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The investigation of the intermediates of spiropyran retinal analogs by laser flash photolysis techniques with different excitation wavelengths

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ABSTRACT

Spectral-kinetic properties of intermediates of spiropyran retinal analogs (SRA), which molecules contain spiropyran and retinoid (with different polyenic chain length and aldehyde terminal group) fragments, have been investigated by nanosecond laser flash photolysis techniques using excitation wavelengths 337 and 380–450 nm in toluene. Relative quantum yields of different SRA intermediates formation relative to those of model compounds, namely triplet excited state and merocyanine form generated upon pyran cycle cleavage have been measured. It has been found that merocyanine form does not form upon photolysis of SRA with polyenic chain length of 5 and 9 using excitation wavelengths of 380–450 nm, the triplet state of retinoid fragment is observed exclusively. The yield of merocyanine (MC) form is the largest one upon SRA photolysis with excitation wavelength of 337 nm for 6′-formylsubstituted spiropyran (it exceeds that of unsubstituted analog in 8 times and forms mainly from the triplet state). The yields of MC for SRA with polyenic chain length of 3, 5 and 9 carbon atoms are 5–10 times smaller than that for unsubstituted spiropyran.

1. Introduction

Indoline spirobenzopyrans are widely known class of photochromic compounds [1]. As other photochromes they are examined as elements of optical materials and devices: sensors (registering materials), optical switches for wide range of different objects (including those of biological nature), data storage, inclusions in finished products (garments, arts, cosmetics, means of information and document protection), special materials with harmful irradiation protective properties [2–4].

The simplicity of preparation and the possibility to vary the spectral properties of these compounds directly by the introduction of the substituents of different nature into the specified positions of molecule or by the medium selection (solvent, polymer, crystal) make the design of new photochromic spiropyran-containing materials very attractive.

Synthetic methods for retinal analogs with trimethylcyclohexenic ring replaced by spiropyran fragment have been developed by us earlier [5,6]. These spiropyran retinal analogs (SRA) possess two various structural fragments with different photochemical properties. In the 6′-nitrosubstituted derivative pyran cycle cleavage is possible with formation of relatively long-lived colored merocyanine (MC) form, absorbed light in the long-wavelength region, in other one – the formation of short-lived triplet state and *cis*-/*trans*-isomers, absorbed in the short-wavelength region [7,8]. This peculiarity of SRA may prove to be useful in applications as molecular switches, especially with implementation of selective photoinitiation of different processes, such as light-driven proton transport by bacteriorhodopsin, membrane protein of

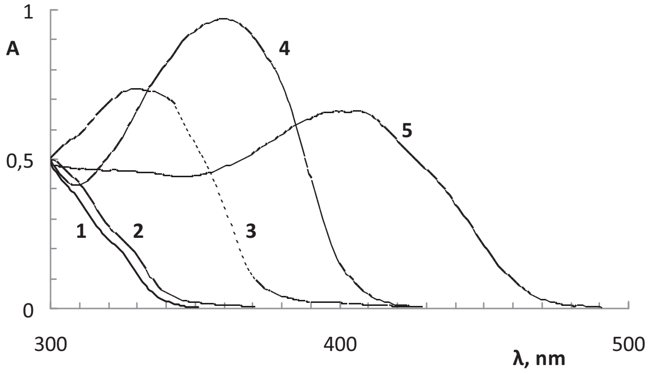

Fig. 1. Normalized absorption spectra of compounds **1**–**5** in toluene.

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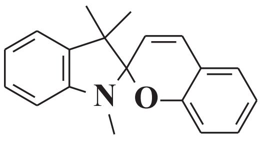
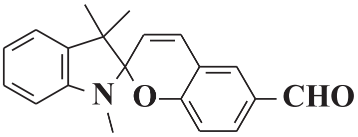
Halobacterium salinarum [6,9], by varying excitation light wavelength and medium.

In the present study spectral-kinetic properties of intermediates formed upon photolysis of compounds synthesized earlier [6] have been investigated using the nanosecond laser flash photolysis techniques:



(1)



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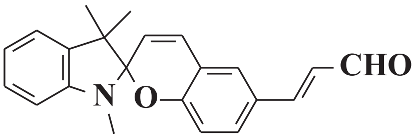

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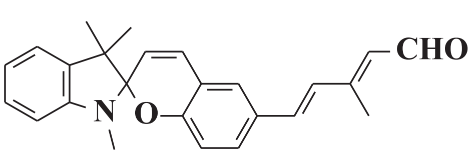

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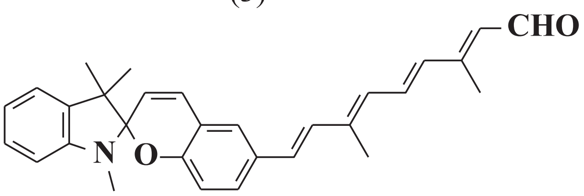
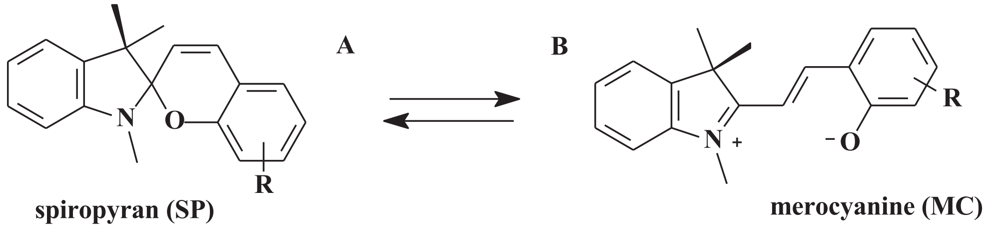


(5)

The selection of **1** as SRA fragment is due to the fact that the initial closed form **A** of compound **1** absorbs at 337 nm, but almost does not absorb at $\lambda \geq 360$ nm (Fig. 1). The photoexcitation of **1** by 337 nm light results in formation of open merocyanine form **B** with relatively large quantum yield [10,11].



Relatively large yield of triplet states is an important property of retinal and its analogs [12–14]. At the same time the presence of absorption at the region $\lambda \geq 380$ nm provides the possibility of selective photoexcitation by light with $\lambda \geq 380$ nm (Fig. 1).

2. Experimental

The retinal analogs (SRA) **3**–**5** were synthesized with the use of a universal experimental procedure that had been proposed by us earlier [6,9]. Model spiropyrans **1**, **2** were prepared as previously described in the literature [15,16]. Purity (≥95%) of all derivatives **1**–**5** was characterized by TLC or HPLC. Their structures were approved by 300 MHz NMR spectroscopy and mass-spectrometry [6].

Methanol and toluene spectral grade were used in UV spectroscopy for preparing solutions.

Electronic spectra were measured in 10-mm quartz cuvettes on Shimadzu UV-2140PC (Japan) spectrophotometer.

Absorption spectra and the kinetics of formation and decay of intermediates were recorded in the time range ≥ 10 ns at $400 \leq \lambda \leq 800$ nm spectral region by the nanosecond laser flash photolysis techniques with registration of electronic absorption [17,18]. A nitrogen laser (PRA LN 1000, with 1 ns pulse duration and 337 nm radiation wavelength), operating in the ≤10 Hz frequency regime, or a dye laser (PRA LN 102, with 0.5 ns pulse duration and 430–470 nm radiation wavelengths) pumped by a N_2 laser were used as an excitation source. Acquisition and averaging of kinetic curves (from 4 to 128 laser pulses) were performed by a UF.258 high speed digitizer (Sweden) interfaced to a personal computer. The data presented in the paper are the average values obtained by processing of at least ten kinetic curves under the indicated conditions.

The yields of the intermediates were determined relative to the yields of corresponding intermediate of **1** (merocyanine form) and **2** (triplet states) by comparison of the corresponding absorption intensities at the absorption maxima, measured at same absorbance of initial solutions at excitation wavelength, assuming similar absorption coefficients of the corresponding intermediates.

All measurements were carried out at room temperature.

3. Results and discussion

3.1. Intermediates of model compound **1**

The appearance of only one intermediate – the merocyanine form **B** (MC) is observed after flash photoexcitation of compound **1** (spiroform **A)** with 337 nm light. MC has the characteristic absorption spectrum with maximum at about 600 nm (λ_B in Table 1) [10,11]. The decay kinetics of MC obeys the first order law (rate constant, k_B, is presented in Table 1). Spiroform A of this compound does not absorb at $\lambda \geq 380$ nm range (Fig. 1, spectrum 5), therefore the measurements upon photoexcitation with light of longer wavelengths were not performed.

3.2. Intermediates of model compound **2**

The photoexcitation of **2** in toluene solution with 337 nm light results in the formation of 2 intermediates (Fig. 2): (1) relatively

Table 1
Absorption bands maxima, relative yields and decay rate constants of merocyanine form **B** (λ_B, φ_B and k_B, respectively) and triplet state (λ_T, φ_T and k_T, respectively) in deoxygenated toluene.

Compound	1	2	3	4	5
λ_B, nm	580	600	620	620	600
φ_B, rel. units	1.0	8.2	0.18	0.093	0.22
k_B, s^{-1}	2.0	0.058	0.19	0.22	0.27
λ_T, nm	–	420	–	430	490
φ_T, rel. units	–	1.0	–	1.5	0.77
k_T, s^{-1}	–	8.4×10^4	–	2.8×10^6	7.4×10^4
k_q, 10^9 l/mol s[a]	–	4.6	–	7.4	7.4

[a] O_2 solubility in air saturated toluene was taken equal to 1.11 mM [20].

long-lived MC form **B** (corresponding values of λ_B and k_B, as well as quantum yield φ_B, as compared to similar value for **1**, are presented in Table 1); (2) relatively short-lived triplet excited state **T2**, which absorbs in 400–500 nm range (position of λ_{max}, λ_T, is presented in Table 1) (Fig. 2) [19].

The decay kinetics of **T2** obeys the monoexponential law (rate constant in deoxygenated toluene, k_T, is presented in Table 1). The disappearance of **T2** is accompanied by simultaneous formation of MC **B2** (Figs. 2 and 3). The introduction of the air oxygen into solutions results in the significant decay acceleration of **T2** (corresponding quenching rate constant, k_q, calculated based on molecular oxygen concentration in air saturated toluene being equal to 1.11×10^{-3} mol/l [20], is presented in Table 1) and in the decrease of **B2** yield. The experimental data analysis allows us to conclude that about 50% of MC **B2** is formed from **T2**. MC **B2** quantum yield is significantly higher than that of **B1** (Table 1). Such behavior is typical for spiropyrans which have possibility of fast (which is able to compete with the spiro-bond cleavage process) intersystem crossing in the singlet excited state, which is provided by the presence of carbonyl or nitro groups as substituents in aromatic rings [21–24]. As a rule, the substituents of this group possess electronegative properties, which lead to significant deceleration of MC **B** form decay [see k_B values for compounds **1** and **2** in Table 1) [19,21–25].

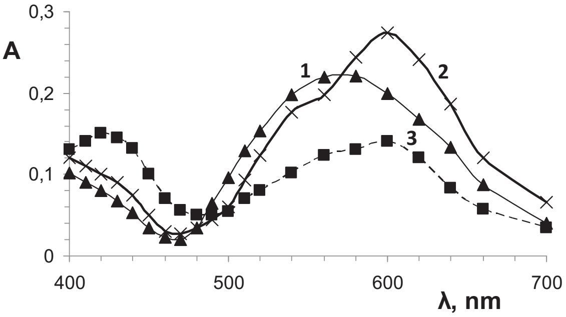


Fig. 2. Absorption spectra of the intermediates produced by laser flash photolysis of **2** in toluene with 337 nm light (optical density of solution at 337 nm equals to 0.4) in 20 ns (3), 50 μs (2) and 20 ms (1) after laser pulse.

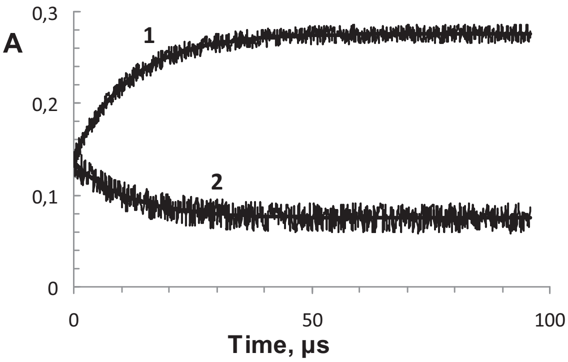


Fig. 3. Decay kinetics of the intermediates, observed at 440 (2) and 600 (1) nm under laser flash photolysis of **2** with 337 nm light (optical density of solution at 337 nm equals to 0.4) in toluene.

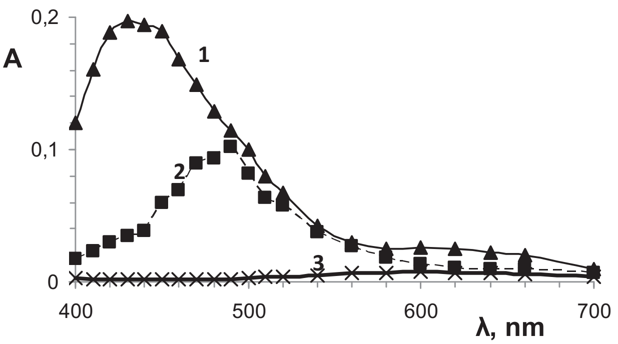


Fig. 4. Absorption spectra of the intermediates produced by laser flash photolysis with 337 nm light of **4** immediately after the laser pulse (1) and **5** 20 ns (2) and 100 μs (3) after the laser pulse (optical density of initial solutions at 337 nm equals to 0.4) in toluene.

Spiroform A of compound **2** does not absorb at $\lambda \geq 380$ region (Fig. 1, spectrum 5), therefore the measurements upon photoexcitation with longer wavelengths light were not performed.

3.3. *Intermediates of compounds **3–5***

The main intermediate of compounds **4** and **5** observed under the photolysis with 337 nm light is the relatively short-living triplet excited state (see Fig. 4, corresponding values of λ_T, k_T and k_q, as well as **T** yields as compared to **T2**, are presented in Table 1). Contrary to **T2**, the disappearance of **T4** and **T5** is not accompanied by the formation of any longer-lived intermediates absorbed in the registration spectral range. The spectral-kinetic properties of **T5** are quite similar to the respective parameters of the retinal triplet state [12–14].

Decrease of the polyenic substituent length (transition from **5** to **4**) is accompanied by the short-wave length shift of **T** absorption band and by the acceleration of its decay (Table 1). Apparently, the compound **3** with short polyenic substituent behaves similarly, but temporal and/or spectral resolution of our device did not allow to observe it.

The formation of small amounts of respective MC **B** forms is observed in addition to the triplet states upon photolysis of **3**, **4** and **5** with 337 nm light (relative yields are presented in Table 1). MC form **B** is barely formed upon photolysis of compounds **4** and **5** with $\lambda \geq 380$ nm light, that is due to the occupation of S_1 state. Thereby the opening of spirocycle in spiropyrans with polyenic substituents containing terminal aldehyde group proceeds with low efficiency (as a result of the presence of the most important competitive internal conversion process) in an excited state higher than S_1.

The characteristic time of the internal conversion from the A_g^- S_2 state of all trans retinal to low-lying $n\pi^*$ state that decays with a 33 ps time constant to form the retinal triplet state is near 0.44 ps [26]. This time is comparable with the typical duration of MC formation from the S_1 state of indolinospiropyran (0.9 ps) [27]. The coloring reaction of spirocompounds proceeds via some intermediate *X*, which corresponds to the molecular electronic state with the practically initial structure, but broken C–O bond. The formation of *X* form can be quite fast, up to 0.25 ps [28] and it can easily compete with the internal conversion from S_2 state of compounds **3**, **4** and **5** to S_1 state localized mainly on the retinoid fragment.

The values of MC decay rate constants in the range of studied compounds increase in the following sequence: $\mathbf{2} \ll \mathbf{3} < \mathbf{4} < \mathbf{5} \ll \mathbf{1}$. Such behavior is probably related to the electron-acceptor ability of the indole fragment substituents of spiropyran molecule. The removing of the polar group away from indole core through a system of double bonds leads to the increase of electron density at spiropyran fragment. The introduction of one double bond results in the order of magnitude increase of MC decay rate constant which is then grows in some arithmetic progression with the increase of the polyenic chain length.

4. Conclusions

Thereby, upon photolysis with UV light two photoprocesses may occur in the studied spiropyrans with polyenic chains as substituents in aromatic ring – the photochromic one in spiropyran fragment as well as the formation of the triplet state, localized mainly at the polyenic fragment.

Acknowledgements

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