SYNTHESIS AND PHOTOCHROMISM OF INDOLINOSPIROCHROMENES WITH CONDENSED FRAGMENTS IN THE INDOLINE PART OF THE MOLECULES

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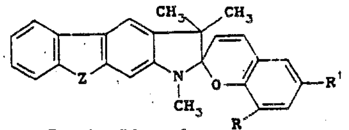
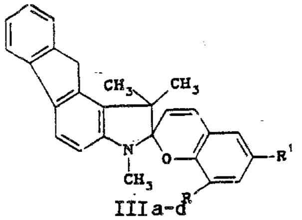
816.07:541.145

Indoline spirochromenes with condensed fragments in the indoline part of the molecules were synthesized. All of the compounds have photochromic properties. The introduction of a condensed fragment into the indoline part of the molecule leads to a bathochromic shift of both the long-wave and short-wave absorption bands of the photomerocyanine; the rate of the dark reaction does not change.

Continuing our investigation of the relationship between the structures of indolinospirochromenes and the parameters of their photochromic transformations [1] we accomplished the synthesis and studied the photochromic properties of spirochromenes of the I-VII type:


Ia-d, IIc, d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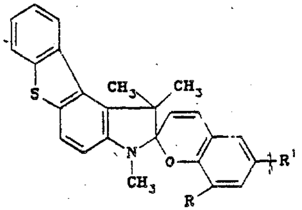
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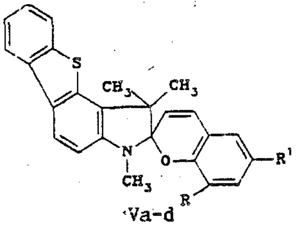
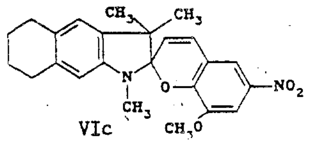

Va-d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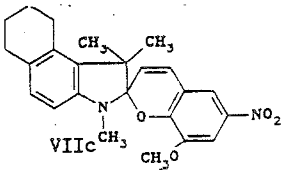
VIIc

I Z=CH$_2$; II Z=CO; ^{a} R=H, R^1=NO$_2$; ^{b} R=Br, R^1=NO$_2$; ^{c} R=OCH$_3$, R^1=NO$_2$; ^{d} R=NO$_2$, R^1=OCH$_3$

The synthesis was carried out via the traditional scheme starting from 2-aminofluorene [2, 3], 2-aminofluorenone [4], 2-aminodibenzothiophene [5, 6], 3-aminodibenzothiophene [6], and 6-aminotetralin [7, 8]. By diazotization of the indicated amino derivatives with subsequent reduction of the diazonium salts with stannous chloride we obtained the corresponding arylhydrazines, from which arylhydrazones were formed by reaction with methyl isopropyl ketone. Fischer cyclization gave trimethylindolenines, methylation of which with methyl iodide led to tetramethylindoleninium iodides with annelated fragments. Decomposition of the quaternary indoleninium salts with alkali gave methylene bases, condensation of which with substituted salicylaldehydes yielded indoline spirobenzopyrans (Table 1).

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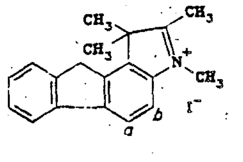
TABLE 1. Spirochromenes II-VII

Compound	R*	mp, °C	Found, %			Empirical formula	Calc., %			Yield, % (based on the amine)
			C	H	N (S)		C	H	N (S)	
IIIa	H	238—240	76,0	5,6	6,6	$C_{26}H_{22}N_2O_3$	76,1	5,4	6,8	3,0
IIIb	Br	282—284	63,8	4,3	5,7	$C_{26}H_{21}BrN_2O_3$**	63,8	4,3	5,7	7,0
IIIc	OCH_3	245—248	73,7	5,4	6,2	$C_{27}H_{24}N_2O_4$	73,6	5,5	6,3	4,4
IIId	NO_2	238—240	73,6	5,8	6,7	$C_{27}H_{24}N_2O_4$	73,6	5,5	6,3	4,4
IIc	OCH_3	260—263	71,7	5,0	6,1	$C_{27}H_{22}N_2O_5$	71,4	4,9	6,2	1,3
IId	NO_2	255—258	71,5	5,1	5,9	$C_{27}H_{22}N_2O_5$	71,4	4,9	6,2	1,7
IVa	H	283—285	81,4	4,7	6,1 (7,4)	$C_{25}H_{20}N_2O_3S$	81,3	4,7	6,5 (7,5)	5,0
IVb	Br	297—298	59,4	3,8	5,5	$C_{25}H_{19}BrN_2O_3S$	59,2	3,8	5,5	9,0
IVc	OCH_3	278—280	68,2	4,9	5,8 (13,7)	$C_{26}H_{22}N_2O_4S$	68,1	4,8	6,1 (14,0)	10,3
IVd	NO_2	212—215	68,0	4,9	6,0 (13,5)	$C_{26}H_{22}N_2O_4S$	68,1	4,8	6,1 (14,0)	12,4
Vb	Br	275—278	59,0	3,8	5,4	$C_{25}H_{19}BrN_2O_3S$	59,2	3,8	5,5	2,5
Vc	OCH_3	240—244	68,2	4,8	6,0	$C_{26}H_{22}N_2O_4S$	68,1	4,8	6,1	7,5
Vd	NO_2	234—236	67,8	4,9	6,0	$C_{26}H_{22}N_2O_4S$	68,1	4,8	6,1	3,0
VIc	OCH_3	258—259	70,8	6,6	7,0	$C_{24}H_{26}N_2O_4$	70,9	6,5	7,0	3,3
VIIc	OCH_3	250—253	71,0	6,6	7,0	$C_{24}H_{26}N_2O_4$	70,9	6,5	7,0	2,1

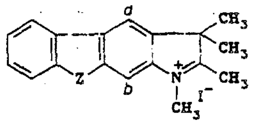
*IIIa-c, IIc, IVa-c, Vb, c, VIc, VIIc $R^1 = NO_2$; IId-Vd $R^1 = OCH_3$.

**Found: Br 15.5%. Calculated: Br 16.3%.



VIII

IX Z=CO; X Z=CH_2



IX, X

The starting aromatic amines have two free structurally nonequivalent ortho positions, as a consequence of which Fischer cyclization could have led to the formation of two different indolenines (with linear and angular structures). The PMR spectrum of the product of cyclization and subsequent methylation obtained from 2-aminofluorene contains a dual set of signals. In particular, singlets with chemical shifts (CS) of 8.03 and 8.20 ppm and two doublets centered at 7.84 and 8.10 ppm are observed in the aromatic-proton region. They can be assigned to two different reaction products – iodides X and VIII (Table 2). The ratio of the intensities of the signals of the protons of the N-methyl groups constitutes evidence for a ratio of the linear and angular compounds in the cyclization product of 3:7. Similar analysis of the PMR spectrum of iodide IX obtained from 2-aminofluorenone showed that only a linear compound is formed as a result of the cyclization (Table 2).

The reaction of the mixture of iodides X and VIII with sodium hydroxide and subsequent condensation of the resulting mixture of 2-methyleneindolines with 3-bromo-5-nitrosalicylaldehyde yielded a substance, the PMR spectrum of which contained, like the starting mixture of iodides, a dual set of signals. In particular, signals of an AB spectrum at 7.89 and 8.20 ppm (J = 8.4 Hz), as well as two singlets at 8.07 and 8.29 ppm, are observed in the spectrum. The first of the indicated pairs of signals can be assigned to the adjacent protons in the 4 and 5 positions of the indoline part of the spirochromene with angular structure III, and the second can be assigned to the noncoupling protons in the 4 and 10 positions in linear structure I. The PMR spectrum of pure isomer IIIb, which was isolated from the indicated mixture by column chromatography, confirmed its angular structure. Compounds IIIa, c, d, which were obtained from 2-aminofluorene using other salicylaldehydes, also have angular structures. On the other hand, spirochromenes IIc, d, which were obtained from 2-aminofluorenone, have linear structures; this follows from the linear structure of methiodide IX.

The PMR spectrum of spirochromene IVd, obtained from 2-aminodibenzothiophene, owing to the presence of doublet signals of an AB spectrum at 6.89 and 7.71 ppm, which belong to the adjacent protons of the middle benzene ring of the indoline part of the molecule, constitutes evidence in favor of an angular structure (Table 3); we also assign a similar structure to spirochromenes IVa-c. The presence in the PMR spectrum of spirochromene Vc of a doublet signal of an AB spectrum at 6.84 and 8.08 ppm also constitutes evidence in favor of an angular

TABLE 2. PMR Spectra of Iodides VIII-X

Compound	δ, ppm					
	N—CH₃	2-CH₃	(CH₃)₂	*a*	*b*	CH₂
VIII	4,76	1,66	1,72	7,84 d*	8,10 d*	4,16
IX	4,09	2,02	1,80	7,55	8,29	
X	4.77	1,72	1,67	8,03	8,20	4,09

*J_{ab} = 8.5 Hz.

TABLE 3. PMR Spectra of Some Spirochromenes

Compound	δ, ppm										J, Hz		
	NCH₃	C(CH₃)₂	4-H	5-H	10-H (9-H)	3′-H	4′-H	5′-H	7′-H	OCH₃	3′—4′	5′—7′	4—5
IIIb	2,78	1,29; 1,46	6,61	7,63	3,88	5,93	6,93	7,97	8,28		10,5	2,90	8,06
IId	2,76	1,20; 1,31	8,32		7,69	5,91	6,89	7,53	7,45	3,74	10,4	2,60	
IVd	2,74	1,55; 1,65	7,71	6,89		6,06	7,16	7,46	7,38	3,76	10,4	2,50	8,30
Vc	2,79	1,24; 1,43	8,08	6,84		6,01	7,19	7,83	7,62	3,90	10,4	2,60	8,20
VIc	2,71	1,18; 1,26	6,23		(6,75)	5,81	6,85	7,62	7,69	3,76	10,0	2,68	
VIIc	2.68	1,21; 1,36	6,91	6,36		5.80	6.87	7.62	7.68	3.77	10,5	2,71	8.60

TABLE 4. Photochromic Characteristics of Spirochromenes

Compound	$k_T \cdot 10^2$, sec^{-1}		λ_{max}, nm	
	toluene	dioxane	ethanol	toluene
IIc	1,95	1,60	575	630 410
IId	—*	—*	620	—* —*
IIIa	5,70	2,70	548	605 390
IIIb	2,00	0,70	545	615 395
IIIc	2,75	2,30	575	627 410
IIId	3,50	2,20	575	623 410
IVa	3,40	2,40	540	613 385
IVb	1,70	0,40	570	610 390
IVc	3,00	2,60	570	620 405
IVd	15,00	12,5	620	648 415

*Measurements could not be made because of the low efficiencies of the photochromic transformations.

structure for spirochromenes Vb-d (Table 3). In the case of compounds obtained from 6-aminotetralin spirochromenes with linear (VIc) and angular (VIIc) structures are isolated from the reaction mixture (Table 3).

The synthesized spirochromenes have the photochromic properties that are typical for spirochromenes of the indoline series with a nitro group in the chromene part of the molecules. The rate constants for thermal decolorization of the photocolored solutions (k_T) at 20°C and the positions of the maxima of the absorption bands of the photoinduced forms (λ_{max}) of some of the compounds obtained are presented in Table 4. A comparison of the spectral characteristics of III and IV with the data for 5-phenylindolinospirochromenes [1] makes it possible to note that fixing of the plane of the phenyl ring, which is realized on passing from the 5-phenyl compounds to substances with annelated fragments, leads to a bathochromic shift of both the long-wave and short-wave absorption bands of the photomerocyanine. This shift may reach 20 nm in some cases. The data obtained confirm the conclusions that we have previously drawn regarding the dependence of the position of the long-wave absorption band in the electronic absorption spectra of photomerocyanines on the structural changes in the indoline part of the spirochromenes [9]. A comparison of the rate constants for the dark decolorization of the photomerocyanines investigated in the present research with the analogous characteristics of compounds that do not have substituents in the indoline part shows that the introduction of linearly or angularly annelated fragments into the indoline part of the spirochromene molecules does not change the indicated constant substantially. This is in good agreement with the previously published data that indicate that the rate of the dark reaction of indolinospirochromenes with a nitro group in the pyran part of the molecules changes substantially only when substituents with an electron-donor or electron-acceptor effect are introduced into the 5 position of the indoline fragment [10].

Thus linear or angular annelation of a two-ring system to the indoline part of the spirochromene molecule makes it possible to shift the absorption bands of the photomerocyanine bathochromically to the visible region of the spectrum and, consequently, to change the color of photochromic materials vis-à-vis a relatively unchanged stability of the colored form; this may prove to be useful in the development of photochromic materials with predesignated properties.

EXPERIMENTAL

The absorption spectra of the photomerocyanines and the kinetic curves of photocoloring and subsequent dark decolorization were measured as described in [11]. The PMR spectra were recorded with a Varian CFT-20 high-resolution NMR spectrometer (80 MHz) with tetramethylsilane as the internal standard.

2-Aminofluorene. This compound was obtained by reduction of 2-nitrofluorene [2] with hydrazine hydrate in alcohol solution in the presence of Raney nickel [3]. The product was obtained in 93% yield and had mp 128°C (from 2-propanol).

2-Aminofluorenone. This compound was obtained by oxidation of 2-nitrofluorene (99% yield) and subsequent reduction of 2-nitrofluorenone with stannous chloride in concentrated HCl [4]. The product had mp 158°C (from ethanol).

2-Aminodibenzothiophene. This compound was obtained in 46% yield by reduction of 2-nitrodibenzothiophene (see below) with stannous dichloride [6]. The product had mp 129°C (mp 133°C [6]).

3-Aminodibenzothiophene. This compound had mp 110-118°C (from 60% ethanol) (mp 113-117°C [6]) and was obtained by nitration of dibenzothiophene 5-oxide (see below) and subsequent reduction of the nitro and sulfoxide groups by the action of stannous chloride [6].

6-Aminotetralin. This compound was obtained as described in [8]. The acetyl derivative had mp 105°C (mp 104-105°C [7]).

2-Nitrodibenzothiophene and Dibenzothiophene 5-Oxide. The nitration of dibenzothiophene was carried out as described in [5]. The reaction product was chromatographed with a column packed with silica gel by successive elution with benzene, benzene—ethyl acetate (1:1), and ethyl acetate. Workup of the benzene fraction gave 2-nitrodibenzothiophene, with mp 180-192°C (mp 186°C [5]) and R_f 0.74, in 30% yield. Workup of the acetate eluent gave dibenzothiophene 5-oxide, with mp 178-180°C (mp 184°C [5]), in 20% yield.

1,3,3-Trimethyl-6'-R^1-8'-R-spiro(indeno[2,3-e]indoline-2,2'-[2H]chromenes) (IIIa-d, Table 2). The diazotization of 5.8 g (32 mmole) of 2-aminofluorene was carried out by the action of 2.5 g (34 mmole) of sodium nitrite dissolved in 30 ml of concentrated HCl with subsequent reduction of the diazonium salt with stannous chloride by the method in [12]. The resulting 2-hydrazinofluorene was dissolved in 30 ml of absolute ethanol, 2.7 g (31 mmole) of methyl isopropyl ketone in 30 ml of absolute ethanol was added, and the mixture was allowed to stand overnight and evaporated. Glacial acetic acid (50 ml) was added to the residue, and the mixture was heated for 1.5 h on a boiling-water bath. Concentrated HCl (10 ml) was added, and the mixture was heated for another hour, cooled, and poured into 150 ml of cold water. The mixture was washed with ether, and the aqueous layer was neutralized with sodium carbonate and extracted with ether. The extract was dried with anhydrous magnesium sulfate and evaporated, 10 ml of methyl iodide was added to the residue, and the mixture was heated for 20 min until the mass solidified. The mixture of methiodides VIII and X was purified by recrystallization from water. For the synthesis of the spirochromenes, 50 ml of 30% NaOH solution was added to 1 g (2.5 mmole) of the mixture of methiodides VIII and X, and the mixture was heated for 30 min. It was then cooled and extracted with ether, and the extract was dried and evaporated. The residue was dissolved in 15 ml of absolute ethanol, a solution of 2.5 mmole of the substituted salicylaldehyde in 20 ml of absolute ethanol was added, and the mixture was refluxed for 30-60 min. It was then cooled, and the precipitate was separated and washed with absolute ethanol.

Spirochromene IIIb with an angular structure was obtained after separation of the mixture of isomers for IIIb with a column packed with silica gel L 100/250 μm (LV, Czech. SSR) (ℓ = 70 cm, d = 5 cm, elution with benzene).

1,3,3-Trimethyl-9-oxo-6'-R^1-8'-R'spiro(indeno[3,2-f]indoline-2,2'-[2H]chromenes) (IIc, d). These compounds were similarly obtained from 2-aminofluorenone.

1,2,3,3-Tetramethylbenzo[4,5]thieno[3,2-e]indoleninium Iodide (XI). A solution of 1.8 g (26 mmole) of sodium nitrite in 10 ml of water was added dropwise at 0°C to a mixture of 4.4 g (22 mmole) of 2-aminodibenzothiophene and 30 ml of concentrated HCl, after which the mixture was stirred for 30 min. A solution of 14.9 g (79 mmole) of stannous chloride in 10 ml of concentrated HCl was added at 0°C, and the mixture was allowed to stand in the cold overnight. The precipitate was washed successively with saturated sodium chloride solution and petroleum ether and treated with 2.5 g (28 mmole) of methyl isopropyl ketone, 2 g (24 mmole) of anhydrous sodium acetate, and 50 ml of absolute ethanol, and the mixture was refluxed for 20 min and evaporated. Glacial acetic acid (50 ml) was added to the residue, and the mixture was heated for 1.5 h on a boiling-water bath. Concentrated HCl (15 ml) was added and the mixture was heated for another hour. It was then cooled and poured into 100 ml of cold water. The aqueous mixture was washed with ether, and the aqueous layer was neutralized and extracted with ether. The extract was dried and evaporated, 3.6 ml (58 mmole) of methyl iodide was added to the residue, and the mixture was refluxed for 15 min until the mass solidified. The precipitate was washed with benzene and recrystallized from water to give 1.6 g (15%) of a product that decomposed at 298-301°C. Found: C 53.2; H 4.5; N 3.3%. $C_{18}H_{18}INS$. Calculated: C 53.1; H 4.4; N 3.4%.

1,2,3,3-Tetramethyl-6,7,8,9-tetrahydrobenzo[3]indoleninium and 1,2,3,3-Tetramethyl-5,6,7,8-tetrahydrobenzo[f]indoleninium Iodides (XII and XIII). These compounds were obtained from 6-aminotetralin by a method similar to that used to prepare XI. Colorless crystals were obtained in 23% yield and had mp 210-213°C (from water). Found: C 54.0; H 6.1; I 34.9; N 3.7%. $C_{16}N_{22}IN$. Calculated: C 54.1; H 6.2; I 35.7; N 3.9%.

1,3,3-Trimethyl-6'-R^1-8'-R-spiro(benzo[4,5]thieno[3,2-e]- and -[2,3-e]indoline-2,2'-[2H]chromenes) (IVa-d and Vb-d). These compounds were obtained as described above from substituted nitrosalicylaldehydes and methiodide XI or its isomer from 3-aminodibenzothiophene, respectively.

1,3,3-Trimethyl-6'-nitro-8'-methoxy-5,6,7,8-tetrahydrospiro(benzo[f]indoline-2,2'-[2H]-chromene) (VIc) and 1,1,3-Trimethyl-6'-nitro-8'-methoxy-6,7,8,9-tetrahydro(benzo[3]indoline-2,2'-[2H]chromene) (VIIc). The reaction of the mixture of methiodides XII and XIII with NaOH was carried out, and the reaction of the resulting mixture with 3-methoxy-5-nitrosalicylaldehyde was then carried out. As described above, the reaction mixture was cooled, and the green crystals of spirochromene VIc were removed by filtration and washed with alcohol. The mother liquor was evaporated, and the black crystals of spirochromene VIIc were separated and washed with alcohol.

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SULFUR-CONTAINING DERIVATIVES OF FIVE-MEMBERED CYCLIC SULFONES.

2.* INTRAMOLECULAR CYCLIZATION OF ISOTHIOUREIDOTHIOLENE 1,1-DIOXIDE SALTS

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cis-2-Imino-4,6,7,8-tetrahydrothieno[3,4-d]thiazole 5,5-dioxides were obtained by intramolecular cyclization of 4-isothioureido-2-thiolene 1,1-dioxide salts. The reaction of N-substituted thioureas with 4-bromo-2-thiolene 1,1-dioxide leads to 3-substituted cis-2-imino-4,6,7,8-tetrahydrothieno[3,4-d]thiazole 5,5-dioxides.

Compounds that contain a thiazolidine ring are of interest as diuretics, CNS stimulators [2], and substances that have anti-inflammatory activity [3]. We have previously reported [1, 4] the synthesis of isothioureidothiolene 1,1-dioxide salts. In a continuation of our research we studied the possibility of the use of these salts to obtain condensed two-ring systems that contain thiazolidine and thiolane 1,1-dioxide rings.

We established that 4-isothioureido-2-thiolene 1,1-dioxide hydrobromides Ia, b in aqueous solutions in the presence of sodium bicarbonate form products of intramolecular cyclization — cis-2-imino-4,6,7,8-tetrahydrothieno[3,4-d]thiazole 5,5-dioxides IIa, b.

Other isothioureidothiolene 1,1-dioxide salts [1] do not undergo this sort of transformation under these conditions. Considering the fact of the formation of salts Ia, b from thiourea and 4-bromo-2-thiolene 1,1-dioxides [1, 4], as well as the ability of these salts to undergo intramolecular cyclization, we investigated the reaction of 4-bromo-2-thiolene

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*See [1] for Communication 1.
†Deceased.

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