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Negative Photochromism of Solutions of Functionalized Spiropyrans in a Water–Acetonitrile Mixture

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Abstract—A spectral-kinetic study of photochromic functionalized nitro-substituted indoline spiropyrans in water-acetonitrile mixtures has allowed to observe for the first time the effect of negative photochromism due to the self-assembly of photochromic molecules in a mixed solvent with the formation of hydrogen bonds and proton complexes.

Keywords: negative photochromism, absorption spectra, spiropyrans, complexes, hydrogen bond

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Special attention in the search for possible application of the photochromism phenomenon has been paid to the systems exhibiting inverse photochromism, which is of interest for the design of diverse photochromic materials, for example, for elaboration of multifunctional clothes and camouflage coatings with dynamic photoinduced color changing [1, 2]. In continuation of our previous studies [3–5], herein we report on the results of the spectral-kinetic study of inverse photochromism of functionalized nitro-substituted spiropyrans.

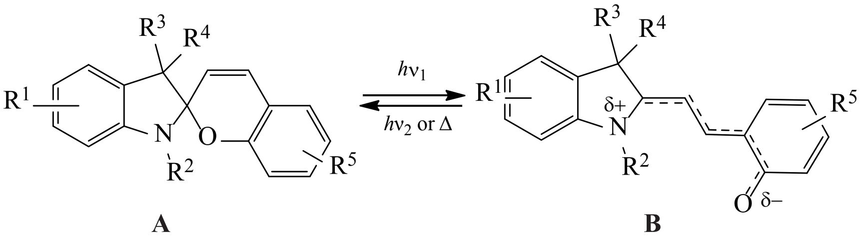
Positive photochromism is typical of nitro-substituted spiropyrans [6]: the starting colorless form **A** exhibits reversible photodissociation of the C–O bond under the action of UV irradiation, followed by *cis*/*trans* isomerization with the formation of colored merocyanine form **B**. The latter is spontaneously relaxed into the initial cyclic form **A**, the process being accelerated by visible light or heating.

In this study, we investigated the indoline nitro-substituted spiropyrans **1** and **2** (Scheme 2).

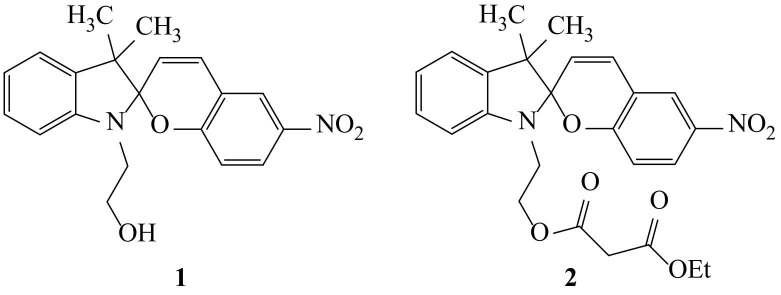
The experimental data collected in the table showed that compound **1** in acetonitrile demonstrated positive photochromism, the colorless cyclic form (Fig. 1, curve *1*) being converted into the colored merocyanine form (curve *2*) under the UV irradiation and recovered into the initial state after turning off the light (curves *3*–*6*).

A solution of compound **1** in a water–acetonitrile mixture (1 : 1) initially was colorless as well and its spectrum was similar to that of the initial solution in acetonitrile. However, after 20 h of storage in the dark, the solution turned colored (Fig. 2, curve *1*) and the absorption band of the merocyanine form of the spiropyran appeared, which was shifted by 50 nm to the shortwave region with respect to the absorption band in acetonitrile (see the table). The formed colored solution demonstrated inverse photochro-

Scheme 1.



Scheme 2.



1 **2**

mism (Fig. 2), but the recovery of the studied compound to the initial state occurred slower, within up to tens of hours (Fig. 2, curves *5*, *6*). The concentration of the colored product decreased during repeated photobleaching and dark relaxation (cf. curves *1*, *3*, *6*), and an absorption band with maximum at 410 nm simultaneously appeared.

Spiropyran **2** demonstrated similar dark and photoinduced spectral changes, although less pronounced (see the table).

Remarkably, the shift of the equilibrium from the cyclic form of spiropyran to the merocyanine structure occurred during prolonged storage of the solutions in the dark. Apparently, that process was due to self-assembly and structurization of the mixed solution. The hypsochromic shift of the absorption band maximums might be indicative of the formation of hydrogen bonding between the molecules of spiropyran and water. The observed decrease in the concentration of the merocyanine

Spectral characteristics of spiropyrans in solution[a]

Compound	Solvent	$\lambda^{\mathbf{A}}_{\max}$, nm ($D^{\mathbf{A}}_{\max}$)	$\lambda^{\mathbf{B}}_{\max}$, nm ($D^{\mathbf{B}}_{\max}$)	Light filter
1	CH_3CN	220 (0.48) 245 (0.45) 265(0.38) 300(0.18) 340(0.21)	560 (0.68)	UFS-1
	CH_3CN–H_2O (20 h in the dark)	220(0.32) – 265(0.17) 360(0.30) 510(0.38)	510 (0.00)	ZhS-10
2	CH_3CN	220(0.53) 240(0.52) 265(0.4) 335(0.24)	568(0,58)	UFS-1
	CH_3CN–H_2O (20 h in the dark)	245(0.45) 270(0.37) 350(0.31) 520(0.11)	520(0,04)	ZhS-10

[a] $\lambda^{\mathbf{A}}_{\max}$ and $\lambda^{\mathbf{B}}_{\max}$ are the maximums of adsorption bands of the initial **A** and longwave-photoinduced forms **B** of spiropyrans, respectively; $D^{\mathbf{A}}_{\max}$ and $D^{\mathbf{B}}_{\max}$ are the values of optical density in the maxima of absorption bands of forms **A** and **B**, respectively. Solutions concentration 2×10^{-4} mol/L.

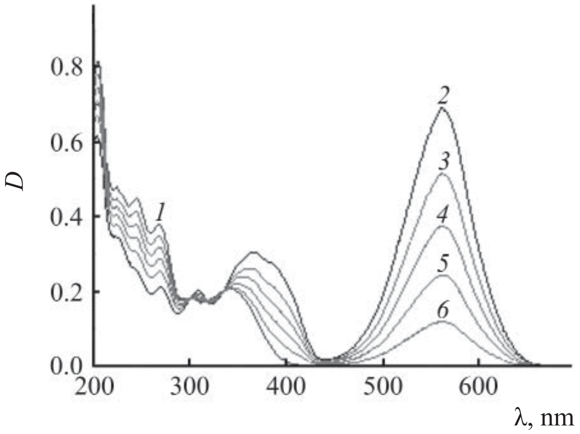


Fig. 1. Absorption spectra of compound **1** in acetonitrile before (*1*) and after UV irradiation (UFS-1 filter) (*2*) and during dark relaxation (*3–6*).

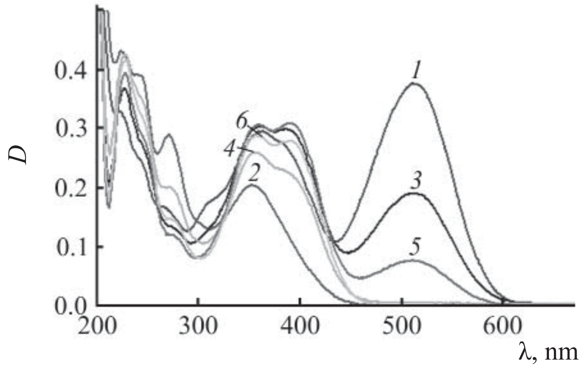


Fig. 2. Absorption spectra of compound **I** in a solution in a water–acetonitrile mixture after 20 h storage in the dark (*1*), after irradiation with visible light (ZhS-10 filter) (*2*, *4*, *6*), and after subsequent dark relaxation for 72 (*3*) and 96 h (*5*).

form and the appearance of a new absorption band with maximum at 410 nm during the repeated processes of photobleaching under visible light and dark relaxation could be explained by the formation of slightly light-sensitive proton complexes.

In summary, in this study we observed for the first time the phenomenon of formation of photochromic systems with negative photochromism of spiropyrans in water-acetonitrile mixed solvent and investigated it by spectral-kinetic method. The revealed peculiarities were explained by self-organization of photochromic molecules in the mixed solvent involving hydrogen bonding and formation of proton complexes.

EXPERIMENTAL

2-[3',3'-Dimethyl-6-nitrospiro(chromene-2,2'-indol)-1'(3'*H*)-yl]ethanol (1) was obtained as described elsewhere [7]. Its spectral parameters fully coincided with those described in the literature.

2-[3',3'-Dimethyl-6-nitrospiro(chromene-2,2'-indol)-1'(3'*H*)-yl]ethyl(ethyl)malonate (2). 3.79 mmol of ethyl malonate, 3.79 mmol of 1,3-dicyclohexylcarbodiimide, and 0.379 mmol of 4-dimethylaminopyridine were added in sequence to a solution of 3.79 mmol of spiropyran **1** in 30 mL of dry methylene chloride in a 50 mL three-neck flask. The reaction mass was stirred at room temperature for 2 h and then filtered. The solvent was evaporated off, the residue was purified by column chromatography eluting with a petroleum ether–ethyl acetate mixture (5 : 1).

Spectral-kinetic measurements were performed in acetonitrile (Aldrich) and its mixtures with bidistilled water. Spectral-kinetic parameters of the solutions were obtained using a Cary 60 bio spectrophotometer (Agilent Technologies) in a 0.2 cm quartz cell, concentration of the solutions being 2×10^{-4} M. The irradiation was performed with an L8253 xenon lamp (LC-4 device, Hamamatsu) equipped with UFS-1 (for UV irradiation) and ZhS-10 ZhS-11 (for visible light irradiation) filters, respectively.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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