EFFECT OF SUBSTITUENTS IN THE 5' AND 7' POSITIONS ON THE SPECTRA OF MEROCYANINES OF 1,3,3-TRIMETHYL-6'-NITROINDOLINE-2-SPIRO-2'-[2H]-CHROMENES

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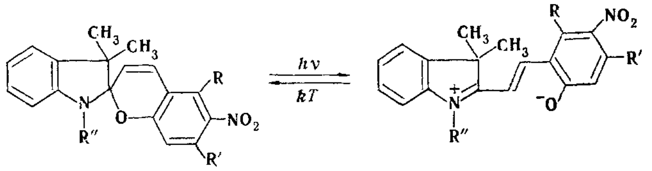
The corresponding photochromic 5',7'-disubstituted indolinospirochromenes were obtained by the reaction of 4,6-dialkoxy-5-nitrosalicylaldehydes, as well as 4,6-dimethyl-5-nitrosalicylaldehyde, with 1,3,3-trimethyl-2-methyleneindoline. Bulky electron-donor substituents in the ortho,ortho' positions relative to the nitro group give rise to a hypsochromic shift of the long-wave absorption band of the photomerocyanine as a consequence of steric hindrance to conjugation of the nitro group in combination with the electronic effect along the chromophore chain on the nitrogen atom of the indoline part of the molecule.

The elucidation of the peculiarities of the effect of structural factors on the photochromism of indolinospirochromenes opens up the possibility of an approach to the purposeful creation of photochromic materials with the necessary properties. It has been shown [1] that substituents in 6'-nitro-substituted indoline spirochromenes can slightly shift the long-wave absorption band of a photomerocyanine bathochromically (donor substituents in the 8' position of the chromene part or acceptors in the 5 position of the indoline part) or hypsochromically (donor substituents in the 5 position or acceptors in the 8' position). Substituents in the chromene part that increase the overall system of conjugated bonds of the molecule may give rise to a more substantial bathochromic shift [2]). According to the data of Taylor and co-workers [3], 1,3,3-trimethyl-5',7'-dimethoxy-6'-nitroindoline-2-spiro-2'-[2H]chromene (Ia) in a polymer matrix under the influence of UV light is converted to a photomerocyanine, the long-wave absorption band of which is shifted hypsochromically as compared with spirochromene Ib, which does not contain methoxy groups. For a more detailed study of this effect we synthesized spirochromenes Ic-g and studied their photochromic properties in comparison with the properties of known spirochromenes Ia, b, h (Table 1).



I a-h

I a,b,d-h $R''=CH_3$; I c $R''=C_{18}H_{37}$; R and $R'=H$, CH_3, OAlk (see Table 1)

The formylation of phloroglucinol monomethyl ether (II) with formanilide in the presence of phosphorus oxychloride led to 4-hydroxy-6-methoxysalicylaldehyde (III), by alkylation of which with ethyl p-toluenesulfonate or butyl iodide we obtained the corresponding 4-alkoxy-6-methoxysalicylaldehydes (IVa, b). In the nitration of these aldehydes we isolated the corresponding 5-nitro-substituted aldehydes (Va, b).

The presence in the PMR spectra of aldehyde III of two doublet signals ($J = 2$ Hz for two aromatic protons and of the signal of one aromatic proton (δ 5.96-5.97 ppm) in the spectra of aldehydes Va, b that is shifted to strong field as compared with the signal of the

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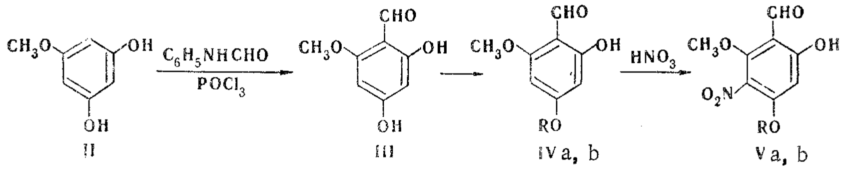
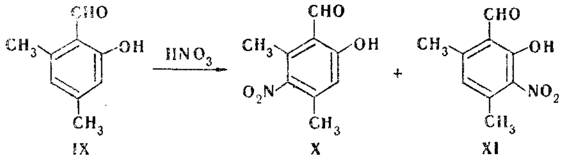


a R = C_2H_5; b R = C_4H_9

proton in the 5 position for aldehydes IVa, b (δ 5.99 ppm) and an analysis of the properties of spirochromenes obtained from these aldehydes unambiguously determine the site of incorporation of the substituents in the indicated formylation and nitration reactions (Table 2).*

Vilsmeier formylation of phloroglucinol diethyl ether (VI) led to 4,6-diethoxysalicylaldehyde (VII), the nitration of which gave 4,6-diethoxy-5-nitrosalicylaldehyde (VIII).

The nitration of 4,6-dimethylsalicylaldehyde (IX) [4] led to a mixture of dimethylnitrosalicylaldehydes (X, XI), the assignment of the structures of which was made by comparison of the properties of spirochromenes obtained from these aldehydes (see below).



The condensation of aldehydes Va, b, VIII, X, and XI with 1,3,3-trimethyl-2-methyleneindoline led smoothly to the corresponding spirochromenes Id-g and 1,3,3,5',7'-pentamethyl-8'-nitroindoline-2-spiro-2'-[2H]-chromene (XII). Spirochromene Ic was obtained from 4,6-dimethoxy-5-nitrosalicylaldehyde [3] and 1-octadecyl-3,3-dimethyl-2-methyleneindoline [5].

Solutions of spirochromenes Ic-g have photochromic properties at room temperature: They are colorless in toluene and dioxane but upon irradiation with UV light, due to conversion of the spirochromene to the open merocyanine form, take on a red (spirochromenes Ic-d) or violet (spirochromene Ig) coloration, which vanishes rapidly after irradiation is discontinued (Table 1).

The introduction of a methoxy group in the 7' position adjacent to the nitro group (spirochromene Ih as compared with spirochromene Ib) leads to a certain hypsochromic shift of the absorption band of the photomerocyanine in toluene; a sharp (up to 55 nm in toluene) hypsochromic shift is observed when two alkoxy substituents are introduced in the ortho,-ortho' positions relative to the nitro group (spirochromenes Ia, c-f). The introduction of two bulky substituents in the ortho,ortho' positions relative to the nitro group leads to its deviation from the plane of the aromatic ring, which hinders transmission of its polar effect. This effect, which was established in the case of a sharp decrease in the lability of the leaving group in the para position relative to the nitro group in aromatic nucleophilic substitution reactions [8, 9], is evidently the reason for the hypsochromic effect that we observed. The data obtained thus, by confirming and expanding the previously drawn conclusions [1, 2], provide evidence that an increase in the conjugation chain of the photomerocyanine due to a substituent in both the indoline and chromene parts of the molecule leads to a bathochromic shift of the long-wave absorption band, while the effect of the substituent via an inductive mechanism depends on its position. The effect of alkoxy groups in spirochromenes Ia, c-f on the spectrum of the photomerocyanine evidently does not reduce only to steric interaction. Methoxy groups give rise to a greater hypsochromic shift as compared with methyl groups (spirochromenes Ia and Ig), although the steric hindrance created by methyl groups is more substantial [9]. The data obtained evidently constitute evidence that methoxy groups in the 5',7' positions of the quinoneallide part of the photomerocyanine transmit their electron-donor effect along the chromophore chain of the molecule to the nitrogen atom, thereby giving rise to an additional hypsochromic shift.

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TABLE 1. Spectral-Kinetic Parameters of the Photochromic Transformations of Spirochromenes Ia-h and XII

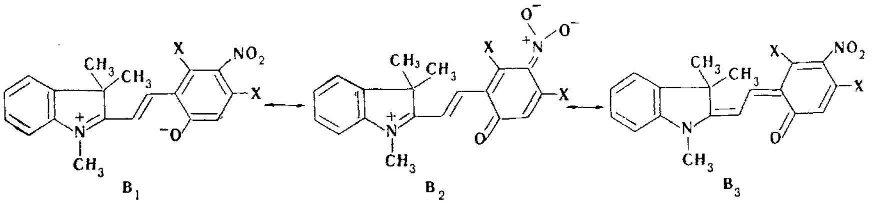
Spirochromene	R	R′	$k \cdot 10^2$ sec^{-1}, 20°		λ_{max} of the photomerocyanine, nm	
			toluene	dioxane	in toluene	in ethanol
Ia	OCH_3	OCH_3	16,1	9,20	533 (567 [7])	520 (515 [7])
Ib[6]	H	H	3,09	2,97	583	532
Ic	OCH_3	OCH_3	12,0	6,00	536	510
Id	OCH_3	OC_2H_5	16,0	7,40	535	516
Ie	OCH_3	OC_4H_9	15,5	4,40	539	515
If	OC_2H_5	OC_2H_5	13,2	3,60	537	516
Ig	CH_3	CH_3	40,0	21,0	563 (565 [7])	545 (558 [7])
Ih	H	OCH_3	2,90	1,60	565	530
XII	—	—	24,5	18,2	574	550

TABLE 2. PMR Spectra of Alkoxysalicylaldehydes

Aldehyde	δ, ppm (in $CDCl_3$)					
	$6\text{-}OCH_3$	3-H	5-H	2-OH	CHO	4-RO
III′	3,79 s	5,85 d	5,93 d	12,35 s	9,98 s	9,88 s (R=H)
IVa	3,85 s	5,90 d	5,99 d	12,49 s	10,09 s	1,43 t; 4,05 q
IVb	3,86 s	5,90 d	5,99 d	12,47 s	10,07 s	0,98 t; 1,18—1,91 m; 4,00 t
Va	3,95 s	5,96 s	—	12,89 s	10,12 s	1,46 t; 4,22 q
Vb	3,96 s	5,97 s	—	12,95 s	10,17 s	0,97 t; 1,12—1,88 m; 4,14 t

The introduction of bulky substituents in the ortho,ortho' positions relative to the nitro group also gives rise to a sharp increase in the rate of dark decolorization of the photomerocyanine (Table 1); this increase is maximal in the case of methyl groups. Deviation of the nitro group from the plane of the photomerocyanine molecule leads to a decrease in stabilization of the dipolar mesomeric structure (for example of the B_2 type), which in turn evidently gives rise to an increase in the contribution of quinoid structure B_3 in the resulting photomerocyanine molecule and, as a consequence, acceleration of the cis-trans isomerization step and the entire dark decolorization of the photomerocyanine as a whole [10].

It has been established empirically in numerous cases that the absorption spectra of photomerocyanines of 8'-nitro-substituted spirochromenes are shifted bathochromically as compared with the corresponding 6'-nitro-substituted compounds [7]. By comparing the spectral characteristics of the photomerocyanine forms of spirochromenes Ig and XII (Fig. 1), which were obtained from two isomeric nitro-substituted 4,6-dimethylsalicylaldehydes (X, XI), one can, by taking into account this principle, make an unambiguous assignment of the structures of aldehydes X and XI and spirochromenes Ig and XII. The spectral characteristics of spirochromene Ig, with mp 228-231°C, were presented (without a description of the synthesis) in a review by Bertelson [7]. It follows from a comparison with the data that we obtained that the American authors were evidently dealing with a mixture of spirochromenes Ig and XII with preponderance of the latter.



EXPERIMENTAL

The rate constants for the dark-decolorization reaction and the absorption spectra of the photomerocyanines (Table 1 and Fig. 1) were measured by means of an automated spectral-kinetic apparatus, and the spectral data obtained were approximated by Gaussian curves by means of a computer as described in [11, 12].

Spirochromenes Ia [mp 210-212°C (mp 212-213°C [3])], Ib [mp 176-177°C (mp 176-177°C [13])], and Ih [mp 179-180°C (mp 180-181°C [3])] were obtained by the method in [13]. The

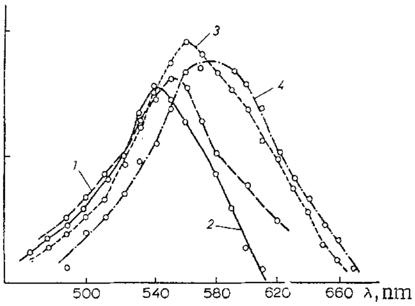


Fig. 1. Absorption spectra of the photomerocyanine forms of spirochromenes: 1) XII in ethanol; 2) Ig in ethanol; 3) Ig in toluene; 4) XII in toluene.

PMR spectra of 0.1 M solutions of the aldehydes in deuterochloroform were measured with an XL-100-12 spectrometer.

4-Hydroxy-6-methoxysalicylaldehyde (III). A mixture of 6 g (0.043 mole) of phloroglucinol monomethyl ether [14], 5.2 g (0.048 mole) of formanilide, 2.2 g (0.014 mole) of phosphorus oxychloride, and 50 ml of ether was refluxed for 1.5 h, after which it was allowed to stand for 24 h. The resulting precipitate was removed by filtration and treated with 200 ml of a boiling 5% solution of sodium hydroxide. The extract was cooled, washed with benzene (two 150-ml portions), and neutralized while cooling with ice by the addition of 50 ml of concentrated HCl. The precipitate was washed with water and dried at 90-100°C to give 5 g (69.4%) of aldehyde III with mp 200-205°C (dec., from water) (mp 201-203°C [15]).

4-Ethoxy-6-methoxysalicylaldehyde (IVa). A mixture of 2.52 g (0.015 mole) of aldehyde III, 3 g (0.015 mole) of ethyl p-toluenesulfonate, 2.07 g (0.015 mole) of potassium carbonate, and 12.5 ml of dimethylformamide (DMF) was stirred at 110-120°C for 8 h, after which it was cooled to 0°C, acidified to pH 2-3 with 10% hydrochloric acid, and subjected to steam distillation. The distillate was cooled with ice, and the precipitate was separated and dissolved in 20 ml of 10% potassium hydroxide solution. The solution was acidified with 10% hydrochloric acid, and the precipitate was removed by filtration and dried.

4-Butoxy-6-methoxysalicylaldehyde (IVb). A mixture of 3 g (0.018 mole) of aldehyde III, 6.2 g (0.035 mole) of butyl iodide, 2.67 g (0.019 mole) of potassium carbonate, and 15 ml of DMF was stirred at 110-120°C for 14-16 h, after which it was worked up as described in the preparation of aldehyde IVa.

4-Alkoxy-5-nitro-6-methoxysalicylaldehydes (Va, b). A solution of 7.9 ml (0.186 mole) of nitric acid (sp. gr. 1.51) in 25 ml of glacial acetic acid was added in the course of 10-15 min to a mixture of 0.045 mole of aldehyde IV and 152 ml of glacial acetic acid at such a rate that the temperature in the reaction mass did not rise above 40°C. Stirring was continued at 45°C for 1 h, after which the mixture was cooled and poured into 550 g of ice. The resulting precipitate was separated and washed with water. For purification, aldehyde Va was crystallized from benzene. Aldehyde Vb was chromatographed with a column filled with D-100/250 μ silica gel using benzene as the eluent; the product has R_f 0.34 (Silufol UV-254, benzene).

4,6-Diethoxysalicylaldehyde (VII). A mixture of 9.1 g (0.05 mole) of phloroglucinol diethyl ether [16] and 7.2 g (0.054 mole) of N-methylformanilide was stirred for 30 min, after which it was cooled to 10°C and treated with 7.95 g (0.052 mole) of phosphorus oxychloride in the course of 40 min. The mixture was then stirred for 1 h, after which it was treated with 100 g of ice and allowed to stand overnight. It was then subjected to steam distillation, and the distillate was allowed to stand for ∿16 h. The resulting precipitate was separated and crystallized from heptane.

4,6-Diethoxy-5-nitrosalicylaldehyde (VIII). A solution of 0.5 mole (11.8 mmole) of nitric acid (sp. gr. 1.51) in 3 ml of glacial acetic acid was added to a solution of 0.63 g (0.3 mmole) of aldehyde VII in 6 ml of glacial acetic acid, and the mixture was stirred at 35°C for 4 h. It was then poured over ice, and the precipitate was washed with water and

TABLE 3. Substituted Salicylaldehydes and Spirochromenes

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
Ic	92—94	73,9	9,4	4,2	$C_{38}H_{56}N_2O_5$	73,5	9,1	4,5	26
Id	140—141	66,5	6,6	6,7	$C_{22}H_{24}N_2O_5$	66,7	6,1	7,1	50
Ie	197—198	68,2	6,5	6,5	$C_{24}H_{28}N_2O_5$	67,9	6,6	6,6	48
If	240	67,4	6,0	6,5	$C_{23}H_{26}N_2O_5$	67,3	6,4	6,8	48
Ig	183—185*	71,8	6,4	7,8	$C_{21}H_{22}N_2O_3$	72,0	6,3	8,0	45
IVa	68—70	61,4	6,1	—	$C_{10}H_{12}O_4$	61,2	6,1	—	12
IVb	46—48	64,4	7,4	—	$C_{12}H_{16}O_4$	64,3	7,1	—	20
Va	223—225,5	50,0	4,6	5,9	$C_{10}H_{11}NO_6$	49,8	4,6	5,8	12
Vb	102—104	53,5	5,5	5,3	$C_{12}H_{15}NO_6$	53,6	5,6	5,2	6
VII	73—75	63,0	6,5	—	$C_{11}H_{14}O_4$	62,8	6,7	—	21
VIII	181—183	52,0	5,0	5,2	$C_{11}H_{13}NO_6$	51,8	5,1	5,5	23
X	187—190	55,1	5,1	7,0	$C_9H_9NO_4$	55,4	4,7	7,2	16
XI	127—130	55,1	5,1	6,8	$C_9H_9NO_4$	55,4	4,7	7,2	29
XII	238—241	72,3	6,7	7,8	$C_{21}H_{22}N_2O_3$	72,0	6,3	8,0	39

*According to the data in [7], this compound has mp 228-231°C.

purified by means of preparative thin-layer chromatography (TLC) on Silufol plates in benzene. The zone with R_f 0.4 was cut out and extracted with chloroform, the extract was evaporated, and the residue was crystallized from hexane.

3- and 5-Nitro-4,6-dimethylsalicylaldehydes (XI, X). A 1.3-ml (30.7 mmole) sample of nitric acid (sp. gr. 1.51) was added at 15°C to a solution of 0.8 g (0.53 mmole) of 4,6-dimethylsalicylaldehyde [4] in 15 ml of glacial acetic acid, after which the mixture was stirred at 15°C for 2 h and poured over ice. The residue was separated, recrystallized from petroleum ether, and separated by means of preparative TLC on Silufol plates in benzene. Workup of the upper zone (R_f 0.62) yielded 0.16 g of 5-nitro-4,6-dimethylsalicylaldehyde (X), which was crystallized from petroleum ether. Workup of the lower zone (R_f 0.39) yielded 0.28 g of 3-nitro-4,6-dimethylsalicylaldehyde (XI), which was crystallized from petroleum ether.

Spirochromenes Ic-g and XII. These compounds were obtained by the method in [13]. Spirochromene If was purified by sublimation at 150°C (0.001 mm), while the remaining compounds were purified by recrystallization from ethanol.

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PYRROLOCARBAZOLES.

4.* ACETYLATION OF 3H-PYRROLO[2,3-c]CARBAZOLE

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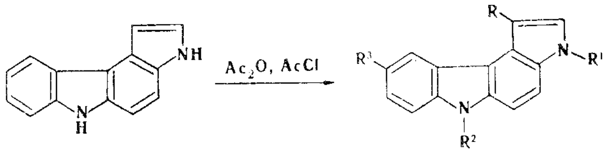
UDC 547.759.52.07:542.951

It is shown that 1-acetyl and 1-chloroacetyl derivatives are formed in the Vilsmeier acylation of 3H-pyrrolo[2,3-c]carbazole. The 3,6-diacetyl derivative is formed by the action of Ac_2O without a catalyst, whereas the presence of catalytic amounts of H_3PO_4 leads to 1,6-diacetyl-3H-pyrrolo[2,3-c]carbazole. Only one reaction product, viz., the 9-acetyl derivative, is formed when $AlCl_3$ is used as the catalyst, while a mixture of acylation products was obtained in the presence of $SnCl_4$.

We have previously shown [2] that in the acetylation of 3H-pyrrolo[2,3-c]carbazole with acetic anhydride in the presence of acetic acid the reaction proceeds unambiguously at the carbazole nitrogen atom to give 6-acetyl-3H-pyrrolo[2,3-c]carbazole.

In the present research we made a detailed study of the acetylation of 3H-pyrrolo[2,3-c]carbazole (I) under various conditions.



I   II–VI

II $R=COCH_3$, $R^1=R^2=R^3=H$; III $R=COCH_2Cl$, $R^1=R^2=R^3=H$; IV $R^1=R^2=COCH_3$, $R=R^3=H$; V $R=R^2=COCH_3$, $R^1=R^3=H$; VI $R=R^1=R^2=H$, $R^3=COCH_3$

For the synthesis of acetyl derivatives of pyrrolocarbazole I we used the general method of Vilsmeier acetylation with complexes of amides and phosphorus oxychloride.

The use of N,N-diethylchloroacetamide in the reaction with I made it possible to obtain 1-chloroacetyl derivative III in 40% yield. The reaction with N,N-dimethylacetamide proceeds with considerably greater difficulty (II is obtained in 10% yield); this is evidently associated with the smaller degree of electrophilicity of the attacking complex [3].

In the PMR spectra of II and III (Table 1) the absence of the signal of the 1-H proton and the appearance in the strong-field region of characteristic singlets of protons of CH_2 group for II at 2.63 ppm and of a CH_2Cl group for III at 4.96 ppm indicate replacement of the hydrogen atom in the 1 position of the pyrrolocarbazole ring by acetyl and chloroacetyl groups, respectively (i.e., C-acylation).

3H-Pyrrolo[2,3-c]carbazole reacts differently with acetic anhydride than indole to give only an N-acetylation product, viz., 3,6-diacetyl derivative IV, while indole gives a mixture of mono- and diacetyl derivatives [4]. Using orthophosphoric acid as the catalyst we also isolated and characterized 1,6-diacetyl-3H-pyrrolo[2,3-c]carbazole (V).

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*See [1] for Communication 3.

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