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Synthesis and spectral kinetic study of photoinduced processes of photochromic nitro-substituted indoline and benzothienopyrroline spiropyrans in solutions

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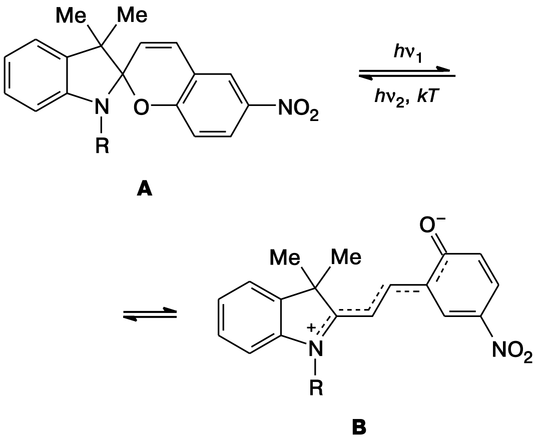
Nitro-substituted benzothienopyrroline spiropyrans containing substituents in the benzothienopyrroline moiety were synthesized. The comparative spectral kinetic study of the photochromic transformations of these compounds and their indoline analogs in solvents of various polarity was carried out. On the basis of the results obtained and literature data, the photoinduced aggregation of molecules of the merocyanine form in weakly polar solvents was suggested.

Key words: photochromism, aggregation, spectroscopy, kinetics, spiropyrans.

Development of nanotechnologies during the recent decade favors a substantial extension of functional possibilities and decreases the sizes of technical facilities of various purpose, because nanoparticles of organic and inorganic substances possess unusual properties providing the creation of novel systems and materials. Photochromic nanoparticles are very important for the development of photocontrolled reversive optical smart devices.[1]

It is known that photochromic nanoparticles, being associates of various type, appear upon the UV irradiation of solutions of spiro compounds, in particular, nitro-substituted indoline spiropyrans.[1] Photochromic spiro compounds are classified as thermally relaxing photochromes, because the photoinduced forms of such compounds at usual temperatures spontaneously return to the initial spiropyran state. Photochromism of compounds of this type is the mutual reversible phototransformation of the starting spiropyran (**A**) and photoinduced merocyanine (**B**) forms (Scheme 1).[2]

Scheme 1



The spontaneous transformation of the merocyanine form to the initial state is accelerated on heating the photochromic system.

In this work, we present the results of the spectral kinetic study of photochromism for a series of the synthesized nitro-substituted indoline and benzothienopyrroline spiropyrans.

Results and Discussion

The objects of the study are nitro-substituted indoline spiropyrans (ISP) **1a—c** (see Refs 3 and 4) and nitro-substituted benzothienopyrroline spiropyrans (BTSP) **2a—d**.

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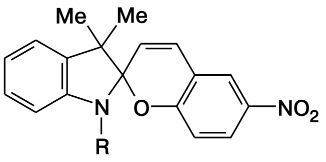
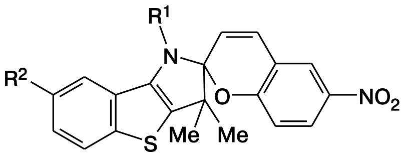


1a—c



2a—d

1: R = Me (**a**), $C_{16}H_{33}$ (**b**), $C_{18}H_{37}$ (**c**)
2: R^1 = Me, R^2 = H (**a**); R^1 = $C_{18}H_{37}$, R^2 = H (**b**);
R^1 = Me, R^2 = NO_2 (**c**); R^1 = $C_{18}H_{37}$, R^2 = NO_2 (**d**)

Synthesis of photochromic compounds. The BTSP studied were synthesized according to Scheme 2 in which the key compounds are benzothienopyrrolenines of type **3** obtained by the reaction of benzothienone hydrazone **4** with 3-methylbutan-2-one under the Fischer reaction conditions. The alkylation of benzothienopyrrolenine **3** by alkyl triflates afforded quaternary salts **5a,b**, whose reaction with 2-hydroxy-5-nitrobenzaldehyde gave target BTSP **2c,d**. The synthesis of BTSP **2a,b** has earlier been described in detail.[5]

The structure of the synthesized compounds was proved by ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis. In the case of BPSP **2d**, we failed to obtain an analytically pure sample, because the substance does not crystallize due to the presence of the long octadecyl substituent.

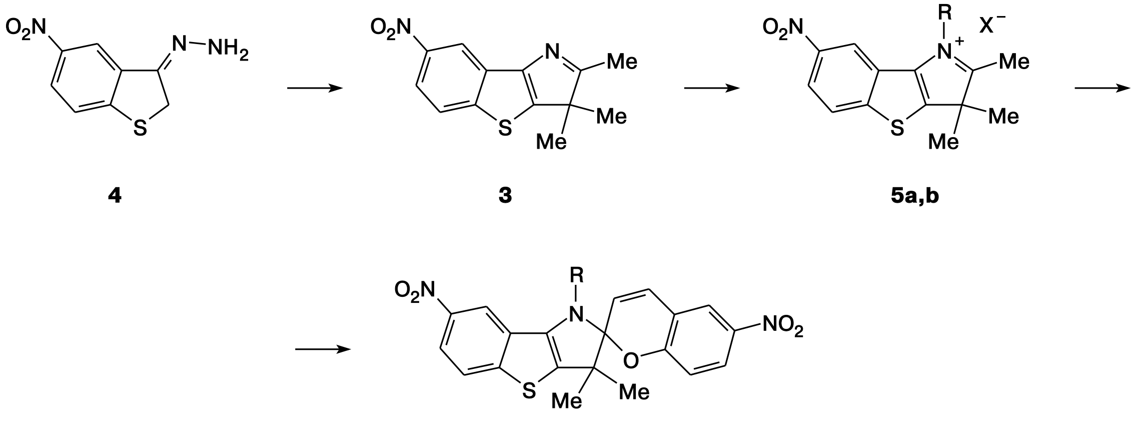
Spectral kinetic study of photochromism of spiropyrans. The results of the spectral kinetic study of nitro-substituted spiropyrans **1a—c** and **2a—d** are presented in Table 1 and Figs 1—3. The studies were carried out in solutions with high concentration of the initial spiropyrans ($C = 2 \cdot 10^{-3}$ mol L^{-1}), since the formation of aggregates of the merocyanine form requires the concentration of the latter to be increased. This concentration was substantially lower than that of the spiropyran form due to the insignificant quantum yield of the merocyanine form, repeated absorption of the activating radiation of the appeared merocyanine form and photoinduced transition to the spiropyran form, and spontaneous decolorization.

The initial spiropyran form of compound **1a** in toluene is characterized by one long-wavelength absorption band with a maximum at 335 nm (see Fig. 1, curve *1*), and the photoinduced merocyanine form is characterized by two absorption bands with maxima at 380 (shoulder) and 604 nm (see Fig. 1, curve *2*). The long-wavelength absorption band consists of several superimposed bands, of which two bands are distinctly pronounced: the bands with maxima at 576 and 604 nm.

An analysis of the absorption spectra of concentrated solutions of ISP **1a** detected at small and large exposures (see Fig. 1) shows that at insignificant concentrations of the photoinduced merocyanine form its absorption band is characterized by the most intense maximum at 576 nm and a less intense naximum at 604 nm (see Fig. 1, curve *2*). The further UV irradiation results in an increase and also redistribution of the absorption band intensity (see Fig. 1, curves *3* and *4*). The long-wavelength absorption band of the photoinduced form at 604 nm is prevailing in intensity.

When weakly polar toluene is replaced by polar ethanol, one absorption band of the photoinduced form with a maximum at 540 nm is observed. Its position remains

Scheme 2



4 **3** **5a,b**

2c,d

R = Me, $C_{18}H_{37}$

Table 1. Spectral kinetic characteristics of nitro-substituted spiropyrans in toluene ($\varepsilon = 2.38$), acetone ($\varepsilon = 20.7$), and acetonitrile ($\varepsilon = 37.5$)

Compound	Solvent	λ_A^{max}	λ_B^{max}	k_{BA}^d/s^{-1}
		nm		
1a	Toluene	335	576 sh	
			604	$5.0 \cdot 10^{-2}$
	Acetone	335	565	$1.1 \cdot 10^{-2}$
	Acetonitrile	335	555	$1.5 \cdot 10^{-2}$
1b	Toluene	335	569 sh	
			605	$4.6 \cdot 10^{-2}$
	Acetone	335	570	$1.1 \cdot 10^{-2}$
1c	Toluene	335	572 sh	
			607	$2.3 \cdot 10^{-2}$
	Acetonitrile	335	564	$3.9 \cdot 10^{-2}$
2a	Toluene	320	580 sh	
			610	$9.9 \cdot 10^{-2}$
	Acetonitrile	320	575	$1.5 \cdot 10^{-2}$
2b	Toluene	328	585 sh	
			625	$2.0 \cdot 10^{-1}$
	Acetonitrile	328	580	$5.6 \cdot 10^{-2}$
2c	Toluene	335 sh	593 sh	
			625	$4.8 \cdot 10^{-1}$
	Acetonitrile	335 sh	580	$7.7 \cdot 10^{-1}$
2d	Toluene	335	590 sh	
			634	$1.9 \cdot 10^{-1}$
	Acetonitrile	335	585	$3.1 \cdot 10^{-1}$

Note. ε is the dielectric constant; λ_A^{max} and λ_B^{max} are the maxima of the long-wavelength absorption bands of the starting spiropyran and photoinduced merocyanine forms, respectively; k_{BA}^d is the rate constant for dark decolorization at the wavelength of the absorption band maximum of the photoinduced merocyanine form.

unchanged with an increase in the duration of UV irradiation (see Fig. 2).

The spectral difference in photochromic transformations observed for ISP **1a** turned out to be characteristic of two other studied nitro-substituted indoline spiropyrans **1b,c** containing alkyl substituents of various length at the nitrogen atom (see Table 1). As in the case of ISP **1a**, the photoinduced complicated absorption band in the visible spectral region is observed only for solutions of these compounds in weakly polar toluene. The influence of the nature of the substituent is manifested only as an insignificant bathochromic shift of the absorption band of the photoinduced form.

The kinetics of dark relaxation processes differs for these three compounds. For compounds **1a** and **1b**, the relaxation is retarded with an increase in the polarity of the solvent, whereas an insignificant acceleration is observed for ISP **1c**.

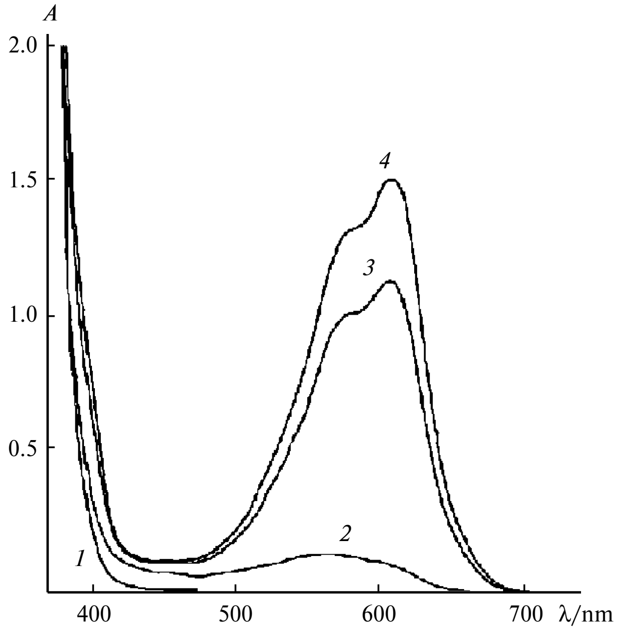


Fig. 1. Absorption spectra of the photoinduced merocyanine form of **1a** in toluene ($C = 2 \cdot 10^{-3}$ mol L^{-1}) before (*1*) and after UV irradiation with the mercury-xenon lamp through the UFS-8 light filter for 3 (*2*), 10 (*3*), and 100 s (*4*).

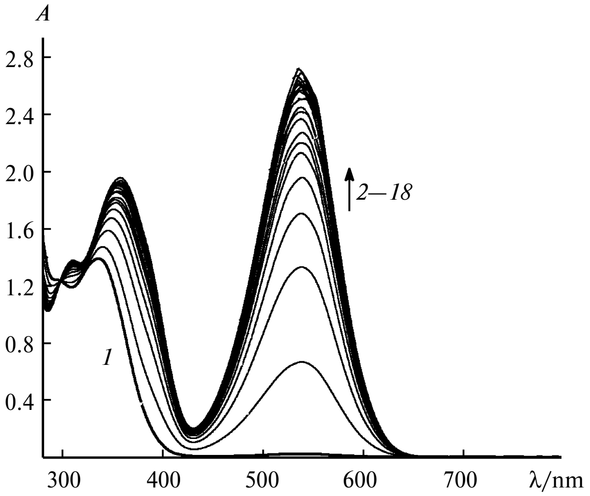


Fig. 2. Absorption spectra of the photoinduced merocyanine form of ISP **1a** in ethanol ($C = 2 \cdot 10^{-3}$ mol L^{-1}) before (*1*) and after successive irradiation with the nonfiltered UV light from the mercury-xenon lamp (*2—18*).

The comparative analysis of the data on photochromism of nitro-substituted benzothienopyrroline spiropyrans **2a,b** and **2c,d**, as well as indoline spiropyrans **1a** and **1b** containing the same substituents at the nitrogen atom (see Table 1) showed that they exhibit similar spectral changes upon the replacement of the weakly polar solvent by the polar one (see Fig. 3, *a*). As in the case of the corresponding indoline analog, the UV irradiation of a solution of this compound first results in the appearance of the short-wavelength absorption band, which is transformed into the absorption band with two maxima with an increase in

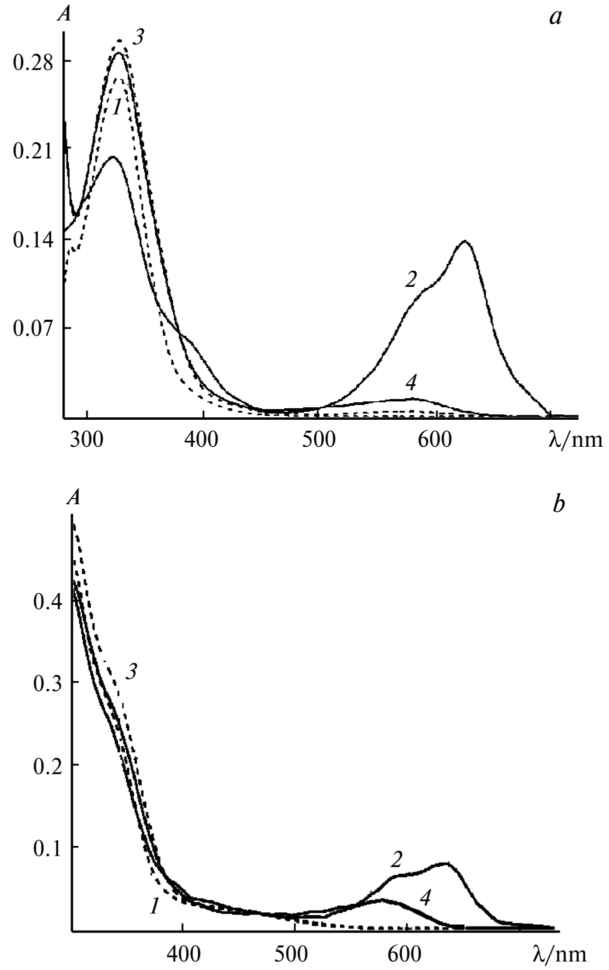


Fig. 3. Absorption spectra of BTSP **2b** (*a*) and **2d** (*b*) in toluene (*1*, *2*) and acetonitrile (*3*, *4*) before (*1*, *3*) and after UV irradiation (*2*, *4*). The concentration of the compounds in solutions is $C = 2 \cdot 10^{-3}$ mol L^{-1}.

the concentration of the photoinduced form, and the intensity of the appeared long-wavelength maximum increases.

The main distinctions of benzothienopyrroline spiropyrans from the indoline analogs are the hypsochromic shift of absorption band maxima of the initial form, the bathochromic shift of the long-wavelength maxima of the absorption bands of the photoinduced form in toluene, and a higher rate of thermal relaxation of the photoinduced form. As in the case of the indoline analogs, for compound **2a** with the methyl group at the nitrogen atom the thermal relaxation rate decreases in a polar solvent and somewhat increases for compound **2b** with the long alkyl substituent. It is noteworthy that the hypsochromic shift of the absorption band of the photoinduced form on going from a weakly polar substituent to a polar one for BTSP is lower than for ISP.

Similar photoinduced spectral kinetic changes are also observed for BTSP **2c,d** (see Fig. 3, *b*), which differ from BTSP **2a,b** only by the presence of the nitro group in the benzothienopyrroline system. The distinctions are the following: the maximum of the photoinduced absorption band in toluene experiences an additional bathochromic shift and the dark relaxation rate to the initial spiropyran state for the both compounds in polar acetonitrile is higher than in weakly polar toluene.

The data presented suggest that in weakly polar toluene at the high concentration of the photoinduced form of the photochromic compounds the absorption spectra of all studied nitro-substituted indoline and benzothienopyrroline spiropyrans contain a complicated band of the photoinduced form with two pronounced maxima. Similar spectral characteristics were observed in cyclohexanone for ISP **1a**, and three maxima were observed in the absorption band of the photoinduced form.[6] This is consistent with the earlier published[7] results of the spectral study of compound **1b** in hexane. For this compound, three maxima at 530, 584, and 618 nm were revealed[7] in the photoinduced absorption spectrum, and only one maximum at 567 nm was observed in acetone.

Based on the earlier substantiated interpretation,[7] it can be assumed that at a low concentration of the merocyanine form of the spiropyrans studied in solutions, which is achieved in a weakly polar solvent at an insignificant duration of UV irradiation (see Fig. 1, curve *2*), only the monomeric merocyanine form of nitro-substituted spiropyrans is formed. Aggregation occurs with an increase in the concentration of the photoinduced form and, perhaps, J-aggregates are formed, because the absorption band maximum of the photoinduced form shifts to the long-wavelength region.

In the case of polar solvents, mainly the monomeric merocyanine form appears in the spectra. The absorption band maximum of the merocyanine form, unlike the initial spiropyran form, experiences the hypsochromic shift with an increase in the solvent polarity, which agrees with the known spectral manifestations of the formation of the zwitterionic structure of the merocyanine form.[2]

There is no substantial difference between the dark relaxation constants for the compounds of each of two groups of the spiropyrans studied, which can be explained by the fact that the dark relaxation of the photoinduced form to the spiropyran one is determined by the disappearance of the monomeric form. The substantial increase in the dark decolorization rate of the BTSP compounds compared to the ISP is due to differences in their structures.

The comparative study of the spectral kinetic characteristics of nitro-substituted indoline and benzothienopyrroline spiropyrans with different substituents at the nitrogen atom of the pyrroline cycle showed no substantial distinctions between them. All spiropyrans studied in weakly polar toluene are characterized by the structured absorption band with two pronounced maxima. In polar solvents the structure of this band is simplified and the absorption band maximum appears, which almost coincides in position with the short-wavelength absorption band of the photoinduced form in toluene. Taking into account the literature data, the results obtained indicate that the difference in the spectral characteristics of the photoinduced form is due to the aggregation of molecules of the photoinduced form with the zwitterionic structure in weakly polar solvents.

Experimental

All absorption spectral kinetic measurements were carried out on a Cary 50 Bio spectrophotometer (Varian) at 25 °C. Absorption spectra were measured in cells with the layer thickness $l = 0.1$ cm.

Toluene (specially pure grade), acetone (specially pure grade), and acetonitrile (specially pure grade) were used as solvents.

Solutions of the studied compounds were obtained by the addition of the calculated amount of the solvent to a weighed sample followed by the immersion of the system into the ultrasonic bath (Sapfir) for mixing. The solutions formed were stored in tightly closed glassware in the dark cold place for several weeks. The concentration of the photochromic compound in solutions was $2 \cdot 10^{-3}$ mol L^{-1}.

A Lightningcure LC4 mercury-xenon lamp (Hamamatsu, Japan) was used for photochemical studies. The light filters composed of one or several colored glasses (UFS5, UFS8, ZhS10, ZhS12, ZhS18, SZS20, SZS22, SZS23, and BS10) from the standard set of colored glasses (GOST 9411-81) were used to pick out the required spectral ranges of photoexcitation of the compounds. In the case of using several glasses, air gaps between them were filled with the immersion liquid (silicone oil with almost the same refractive index as that of the glasses) to avoid refraction losses.

Benzothienopyrrolines **2a** and **2b** were synthesized according to the procedure described earlier.[8]

For the syntheses of benzothienopyrroline **2c** and benzothienopyrrolenine **3**, see Ref. 5.

3,3-Dimethyl-6r,7-dinitro-1-octadecylspiro[2,3-dihydro-1*H*-[1]benzothieno[3,2-b]pyrrole-2,2r-2*H*-chromene] (2d). Octadecyl triflate (0.44 g, 1.1 mmol) was added to a solution of pyrrolenine **3** (0.26 g, 1 mmol) in anhydrous acetonitrile (5 mL). The reaction mixture was refluxed for 1.5 h, then cooled, and concentrated *in vacuo*. Anhydrous ethanol (5 mL), 5-nitrosalicylaldehyde (0.17 g, 1 mmol), and piperidine (0.11 mL, 1.1 mmol) were added to the residue. The reaction mixture was refluxed for 4 h and then concentrated by evaporation. The residue was purified by chromatography on a column with silica gel (petroleum ether—ethyl acetate (10 : 1) as eluent). The yield was 0.2 g (30%). The product is an amorphous powder, which we could not additionally purify. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 0.89 (t, 3 H, Me, $J = 6.6$ Hz); 1.24—1.32 (m, 33 H, 0.5 $CMe_2 + (CH_2)_{15}$); 1.36 (s, 3 H, 0.5 CMe_2); 1.69—1.83 (m, 2 H, CH_2); 3.34—3.54 (m, 2 H, NCH_2); 5.95 (d, 1 H, CH, $J = 10.3$ Hz); 6.84 (d, 1 H, H arom., $J = 8.8$ Hz); 6.96 (d, 1 H, CH, $J = 10.6$ Hz); 7.88 (d, 1 H, H arom.); 8.00—8.14 (m, 3 H, H arom.); 8.60 (s, 1 H, H arom.). MS, m/z (I_{rel} (%)): 661 $[M]^+$ (100), 615 $[M - NO_2]^+$ (7), 408 $[M - C_{18}H_{36}]^+$ (58).

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