SYNTHESIS AND PHOTOCHROMIC PROPERTIES OF 6',7'-TETRAMETHYLENE-SUBSTITUTED SPIROCHROMENES OF THE INDOLINE SERIES

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6-Nitro-6',7'-tetramethylene-substituted photochromic spirochromenes were synthesized from 5-aminotetralin. In the series of compounds thus obtained the electronic effect of the substituents in the 8 position on the dark decolorization reaction is substantially more noticeable than in the corresponding series of standard spirochromenes. The spectral characteristics of the merocyanine form of the tetramethylene-substituted spirochromenes practically coincide with the characteristics of the analogous unsubstituted compounds.

The relationship between the structure and the properties of photochromic compounds has been studied most intensively in a series of indolinespirochromenes, which constitute one of the most promising classes of photochromic compounds [1]. In addition to their spectral-kinetic properties, the stability of spirochromenes with respect to the action of UV and visible radiation is of great importance. Research by Gautron [2] has shown that the introduction of alkyl substituents in the indoline fragment of the spirochromene molecule increases the photostability of these compounds. In the present research we synthesized a number of compounds of the type and measured their spectralkinetic characteristics.

By catalytic hydrogenation of a mixture of 5- and 6- nitrotetralins [3] we obtained a mixture of 5- and 6-aminotetralins, which we were able to separate by means of fractional crystallization of the hydrochlorides.

TABLE 1. Kinetic Parameters of the Dark Decolorization of Spirochromenes

Compound	Solvent	k. sec^{-1} · 10^{2} at				Activation parameters			
		12°C	20°C	30°C	40°C	$\Delta H^{\#}$		$\Delta S^{\#}$	
						kJ/mole	kcal/mole	J/mole · deg K	cal/mole · deg
I	Toluene	2,42	6,20	17,4	43,8	76,1	18,2	−15,1	−3,6
	Dioxane	0,868	2,61	8,87	24,6	88,3	21,1	18,9	4,5
II	Toluene	3,95	7,40	16,0	31,6	55,2	13,2	−85,8	−20,5
	Dioxane	1,84	5,60	14,4	36,0	77,4	18,5	−13,4	−3,2
III	Toluene	0,14	0,53	2,75	10,3	114,2	27,3	94,1	22,5
	Dioxane	0,056	0,18	0,87	2,63	102,9	24,6	48,1	11,5
IV*	Toluene	1,80†	3,09	8,24	18,0	57,7	13,8	−83,7	−20,0
	Dioxane	1,10	2,97	9,67	33,8	89,1	21,3	20,9	5,0
V	Toluene	0,70†	1,66	3,60	11,0	66,1	15,8	−60,2	−14,4
	Dioxane	0,77	1,53	4,17	11,4	71,5	17,1	−41,8	−10,0
VI	Toluene	0,57†	1,78	6,60	18,6	86,2	20,6	9,6	2,3
	Dioxane	0,16	0,54	1,94	5,50	93,3	22,3	22,6	5,4

*Data from [6].

† At 10°C.

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TABLE 2. Spectral Characteristics of the Merocyanine Forms of Spirochromenes

Compound	λ_{max}, nm		Position of center of band in toluene, mm
	alcohol	toluene	
I	535	595	583
II	560	610	601
III	533	595	583
IV	532	595*	583
V	560	610†	601
VI	534	600‡	583

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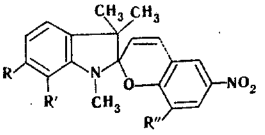
* λ_{max} 598 nm [1].

† λ_{max} 590 nm [1].

‡ λ_{max} 600 nm [1].

Using previously described methods [4, 5], we obtained spirochromenes I-III, which contain a tetramethylene fragment in the 6,7 position.

Solutions of the spirochromenes have photochromic properties at room temperature: the colorless solutions in toluene and dioxane turn blue-azure when they are irradiated with UV light due to conversion of the spirochromene to the open merocyanine form; this blue-azure color vanishes when irradiation is discontinued. Red (spirochromenes I and III) or red-violet (spirochromene II) alcohol solutions undergo an increase in the intensity of the color under the influence of UV irradiation.



I-VI

I R+R'=(CH$_2$)$_4$, R''=H; II R+R'=(CH$_2$)$_4$, R''=OCH$_3$; III R+R'=(CH$_2$)$_4$, R''=Br; IV R=R'=R''=H; V R=R'=H, R''=OCH$_3$; VI R=R'=H, R''=Br

A study of the kinetics of the thermal decolorization of spirochromenes I-III in toluene and dioxane made it possible to ascertain some peculiarities of their behavior as compared with spirochromenes IV-VI of the standard series. The rate constants at various temperatures and the activation parameters for I-VI are presented in Table 1. The introduction of a methoxy group or a bromine atom in the 8 position in the standard series of spirochromenes (V and VI as compared with IV) slows down dark decolorization somewhat; passing from toluene to dioxane has little effect on the rate of decolorization.

The effect of a substituent in the 8 position is more appreciable in the series of tetramethylene-substituted compounds (spirochromenes I-III) than in the standard series, as well as in the series of spirochromenes with aryl substituents in the 5' or 3 position [6]. We note that the rate of the dark reaction for spirochromenes I-III changes in conformity with the electronic effect of the substituent in the 8 position in a manner opposed to the change in the activation energy; the change in the activation entropy partially compensates this effect. Passing from toluene to dioxane slows down the dark reaction, and this tendency is manifested more clearly as compared with unsubstituted compounds IV-VI.

The characteristics of the absorption spectra of the merocyanine forms of I-VI in the visible region are presented in Table 2. The absorption spectra of ethanol solutions of the compounds were measured with a spectrophotometer by the usual method; a special method [7] was used for the measurement of the spectra of toluene solutions of the compounds. In addition to the position of the center of the long-wave absorption band in toluene, which was determined by approximation of the experimental curve [7], we also present the λ_{max} value on this curve. The spectral characteristics of tetramethylene-substituted photomerocyanines I-III practically coincide with the characteristics of the corresponding standard compounds.

EXPERIMENTAL

The measurement of the absorption spectra of solutions of the spirochromenes in the photoelectric steady state and the approximations of the data by Gaussian curves by means of a computer were accomplished as described in [7]. The purification of the solvents, the preparation of the solutions, and the measurement of the rate constants of dark decolorization of the photomerocyanines were accomplished as described in [8].

TABLE 3. Characteristics of the Spirochromenes Obtained

Spirochromene	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %*
		C	H	N		C	H	N	
I	175—176	73,8	6,7	7,3	$C_{23}H_{24}N_2O_3$	73,4	6,4	7,4	7,5
II	222—223	70,4	6,4	6,7	$C_{24}H_{26}N_2O_4$	70,9	6,5	6,9	2,4
III	272—275	60,7	5,0	6,0	$C_{23}H_{23}BrN_2O_3$	60,7	5,1	6,2	2,4

*Based on 5-aminotetralin.

5-Aminotetralin. A solution of 124.8 g (0.7 mole) of a mixture of 5- and 6- nitrotetralins [3] in 800 ml of isopropyl alcohol was hydrogenated for 8 h in the presence of 20 g of Raney nickel at 40°C and 100 atm, after which the mixture was filtered, the filtrate was evaporated, and the residue was vacuum distilled to give 73 g (70%) of a mixture of 5- and 6-aminotetralins with bp 115° (4 mm). A total of 100 ml of 1 N hydrochloric acid was added to 61.5 g (0.42 mole) of the mixture of 5- and 6-aminotetralins, and the mixture was heated to 60° and cooled to 0°C. The resulting crystals were separated, washed with ether, and crystallized from a threefold (by weight) amount of water to give 21 g (27%) of 6-aminotetralin hydrochloride with mp 185°C. The acetyl derivative of 6-aminotetralin had mp 105°C (mp 104-105°C [3]). The mother liquor remaining after the separation of 6-aminotetralin hydrochloride was neutralized to pH 6 with a 10% solution of sodium hydroxide, and the liberated oil was extracted with ether. This extract was combined with the ether solution obtained by washing the crystals of 6-aminotetralin hydrochloride, and the combined solutions were washed with water, dried, and evaporated to give 12.4 g (20%) of 5-aminotetralin with bp 112-114°C (3-4 mm). The acetyl derivative had mp 155° (mp 154-155° [3]). An additional amount of 5-aminotetralin containing the 6 isomer could be isolated by alkalization of the aqueous solution to pH 10. The properties of the spirochromenes obtained from 5-aminotetralin in conformity with the methods in [4, 5] are presented in Table 3.

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