SYNTHESIS AND SPECTRAL CHARACTERISTICS OF PHOTOCHROMIC SPIROCHROMENES – 2,3-DIHYDRO-1H-PYRROLO[3,2-h]QUINOLINE DERIVATIVES

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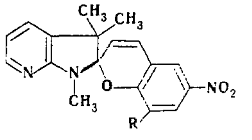
Photochromic spirochromenes that differ from the standard indoline spirochromenes with respect to an angularly annelated pyridine ring were synthesized from 8-hydrazinoquinoline. The spectral characteristics of the merocyanine form of the compounds practically coincide with the characteristics of the analogous spirochromenes containing an annelated benzene ring.

The creation of new photochromic materials requires a thorough study of the relationship between the structure and properties of photochromic compounds. Studies in this direction in a series of indoline spirochromenes, which are promising photochromic compounds, are currently under way.

A number of investigations of recent years have been devoted to the study of the properties of azaindolinospirochromenes that contain a nitrogen atom in the most diverse portions of the molecule. Thus indoline spiropyridopyrans were obtained when pyridine o-hydroxy aldehydes were used [1, 2]. A large number of similar compounds have been synthesized from o-hydroxy aldehydes of the quinoline and indole series [1,3,4]. Indoline spiro compounds that contain a benzoxazine ring instead of a pyran ring are known [1]. A communication [5] regarding photochromic compounds obtained from 1,3,3-trimethyl-2-methylene-1,7-diazaindene was recently published. As compared with their indoline analogs, I have dark reactions that proceed at high rates; this is associated with the decrease in the basicity of the nitrogen atom of the pyrrole ring and the increase in the thermodynamic stabilities of the colorless (closed) form.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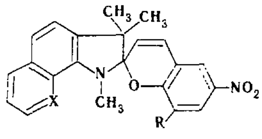
II-IV, V-VII

II-IV X=N; II R=H; III R=OCH_3; IV R=Er; V-VII X=CH

In the light of the material set forth above, it seemed of interest to obtain spirochromenes from 8-hydrazinoquinoline and compare their properties with the properties of their indoline and benzoindoline analogs.

The spirochromenes (II-IV) that we obtained in this study have photochromic properties, but their capacity for photodyeing is manifested to a considerably lesser extent than in the case of spirochromenes of the indoline series.

Using the method in [6, 7], we determined the position of the maximum of the long-wave absorption band of the merocyanine form of spirochromenes II-IV. For comparison, we also determined the spectral charac-

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TABLE 1. Position of the Maxima of the Long-Wave Absorption Band of the Merocyanine Form of Spirochromenes

Spirochromene	R	X	Solvent	λ_{max}, nm
II	H	N	Ethanol	544
III	OCH_3	N	Ethanol	570
IV	Br	N	Dioxane	576
			Ethanol	538
			Toluene	601
V	H	CH	Ethanol	540*
VI	OCH_3	CH	Ethanol	568†
VII	Br	CH	Ethanol	537
			Dioxane	575
			Toluene	601
VIII	H	—	Ethanol	523[8]
IX	Br	—	Toluene	586[6]

*λ_{max} 547 nm [1].
†λ_{max} 570 nm [1].

teristics of the similarly substituted 2H-chromene-2-spiro-2'-benzo[g]indolines (V-VII), which were previously synthesized in the All-Union Scientific-Research Institute of Chemical Reagents and Ultrapure Chemical Substances.*

In view of the low photosensitivity of the compounds, we were unable to sufficiently accurately measure the spectral characteristics in toluene and dioxane of spirochromenes I, III, V, and VI, nor were we able to measure the long-wave extinction coefficients and all the spectral characteristics of the short-wave absorption bands of the merocyanine form.

The data obtained in this study are presented in Table 1, which also includes the λ_{max} values for 1',3',3'-trimethyl-6-nitro-2H-chromene-2-spiro-2'-indoline (VIII) and 1',3',3'-trimethyl-6-nitro-8-bromo-2H-chromene-2-spiro-2'-indoline (IX), which we previously obtained in [6, 8].

The negative solvatochromism typical for the analogous merocyanine dyes [9] is characteristic for the long-wave absorption band of the colored form of the spirochromenes: the band undergoes a hypsochromic shift of 25 nm on passing from toluene to dioxane, and the shift is ~65 nm on passing from toluene to alcohol. The introduction of a methoxy group in the 8 position gives rise to a bathochromic shift of 26-28 nm, whereas the introduction of a bromine atom produces only a slight hypsochromic shift. The established regularities are in good agreement with those that we previously observed in [10]. The spectral characteristics of spirochromenes II-IV, which contain an angularly annelated pyridine ring, practically coincide with the characteristics of the analogously substituted spirochromenes V-VII, which contain an annelated benzene ring. The introduction of an angularly annelated benzene or pyridine ring in the indoline spirochromene molecule leads to a bathochromic shift of 15-20 nm of the long-wave photomerocyanine bands. These results are in good agreement with the data presented in [11, 12].

EXPERIMENTAL

The absorption spectra of solutions of the spirochromenes in the photochemical steady state were measured as described in [6, 7], and the approximation of the data by means of Gaussian curves with an M-220 computer was accomplished as in [6, 7]. Compounds having the following characteristics were used for the determination of the spectral data: spirochromene V with mp 212-213° (mp 216-219° [1]), spirochromene VI with mp 212-213° (mp 214-215° [1]), and spirochromene VII with mp 238-238.5°. Found: C 61.1; H 4.3; Br 17.8; N 6.1%. $C_{23}H_{19}BrN_2O_3$. Calculated: C 61.2; H 4.2; Br 17.7; N 6.2%.

The synthesis of spirochromenes from 8-hydrazinoquinoline (hydrochloride, mp 202-205° [13]) was realized by means of previously described methods [10, 14].

2,3,3-Trimethylpyrido[2,3-g]indolenine (X). This compound was obtained as colorless crystals with mp 158-160° (from water). Found: C 79.6; H 6.7; N 13.4%. $C_{14}H_{14}N_2$. Calculated: C 80.0; H 6.7; N 13.3%. The product was obtained in 75% yield based on the starting hydrazine.

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1,2,3,3-Tetramethylpyrido[3,2-g]indoleninium Iodide [11]). This compound was obtained as colorless needles with mp 350° (sublimation and crystallization from alcohol with charcoal). Found: C 51.2; H 5.3; I 36.2; N 8.1%. $C_{15}H_{17}N_2$. Calculated: C 51.2; H 4.9; I 36.0; N 8.0%. The product was obtained in 61.5% yield based on indoline X.

1',3',3'-Trimethyl-6-nitro-2H-chromene-2-spiro-2'-(2,3-dihydro-1H-pyrrolo[3,2-h]quinoline) (II). This compound was obtained as fine yellow crystals with mp 216-217° (from benzene-hexane). UV spectrum in ethanol, λ_{max}, nm: 255 (ε 50,500) and 245 (ε 12,400). Found: C 70.9; H 5.1; N 11.4%. $C_{22}H_{19}N_3O_3$. Calculated: C 70.8; H 5.1; N 11.3%. The product was obtained in 22% yield based on 8-hydrazinoquinoline.

1',3',3'-Trimethyl-6-nitro-8-methoxy-2H-chromene-2-spiro-2'-(2,3-dihydro-1H-pyrrolo[3,2-h]quinoline) (III). This compound was obtained as light-yellow crystals with mp 241-243°. UV spectrum in ethanol, λ, nm: 257 (ε 53,000) and 360 (ε 13,000). Found: C 68.7; H 5.3; N 10.3%. $C_{23}H_{21}N_3O_4$. Calculated: C 68.5; H 5.3; N 10.4%. The product was obtained in 17.3% yield based on the starting hydrazine.

1',3',3'-Trimethyl-6-nitro-8-bromo-2H-chromene-2-spiro-2'-(2,3-dihydro-1H-pyrrolo[3,2-h]quinoline) (IV). This compound was obtained as dark-green crystals with mp 305°. UV spectrum in ethanol, λ_{max}, nm: 252 (ε 40,300) and 341 (ε 6500). Found: C 57.8; H 4.2; Br 17.3; N 9.1%. $C_{22}H_{18}BrN_3O_3$. Calculated: C 58.0; H 4.0; Br 17.7; N 9.3%. The product was obtained in 16% yield based on the starting hydrazine.

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