

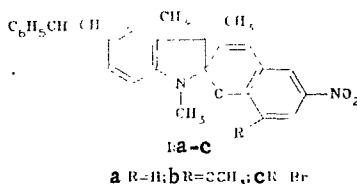
PHOTOCHROMIC 5-STYRYL-SUBSTITUTED INDOLINOSPIROCHROMENES

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Three photochromic indoline spirochromenes that contain styryl-substituents in the 5 position of the indoline part of the molecule were synthesized. The introduction of a styryl substituent into this position gives rise to a 15-20 nm bathochromic shift of the long-wave absorption band of the merocyanine isomers; the rate constant for the dark decolorization of the reaction does not change substantially in this case. In the case of one 5-styryl-substituted spirochromene we evaluated the photocolorization quantum yield, which, both for the forward and reverse photoreactions, is considerably lower than in the case of the spiropyran that is unsubstituted in this position.

It has been previously established [1] that the introduction of a styryl substituent into the pyran part of the spirochromene molecule gives rise to a substantial bathochromic shift of the long-wave absorption band of the photomerocyanine. It seemed of interest to study how strong the effect on the photochromic characteristics of spirochromenes of a styryl substituent in the indoline part of the molecule could be. With this end in mind, we accomplished the synthesis of three spirochromenes with this sort of substituent in the 5 position. Cyclization in acetic acid of methyl isopropyl ketone (4-styrylphenyl) hydrazone gave 5-styryl-2,3,3-trimethylindolenine, which, by alkylation with methyl iodide and subsequent treatment of the quaternary salt with aqueous sodium bicarbonate, was converted to 5-styryl-1,3,3-trimethyl-2-methyleneindoline. 5-Styryl-substituted indolinospirochromenes Ia-c were obtained by condensation of the methylene base with substituted salicylaldehydes.



Spirochromenes Ia-c have photochromic properties. Colorless solutions in nonpolar or slightly polar solvents upon irradiation with UV light, as a consequence of conversion to the merocyanine form, are blue; the solutions gradually become colorless when irradiation is discontinued. Alcohol solutions of the spirochromenes are violet (Ia, c) or blue (Ib) due to partial conversion to the merocyanine form. In the case of irradiation with UV light the intensity of the coloration increases, whereas it decreases in the case of irradiation with visible light. When irradiation is discontinued, the solutions gradually return to their initial state. The positions of the maxima of the long-wave absorption bands of the merocyanine forms of Ia-c and the rate constants (k) of the dark decolorization reactions of the photomerocyanines at 20°C are presented in Table 1.

A comparison of the data obtained with the characteristics of compounds that do not contain a substituent in the 5 position [2] makes it possible to establish that the introduction of a styryl substituent in the 5 position in the indoline part of the photomerocyanine molecule gives rise to a 15-20 nm bathochromic shift of the long wave absorption band. Although a similar structural change in the pyran part of the spirochromene molecule leads to an 80 nm bathochromic shift of the long-wave absorption band [1], nevertheless it may be stated that there is incomplete agreement with the results obtained with respect to the theoretical conclusions of V. I. Minkin and co-workers [3], according to which, the long-

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TABLE 1. Spectral-Kinetic Characteristics of the Photomerocyanines of Spirochromenes Ia-c

Compound	$k \cdot 10^2$ (20°)		$\lambda$ , nm		
	toluene	dioxane	ethanol, $\lambda_{\max}$	toluene	
				$\lambda_{\max}$	center of the band
Ia	3,60	2,75	553	610	598
Ib	2,40	2,00	580	617	610
Ic	3,50	2,60	548	608	599

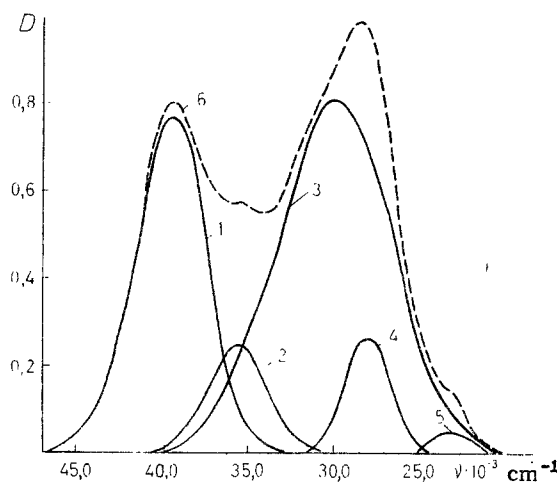


Fig. 1. Breakdown of the overall spectral curve into individual absorption bands for spirochromene Ib: 1-5) individual absorption bands: 6) overall spectral curve.

wave transition is localized in the quinonallide fragment of the photomerocyanine molecule, and consequently, its energy should not depend substantially on structural changes in the indoline fragment. Let us note that, according to the data in [4], the introduction of a nitro group in the 5 position of the indoline part of the photomerocyanine molecule gives rise to a 30-40 nm bathochromic shift of the long-wave absorption band, which also illustrates a certain degree of sensitivity of the position of the indicated band to structural changes in the indoline part of the molecule, which lead to an increase in the overall conjugation system.

The introduction of a styryl substituent in the 5 position of the indoline part of the molecule does not substantially change the rate constant of the dark decolorization reaction. This result is in agreement with the previously published data to the effect that the rate of the dark reaction of indolinspirochromenes with the nitro group in the pyran part changes substantially only when substituents with strong electron-acceptor or electron-donor effects are introduced in the 5 position of the indoline fragments [5].

According to our previously developed methods [6], in the case of Ib we attempted to evaluate the quantum yield of the photocolorization of styryl-substituted spirochromenes upon irradiation with UV light with a wavelength of 366 nm. We found that the quantum yields of both the forward ( $F_1 = 0.01$ ) and the reverse ( $F_2 = 0.002$ ) photoreactions are substantially lower for the 5-styryl-substituted spirochromene as compared with 5-unsubstituted IIb ( $F_1 = 0.68$ ,  $F_2 = 0.16$ ) [6]. For an analysis of the possible reasons for this phenomenon we broke down the overall absorption spectrum of the colorless form of the spirochromene into individual bands by means of the method that we previously used in [7] (Fig. 1). The characteristics of the individual absorption bands of spirochromene Ib and 5-unsubstituted spirochromene IIb are presented in Table 2. It is apparent from the data in Table 2 that the spectrum of spirochromene Ib consists of five individual bands. Two bands ( $\lambda_{\max}$  251 and 357 nm) correspond to electronic transitions in the chromene part of the molecule; with respect

TABLE 2. Characteristics of the Individual Absorption Bands of the Spirochromenes

Compound	Ib					IIb			
	1	2	3	4	5	1	2	3	4
$\lambda_{\max}$ , nm	252	281	333	357	438	254	281	301	357
$\epsilon_{\max} \cdot 10^{-4}$	2,33	0,74	2,43	0,80	0,15	2,01	0,97	0,43	1,04
$\sigma$ , cm <sup>-1</sup>	1978	1691	3556	1475	1055	658	1094	1448	1375
$P^*$	0,42	0,11	0,79	0,11	0,01	0,12	0,098	0,0057	0,13

\*Oscillator force of the bands  $P = 0.92 \cdot 10^{-8}$ ;  $\epsilon_{\max} \sigma$  [19].

TABLE 3. Characteristics of the Spirochromenes Obtained

Compound	R	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
			C	H	N (Br)		C	H	N (Br)	
Ia	H	206	76,2	5,6	6,4	C <sub>27</sub> H <sub>24</sub> N <sub>2</sub> O <sub>3</sub>	76,6	5,7	6,6	3
Ib	OCH <sub>3</sub>	201	73,7	5,6	5,9	C <sub>28</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4</sub>	74,0	5,8	6,2	2
Ic	Br	243	63,5	4,8	5,3 (15,33)	C <sub>27</sub> H <sub>23</sub> BrN <sub>2</sub> O <sub>3</sub>	64,4	4,6	5,6 (15,88)	2

\*The overall yield was based on 4-aminostilbene.

to the position of the center of the band, the extinction coefficient, and the oscillator force, these bands are rather close. Two other bands ( $\lambda_{\max}$  252 and 333 nm) correspond to transitions in the indoline part and, as compared with the analogous bands of IIb, undergo the same changes as in the case of the transition from dimethylaniline [8] to 4-dimethylaminostilbene [9]; the parameters of the short-wave band did not change substantially ( $\lambda_{\max} \sim 250$  nm,  $\log \epsilon$  4.3 for dimethylaniline;  $\lambda_{\max} \sim 240$  nm,  $\log \epsilon$  4.1 for 4-dimethylaminostilbene), whereas the long-wave band experiences a bathochromic shift and a hyperchromic effect ( $\lambda_{\max} \sim 290$  nm,  $\log \epsilon$  3.3 for dimethylaniline;  $\lambda_{\max} \approx 340$  nm,  $\log \epsilon$  4.5 for 4-dimethylaminostilbene). The rather close coincidence of the parameters of the individual absorption bands in the spectra of spirochromenes Ib and IIb with the analogous parameters of model compounds confirms the correctness of the assignments made above. It is apparent from Fig. 1 that only 25% of the absorption of the indoline part goes into the wavelength of the activating light (366 nm). However, the quantum yield of the photocolorization reaction of spirochromene when a styryl substituent is introduced in the 5 position of the indoline part decreases to a considerably greater extent (by a factor of more than 1.5 orders of magnitude) than would follow with allowance for filtration of the activating light of the indoline part of the molecule. Other reasons for the sharp decrease in the quantum yield also probably exist. In particular, if one takes into account the fact that the introduction of a styryl substituent into the molecule should evidently lead to an appreciable decrease not only in the singlet but also in the triplet level of the indoline part [10], it may be assumed that, as for several previously studied spirochromenes [11, 12], in the case under consideration there is a possibility for transmission of the excitation energy from the chromene to the indoline part, which leads to a substantial decrease in the efficiency of the photocolorization reaction.

#### EXPERIMENTAL

The measurement of the absorption spectra of the photomerocyanines, the kinetic curves of the photocolorization and subsequent dark decolorization, and the determination of the quantum yields were carried out as described in [6]. Breakdown of the experimental spectral curve into a combination of Gaussian bands was carried out in [7]. The electronic absorption spectra of solutions of the spirochromenes were measured with a Specord UV-vis spectrophotometer.

The 4-nitrostilbene was obtained from cinnamic acid and p-nitrobenzenediazonium chloride in the presence of cupric chloride [13]. The 4-nitrostilbene was reduced to 4-aminostilbene by means of hydrazine hydrate in isopropyl alcohol in the presence of Raney nickel [14]. 4-Hydrazinostilbene was obtained by diazotization of the amine with subsequent reduction of the diaxonium salt with stannous chloride [15]. 5-Styryl-2,3,3-trimethylindolenine was formed by cyclization of the corresponding methyl isopropyl ketone (4-styrylphenyl)-hydrazone

in acetic acid [16]. 5-Styryl-2,3,3-trimethylindolenine methiodide was synthesized by the method in [17] by heating the indolenine with methyl iodide. Condensation of 5-styryl-1,3,3-trimethyl-2-methyleneindoline with substituted salicylaldehydes was accomplished by the method in [18]. The properties of the 1,3,3-trimethyl-5-styryl-6'-nitroindoline-2-spiro-2'-[2H]chromene (Ia), 1,3,3-trimethyl-5-styryl-6'-nitro-8'-methoxyindoline-2-spiro-2'-[2H]-chromene (Ib), and 1,3,3-trimethyl-5-styryl-6'-nitro-8'-bromoindoline-2-spiro-2'-[2H]chromene (Ic) are presented in Table 3.

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