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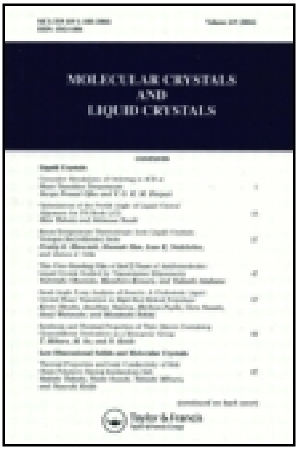

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Photochromic Spiro[7H-furo(3,2-f)-(2H-1)-benzopyran-7,2′-indolines]: Experimental and Computational Evidence for the Elusive Intermediate of the Photoinitiated Ring Opening Reaction of Spiropyrans

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The photochromic behavior, absorption and luminescence spectra of a series of 1′,3′,3′-trimethyl-1,2-tetramethylenespiro[7H-furo(3,2-f)-(2H-1)-benzopyran-7,2′-indolines] ***1*** *have been studied. In the case of 6-(*tert*-butyl) derivative* ***1d****, the formation of an acoplanar* cis-cisoid *intermediate, the lifetime of which at 77 K is long enough to observe its absorption and fluorescence spectra, has been detected. The occurrence of the intermediate on the reaction paths for the thermal and photoinitiated ring-opening processes has been also shown by DFT calculations.*

Keywords: DFT; intermediate; photochromism; spiropyrans

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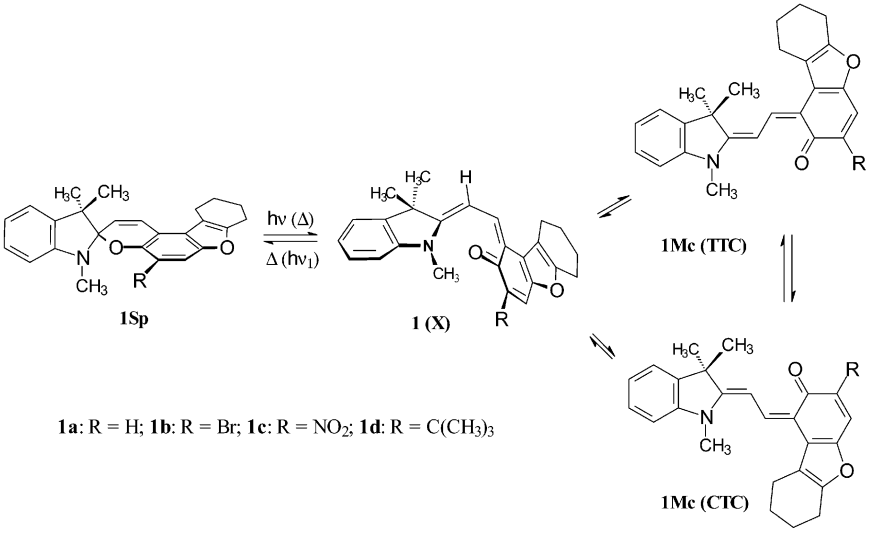
INTRODUCTION

Thanks to high quantum efficiency of their photoinitiated rearrangements governed by the reversible photochemical cleavage of the C_{spiro}—O bond in the 2H-chromene ring and high two-photon absorption coefficients spiropyrans continue to hold an important place among the families of photochromic compounds with a potential for such technical applications as molecular switches and high-density photochemical erasable memories [1–3]. To further improve these properties of spiropyrans and to amend the drawbacks of this class of photochromic compounds caused by the relatively low energy barriers to their dark back ring-closing reactions and insufficient fatigue resistance, various structural modifications of spiropyran molecules were undertaken, which revealed the role of the 2H-chromene moiety of the compounds as the principal structural element responsible for their photochemical behavior and spectral properties. One way to follow these objectives, in particular to increase the energy barrier to the dark back reaction, is to fuse a heterocyclic fragment to the photoresponsive 2H-chromene ring of spiropyrans. In this paper, we report on the study of spectral properties and mechanism of the photochromic rearrangements of a new group of spiropyrans, spiro[7H-furo(3,2-f)-(2H-1)-benzopyran-7,2′-indolines] **1** shown in Scheme 1.



1a: R = H; **1b**: R = Br; **1c**: R = NO_2; **1d**: R = $C(CH_3)_3$

SCHEME 1

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RESULTS AND DISCUSSION

In toluene, spiropyrans **1a–d** exist as their ring-closed spiro forms **1** (**Sp**). The longest wavelength absorption of compounds **1a–d** (**Sp**) consists of a band with the maximum in the spectral region of 301–312 nm having a shoulder at 352–380 nm. Ethanol and acetonitrile solutions of spiropyrans **1a–d** weakly colored, which fact is indicative of the presence of small amounts of respective merocyanine isomers in the equilibrium (Scheme 1). Table 1 contains the data on spectral properties of spiropyrans **1**.

UV-Irradiation of isopentane/isopropanol (4:1) solutions of spiropyrans **1** cooled to the temperature lower than 250 K results in the intense coloration caused by the photoinitiated ring- opening reaction resulting in the formation of the merocyanine isomers. Figure 1 pictures the spectral changes occurring at the formation of the photostationary state of the rearranged system, as exemplified by spiropyran **1b**.

The spectral behavior of spiropyran **1d** in isopentane/isopropanol (4:1) solutions at the temperature higher than ~100 K is similar to that of **1a–c**. However, at 77 K irradiation of an isopentane/isopropanol solution of **1d** with the light at 365 nm leads to the appearance of the longest wavelength absorption with a maximum at 471 nm (Fig. 2). Under prolonged irradiation of the system already attained its photostationary state at 77 K with non-filtered light of a mercury lamp or heating the solution to 178 K the spectrum transforms to the shape similar to that shown in Figure 1 with the 585–625 nm longest wavelength absorption bands typical of trans-merocyanines. The observed spectral behavior may be explained as a consequence of the kinetic stabilization of the intermediate *cis-cisoid* isomer **1d** (**X**) (R = *t*-Bu), the bulky *tert*-butyl group of which creates a sufficiently high energy barrier to the rotations about the central CC bonds and, thus, hinders the dark reaction in the rigid matrix at 77 K. Rising the temperature of the rigid glass solution accelerates the thermal rearrangements resulting in converting **1d** (**X**) to its more stable **1d** (**CTC**) and **1d** (**TTC**) isomers as depicted in Scheme 1. This assignment is supported by the TDDFT calculation of the absorption spectrum of **1d** (**X**). The occurrence of the nonplanar intermediate on the reaction paths of the ring-opening reaction emerged at the initial stages of both thermal and photoinitiated rearrangements has been confirmed by the results of the DFT calculations performed at B3LYP/6-31G** and time-dependent (TD) B3LYP/6-31G** levels of approximation. The computed position ($\lambda_{\max} = 473$ nm) of its longest wavelength absorption band for the B3LYP/6-31G**//HF/6-31G**

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TABLE 1 Absorption and Luminescence Properties of Isomeric Forms for Spiropyrans **1a–d** in Mixture of Isopentane and Isopropyl Alcohol (4:1) at 77 K

Compound	Form	$\lambda_{\max}$, nm				
		Absorption	Excitation of fluorescence	Fluorescence	Excitation of phosphorescence	Phosphorescence
1a	**Sp**	301				
		346sh	–	–	346	540
						585
	Mc	482	470			
		546			–	–
		587	610	648		
		627		695		
1b	**Sp**	302				
		348sh	348	374	345	548
						577
	Mc	458				
		482	473			
		550sh	550	659	–	–
		585	585	718		
		625sh	626			

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1c	**Sp**	298				
		380sh	–	–	382	512
						553
						598
	Mc	483	468			
		592sh			–	–
		625	620	656		
		644sh		710		
1d	**Sp**	312				
		379	379	540	–	–
				570sh		
	X	471	468	543	–	–
				572		
	Mc	482	468			
		550sh			–	–
		585	582	653		
		625sh	625	698sh		

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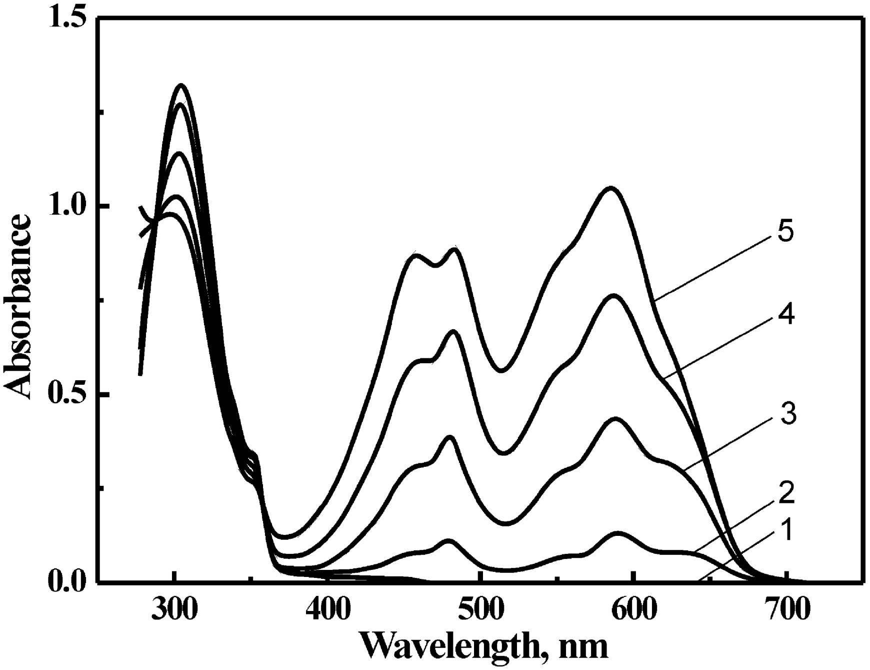

FIGURE 1 Absorption spectra of spiropyran **1b** in mixture of isopentane and isopropyl alcohol (4:1) ($[C]_0 = 6.3 \cdot 10^{-5}$ mol·L^{-1}, T = 77 K) before (1) and during of 60 (2), 180 (3), 360 (4), 630 s (5) of 313 nm irradiation.

optimized geometry is in excellent agreement with that observed in its rigid glass solution.

Of spiropyrans **1a–c**, only **1b** displays low intense fluorescence of the ring-closed form at 374 nm with a Stokes shift $\Delta\nu \cong 2000$ cm^{-1} in isopentane/isopropanol solution (Table 1). The phosphorescence observed for the ring-closed forms of spiropyrans **1b** and **1c** witnesses an existence of a triplet channel of deactivation of the excited state of these compounds characteristic of spiropyrans with nitro and heavy atom group substituents [1–3]. By contrast with **1a–c**, the fluorescence of spiropyran **1d** is characterized by the anomalous Stokes shift (ASS) $\Delta\nu = 7200–8150$ cm^{-1}. The fluorescence of the intermediate photoproduct **1d** (**X**) initially formed on irradiation of a rigid isopentane/isopropanol solution of **1d** (**Sp**) at 77 K appears as the bands at 543 and 572 nm in the same spectral region as the ASS fluorescence of the latter observed at room temperature. Prolonged irradiation at the longest wavelength of **1d** (**X**) transforms its fluorescence spectrum

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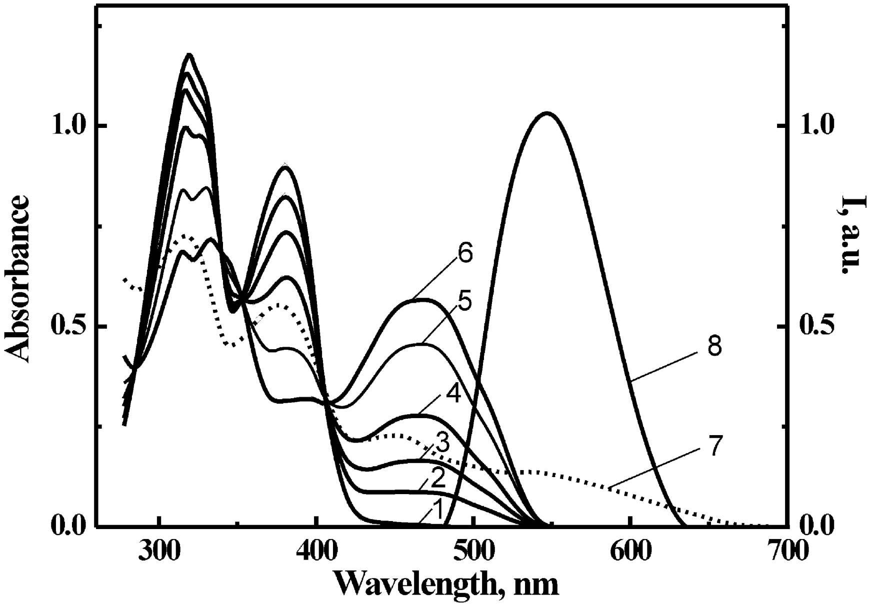

FIGURE 2 Absorption spectra of spiropyran **1d** in mixture of isopentane and isopropyl alcohol (4:1) ($[C]_0 = 9.4 \cdot 10^{-5}$ mol·L^{-1}, T = 77 K) before (1) and during of 180 (2), 480 (3), 1080 (4), 4800 s (5), 9600 s (6) of 365 nm irradiation and after that 1800 s (7) non filter irradiation of Mercury lamp. Fluorescence spectrum (8) of spiropyran **1d** in mixture of isopentane and isopropyl alcohol (4:1) ($[C]_0 = 1.2 \cdot 10^{-5}$ mol·L^{-1}, T = 293 K).

to that characteristic of the merocyanine form **1d** (**Mc**) with λ_{max}^{flu} = 653 nm and a shoulder at 698 nm. These results indicate that the origin of the ASS fluorescence of **1d** (**Sp**) is in the fast transformation of its structure occurring in the S_1 electronic excited state due to the cleavage of the C_{spiro}–O bond and the formation of the *cis-cisoid* merocyanine **1d** (**X**). Deactivation of electronic energy from the S_1 level of the latter may involve both radiative (fluorescence) and nonradiative (internal conversion to the ground state) pathways as well as other possible mechanisms, *e.g.* intersystem crossing to the T_1 triplet state. Because of the steric hindrances produced by a bulky *tert.*-butyl group in **1d** (**X**), the energy barriers against these rearrangements are substantially increased compared with those for spiropyrans **1a–c**, which prolongs the lifetime of **1d** (**X**) in the S_1 excited state to the value sufficient for observation of the fluorescence.

CONCLUSION

The formation of a long-lived intermediate **1** (**X**) on the reaction pathway of the photochromic rearrangement of 6-R-1′,3′,3′-trimethyl-1,2-tetramethylenespiro[7H-furo(3,2-f)-(2H-1)-benzopyran-7,2′-indolines] **1** occurring under the conditions of continuous UV-irradiation of rigid isopentane/isopropanol solution of a *tert.*-butyl derivative (R = *tert.*-butyl) at 77 K has been proved based on the measurements of the absorption and emission spectra and corroborated by the results of quantum mechanical calculations of the structure and spectral properties of the elusive intermediate.

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