photochemical degradation [1]. The photochromic properties of spirooxazines and spiropyrans [1–4] are determined by the existence and mutual transitions (Scheme 1) of a closed colorless spiro-form A and an open colored merocyanine form B. In the closed A-form, the π-systems of the two parts of the molecule are mutually perpendicular and have no conjugated bond. Therefore, this form absorbs in the UV region. In the open B-form, spiropyrans and spirooxazines display a flat geometry and a single π-system [1,2], which gives rise to a strong absorption band in the red spectral region. Irradiation in the UV region leads, as a rule, to the appearance of a blue color of solution due to the A → B transition. The back reaction B → A occurs in the dark but can be accelerated by exciting the B-form by radiation falling on a long-wave absorption band at 500–700 nm.

Photochemical transformations of spirooxazines in solutions have been studied using the stationary photolysis

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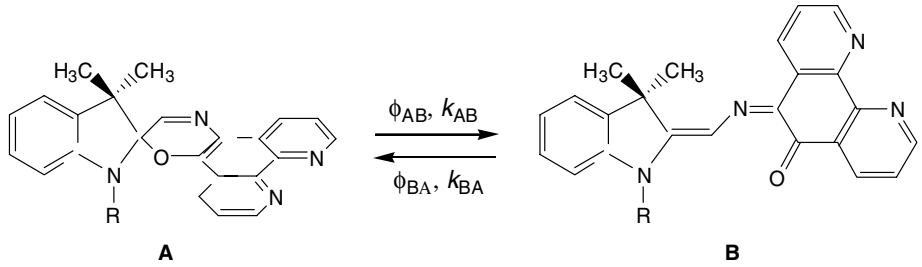
doi:10.1016/j.chemphys.2005.10.017



Scheme 1. Closed A spiro-form and open merocyanine B-form of spirooxazines SPO1 (R ≡ CH3) and SPO2 (R ≡ n-$C_{16}H_{33}$).

[5–10] and laser flash photolysis within nano- [11–15], pico- [16–19], and femtosecond [20–26] time domains. In the literature, available are the data on the photolysis of spirooxazines in crystalline state [22,23,27], polymer films and frozen solutions [28–35]. The primary photochemical processes in the photochemistry of spirooxazines are generally similar to these for spiropyrans [36–40]. When a light quantum is absorbed by the A-form, the primary process is the break of the bond between the spiro carbon atom and the oxygen atom, which results in the formation of an intermediate *cis*-cisoide X-isomer where the planes of the two molecule parts are mutually perpendicular. Rotating the indoline and oxazine parts of the molecule relative to each other gives rise to the B-form isomers with a flat geometry.

Hypothesis for the existence of X-isomer was first put forward by Fischer et al. [41,42] in the studies on phototransformations upon stationary irradiation of spiropyrans in frozen matrices. In these and later works [43–45], X-isomer was assumed to be stabilized at liquid nitrogen temperature. Absorption bands arising under irradiation in the red region at the location of the B-form band typical of solutions at room temperature were assigned to this species. A slight shift and the differences in the structure and width of the bands were attributed to the manifestation of the difference in the geometry of X-isomer and B-form isomers.

Flash photolysis with pico- and femtosecond time resolution indicates [16–25] that after a laser pulse (absorption of the excited A* state and X-isomer) the intermediate absorption in the range of 400–500 nm is usually formed. The characteristic lifetime of this absorption is less than 10 ps. The B-form absorption band in the red region (550–700 nm) is commonly formed 1–10 ps after the laser pulse. Thus, a characteristic lifetime of spirooxazine X-isomers in a nonviscous solvent at room temperature is in the picosecond time range. Obviously, a substantial decrease in temperature and moreover, the photolysis in a frozen rigid matrix should increase much the time of X-isomer transformation into the B-form. The nano- and microsecond laser flash photolysis of spirocompounds in a frozen matrix is likely to solve the problem on the possibility of X → B transformations at liquid nitrogen temperature and of possible X-isomer stabilization. In addition, when the X-isomer absorption is revealed in the range of tens of nanoseconds to seconds, it could be claimed that the B-form originates from X-isomer, which is in the ground electronic state. The data of femto- and picosecond experiments give no way of solving this problem. Therefore, for the case of spiropyrans, there are the works giving a scheme with both the reactions X* → B [20] and X → B [46].

Thus, the goal of the present work is to record intermediate optical spectra upon nanosecond laser flash photolysis of spirooxazines in a frozen matrix for determining the kinetics of X-isomer transformation at liquid nitrogen temperature. The objects of investigation (Scheme 1) were the A-forms of phenanthroline-containing spirooxazines, one of which had no substituents (SPO1) and the other had a long alkyl substituent (n-$C_{16}H_{33}$) in the indoline part of the molecule (SPO2). The existence of a long substituent is likely to increase substantially the X-isomer lifetime.

2. Experimental

Spirooxazine SPO1 (3,3-dimethyl-1-methyl-2,2′-[2H]bipyrido-[3,2-f][2,3-h][1,4]benzoxazine) was synthesized as described in [47]. The synthesis of SPO2 (3,3-dimethyl-1-hexadecylspiro[indoline-2,2′-[2H]bipyrido-[3,2-f][2,3-h]-[1,4]benzoxazine]) is described in [7]. Methanol with 5 vol% of water was used as a solvent to produce transparent glass at 77 K. Determining the concentration of spirooxazines in a matrix, it was necessary to take into account a decrease in the volume of liquid upon freezing to 77 K which, for a mixture of methanol with 5% water, was 23%. Experiments were performed using a laser flash photolysis setup (radiation wavelength – 308 nm, pulse duration – 15 ns, pulse energy ca. 30 mJ) described elsewhere [48]. In experiments performed at 77 K, an optical cryostat described in [49] was used. A 0.49 mm thick cell with a solution was frozen and placed into liquid nitrogen in the cryostat. To exclude sample photolysis by the probing light of the xenon lamp, it passed through a monochromator. The exciting and probing light beams fell on the cell at a small angle (∼2°) to each other. To decrease the influence of matrix inhomogeneity (the cracks appearing upon sample freezing) and to increase the signal-to-noise ratio, each experimental kinetic curve was obtained by averaging 5–10 curves recorded by means of either fresh samples or fresh parts on the sample.

Experiments on stationary photolysis were carried out using the XeCl laser radiation (308 nm), the second harmonic of YAG:Nd^{3+} laser (532 nm) or high pressure mercury lamp with a set of glass filters to separate light

with the necessary wavelength. The optical absorption spectra were recorded using an HP 8453 spectrophotometer (Hewlett–Packard). The diode array of this setup can be used to record a spectrum over the entire range (190–1100 nm) during several seconds, which is of importance for studying fast photochromic transformations. To distinguish the processes concerning A-form, experiments were performed using the samples with a high content of this form. Before freezing, spirooxazines were transformed into the A-form by irradiating cooled solution (276 K) at 532 nm. The intensity of laser pulses was measured by the value of T–T absorption of anthracene in oxygen-free benzene solutions at 431 nm (the triplet state quantum yield is 0.53 and the absorption coefficient of the T–T band is 42 000 M^{-1} cm^{-1} [50]).

Table 1 summarizes the equilibrium content of the open A-form for SPO1 and SPO2 in methanol at room temperature [7]. It also presents information on the quantum yield of phototransformations and isomerization rate constants for open and closed forms.

3. Results and discussion

3.1. Optical absorption spectra of spirooxazines SPO1 and SPO2 in a methanol matrix

Figs. 1 and 2 show the optical absorption spectra of the closed and open forms of spirooxazines SPO1 and SPO2 in a methanol matrix at 77 K. The spectra of A- and B-forms were determined from the data in Table 1, which indicates the content of the B-form at 298 K and the absorption coefficient of its long-wave absorption band (which does not overlap the A-form bands). The starting solution containing both of the forms was irradiated by pulses of XeCl laser (308 nm) at low temperature (273 K) to increase the content of the B-form. The two spectra, with a substantially different content of the B-form, can be used to calculate the spectra of both A- and B-forms. These calculations were performed in assumption that the spectrum shapes of these species and the absorption coefficients of the long-wave absorption bands of the B-form are temperature independent over the range of 298–273 K.

In a rigid matrix, the shape of spectra of isomers can be changed at liquid nitrogen temperature. However, the spectra of the two rapidly frozen samples with different relative contents of the B-form allow one to calculate the spectra of A- and B-forms separately. The calculations will be true in assumption that during the fast freezing the A- and B-forms do not transform into each other. This is valid because a decrease in temperature reduces sharply the rate constants of both A → B and B → A transformations due to high activation energies (Table 1). The spectra of the A- and B-forms of spirooxazines at 77 K are not too different from those of the solutions of these molecules at room temperature. A substantial decrease in temperature mainly leads to a small reduction of band widths and an increase in the absorption coefficients.

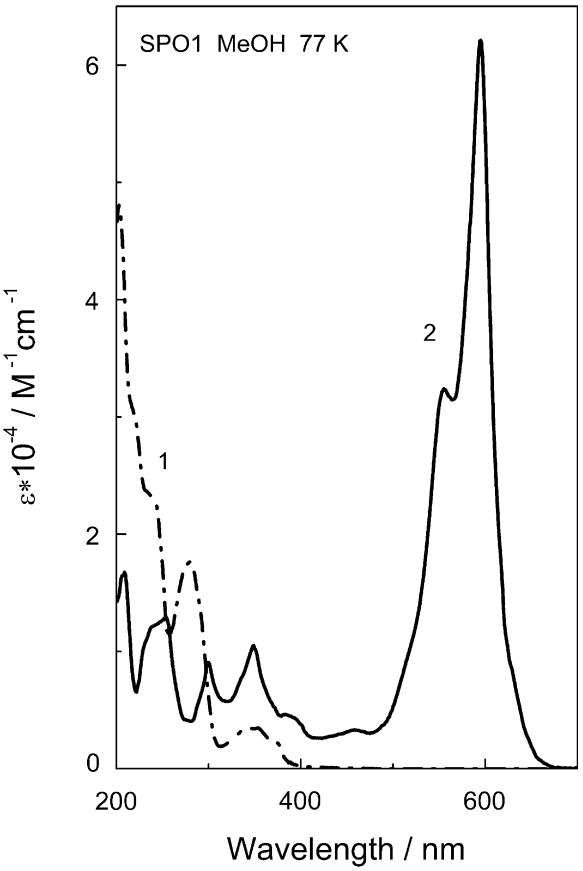


Fig. 1. UV absorption spectra of A- (1) and B-forms (2) of SPO1.

3.2. Photolysis of spirooxazine solutions at room temperature (298 K)

Irradiating SPO1 and SPO2 solutions at room temperature by XeCl laser pulses (308 nm) leads to photoinitiation of both the direct (A → B) and back (B → A) reactions. The quantum yields of phototransformations (φ_{AB}) in solutions are independent of the excitation wavelength in the range of 300–400 nm and are summarized in Table 1. Due to a small initial content of the B-form and a low

Table 1
The content of B-form, maxima and absorption coefficients of the long-wave absorption bands of B-form, the quantum yields of the photolysis of A- and B-forms, and the kinetic parameters of dark isomerization for spirooxazines SPO1 and SPO2 in methanol at 298 K [7]

SPO	B-form (%)	λ_{max} (nm)	ε_B^{max} (M^{-1} cm^{-1})	φ_{AB}	φ_{BA}	k_{AB} (s^{-1})	k_{BA} (s^{-1})	E_{AB} (kJ/mol)	E_{BA} (kJ/mol)
SPO1	7.0	595	57 700	0.24	0.022	0.0112	0.146	85.7	77.5
SPO2	23.5	605	56 200	0.24	0.015	0.0376	0.124	79.3	78.5

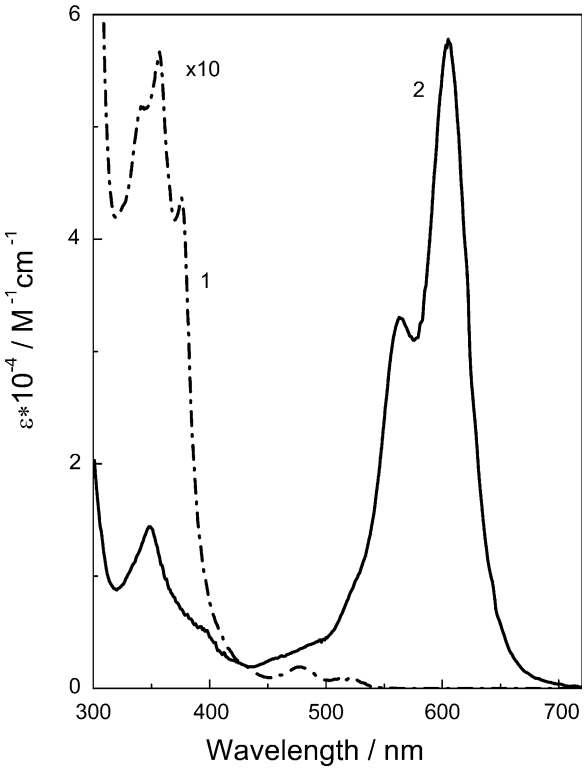


Fig. 2. UV absorption spectra of A- (1) and B-forms (2) of SPO2.

quantum yield of the back reaction, (φ_{BA}), only the A → B reaction is observed in the initial photolysis stage. A new equilibrium with a high content of B-form is reached under prolonged irradiation. When irradiation is over, the initial equilibrium between the open and closed forms is restored during several seconds (transition rate constants are shown in Table 1).

The laser flash photolysis of SPO1 and SPO2 solutions indicates that at room temperature the open B-form of spirooxazine is formed under the action of a laser pulse (for less than 15 ns). This corresponds to the literature data on a fast transformation of X-isomer into the B-form for both spirooxazines [16,17,20,21,26] and spiropyrans [20,46,51,52]. Minor changes in the absorption of B-form during several tens of microseconds can be determined by equilibrium established between the B-form isomers. The similar small spectral changes caused by the flash photolysis of spirooxazines over the microsecond time domain were observed in [11,14].

3.3. Stationary and laser flash photolysis of SPO1 in a frozen matrix

Fig. 3 shows a change in the optical spectrum upon the stationary photolysis (308 nm) of a frozen matrix containing nonsubstituted SPO1. An increase in the intensity of the long-wave absorption band of B-form (595 nm) indicates the A → B phototransformation. Accumulation of B-form increases its absorption and initiates reverse phototransformation (B → A). A new stationary state is reached

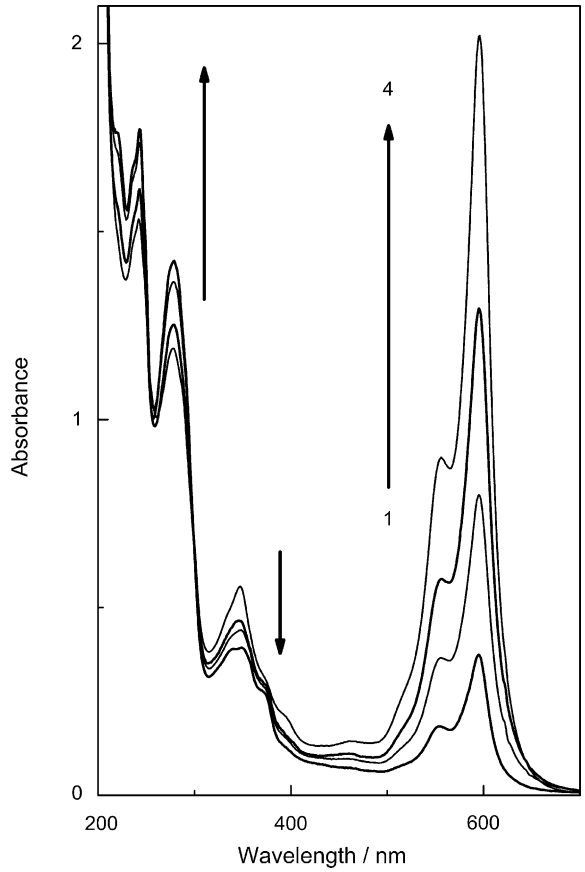


Fig. 3. Stationary photolysis of SPO1 (1.6×10^{-3} M) at 77 K. Irradiation by XeCl laser (308 nm). Curves 1–4 correspond to 0; 15; 100; 4000 pulses.

with a content of the B-form of about ~40% (Fig. 3, spectrum 4). When the irradiated sample is unfrozen, the system acquires its initial state and the B-form content decreases substantially. The spectrum shape and the band width of the B-form produced by the photolysis of the A-form in a matrix practically coincide with those obtained by freezing the initially liquid samples in which the B-form has been accumulated under preliminary irradiation.

Experimental results on the laser flash photolysis performed for SPO1 in a frozen matrix are listed in Fig. 4 (kinetic curves) and Fig. 5 (the spectra of intermediate absorption). The kinetic curves shape indicates that the processes following a light pulse are characterized by several characteristic times. A narrow absorption band which is located near the B-form band obtained under the stationary irradiation of SPO1 (a maximum is shifted by 5 nm to the red region from 595 to 600 nm) is formed under the action of a laser pulse (~15 ns). In addition, a wide band arises with a maximum at 400 nm and absorption appears in the red region with $\lambda > 620$ nm (Fig. 4, spectrum 1). Thus, the characteristic time of the appearance of new absorption is shorter than 15 ns.

The laser pulse is followed by an increase in the intensity of the band with a maximum at 600 nm and a decrease in absorption both in the blue (400 nm) and red ($\lambda > 620$ nm) regions (Fig. 5, spectrum 2) with a character-

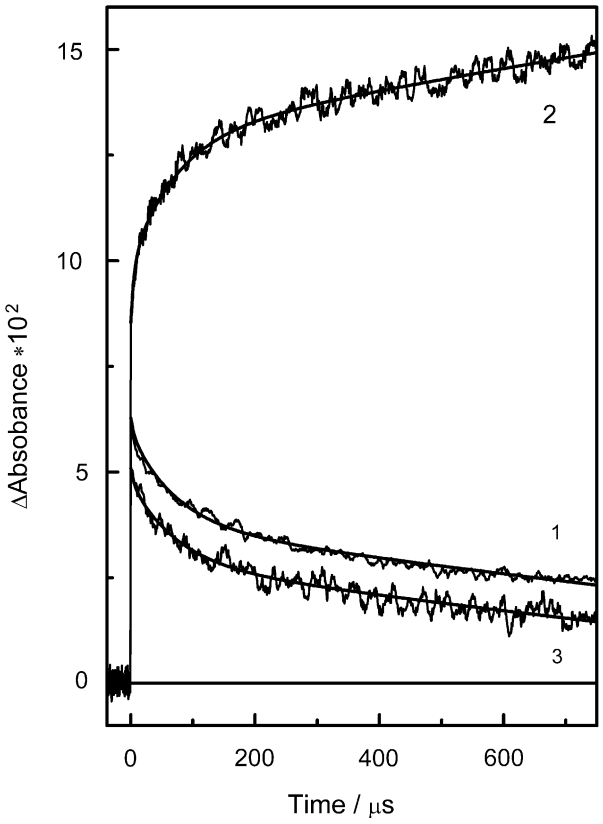


Fig. 4. Kinetic curves of changes in intermediate absorption caused by laser flash photolysis (308 nm) of SPO1 (1.6×10^{-3} M) at 77 K. Curves 1–3 correspond to registration wavelengths of 400, 590, and 660 nm. Smooth curves – three-exponential fit with the characteristic times 5.5; 72.5; and 5260 μs and varied relative amplitudes.

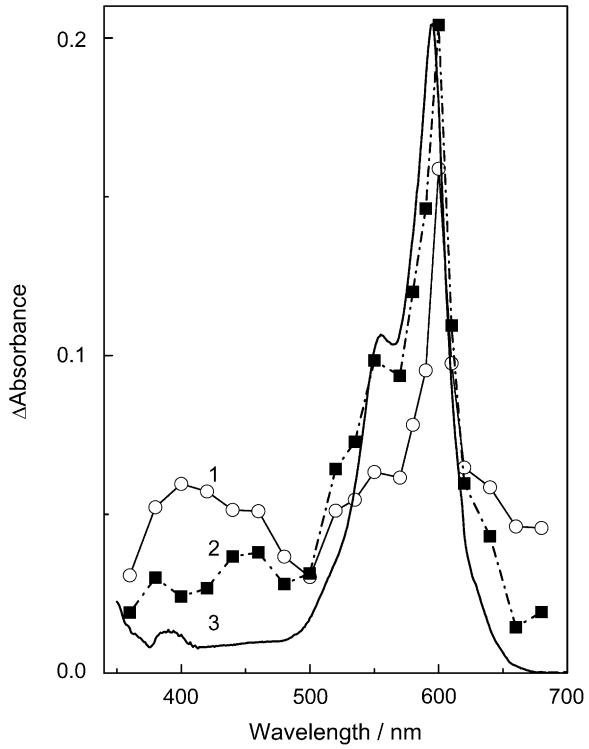


Fig. 5. Intermediate absorption spectra caused by laser flash photolysis (308 nm) of SPO1 (1.6×10^{-3} M) at 77 K. Curves 1, 2 correspond to 0 and 750 μs after laser pulse. Curve 3 is the difference UV absorption spectra of B- and A-forms of SPO1.

istic time of several hundreds of microseconds. The kinetic curves in Fig. 4 cannot be described by one exponential function. It is necessary to make use of a set of such functions with quite different times. The smooth curves in Fig. 4 denote a three-exponential fit with the characteristic times of 5.5, 72.5, and 5260 μs, which are in fair agreement with the experimental curves at 400 and 600 nm. The synchronism of absorption change at various wavelengths indicates that a species which appears just after the laser pulse transforms into the merocyanine B-form of spirooxazine.

The available concepts of the mechanism of phototransformations of spirocompounds [1,2] allow one to assign the intermediate absorption at 400 nm to the X-isomer which results from A-form excitation. Some molecules are likely to pass rapidly from the X-isomer state to the B-form (during the time shorter than the laser pulse duration) due to the relaxation of electron energy and the local heating of matrix [52]. However, when the local surrounding has been cooled, a substantial part of molecules remains long in the X-isomer state.

At present, it is well known that the low-temperature frozen and polymeric matrices display inhomogeneous composition, which manifests itself in the non-exponential time dependence of the kinetics of the first- or pseudo-first order reactions. This inhomogeneity is particularly vivid in the appearance of the "inhibited" kinetics, where the reaction rate decreases sharply with a small transformation degree. This effect holds for the reactions of radical oxidation [53] and *cis–trans* isomerization of dye molecules [54]. A similar inhibition of the reaction was also observed upon the B → A transformations for spirocompounds in polymeric films [28,34,35], gel [55], and frozen matrices [56]. Most likely, this also accounts for the nonexponentiality of the kinetics of X-isomer transformation into the B-form in Fig. 4. Thus, depending on local surrounding (more particularly, on the value of free volume), each X-isomer molecule has its own rate constant of the transition into the B-form. According to a fairly simple modeling, the total kinetics for molecules with a continuous rate constant distribution is well described by either two or three-exponential functions. Usually, the characteristic times of exponents determine the boundaries of the continuous rate constant distribution. The stiffness of a methanol matrix at liquid nitrogen temperature causes an extremely wide distribution of the rate constant of X-isomer transformation into the B-form. The kinetic curves in Fig. 4 denote the characteristic times from 5 μs to 5 ms. Registration performed at a shorter time domain indicates that the characteristic time can be extended to several hundreds of nanoseconds. For longer times, the range is also much wider and stretches to hundreds of milliseconds (the time of the complete disappearance of X-isomer absorption unobservable in stationary measurements). Thus, in a fro-

zen matrix, the distribution of the rate constants of X-isomer transformation takes 5–6 orders of magnitude.

A relative change in absorption at 600 and 400 nm (Fig. 4) allows one to estimate the absorption coefficient of X-isomer absorption bands in a methanol matrix. Assuming that the X-isomer weakly absorbs at 600 nm, one can write down the following equation

$$\frac{|\Delta D(400)|}{|\Delta D(600)|} = \frac{\varepsilon_X^{400} - \varepsilon_B^{400}}{\varepsilon_B^{600}}. \quad (1)$$

Using the absorption coefficients of the B-form absorption bands (Fig. 1), one can obtain $\varepsilon_X^{400} \approx 42\,000\ M^{-1}\ cm^{-1}$ and $\varepsilon_X^{650} \approx 35\,000\ M^{-1}\ cm^{-1}$.

3.4. Stationary photolysis of SPO2 in a frozen matrix

The spectral changes upon the stationary photolysis of the SPO2 A-form in a frozen methanol matrix are shown in Fig. 6. Initially, irradiation causes a fast increase in the absorption of the B-form band in the red region (a maximum at 605 nm). Simultaneously, an increase in the absorption at 390–530 nm is observed, which has no relation to the B-form. Under prolongated photolysis, an increase in absorption in the long-wave B-form band stops, and the new absorption bands are formed with maxima at 415 and 508 nm. Their intensities are compared with those of the band at 605 nm. In the final spectrum, the long-wave absorption band of the B-form obtained by irradiation is broader than that formed by freezing solutions that initially contained the B-form of spirooxazines (equilibrium B-form).

3.5. Laser flash photolysis of A-form of SPO2 in a frozen matrix

Fig. 7 shows the kinetic curves of a change in intermediate absorption over the range of 0–400 μs at 77 K for a specially prepared sample containing only the A-form of SPO2. The kinetics of absorption change (as in the case of SPO1) is nonexponential. A laser pulse is followed by a "fast" region after which the absorption change rate decreases substantially and by 400 μs, tends to zero. In the blue region (400 nm), the absorption intensity over the range of 0–400 μs decreases by a factor of 2. In the long-wave absorption band of the B-form (605 nm), absorption starts to increase almost from zero over a fast region after which the growth also slows down.

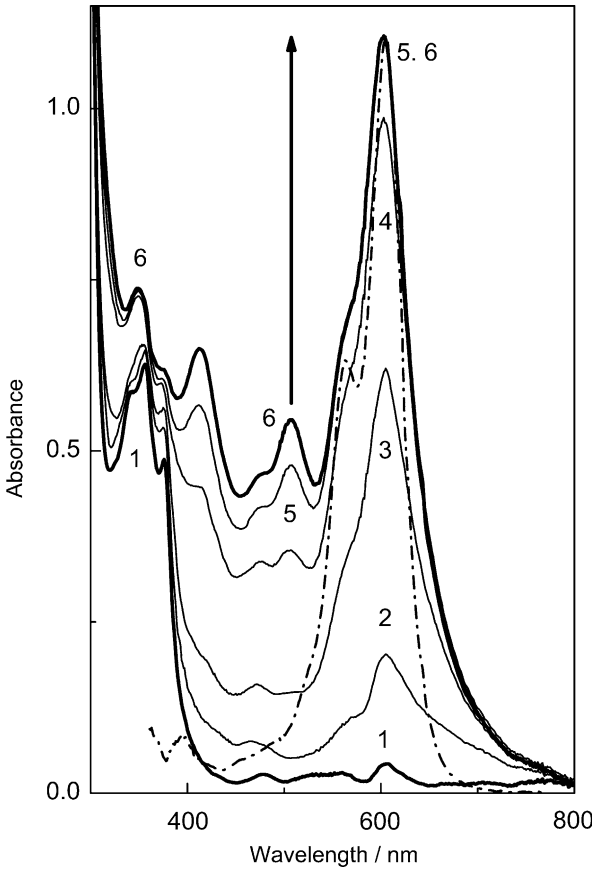


Fig. 6. Stationary photolysis of SPO2 (1.8×10^{-3} M) at 77 K. Irradiation by XeCl laser (308 nm). Before freezing, the solution of SPO2 was transformed to A-form by irradiation of cooled sample (280 K) at 532 nm (2nd harmonics of Nd^{3+}:YAG laser). Curves 1–6 denote to 0, 500, 3000, 9000, 18 000, and 27 000 XeCl laser pulses. Dash line is the UV absorption spectrum of B-form of SPO2.

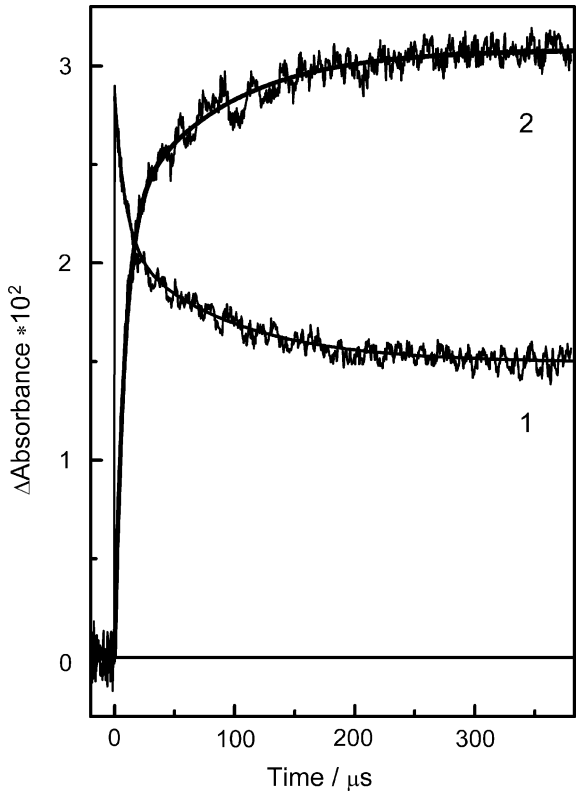


Fig. 7. Kinetic curves of changes in intermediate absorption caused by laser flash photolysis (308 nm) of A-form of SPO2 (1.7×10^{-3} M) at 77 K. Curves 1, 2 correspond to registration wavelengths of 400 and 605 nm. Smooth curves – three-exponential fit with the characteristic times 8.6; 86; and 1 000 000 μs and varied relative amplitudes.

The solid lines in Fig. 7 denote the fit of kinetic curves by a set of three-exponential functions. The characteristic times of the two exponents were 8.7 and 86 μs (these values were obtained for kinetics at both 440 and 605 nm). The characteristic time of the third exponent is too long, which is in fair agreement with the recording of the residual absorption at these wavelengths upon stationary photolysis. Similar to SPO1, absorption in the blue region (400 nm) is assumed to belong to X-isomer. The kinetics of X → B transformation, in this case, is too delayed and the absorption of X-isomer can be recorded under stationary experiments. An increase of the B-form absorption (605 nm) from zero value indicates the process has no characteristic times shorter than 8 μs. Thus, the existence of a long alkyl substituent in SPO2, has shifted the time domain of the transformation of X-isomer into B-form toward long times as compared with SPO1. For SPO2, this range in a methanol matrix stretches from ~10 μs to thousands of seconds (8–9 orders of time).

Fig. 8(a) shows the spectra of intermediate absorption upon the photolysis of the A-form of SPO2 in a methanol matrix at 77 K. For comparison, Fig. 8(a) gives the difference in spectra of equilibrium B- and A-forms (obtained from solution freezing). Fig. 8(b) demonstrates that the kinetic curves at 400 and 760 nm could be fitted by a set of exponential functions with the same parameters. The absorption bands with maxima at 400 and 750 nm that follow the laser pulse so as in the case of SPO1, can be referred to the X-isomer. The width of the B-form band with a maximum at 605 nm formed at short times is much smaller (about twofold) than the widths of both the band formed by stationary photolysis and the band of the equilibrium B-form. A substantially smaller width is, probably, due to the fact that in the X → B process only one B-form isomer is first formed. Thus, at long times (tens, hundreds of milliseconds, and more) the process of X-isomer transformation into B-form can be superimposed by the processes of B-form redistribution over its isomeric forms that lead to the broadening of absorption band at 605 nm. In this time domain, the X-isomer structure is likely to evolve so that upon stationary photolysis the bands with maxima at 414 and 508 nm are formed in the spectrum (Fig. 6).

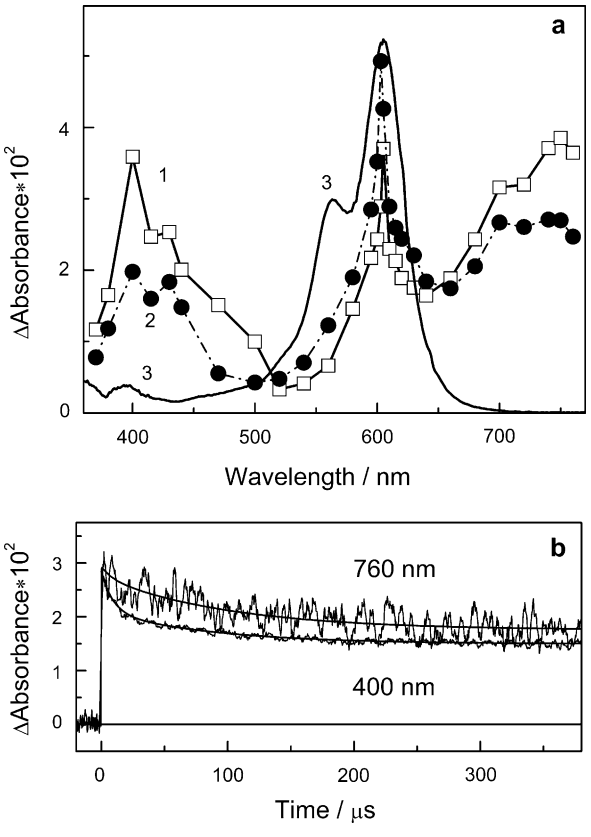


Fig. 8. (a) Intermediate absorption spectra caused by laser flash photolysis (308 nm) of A-form of SPO2 (1.8×10^{-3} M) at 77 K. Curves 1, 2 correspond to 30 and 380 μs after laser pulse. Curve 3 is the difference UV absorption spectra of B- and A-forms of SPO2. (b) Kinetic curves of changes in intermediate absorption at the wavelengths of 400 and 760 nm. Smooth curves – three-exponential fit with the characteristic times 8.6; 86; and 1 000 000 μs and varied relative amplitudes.

Using a relative change in optical density at 400 and 605 nm (Fig. 7) and Eq. (1), it is possible to estimate the absorption coefficients of X-isomer bands for SPO2 ($\varepsilon_X^{400} \approx 33\,600\ M^{-1}\ cm^{-1}$ and $\varepsilon_X^{750} \approx 35\,000\ M^{-1}\ cm^{-1}$). These estimates and the measurement of laser pulse intensity make it possible to determine the quantum yield of X-isomer appearance. In a frozen matrix, at 77 K, it decreases more than by order of magnitude ($\varphi \sim 0.01$) as compared with the case of liquid solutions ($\varphi = 0.24$, Table 1). Similar estimates of quantum yield are given for naphthospiroxazines in the glass of petroleum ester at 77 K [57].

3.6. Spectroscopy and kinetics of X-isomer

The origin of intermediates (including X-isomer) has being studied in the photochemistry of spirooxazines and spiropyrans since 1962 [41,42]. Prior to the appearance of pico- and femtosecond spectrometers, in low-temperature experiments, the absorption bands of the red region [43,44,56,57], actually located where the final B-form was absorbed, were assigned to X-isomer. The fast and superfast measurements for the solutions of spirocompounds substantially changed these concepts. Intermediate absorption appeared to arise at 400–500 nm even before the formation of the B-form absorption band in the red spectral region. This absorption can refer to both the A (S_1) → A (S_n) transitions and X-isomer. The characteristic examples for both spiropyrans and spirooxazines are followed.

For the photolysis of 6′-methoxyindolinobenzospiropyran in toluene, it was established that X-isomer forms for 25 ps and has a wide absorption band with a maximum at 380 nm [58]. The bands with maxima at 405 and 570 nm belonging to the B-form, arise 100 ps after the laser pulse. Exciting 3′,3′-dimethyl-1′-methylspiro[2H-naphtho[1,2-*e*]-1,4-oxazine-2,2′-indoline] in butanol, the laser pulse is followed by the formation of A (S_1) → A (S_n) absorption band with a maximum at 490 nm [21]. A wide

absorption band of X-isomer in the range of 550–700 nm evolves during 0.5–2 ps. After 2 ps, a wide B-form band arises (580 nm), which narrows and shifts during several tens of picoseconds.

For 1′,3′,3′-trimethyl-6-hydroxyspiro-[2H-1-benzopyran-2,2′-indoline] (HBPS) in propanol, a complex kinetics of the appearance of intermediate absorption has been revealed [46]. To account for the results obtained, the authors have considered various models of C–O bond dissociation under UV excitation of spiropyran. The independence of the quantum yield of the photochromic transformations of indolinespiropyrans on temperature (0–100 °C) [59] and the observation of reaction at low temperature (4 K) in a polymeric matrix [60] allowed the assumption [46] that there is no activation barrier for the A* → X transition and the direct C–O band rupture occurs for less than 100 fs.

For nonsubstituted spironaphthopyrans and spironaphthooxazines, a model is proposed on the basis of femtosecond spectroscopy data [20] in which X-isomer exists only in the excited state (X*). This species absorbs in the range of $\lambda < 460$ nm. The authors of [52] assume that the conversion of the A (S_1) state into the B-form for 1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (BIPS) in *n*-pentane involves no intermediate X-isomer. 1 ps after the pulse, a wide absorption spectrum arises from the A (S_1) state in the range of 380–680 nm with a maximum at 400 nm [52]. The B-form band (540 nm) starts to manifest itself 1 ps after laser pulse, narrows, and 7.5 ps later a partially resolved vibrational structure of this band appears. Analyzing the possibility of the appearance of various B-form isomers allowed one to estimate the inner molecule temperature after UV excitation (~900 K). In [19] (picosecond photolysis of substituted spironaphthooxazines), the isomers of B-form were also assumed to form directly from the excited A (S_1) state without appearance of X-isomer. The intermediate absorption in the range of 400–460 nm arising during the first 50 ps is referred to the absorption of the B-form isomer.

For the photolysis of 6′-cyano-spiroindolinenaphtoxazine, the formation of a metastable species with intense absorption bands in the 400–600 and 650–975 nm was demonstrated [26]. The decay of these bands was fitted by a two-exponential kinetics with time constants of 6.5 and 30 ps. The bands were assigned to an "Y" intermediate, which transformed to the ground state of the closed form. The spectrum of X-isomer as a precursor of merocyanine was not observed in [26], probably, due to weak absorption.

By this means most of the works on the photochemistry of spiropyrans and spirooxazines assume the existence of an intermediate X-isomer. However, its spectral and kinetic parameters obtained in various works are varied over a wide range. Moreover, some authors assume the absence of intermediate X-isomer in the A → B process. The superfast measurements indicate that if this isomer does exist, its absorption is in the range of 400–500 nm.

The results for SPO1 and SPO2 in a frozen matrix indicate that the intermediate spirooxazine form (*cis*-cisoid X-isomer) does exist and has absorption bands in the blue (400–500 nm) and far red (750 nm) regions. The lifetime of X-isomer in a rigid matrix at liquid nitrogen temperature varies over a wide range from tens of nanoseconds to milliseconds for SPO1 and to hours for substituted spirooxazine (SPO2). The lifetime is determined by the local surrounding of a molecule and can be rather short due to a free volume. If a spirooxazine molecule is "clamped" by surrounding molecules, the times of X → B transformation increase by many orders of magnitude.

In solutions, at room temperature the X → B transition for spiropyrans and spirooxazines takes 10^{-12}–10^{-11} s [20–22,24,25,39,40,46,52,61]. For SPO1 in a methanol matrix, at 77 K this transformation, depending on the local molecule environment, takes 10^{-7}–10^{-1} s. Assuming that the preexponential factor of the rate constant is weakly dependent on the state of aggregation (either liquid or amorphous glass), these two time domains allow one to estimate the activation energy range of X → B transformation in a matrix (8–21 kJ/mol). The range width is determined by inhomogeneity of the local environment of X-isomer, and the activation energy distribution is wider in a harder matrix [35]. The existence of a long substituent in the SPO2 molecule shifts the time domain of X → B transformation in a methanol matrix to the range of 10^{-5}–10^{4} s. The estimates similar to those for SPO1, in the case of SPO2, give the activation energy range of 12–32 kJ/mol.

For spironaphthooxazine in a polystyrene film, the X → B transition was found to occur even at very low temperatures (ca. 10^4 s at 25 K [33]). This time domain of transformation leads to an activation energy of about 8 kJ/mol, which is the lower distribution boundary. Transformations with larger activation energies should occur at very long times that are practically impossible to record. In [33], it was shown that at 77 K the B → A transition takes about 10^3 s. Thus, the X → B transformation is much faster. The reaction kinetics was not studied in detail in [33]. Therefore, the inhomogeneity of a polystyrene matrix and its influence on the transformation rate are uncertain. Nevertheless, our results and the data of [33] indicate that the processes X → B and B → A can be fast enough despite matrix rigidity and low temperatures.

A weak dependence of the quantum yield of A → B transformation in the range of 0–100 °C [59] assumes that the barriers created by medium molecules do not exceed 1 kJ/mol at room temperature and higher. A decrease in temperature substantially reduces solution volume (upon methanol freezing the volume decreases by 23%), which leads to a decrease in a free volume for a molecule in a matrix. In this case, the "clamped" molecules almost stop to participate in phototransformations and the quantum yield at low temperatures decreases substantially. Thus, the potential surface of A → X → B transformation includes, most probably, the additional barriers determined by the existence of surrounding molecules.

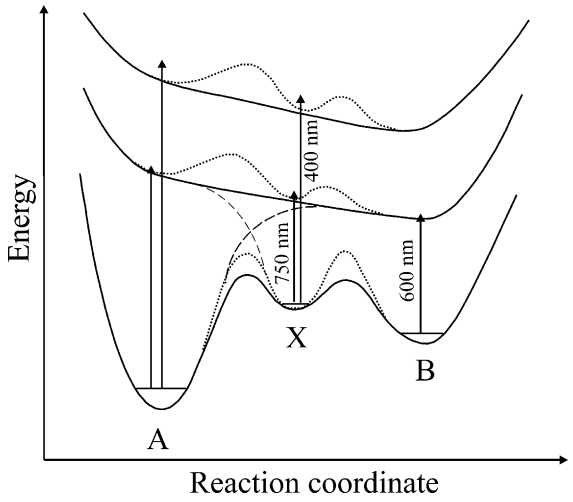


Fig. 9. Scheme of potential surfaces for phototransformation A → X → B. Dotted line – additional barriers caused by molecules of local surrounding. Dashed line – diabatic surface.

Fig. 9 shows potential surfaces for the A → B phototransformation. The additional barriers are denoted by dotted lines. The reaction proceeds along the diabatic surface (dashed lines). The values of the barriers depend on the local environment of a spirooxazine molecule and are likely to vary over wide ranges. Since the reaction coordinate is determined by the rotation of molecule fragments, barriers in a matrix can also exist on the surface of the excited state from which the photoreaction starts. The existence of these barriers can determine a complex kinetic pattern in a rigid polymeric or frozen matrix, dispersion of quantum yield and transformation rate constants.

3.7. Formation of B-form absorption

The character of B-form absorption formation at 600 nm suits well the framework of these concepts. For both spirooxazines, first the absorption band arises (Figs. 5 and 8), whose width is substantially smaller than that for the B-form band observed in both solutions and matrices (Figs. 1 and 2). For SPO1, after 800 μs the width increases (Fig. 5) and 5 s later (the time during which the optical spectrum is recorded upon stationary measurements) it becomes close to the usual width. For substituted spirooxazine (SPO2), after 400 μs the band remains narrow (Fig. 8). However, over a range of several seconds, its width also increases substantially (Fig. 7). This behavior of the absorption band at 600 nm can be assigned to the appearance of only one B-form isomer in the X → B process.

The existence of isomeric forms of the open merocyanine structure was assumed in [41]. The *cis–trans* positions relative to three bonds linking the fragments of the spirocompound molecule make probable the existence of 8 isomers [16,62]. Below, we shall use the well-known designations [62] indicating position starting with the indoline part of the molecule. Among 8 possible configurations, *cis*-isomers relative to the central bond are considered unstable (TCT, TCC, CCT, and CCC) due to the repulsion of two molecule fragments [62]. *trans*-Isomers relative to the central bond are considered as B-form isomers, which are in equilibrium at room temperature. The quantum-chemical calculations [63] indicate that the TTC isomer with the largest dipole moment has the lowest energy [20]. The energy of remaining *trans*-isomers (TTT, CTT, and CTC) is by 0.4–11 kJ/mol higher.

Studying the Raman spectra with nanosecond time resolution demonstrated [62,64] that upon UV photolysis of BIPS and 6-nitro-BIPS spiropyrans the TCC isomer of B-form is first to appear. At longer times, there are transitions between the various forms of isomers TCC ⟺ TTC ⟺ TTT ⟺ CTT ⟺ CTC. The difference in the energies of isomers [62] determines the temperature dependence of the transition rate constants. The existence of similar isomers is shown for the B-form of nonsubstituted and substituted spironaphthooxazines in solvents of various polarities [65].

Thus, the appearance of a narrow line at 600 nm in a microsecond time domain after the X → B transformation is, probably, due to the formation of TCC isomer whose structure is close to that of X-isomer. Transition of the TCC isomer into other isomer forms leads to the broadening of the absorption band. The low energy barriers (and activation energies for transitions) between isomers determine the transition time range 10^{-4}–10^{0} s in a methanol matrix. A potential surface of the ground state in the region of the final product contains several minima that correspond to isomer forms (omitted in Fig. 9). Barriers between the forms in a rigid matrix are modulated by the local environment, which also has an effect on the transformation kinetics.

4. Conclusions

Photochemistry of the closed A-form of phenanthroline-containing spirooxazines in a frozen methanol matrix was studied. For nonsubstituted spirooxazine (SPO1), excitation of A-form gives rise to the absorption of B-form under the action of a laser pulse. The kinetics of further increase in B-form concentration is determined by inhomogeneity of a rigid matrix and is described by a set of exponents with characteristic times from hundreds of nanoseconds to tens of milliseconds. The appearance of B-form in a matrix is accompanied by the appearance of X-isomer whose disappearance is determined by the same characteristic times as of the B-form appearance. For SPO2, having a long alkyl substituent, the range of characteristic times shifts to longer times so that even upon stationary photolysis the X-isomer absorption manifests itself. Thus, a long lifetime of X-isomer indicates that the B-form arises from the ground state of this intermediate form of SPO and the existence of a long substituent increases substantially the time of this transformation in a frozen matrix. The formation of a narrow absorption band at 600 nm immediately after the laser pulse assumes the initial appearance of only one isomer of the open form.

Acknowledgements

The work was supported by the INTAS (Grant 2000-00152), the Russian Foundation for Fundamental Research (Grants 05-03-32474, 03-03-33314, 03-03-39008GFEN) and the Ministry of Education of RF (program "Universities of Russia", Grant UR.05.01.020).

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