zene until the solid material became colorless and dissolved. The resulting benzene solution was filtered, and the filtrate was chromatographed with a column filled with Al_2O_3 (with benzene as the mobile phase). The fraction with R_f 0.9 was collected, and the benzene was removed by distillation at reduced pressure. Recyrstallization of the residue from isopropyl alcohol–benzene gave the spiropyrans in the form of colorless or slightly colored crystalline substances.

4,4,5,5-Tetramethylspiro(1,3-dioxolane-2,2'-[2H]benzo[f]chromene) (V). This compound was synthesized from 2,4,4,5,5-pentamethyl-1,3-dioxolanium perchlorate [8] and 2-hydroxynaphthaldehyde by a method similar to that used to obtain spiropyrans III. The product, with mp 98-99°C (from glacial acetic acid), was obtained in 56% yield. Found: C 77.2; H 6.6%. $C_{19}H_{20}O_3$. Calculated: C 77.0; H 6.7%.

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1-OCTADECYL- AND 3,3-DIPHENYL-SUBSTITUTED PHOTOCHROMIC INDOLINOSPIROCHROMENES

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A number of photochromic indolinospirochromenes that contain an octadecyl substituent in the 1 position were synthesized. The introduction of an octadecyl group in place of a methyl group increases the stability of the merocyanine form in solution but does not change its spectral characteristics. On the other hand, the introduction of phenyl groups in place of methyl groups in the 3 position does not change the stability of the merocyanine but gives rise to a bathochromic shift of the long-wave absorption band.

The modification of the structures of photochromic indolinospirochromenes through the introduction of substituents that increase the possibility of steric interactions in the molecule is of interest in the development of photochromic compositions with predesignated properties. The introduction of bulky substituents may lead both to an increase in the stability of the colored photomerocyanine form by hindering its isomerization to the cisoid isomer and subsequent cyclization to the colorless spirochromene and to a decrease in the efficiency of the photocoloration process by hindering cis-trans isomerization of the photomerocyanine [1].

It has been recently shown that the introduction of a hexadecyl substituent in the 1 position of the photochromic spirochromene increases the stability of the photomerocyanine form in solution [2]. We have confirmed this interesting principle in a new case. We ob-

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TABLE 1. Spectral Characteristics of the Merocyanine Forms of Spirochromenes I and II and Equilibrium Parameters at 20°C in Absolute Ethanol

Compound	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$, liter·mole^{-1}·cm^{-1}	$K \cdot 10^2$	ΔH, kcal/mole	ΔG, kcal/mole	ΔS, cal·mole^{-1}·deg^{-1}
Ia	537	3,4	1,7	1,0	2,4	−4,8
IIa*	532	3,4	0,83	2,2	2,8	−1,9
Ib	562	3,0	37,8	1,1	0,6	1,6
IIb	560	2,7	14,6	1,7	1,1	2,0
Ic	528	2,8	111	1,0	~0	3,4
IIc	530	2,8	39,5	1,3	0,5	2,6
Id	545	3,4	1,58	1,8	2,4	−2,1
IId	540†	3,4	0,83	3,1	2,8	1,2
Ie	550	2,6	10,7	3,6	1,3	−3,2
IIe	550	2,7	4,5	1,3	1,8	−1,7
If	510	3,1	—‡	—	—	—
IIf	515	3,2	88,2	1,6	~0	5,3

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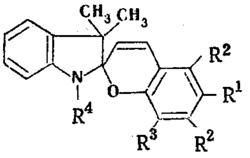
*For IIa it was found [3] that K = 0.84 ± 0.27 at 25°C, ΔH = 2.1 ± 0.4 kcal/mole, ΔG = 2.8 ± 0.2 kcal/mole, and ΔS = −2.4 ± 2.0 cal·mole^{-1}·deg^{-1}.

†According to the data in [1], 550 nm.

‡The equilibrium is shifted virtually completely to favor the merocyanine form.

tained 1-octadecyl-3,3-dimethyl-2-methyleneindoline by reaction of octadecyl iodide with 2,3,3-trimethylindolenine and subsequent treatment of the resulting 1-octadecyl-2,3,3-trimethylindoleninium iodide with alkali. Condensation of this compound with various nitrosalicylaldehydes led to the corresponding photochromic spirochromenes Ia-g.



I, II a-g

I $R^4=C_{18}H_{37}$; II $R^4=CH_3$; I—II a $R^1=NO_2$; b $R^1=NO_2$, $R^3=OCH_3$; c $R^1=NO_2$, $R^3=Br$; d $R^1=NO_2$, $R^3=CH_2CH=CH_2$; e $R^3=NO_2$; f $R^1=NO_2$, $R^2=OCH_3$; g $R^1=CH_3$, $R^3=NO_2$; unspecified R=H

The parameters of the equilibrium in absolute ethanol between the spiran and merocyanine forms of spirochromenes Ia-f and the corresponding methyl-substituted compounds (IIa-f) measured by the method in [3] are presented in Table 1. As in the case of N-hexadecyl-substituted compounds [2], the introduction of an octadecyl substituent in place of the methyl group attached to the nitrogen atom increases the stability of the merocyanine form appreciably, and the change in the equilibrium constant is in conformity with the change in the enthalpy partially compensated by an opposite change in the entropy factor. The spectral characteristics of the merocyanine forms of spirochromenes I are virtually the same as the characteristics of the N-methyl compounds (II); however, the rate constants for dark decolorization for all I except Ic, g in dioxane are appreciably lower than in the case of the corresponding spirochromenes II (see Table 2 and the characteristics of IIa-c, e, g given in [4-7]). It should be noted that the stability of the merocyanine form of nitro-substituted indolinospirochromenes increases when additional substituents are introduced in the pyran part of the molecule, regardless of their electronic effect; this is possibly a consequence of an additional increase in the solvation energy. A similar increase in solvation in an aqueous ethanol medium when other substituents are introduced in the aromatic ring has been previously observed in the case of benzoic acids [8].

A somewhat different pattern is observed when the methyl groups in the 3 position of the spirochromene molecule are replaced by bulky phenyl substituents. We synthesized photochromic spirochromenes IIIa, b, which contain two phenyl substituents in the 3 position, by reaction of 2-methyl-3,3-diphenylindoline with methyl iodide, subsequent treatment of the

TABLE 2. Kinetic and Spectral Characteristics of the Photochromic Transformations of Spiropyrans

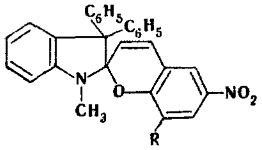
Compound	$k \cdot 10^2$, sec^{-1}, at 20°C		In toluene, λ, nm	
	toluene	dioxane	λ_{max}	center of band
Ia	1,21	1,41	600	587
Ib	0,84	0,61	610	604
Ic	1,28	0,95	590	584
Id	1,05	0,75	600	592
IId	1,90	1,84	600*	591
Ie	1,90	1,80	603	598
If	12,0	6,0	542	536
IIf	16,1	9,2	540	533
Ig	3,6	3,0	627	618
IIIa	3,95	1,03	608†	—
IIIb	2,09	0,83	596‡	—

*According to the data in [1], 600 nm.

†In alcohol this band is found at 580 nm.

‡In alcohol this band is found at 555 nm.

resulting 1,2-dimethyl-3,3-diphenylindoleninium iodide with alkali, which leads to 1-methyl-3,3-diphenyl-2-methyleneindoline, and condensation of the compound obtained with 5-nitro- or 3-methoxy-5-nitrosalicylaldehyde.



III a,b

a $R=OCH_3$; b $R=H$

The introduction of one phenyl group in place of the methyl group in the 3 position slows down the dark decolorization of the photomerocyanine somewhat [4, 6]; the introduction of a second phenyl substituent in some cases gives rise to the opposite effect (Table 2). The spectral characteristics of the photomerocyanines change considerably more regularly. The successive replacement of methyl substituents by phenyl groups in the 3 position gives rise to a bathochromic (up to 15 nm in alcohol) shift of the long-wave absorption band (compare the data in Table 2 and in [4, 10]). This bathochromic shift may evidently constitute evidence for the existence of steric effects that tend to disrupt the coplanarity of the chromophore chain of the photomerocyanine due to rotation relative to the bond with increased order [11]. Let us note that in the structure of the most stable isomer of the merocyanine form of the indolinospirochromenes the hydrogen atom in the 3' position and the substituent in the 3 position are drawn together in space [12], and an examination of Stuart–Briegleb models for the corresponding structures makes it possible to detect a substantial increase in the steric hindrance in the case of successive replacement of the methyl groups by phenyl groups in this fragment of the molecule.

Thus replacement of the methyl groups in the indoline part of the spirochromene molecule by bulkier substituents may, as a consequence of an increase in the steric interactions, lead either to a change in the coplanarity of the merocyanine form, which is manifested in a change in its spectral characteristics, or to an increase in its stability as a consequence of hindrance to trans-cis isomerization.

EXPERIMENTAL

The constants of the equilibrium between the spiran and merocyanine forms of spirochromenes in absolute ethanol at 20-60°C were measured by the method in [3]. The measurement of the kinetics of the dark decolorization reaction and the subsequent statistical treatment of the results were accomplished as described in [13]. The measurement of the absorption spectra of solutions of the spirochromenes in the photochemical steady state and the approximation of the results by means of Gaussian curves with a computer were realized by the methods in [14].

TABLE 3. Spirochromenes I and III

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
Ia	75—78	77,3	9,5	4,6	$C_{36}H_{52}N_2O_3$	77,1	9,3	5,0	31
Ib	56—58	75,5	9,1	4,8	$C_{37}H_{54}N_2O_4$	75,2	9,2	4,7	17
Ic	105—107	67,6	8,5	4,5	$C_{35}H_{51}BrN_2O_3$	67,6	8,0	4,4	64
Id	62—65	78,0	9,4	4,6	$C_{39}H_{56}N_2O_3$	78,0	9,4	4,7	10
Ie	62—65	76,6	9,3	4,8	$C_{36}H_{52}N_2O_3$	77,1	9,3	5,0	87
If	92—94	73,9	9,4	4,2	$C_{38}H_{56}N_2O_5$	73,5	9,1	4,5	25
Ig	67—68	76,9	9,5	5,0	$C_{37}H_{54}N_2O_3$	77,3	9,5	4,9	31
IIIa	230—233	75,8	5,3	5,6	$C_{30}H_{24}N_2O_4$	75,6	5,1	5,9	88
IIIb	215	78,4	5,0	6,0	$C_{29}H_{22}N_2O_3$	78,0	5,0	6,3	83

Spirochromenes Ia-g (Table 3). A 4.4-g (28 mmole) sample of 2,3,3-trimethylindolenine [15] was added to a solution of 15 g (39 mmole) of octadecyl iodide in 50 ml of chloroform, and the mixture was refluxed for 20 h. The solvent was removed by distillation, and the residue was triturated with 50 ml of absolute ether and dried to give 9.3 g (61%) of 1-octadecyl-2,3,3-trimethylindoleninium iodide with mp 85-88°C. The iodide obtained was suspended without further purification in 70 ml of water, 55 ml of a concentrated potassium hydroxide solution was added, and the mixture was stirred at 50°C for 40 min. It was then cooled and extracted with ether. The extract was dried over potassium hydroxide and evaporated to give 5.55 g (79%) of 1-octadecyl-3,3-dimethyl-2-methyleneindoline in the form of an oil. This oil was used without further purification for the preparation of the spirochromene. A 0.35-g (0.85 mmole) sample of 1-octadecyl-3,3-dimethyl-2-methyleneindoline was added to a solution of 0.9 mmole of the corresponding salicylaldehyde in 10 ml of absolute alcohol, and the mixture was refluxed for 6 h. The precipitate was separated and crystallized three times from absolute alcohol.

1-Methyl-3,3-diphenyl-6'-nitroindoline-2-spiro-2'-[2H]chromenes (IIIa, b). A mixture of 1.41 g (5 mmole) of 2-methyl-3,3-diphenylindolenine [8] and 10 ml (162 mmole) of methyl iodide was refluxed for 10 h, after which it was evaporated, and the residue was crystallized from aqueous methanol to give 1.82 g (85%) of 1,2-dimethyl-3,3-diphenylindoleninium iodide with mp 230°C. The iodide obtained was heated without further purification with 10 ml of a 10% solution of sodium hydroxide, and the mixture was cooled and extracted with ether. The extract was dried with potassium hydroxide and evaporated to give 0.9 g (70%) of 1-methyl-3,3-diphenyl-2-methyleneindoline in the form of light-yellow crystals with mp 101°C. The latter was used in the synthesis of the spirochromenes without further purification. A 0.5-g (1.6 mmole) sample of 1-methyl-3,3-diphenyl-2-methyleneindoline was added to a solution of 1.8 mmole of 3-methoxy-5-nitro- or 5-nitrosalicylaldehyde in 10 ml of ethanol, and the mixture was refluxed for 2 h. The precipitate was separated and crystallized from a mixture of chloroform with heptane (1:2).

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