2.81 ppm (2H, m, NCH_2). Found: C 63.0; H 11.9; N 3.1; S 8.0; Si 12.7%. $C_{22}H_{51}NSSi_2$.
Calculated: C 63.2; H 12.3; N 3.3; S 7.7; Si 13.4%.

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SYNTHESIS AND PHOTOCHROMIC PROPERTIES OF 5-ACETYL-SUBSTITUTED
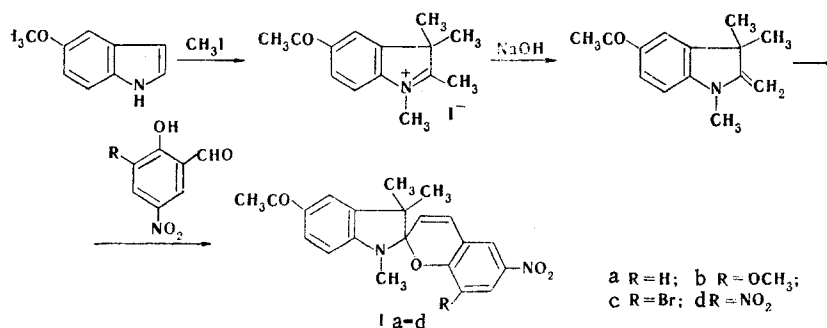
INDOLINOSPIROCHROMENES

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Four photochromic 5-acetyl-substituted indolinospirochromenes were synthesized. The introduction of an acetyl group does not change the spectral characteristics of the merocyanine form but leads to a decrease in the efficiency of photocoloring.

The photocoloring of indolinospirochromenes can be sensitized in a number of cases by aromatic ketones, particularly acetophenone derivatives [1, 2]. The existence of triplet-triplet transfer of energy between the two halves of the spirochromene molecule makes it possible to assume that the indoline part is an internal sensitizer with respect to the chromene part, in which the photoreaction occurs [3]. In this connection, it seemed of interest to synthesize and study the properteis of 5-acetyl-substituted indolinospirochromenes, the indoline part of which can be regarded as a 4-aminoacetophenone derivative.

By exhaustive methylation of 5-acetylindole [4] by the action of methyl iodide in an autoclave and subsequent treatment of the resulting 1,2,3,3-tetramethyl-5-acetylindoleninium iodide with alkali we obtained 1,3,3-trimethyl-5-acetyl-2-methyleneindoline, which reacted readily with substituted nitrosalicylaldehydes to give indolinospirochromenes Ia-d:

a R=H; b R=OCH₃;
c R=Br; d R=NO₂

TABLE 1. Position of the Maximum
of the Long-Wave Absorption Band
of Photomerocyanines

Com-pound	λ_{max}, in alcohol, nm	Spectra of toluene solutions, nm	
		λ_{max}	band center
Ia	535	595	583
Ib	565	610	602
Ic	535	595	585
Id	522	*	—

*We were unable to measure this
band because of the low solubil-
ity of the compound in toluene.

TABLE 2. Calculation of the Kinetic Curve of the Dark
Decolorization of Spirochromene Ib in Toluene in Con-
formity with Eq. (1) for $D_0^1 = 0.21$, $D_0^2 = 0.29$, $k_1 = 2.66 \cdot 10^{-2}$ sec^{-1}, and $k_2 = 0.27 \cdot 10^{-2}$ sec^{-1}

t, sec	D_i^{expt}*	D_i^{calc}†	Relative error, %	t, sec	$D_i$expt*	$D_i$calc†	Relative error, %
0	0.507	0.497	2.06	82.4	0.264	0.255	3.39
10.3	0.434	0.439	−1.25	92.7	0.245	0.243	0.67
20.6	0.379	0.394	−3.77	103.0	0.230	0.233	−1.44
30.9	0.347	0.356	−3.16	113.3	0.224	0.224	−0.05
41.2	0.331	0.328	0.80	123.6	0.215	0.216	−0.30
51.5	0.309	0.305	1.30	133.9	0.198	0.210	−5.17
61.8	0.291	0.285	1.99	144.2	0.195	0.200	−3.14
72.1	0.284	0.269	5.34				

*This is the experimentally determined optical density.
†This is the optical density calculated from Eq. (1).

It should be noted that exhaustive alkylation for the preparation of 1,2,3,3-tetra-
alkylindoleninium salts of the corresponding 1,3,3-trialkyl-2-alkylideneindolines has been
described repeatedly only as applied to 2-substituted indole derivatives. Our reaction is
a second (after unsubstituted indole [5, 6]) instance of the exhaustive alkylation of indole
derivatives that do not have substituents in the 2 and 3 positions.

The data from the IR spectra of spirochromenes Ia-d are in good agreement with their
structure: absorption bands at 1670-1710 (C=O), 1520-1535 and 1340-1380 (NO$_2$), and 960-980
cm^{-1} (C$_{spiro}$-O) are observed in the spectra.

Spirochromenes Ia-c have photochromic properties. When colorless solutions in nonpolar
or slightly polar solvents are irradiated with UV light, they turn blue as a consequence of
conversion to the merocyanine form, these blue solutions gradually become colorless again
when irradiation is discontinued. Alcohol solutions of spirochromenes Ia-d are red-violet
due to partial conversion to the merocyanine form. The intensity of the color increases
when the solutions are irradiated with UV light and decreases when they are irradiated with
visible light. The solutions gradually return to their original state when irradiation is
discontinued. The positions of the maxima of the long-wave absorption bands of the mero-
cyanine forms of Ia-d (Table 1) and of compounds that do not contain substituents in the
5 position (spirochromenes IIa-d, see [7, 8]) are almost the same (they differ by no more
than 8 nm), and this is in good agreement with the theoretical conclusions obtained by V. I.
Minkin and co-workers [9].

In contrast to most of the spirochromenes that we have previously investigated [10],
the kinetics of the dark decolorization of photocolored solutions of Ia-d in toluene and
dioxane were not described by a simple first-order equation. An analysis of the kinetic
curves showed that they may correspond to the sum of two monomolecular processes with rate
constants that differ by approximately an order of magnitude, in conformity with Eq. (1).
An example of the indicated treatment of the kinetic curve is presented in Table 2.
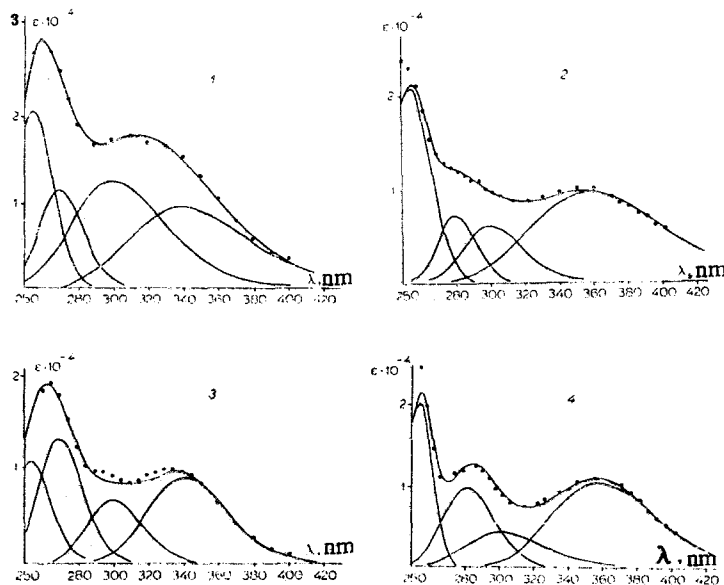
Fig. 1. Breakdown of the overall spectral curves into individual absorption bands of spirochromenes: 1) Ia; 2) Ib; 3) IIa; 4) IIb.

$$D_i = D_0{}^1 e^{-k_1 t} + D_0{}^2 e^{-k_2 t} \tag{1}$$

The failure of the dark decolorization of the photomerocyanine to follow the first-order kinetic law that is characteristic for such reactions in alcoholic media [11] or in a solid polymeric matrix [12] may evidently constitute evidence that some of the individual steps of the overall decolorization process, viz., dissociation of the dimers, interconversions of the various trans isomers of the photomerocyanine, trans-cis isomerization, and cyclization [14], proceed at comparable rates.

Despite the impossibility of description of the dark decolorization process by one first-order rate constant, we attempted in the case of Ib to estimate the quantum yield of the photocoloration reaction in the case of irradiation with UV light with a wavelength of 366 nm by our previously developed method [14]. It was found that the photocoloration quantum yield ($\Phi_1 \approx 0.24 \pm 0.02$) is independent of the value of the dark decolorization rate constant (k) used in the calculation: when the k value was varied over a wide range, the Φ_1 value remained constant within the limits of the experimental accuracy, and only the quantum yield (Φ_2) of the photodecolorization reaction changed. A comparison of the Φ_1 value of 0.24 determined for spirochromene Ib by this method with $\Phi_1 = 0.68$ for the corresponding 5-unsubstituted spirochromene (IIb) [14] shows that the introduction of an acetyl group in the 5 position leads to an appreciable decrease in the efficiency of the photoreaction, despite the assumption of the possible internal sensitization of the photocoloring reaction.

To ascertain the reasons for this phenomenon, we attempted to determine whether direct excitation of the indoline part of the compounds occurs in the case of spirochromenes Ia, b and the corresponding spirochromenes without an acetyl group (IIa, b) when they are irradiated with activating UV light (λ 366 nm). Proceeding from the concepts that the indoline and chromene parts of the molecule are orthogonal and absorb light independently [15] and taking into account the spectral properties of a model compound, viz., 1,2,3,3-tetramethylindoline (λ_{max} 254 and 301 nm) [16] and the position of the absorption bands of the chromene part of the spirochromene IIa molecule (λ_{max} 269 and 340 nm) [15], we broke down the absorption spectrum of spirochromene IIa in ethanol into four absorption bands (Fig. 1) after initially establishing the position of these bands (ν_{max}) and calculating the amplitudes (ε_{max}) and half-widths (σ) of the bands under the assumption that the bands have the form of Gaussian curves [17]:

TABLE 3. Characteristics of the Individual Absorption Bands of Spirochromenes

Compound	λ_{max}, nm	$\varepsilon_{max} \cdot 10^{-4}$	σ, cm^{-1}	P^*	λ_{max}, nm	$\varepsilon_{max} \cdot 10^{-4}$	σ, cm^{-1}	P^*	λ_{max}, nm	$\varepsilon_{max} \cdot 10^{-4}$	σ, cm^{-1}	P^*	λ_{max}, nm	$\varepsilon_{max} \cdot 10^{-4}$	σ, cm^{-1}	P^*
	1				2				3				4			
IIa	254	1,07	953	0,094	270	1,32	1006	0,12	301	0,65	1023	0,061	341	0,90	1141	0,094
Ia	255	2,08	950	0,18	270	1,16	1003	0,11	301	1,26	1742	0,20	340	0,96	1721	0,15
IIb	254	2,01	658	0,12	281	0,97	1094	0,098	301	0,43	1448	0,057	357	1,04	1375	0,13
Ib	255	1,36	992	0,12	281	0,48	834	0,037	301	0,39	1128	0,04C	357	0,98	1759	0,16

*The oscillator force (P) of the band is $0.92 \cdot 10^{-8} \varepsilon_{max} \sigma$ [17].

TABLE 4. Spirochromenes Ia–d

Compound	mp, °C *	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
Ia	>350 (dec.)	69.4	5,5	7,1	$C_{21}H_{20}N_2O_4$	69,2	5,5	7,7	23,4
Ib	195–197	67,5	5,5	6,4	$C_{22}H_{22}N_2O_5$	67,0	5,6	7,1	38,0
Ic	155–157	56,6	4,8	6,3	$C_{21}H_{19}BrN_2O_4$†	56,9	4,3	6,3	33,0
Id	220 (dec.)	61,7	5,3	10,8	$C_{21}H_{19}N_3O_6$	61,6	4,7	10,3	53,0

*Compounds Ia, b were recrystallized from aqueous acetone, and Ic,d were recrystallized from aqueous ethanol.
†Found: Br 17.3%. Calculated: Br 17.9%.

$$\varepsilon = \varepsilon_{max} e^{-\frac{(\nu - \nu_{max})^2}{\sigma^2} \ln 2} \qquad (2)$$

On the basis of the data obtained we then determined the parameters of the individual absorption bands of other spirochromenes (see the experimental section). The results are presented in Table 3 and Fig. 1.

The introduction of an acetyl group in the 5 position of the indoline part of the molecule does not cause a change in the position of the individual absorption bands of the spirochromene; however, the relative intensities of the absorption bands of the indoline part increase appreciably in some cases as compared with the intensities of the absorption bands of the chromene part. It follows from the spectral curves (Fig. 1) that absorption of the indoline part of the molecule is virtually absent at the wavelength of the activating light (366 nm) (in the case of spirochromenes Ib and IIa, b) or does not exceed 15% of the overall absorption (in the case of spirochromene Ia).

Thus in the case under consideration the prerequisites for appreciable absorption of the energy of the indoline part of the spirochromene molecule and its subsequent transfer to the chromene part are absent. The decrease in the efficiency of photocoloring when an acetyl group is introduced in the 5 position may most likely constitute evidence for the reverse process, viz., energy transfer from the pyran to the indoline part with subsequent emission-less deactivation. A similar phenomenon due to a decrease in the triplet π,π^* level of the indoline part below the corresponding level of the pyran part of the spirochromene when annelated benzene rings are introduced in the indoline part has been described [18].

EXPERIMENTAL

The measurement of the absorption spectra of the photomerocyanines and the kinetic photocoloring and subsequent dark decolorization curves and the determination of the quantum yields were carried out as described in [14]. The calculation of the kinetics of the dark decolorization reaction from Eq. (1) was accomplished by the coordinate descent method. The experimental spectral curve was broken down into the combination of four Gaussian bands by means of the criterion of least squares. The system of differential equations that follow from the condition of least squares was solved by the Newton method of successive approxi-

mation [19]. The subsequent refinement of the desired parameters included the transformation of the starting function to a linear regression equation successively relative to each of the parameters at fixed values of all the remaining parameters. The programs were realized in extended Basic language with a Nova-1200 computer. The parameters of the individual absorption bands in the spectrum of spirochromene IIa were determined initially. After which for a fixed position of the absorption bands of the chromene part of the molecule (λ_{max} 269 and 340 nm) the characteristics of individual absorption bands of spirochromene Ia were determined. These characteristics were similarly determined successively at a fixed position of the bands of the indoline part of the molecule (λ_{max} 254 and 301 nm) for spirochromene IIb and spirochromene Ib. The electronic absorption spectra of solutions of the spirochromenes were measured with a VSU-2P spectrophotometer. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer.

1,3,3-Trimethyl-5-acetyl-6'-nitro-8'-R-spiro(indoline-2,2'-[2H]chromenes) (Ia-d, Table 4). A mixture of 7.96 g (0.05 mole) of 5-acetylindole [4], 32 g (0.225 mole) of methyl iodide, and 10 ml of methanol was heated with shaking in an autoclave at 150°C for 15 h, after which it was extracted repeatedly with hot water, and the aqueous extract was refluxed with activated charcoal and filtered. The filtrate was made alkaline to pH 10 with solid alkali and refluxed for a few minutes. The resulting solution was cooled and extracted with ether, and the extract was dried rapidly over sodium sulfate and evaporated. The residue, which was unstable 5-acetyl-1,3,3-trimethyl-2-methyleneindoline, was dissolved in 20 ml of absolute ethanol, the solution was mixed with a solution of 0.025 mole of the corresponding nitrosalicylaldehyde in 40 ml of absolute ethanol, and the mixture was refluxed for 3 h. It was then cooled, and the precipitate was separated, washed with ethanol and ether, and recrystallized from aqueous acetone or ethanol.

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