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SYNTHESIS AND PHOTOCHROMIC PROPERTIES OF INDOLINOSPIROCHROMENES WITH ELECTRON-DONOR SUBSTITUENTS IN THE INDOLINE PART OF THE MOLECULE

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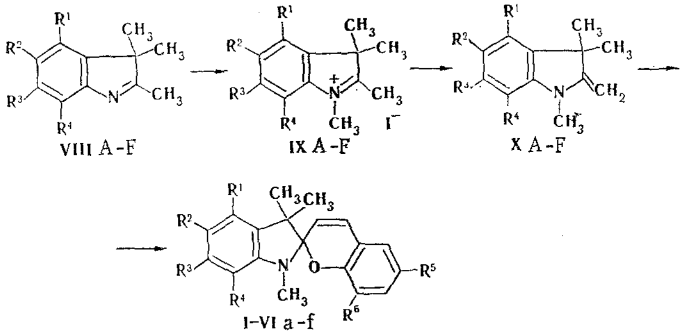
1,3,3-Trimethylspiro(indoline-2,2'-[2H]chromenes) with CH_3 and CH_3O groups in the 4-7 positions and NO_2 and CH_3O groups in the 6' and 8' positions were obtained by the reaction of 4,6-, 4,7-, 5,6-, and 6,7-dimethoxy- and 4-methyl-7-methoxy-2-methyleneindolines and 1,3,3,4,5,6,7-heptamethyl-2-methyleneindoline with 3- and 5-nitrosalicylaldehydes and their derivatives. Most of the compounds have photochromic properties. The introduction of electron-donor groups into the indoline fragment of the spirochromene molecules changes the rate of the dark reaction within the limits of one order of magnitude and has a small effect on the position of the long-wave absorption band of the photomerocyanine.

A large amount of research has been devoted to the study of the relationship between the structure of indolinospirochromenes and their photochromic properties [1]; however, the peculiarities of the effect of substituents from the 4-7 positions of the indoline part of the molecule have not been adequately revealed. In order to study the problem of the degree to which the introduction of electron-donor substituents into these positions can change the photochromic properties of the molecule we synthesized several series of indolinospirochromenes that contain methoxy and methyl groups in the 4-7 positions. Indolinospirochromenes (I-VI) were obtained by the reaction of substituted 1,3,3-trimethyl-2-methyleneindolines (X) with substituted salicylaldehydes.



I B $R^1=R^4=OCH_3$; II E $R^3=R^4=OCH_3$; III D $R^2=R^3=OCH_3$; IV A $R^1-R^3=OCH_3$; V C $R^1=CH_3$, $R^4=OCH_3$; VI F $R^1=R^2=R^3=R^4=CH_3$; I—VI a $R^5=NO_2$; b $R^5=NO_2$, $R^6=OCH_3$; c $R^5=NO_2$, $R^6=Br$; d $R^5=R^6=NO_2$; e $R^6=NO_2$, f $R^5=OCH_3$, $R^6=NO_2$. not indicated $R^i=H$

The methods for the synthesis of the indolenines VIII that are necessary for the preparation of substituted 2-methyleneindolines X differed depending of the position of the substituents. Thus for the preparation of 4,6-dimethoxy- (VIIIA), 4,7-dimethoxy- (VIIIB), and

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TABLE 1. Substituted 1,3,3-Trimethylspiro(indoline-2,2'-[2H]chromenes) (I-VI)

Compound	R^5	R^6	mp, °C	Found, %			Empirical formula^a	Calc., %			Yield, % (with respect to amine)
				C	H	N		C	H	N	
Ia	NO_2	H	180—182	65,4	5,9	7,2	$C_{21}H_{22}N_2O_5$	65,9	5,8	7,3	1,5
Ib	NO_2	OCH_3	212—214	64,4	6,1	6,9	$C_{22}H_{24}N_2O_6$	64,1	5,9	6,8	2,4
Ic	NO_2	Br	235—240	54,6	4,8	6,5	$C_{21}H_{21}N_2O_5$	54,7	4,6	6,1	3,0
Id	NO_2	NO_2	212—215	58,5	5,1	9,5	$C_{21}H_{21}N_3O_7$	59,0	5,0	9,8	1,5
IIa	NO_2	H	132^b	65,9	5,9	7,4	$C_{21}H_{22}N_2O_5$	65,9	5,8	7,3	29,3
IIb	NO_2	OCH_3	171—172^c	64,5	5,9	6,5	$C_{22}H_{24}N_2O_6$	64,1	5,9	6,8	14,0
IIc	NO_2	Br	163—164^b	54,4	4,9	6,5	$C_{21}H_{21}BrN_2O_5$	54,7	4.6	6,1	14,8
IId	NO_2	NO_2	174—176^d	58,4	4,7	10,3	$C_{21}H_{21}N_3O_7$	59,0	5,0	9,8	30,0
IIe	H	NO_2	120—121,5^e	66,3	5,9	7,3	$C_{21}H_{22}N_2O_5$	66,0	5,8	7,3	20,0
IIf	OCH_3	NO_2	132—133^b	64,5	6,0	7.0	$C_{22}H_{24}N_2O_6$	64,1	5,9	6,8	13,0
IIIa	NO_2	H	179—181^e	65,3	5,9	7,7	$C_{21}H_{22}N_2O_5$	66,0	5,8	7,3	13,0
IIIb	NO_2	OCH_3	255—257^b	63,7	5,9	6,7	$C_{22}H_{24}N_2O_6$	64,1	5,9	6,8	16,0
IIIc	NO_2	Br	272—273^f	54,3	4,5	5,8	$C_{21}H_{21}BrN_2O_5$	54,7	4,6	6.1	21,6
IIId	NO_2	NO_2	303—304^f	58,7	5,2	9,3	$C_{21}H_{21}N_3O_7$	59,0	5,0	9,8	22,3
IIIe	H	NO_2	263—265^c	65,7	5,9	7,5	$C_{21}H_{22}N_2O_5$	66,0	5,8	7,3	11,6
IIIf	OCH_3	NO_2	175—177^e	63,9	6,1	6,7	$C_{22}H_{24}N_2O_6$	64,1	5,9	6,8	15,4
IVa	NO_2	H	134—135^b	65,7	5,4	7,5	$C_{21}H_{22}N_2O_5$	66,0	5,8	7,3	12,8
IVb	NO_2	OCH_3	200—201^g	64,4	5,9	7,1	$C_{22}H_{24}N_2O_6$	64,1	5,9	6.8	11,5
IVc	NO_2	Br	199—200^b	54,3	4,6	6,2	$C_{21}H_{21}BrN_2O_5$	54,7	4,6	6,1	19,0
IVd	NO_2	NO_2	245—247^f	57,7	5,2	9,8	$C_{21}H_{21}N_3O_7 \cdot H_2O$	57,9	5,2	9,4	24,5
IVe	H	NO_2	132—134^h	65,8	5,9	7,7	$C_{21}H_{22}N_2O_5$	66,0	5.8	7,3	3,5
IVf	OCH_3	NO_2	191—192^g	64.0	5,9	6,9	$C_{22}H_{24}N_2O_6$	64,1	5,9	6,8	15,0
Va	NO_2	H	168	68,9	6,1	7.6	$C_{21}H_{22}N_2O_4$	68,8	6,1	7,7	3,6
Vb	NO_2	OCH_3	228—230	66,7	6,2	7,1	$C_{22}H_{24}N_2O_5$	66,6	6,1	7,1	5,2
Vc	NO_2	Br	285—286	56,7	5,0	6,1	$C_{21}H_{21}BrN_2O_5$	56,6	4,8	6,3	7,3
VIa	NO_2	H	212—215^i	73,0	7,1	7,4	$C_{23}H_{26}N_2O_3$	73,0	6,9	7.4	8,7
VIf	OCH_3	NO_2	140—145^i	70,8	7,2	6,9	$C_{24}H_{28}N_2O_4$	70,6	6,9	6,9	5,5

[a] In the case of Ic-Vc the compositions were also confirmed from the bromine content. [b] From ethanol. [c] From benzene. [d] From a mixture of acetone with ethanol. [e] From heptane. [f] From a mixture of acetone with water. [g] From a mixture of benzene with heptane (1:1). [h] From 2-propanol. [i] From hexane.

4-methyl-7-methoxy-2,3,3-trimethylindolenines (VIIIC) the corresponding amines (2,5- and 3,5-dimethoxy- and 2-methoxy-5-methylanilines) were diazotized, and the solutions of the diazonium salts were reduced with stannous chloride as in [2]. The isolated arylhydrazines were condensed with methyl isopropyl ketone to the corresponding hydrazones, which were subjected without isolation to cyclization by refluxing in glacial acetic acid. The indolenine was isolated, as described in [3], from the reaction mixture containing the indole and indolenine derivatives.

It is known [4] that o- and p-methoxyphenylhydrazines are unstable and are formed in low yields in the case of reduction of the diazonium salts with stannous chloride even at −15°C [5]. Compounds such as 2,3-dimethoxy-, 3,4-dimethoxy-, and 2,3,4,5-tetramethylphenylhydrazines were therefore obtained in the form of stable hydrazinesulfonates by reduction of the diazosulfonates with zinc in acetic acid [6]. The arylhydrazinesulfonates are converted to indolenines in one step by reaction with methyl isopropyl ketone in the presence of hydrogen chloride in absolute ethanol. This method was used to obtain 5,6-dimethoxy- (VIIID), 6,7-dimethoxy- (VIIIE), and 4,5,6,7-tetramethyl-2,3,3-trimethylindolenines (VIIIF). The indolenines were methylated, without purification, by means of methyl iodide. The resulting crystalline salts of substituted 1,2,3,3-tetramethylindoleninum iodide (IXA-F) were converted to the corresponding 1,3,3-trimethyl-2-methyleneindolines (XA-F) by the action of a solution of alkali.

Two pathways of Fischer cyclization to give 4,5-dimethoxy- or 5,6-dimethoxy-2,3,3-trimethylindolenine are possible in the case of methyl isopropyl ketone 3,4-dimethoxyphenylhydrazone. In conformity with [7], one might expect primarily the formation of 5,6-dimethoxy-2,3,3-trimethylindolenine (VIIID) and, after its methylation, 5,6-dimethoxy-1,2,3,3-tetramethylindoleninium iodide (IXD). The PMR spectrum of the indoleninium salt contains singlets of methyl groups in the 3 position (1.61 ppm), a methyl group in the 2 position (2.37 ppm), an N-methyl group (4.18 ppm), and methoxy groups (3.96 and 3.90 ppm). The aromatic protons give one-proton signals with δ 7.27 (4-H) and 7.54 ppm (7-H). The absence of splitting of these signals makes it possible to draw a conclusion in favor of 5,6-dimethoxy-1,2,3,3-tetramethylindoleninium iodide (IXD).

TABLE 2. Spectral-Kinetic Characteristics of the Photomerocyanines

Compound	$k_T \cdot 10^2$, sec^{-1} (20°C)		λ_{max}, nm	
	toluene	dioxane	toluene	ethanol
Ia	4,70	2,90	605 (607) [a]	536 (535)[a]
Ib	3,40	3,30	610 (630) [a]	565 (563)[a]
Ic	0,90	0,23	600	535
Id[b]	—	—	—	505 (558)[a]
IIa	4,71	3,76	595	540
IIb	1,80	1,70	615	565
IIc	2,76	1,00	595	532
IIe	5,31	5,00	615	558
IIIa	2,70	0,75	610	542
IIIb	8,66	4,81	616	565
IIIc	1,88	1,07	605	538
IIId[b]	—	—	—	515
IIIe[c]	—	—	—	560
IIIf[c]	—	—	—	605
IVa	6,50	3,70	590	540
IVb	2,80	1,80	610	563
IVc	2,20	1,10	595	536
IVd[b]	—	—	—	515
IVe	7,50	3,20	593	557
IVf	18,50	7,00	645	613
Va	5,30	1,07	592	525
Vb	6,80	3,00	610	552
Vc	0,53	0,14	590	522
VIa	3,90	2,20	600	520
VIf[c]	—	—	—	605
VIIa[d]	3,09	2,97	595	532
VIIb[d]	1,66	1,53	610	560
VIIc[d]	1,78	0,54	600	534
VIId[b]	—	—	—	515
VIIe	1,26	0,94	598	555
VIIf	55,0	—	640	615

[a] According to the data in [1]. [b] In view of the extremely low solubility, we were unable to observe photochromic properties upon irradiation with UV light.

[c] This compound does not display photochromic properties upon irradiation with UV light. [d] According to the data in [10].

Most of the spirochromenes obtained (Table 1) have photochromic properties. Colorless solutions in nonpolar or slightly polar solvents turn blue or blue-green upon irradiation with UV light as a consequence of conversion to the merocyanine form; they gradually become colorless when irradiation is discontinued. Alcohol solutions of the spirochromenes are red or red-violet due to partial conversion to the merocyanine form. The intensity of the color increases upon irradiation with UV light, whereas it decreases upon illumination with visible light. The solutions gradually return to their original state after irradiation is discontinued. The positions of the maxima of the long-wave absorption bands of the merocyanine forms and the rate constants (k_T) of the dark decolorization reaction of the photomerocyanines at 20°C for the compounds obtained and (for comparison) spirochromenes of the VII type ($R^1 = R^2 = R^3 = R^4 = H$) that do not contain substituents in the 4-7 positions of the indoline part are presented in Table 2.

The rate of the dark decolorization reaction for the compounds obtained changes only slightly when the substituents in both the indoline and pyran parts of the molecule are varied. The maximum differences in the rate constants generally do not exceed one order of magnitude. The character of the effect of the substituents differs in the different series, and no definite relationships between the rate of dark decolorization and the peculiarities of the electronic effects of the substituents can be established. The slight dependence of the rate of dark decolorization of the photomerocyanines on the character of the substituents in the 4-7 and 6' and 8' positions of the spiropyran molecule is evidently associated with the complex character of the effect of structural factors on the ease of trans-cis isomerization, which is the rate-determining step in the process, as we have previously noted in [8].

The effect of the substituents in the phenolate part of the photomerocyanine molecule on the position of the maximum of the long-wave absorption band is in complete agreement with the previously established principles [9]: a methoxy group gives rise to a bathochromic shift of the band (up to 20 nm in toluene and 25 nm in ethanol; spirochromenes IIb-Vb as compared, respectively, with spirochromenes IIa-VA), whereas a nitro group gives rise to a hypsochromic shift (up to 25 nm in ethanol; spirochromenes IIId and IVd as compared, respectively, with spirochromenes IIIa and IVa).

A distinct regularity is displayed in the effect of the substituents in the indoline part of the molecules on the spectral characteristics. Regular shifts of the spectral band are not observed when methoxy groups are introduced into the meta position relative to the nitrogen atom of the indoline part of the molecules (spirochromenes IV); at the same time the presence of a methoxy group in a position that is conjugated with the nitrogen atom (spirochromenes I-III) gives rise to a certain (up to 10-15 nm) bathochromic shift of the absorption band, which is evidently associated with the possibility of enlargement of the overall π system of the molecule due to the participation of the unshared electron pairs of the oxygen atom of the methoxy group [9]. In the case of replacement of a methoxy group in the 4 position by a methyl group, which has a positive inductive effect, in series of 4-methyl-7-methoxy-substituted compounds (spirochromenes V) one observes a hypsochromic shift of the long-wave absorption band as compared with series of both 4,7-dimethoxy-substituted compounds and unsubstituted compounds. The introduction of four methyl groups into the indoline ring (spirochromenes VI), in conformity with the indicated regularity, also leads to appreciably hypsochromic shifts. Thus the introduction of electron-donor substituents into the indoline fragment of the spirochromene molecules, while not having a substantial effect on the relative stabilities of the spiran and merocyanine forms, makes it possible, within certain limits, to shift the long-wave absorption band of the photomerocyanine; this may prove to be important in the solution of a number of applied problems.

EXPERIMENTAL

The measurements of the dark decolorization rate constants and the absorption spectra of the photomerocyanines by means of an automated spectral-kinetic apparatus were made as described in [11].

The course of the reactions and the purity of the compounds obtained were monitored by thin-layer chromatography (TLC) on plates of the Silufol UV-254 type in a benzene—ethyl acetate system (9:1) or in chloroform. The spots were developed by heating the plates.

Sodium 3,4-Dimethoxyphenylhydrazinesulfonate (XID). A 4-1-g (25 mmole) sample of 3,4-dimethoxyaniline was dissolved in 20 ml of water and 6 ml (66 mmole) of concentrated HCl, the solution was cooled to −1°C, and a solution of 1.75 g (25 mmole) of sodium nitrite in 10 ml of water was added with stirring in a stream of nitrogen in the course of 15 min, after which the mixture was stirred for 30 min. An 80-ml sample of a freshly prepared 20% solution (~130 mmole) of sodium sulfite was cooled to 0°C, the solution of 3,4-dimethoxybenzenediazonium chloride was added to it, and the mixture was cooled with ice water and stirred for 1.5 h. The red precipitate was separated and suspended in 20 ml of water and 4 ml of acetic acid, and 2 g (30.5 mmole) of zinc dust was added gradually to it. The precipitate dissolved as the reaction mixture heated up spontaneously, and white plates formed when the mixture was cooled. The mixture was allowed to stand overnight, after which the precipitate was removed by filtration, squeezed thoroughly to remove water, and washed successively with alcohol and ether to give 7.3 g of product. Recrystallization from 70% ethanol gave 3.8 g of XID (54% based on the amine), which decomposed above 240°C. Found: C 35.4; H 4.2%. $C_8H_{11}N_2NaSO_5$. Calculated: C 35.5; H 4.1%.

Sodium 2,3-Dimethoxyphenylhydrazinesulfonate (XIE). This compound was obtained in 87% yield (based on the amine) by a procedure similar to that used to prepare the preceding compound. It decomposed above 240°C. Found: C 35.3, H 4.1%. $C_8H_{11}N_2NaSO_5$. Calculated: C 35.5, H 4.1%.

Sodium 2,3,4,5-Tetramethylphenylhydrazinesulfonate (XIF). This compound was obtained in 57% yield and decomposed above 250°C. Found: C 44.9, H 5.8%. $C_{10}H_{15}N_2NaSO_5$. Calculated: C 45.1, H 5.7%.

5,6-Dimethoxy-1,2,3,3-tetramethylindoleninium Iodide (IXD). A 45-ml sample of an 18% solution of hydrogen chloride (220 mmole) in absolute alcohol and 6.6 g (77 mole) of methyl isopropyl ketone were added to 11.75 g (43 mmole) of pulverized hydrazinesulfonate XID, and the mixture was refluxed with stirring in a stream of nitrogen for 1.5 h, after which it was poured into 350 ml of cold water. The aqueous mixture was extracted six times with ether to remove the resulting indole. The aqueous solution was made alkaline to pH 9 with crystalline sodium carbonate while cooling with ice water, after which it was extracted six times with ether to remove the indolenine, and the extract was dried with sodium sulfate. The ether was removed by distillation to give 10.5 g of an oil, to which 15 ml of methyl iodide was added, and the mixture was refluxed for 30 min until a precipitate formed. Absolute ether (30 ml) was added to the mixture, and the precipitate was removed by filtration and washed thoroughly with ether to give 12.45 g (27% based on the amine) of product. Recrystallization from alcohol gave 7 g of iodide IXD with mp 203-205°C. Found: C 46.7, H 5.3, I 35.5%. $C_{14}H_{20}INO_2$. Calculated: C 46.5, H 5.6, I 35.2%. The PMR spectrum of a solution of IXD in $CDCl_3$ was recorded with a Varian CFT-20 high-resolution NMR spectrometer relative to tetramethylsilane as the internal standard.

4,6-Dimethoxy-1,2,3,3-tetramethylindoleninium Iodide (IXA). This compound was obtained in 35% yield (based on the amine) and had mp 230-232°C.

4,7-Dimethoxy-1,2,3,3-tetramethylindoleninium Iodide (IXB). This compound was obtained in 17% yield (based on the amine) and had mp 220-223 °C.

7-Methoxy-1,2,3,3,4-pentamethylindoleninium Iodide (IXC). This compound was obtained in 26% yield (based on the amine) and had mp 236-238°C.

6,7-Dimethoxy-1,2,3,3-tetramethylindoleninium Iodide (IXE). This compound was obtained in 32% yield (based on the amine) and had mp 174-176°C.

1,2,3,3,4,5,6,7-Octamethylindoleninium Iodide (IXF). This compound was obtained in 27% yield (based on the amine) and had mp 238-240°C.

Substituted 1,3,3-Trimethylspiro(indoline-2,2'-[2H]chromenes) (I-VI). A 5-g (13 mmole) sample of indoleninium iodide (IXA-F) was added to 75 ml of a 30% solution of sodium hydroxide, and the mixture was heated to 80°C with stirring. It was then cooled, and the resulting oil was extracted with ether. The extract was dried with magnesium sulfate for 2 h and evaporated. The residue [2.9 g (90% based on the methiodide)] was substituted 1,3,3-trimethyl-2-methyleneindoline (XA-F). An 8-mmole sample of the indoline (XA-F) dissolved in 15 ml of absolute ethanol was added to a hot solution of 8 mmole of the corresponding nitrosalicylaldehyde in 20 ml of absolute ethanol, and the mixture was refluxed from 30 min to 1 h. It was then cooled, and the precipitate was separated, washed with ethanol and ether, and recrystallized. This procedure was used to obtain I-VI (Table 1).

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