SYNTHESIS AND PROPERTIES OF PHOTOCHROMIC BISINDOLINOSPIROPYRANS*

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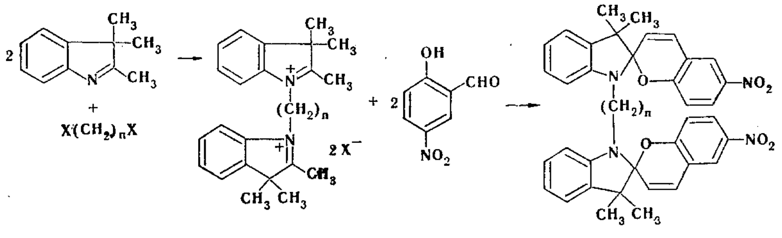
Bisspiropyrans were obtained by reaction of diquaternary salts – 1,1'-polymethylenebis-(2,3,3-trimethylindoleninium) halides – or the corresponding methylene bases with 5-nitrosalicylaldehyde in the presence of piperidine. Bisspiropyrans of another type were obtained by reaction of 1-propyl-2,3,3-trimethylindoleninium iodide with 5,5'-methylenedisalicylaldehyde and 5,5'-methylenedi(3-nitrosalicylaldehyde). The photochemical and spectral properties of the bisspiropyrans were compared with those of the corresponding monospiropyrans.

Photochromic spiropyrans are presently the most investigated class of photochromic materials (for example, see [2]). The literature contains a large number of studies devoted to monospiropyrans, but there is practically no information regarding bisspiropyrans. The latter were described only in a few patents [3-6], whereas they seem of interest as model compounds for the investigation of methods of synthesis and properties of photochromic polymers that contain spiropyran groupings. In the case of bisspiropyrans in which the spiropyran groupings are bonded together by a chain of methylene groups, it becomes possible to study the mutual effect of closely situated photochromic groups on their photochromic properties as a function of the manner of connection of the photochromic fragments and the length of the polymethylene chain.

Bisspiropyrans I-III were obtained by reaction of diquaternary salts – 1,1'-polymethylenebis(2,3,3-trimethylindoleninium halides) (IV-VI) – or the corresponding methylene bases with 5-nitrosalicylaldehyde in the presence of piperidine. Salts IV-VI were synthesized by reaction of α,ω-dihaloalkanes with 2,3,3-trimethylindolenine.



IV–VI

I–III

X = Br, I; I, IV n = 2; II, V n = 4; III, VI n = 6

Monoquaternary salts – 1-(ω-iodoalkyl)-2,3,3-trimethylindoleninium iodides – are also formed in the synthesis of the diquaternary salts (V, VI). Their percentage in the reaction mixture increases as the reaction temperature is lowered and the amount of excess indolenine is decreased. At 85°C in the presence of excess diiodoalkanes primarily iodoalkylindoleninium iodides are formed. The latter react with 5-nitrosalicylaldehyde to give monospiropyrans (VII, VIII).

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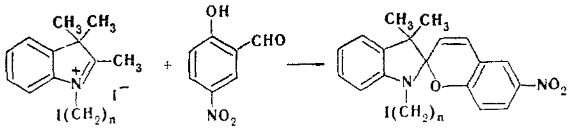
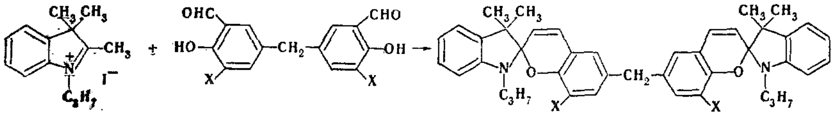


VII n=4; VIII n=6

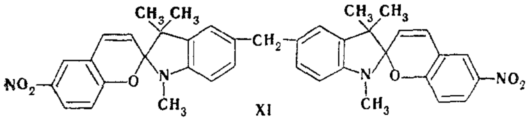
Bisspiropyrans I-III are readily separated from the monospiropyrans by recrystallization. However, we were unable to separate monospiropyrans VII and VIII from traces of bisspiropyrans by recrystallization as indicated in [7] for VII. Pure monospiropyrans VII and VIII were obtained by preparative thin-layer chromatography (TLC).

We also synthesized bisspiropyrans in which the spiropyran units are connected to the methylene group situated between the benzene rings of the benzopyran (IX, X) or indoline (XI) portion of the molecule.



IX X=H; X X=NO_2

Bisspiropyran XI was synthesized in accordance with patent data [6] by reaction of 5,5'-methylenebis(1,2,3,3-tetramethylindoleninium iodide) with 5-nitrosalicylaldehyde.



XI

The photochromic properties of bisspiropyrans I-III, IX-XI, and 1,3,3-trimethyl-6'-nitro- and 1,3,3-trimethyl-8'-nitrospiro(indoline-2,2'-[2H-1]benzopyrans) (XII and XIII) were studied at room temperature in toluene and alcohol. Except for IX, toluene solutions of the compounds listed above are blue when irradiated with UV light (303-313 nm) and gradually become colorless when the light source is switched off. The photocoloration of the spiropyran solutions is due to photodissociation of the C—O bond of the spiropyran ring (of starting form **A**) and the formation of a dipolar merocyanine structure (form **B**) [8]. Typical absorption spectra of solutions of spiropyrans III, X, and XII in toluene and alcohol before and after irradiation with UV light are presented in Figs. 1 and 2. The other investigated spiropyrans have similar absorption spectra.

At room temperature, form **B** is thermodynamically unstable and is gradually converted to starting form **A** via a dark route. The **B** ⇢ **A** conversion is also possible by the action of light absorbed by form **B**. Thus, the simplest kinetic scheme for the photochromic cycle for spiropyran solutions can be represented in the following form:

$$\mathbf{A} \underset{h\nu,\, kT}{\overset{h\nu}{\rightleftarrows}} \mathbf{B}.$$

A similar examination of the kinetic equations flowing out of this scheme was previously accomplished in [9]. The overall rate of the process in conformity with this scheme can be represented as a differential equation (1):

$$\frac{d\mathrm{B}}{dt} = \Phi_\mathrm{B} I_0 \varepsilon'_\mathrm{A} l' (\mathrm{A}_0 - \mathrm{B}) f(D') - \Phi_\mathrm{A} I_0 \varepsilon'_\mathrm{B} l' \mathrm{B} f(D') - k\mathrm{B}, \tag{1}$$

in which the first two terms in the right-hand portion of the equation describe the rates of photocoloration ($\mathbf{A} \xrightarrow{h\nu} \mathbf{B}$) and photodecolorization ($\mathbf{B} \xrightarrow{h\nu} \mathbf{A}$), while the last term describes the rate of dark decolorization ($\mathbf{B} \xrightarrow{kT} \mathbf{A}$). In Eq. (1), Φ_B is the quantum yield of photocoloration, Φ_A is the quantum yield of photodecolorization of the solutions (in moles per einstein), ε'_A and ε'_B are the extinction coefficients of forms **A** and **B** at the wavelength of the activating light (in liters per mole per centimeter), l' is the cuvette thickness in the direction of the activating light (in centimeters), A_0 is the starting concentration of form **A**, B is the concentration of form **B** (in moles per liter), I_0 is the intensity of the activating light (in einsteins

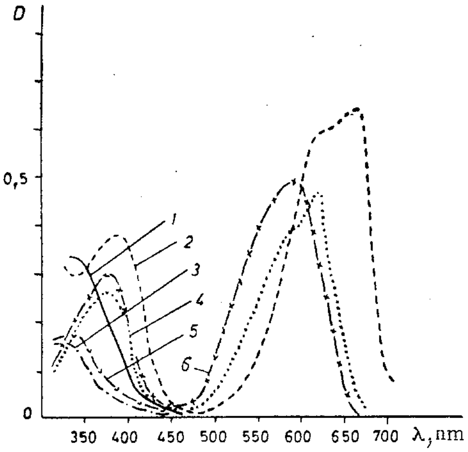


Fig. 1. Absorption spectra of mono- and bisspiropyrans in toluene (l 0.2 cm) before irradiation (1, 3, and 5) and after irradiation (2, 4, and 6) of the solutions with UV light (λ 303-313 nm): 1 and 2) X, c $2.0 \cdot 10^{-5}$ M, 235°K; 3 and 4) XII, c $2.5 \cdot 10^{-5}$ M, 243°K; 5 and 6) III c $1 \cdot 10^{-5}$ M, 253°K.

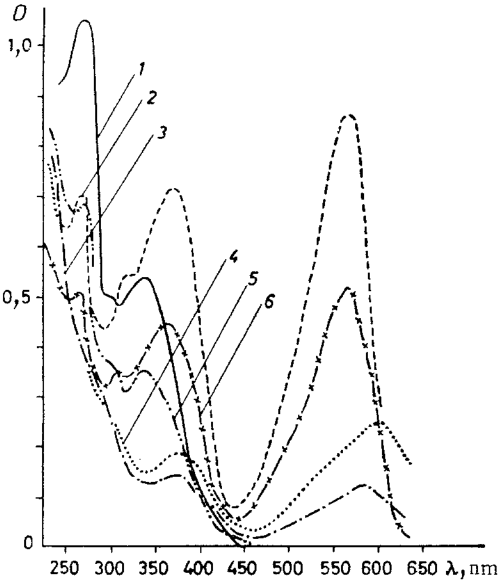


Fig. 2. Absorption spectra of mono- and bisspiropyrans in alcohol (l 1 cm, 296°K) before irradiation (1, 3, and 5) and after irradiation (2, 4, and 6) with UV light: 1 and 2) X, c $5.9 \cdot 10^{-5}$ M; 3 and 4) XII, c $2.5 \cdot 10^{-5}$ M; 5 and 6) III, c $2.4 \cdot 10^{-5}$ M.

per liter per second), k is the rate constant for dark decolorization of the colored solutions (in liters per mole per second), D' is the optical density of the solution in the range of the activating light, and $f(D') = (1-10^{-D'})/D =$ const, if D' = const.

In special cases, Eq. (1) takes on the form of Eqs. (2) and (3):

$$dB/dt = -kB \text{ when } I_0 = 0, \tag{2}$$

$$dB/dt = 0 \text{ (for the photosteady state).} \tag{3}$$

By multiplying each of Eqs. (1)-(3) by $\varepsilon_B l$, where ε_B is the extinction coefficient of form **B** at the wavelength of the scanning light (600 nm in toluene and 540 nm in alcohol) and l is the length of the cuvette in the direction of scanning, we obtain

$$\frac{dD_B}{dt} = a - bD_B, \ D_B = 0 \text{ when } t = 0, \tag{4}$$

where $a = \Phi_B \varepsilon_B I_0 D'_0 l f(D')$; $b = \Phi_B \varepsilon'_A l' I_0 f(D') + \Phi_A \varepsilon'_B l' I_0 f(D') + k$,

$$\frac{dD_B}{dt} = -kD_B, \ D_B = D_0 \text{ when } t = 0, \tag{5}$$

$$\frac{dD_B}{dt} = 0. \tag{6}$$

Using Eq. (4) and the condition of photosteady-state character (6), we find

$$\frac{dD_B}{dt} = b(D_{st} - D_B), \ D_B = 0 \text{ when } t = 0, \tag{7}$$

where D_{st} is the optical density of the system in the steady state. By solving Eq. (7) and determining the integration constant from the condition $D_B = 0$ when $t = 0$, we obtain

$$\lg(1 - D_B/D_{st})^{-1} = 0.43bt. \tag{8}$$

By solving (6), we find that

$$\lg(D_0/D_B) = 0.43kt. \tag{9}$$

It should be noted that a and b in Eq. (4) remain constant only if $f(D')$ is held constant during the entire time of irradiation of the photochromic system. This was achieved by the fact that the irradiation of the samples was carried out in the vicinity of the isosbestic point. In this case, $D' \leq 0.1$; this insured uniformity of the light absorption in the volume of the sample.

Typical kinetic dependences for solutions of some mono- and bisspiropyrans in toluene and alcohol are shown in Figs. 3 and 4. In conformity with Eqs. (8) and (9), straight lines are obtained in coordinates of log $(1-D_0/D_{st})^{-1}$ and t and log (D_0/D_B) and t; from the slopes of these lines we find constants b and k. Considering that $a = bD_{st}$, we calculate a from the found b and D_{st} values. A knowledge of the a, b, and k constants provides a possibility for finding $\Phi_B \varepsilon_B$ and $\Phi_B + \varkappa \Phi_A$ $(\varkappa = \varepsilon'_B/\varepsilon'_A)$. For toluene solutions of bisspiropyrans, $\varkappa \simeq 1.0$, while $\varkappa = 2$ for alcohol solutions (according to the data in [10]). The $\Phi_B \varepsilon_B$ and $\Phi_B + \varkappa \Phi_A$ values, as well as the ε'_A and ε'_B values, pertain to one spiropyran group of the bisspiropyran molecule.

A decrease in the temperature of toluene solutions of monospiropyran XII will lead to a sharp decrease in the efficiency of both the dark and photochemical processes of decolorization of colored spiro-

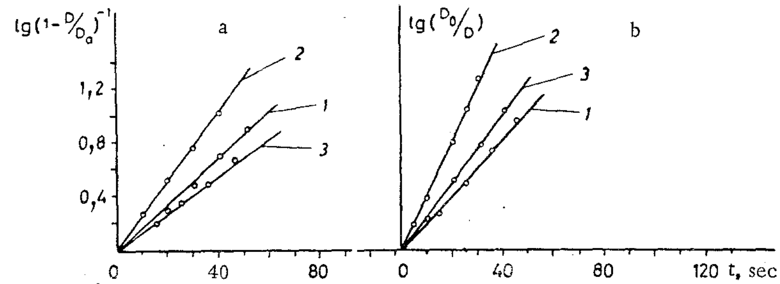


Fig. 3. Kinetics of the photochromic transformations of mono- and bisspiropyrans in toluene (l' 0.5 cm, l 3 cm, λ 303-313 nm, 23°C): a) colored solutions: linear anamorphoses of the kinetic curves in coordinates of $\log(1-D_B/D_{st})^{-1}$ and t; b) dark decolorization of the solutions: linear anamorphoses of the kinetic curves in coordinates of $\log D_0/D_B$ and t; 1) III; 2) XII; 3) X.

TABLE 1. Quantum Yields of Photocoloration (Φ_B) and Photodecolorization (Φ_A)* and Rate Constants for the Dark Decolorization (k) of Mono- and Bisspiropyrans in Toluene and Alcohol at 23°C

Compound	Toluene			Alcohol		
	Φ_B	Φ_A	k	Φ_B	Φ_A	k
I	0,5	0,6	$2\cdot10^{-2}$	—	—	—
II	0,3	0,8	$2\cdot10^{-2}$	0,05	0,06	10^{-4}
III	0.6	0,4	$2\cdot10^{-2}$	0,03	0.07	10^{-4}
XII	0,7	0,3	$4\cdot10^{-2}$	0,08	0,07	10^{-4}
XIII	0,1	1,0	$6\cdot10^{-2}$	—	—	—
X	0,04	0,25	$3\cdot10^{-2}$	—	—	—
XI	0,3	1,0	$4\cdot10^{-2}$	0,06	0,07	10^{-4}

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* The error in the measurement of Φ_B was ± 20%, while that in the measurement of Φ_A was ± 40%.

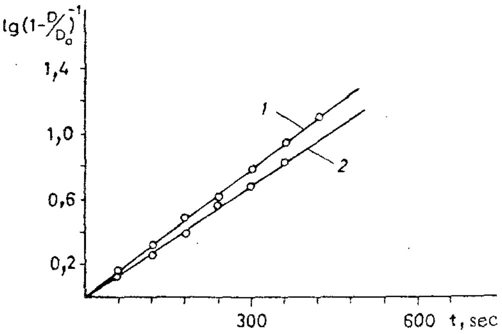
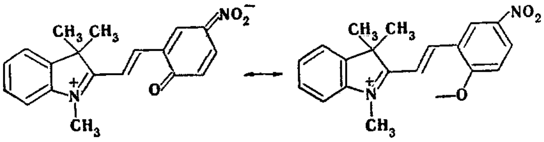


Fig. 4. Kinetics of the photocoloration of mono- and bisspiropyrans in alcohol (l' 0.5 cm, l 3 cm, λ 303-313 nm, 23°C). Linear anamorphoses of the kinetic curves in coordinates of $\log(1-D_B/D_{st})^{-1}$ and t: 1) XII; 2) III.

pyran solutions, i.e., it will lead to a sharp decrease in the Φ_A and k values, while Φ_B changes only slightly. The result of this is the fact that the rate of decolorization can be disregarded as compared with the rate of coloration. Irradiation of spiropyran XII at −30° with 303-313-nm light will therefore lead to intense coloration of solutions of the photochrome. When the steady state was reached, the system was again irradiated with 365-nm light. In this case, the optical density of the solution in the region of the absorption maximum of form **B** did not change. This fact attests to practically complete $\mathbf{A} \dashrightarrow \mathbf{B}$ conversion. This circumstance can be used for the determination of ε_B of the spiropyran photochrome in toluene. In fact, under the condition of complete conversion of the starting form to the colored form, $\varepsilon_B = D_{st}/A_0 l$ and ε_B (toluene) $\simeq 5.5 \cdot 10^4$ liter/mole · cm. According to the data in [10], ε_B (alcohol) $\simeq 3.54 \cdot 10^4$ liter/mole · cm. It should be noted that the direction determination of ε_B for bisspiropyrans is difficult because of the low solubility of the colored forms in toluene: irradiation of cooled solutions of the bisspiropyrans will lead to the formation of a colored precipitate. If it is assumed that ε_B does not change on passing from mono- to bisspiropyrans (the absorption spectra of the **B** forms of the mono- and bisspiropyrans are similar to one another, Figs. 1 and 2), this provides a possibility for the approximate evaluation of Φ_B and Φ_A for the bisspiropyrans. These estimates are presented in Table 1. Considering the errors in the measurements, one can conclude that Φ_A and Φ_B change little on passing from mono- to bisspiropyrans (I and III). In the case of bisspiropyran II, an unexpected decrease in Φ_B is observed. This fact as yet remains unclear. All of the investigated spiropyrans, except for IX, contain an NO_2 group in the benzopyran portion of the molecule, which is known [8] to slow down the dark decolorization of spiropyrans. This can be explained by stabilization of merocyanine form B owing to a decrease in the negative charge on oxygen.



It is apparent from a comparison of the absorption spectra of the bisspiropyrans in alcohol and toluene that the long-wave absorption band of form B in alcohol is shifted to the short-wave region as compared with the analogous band in toluene, i.e., the colored forms of the investigated compounds have negative solvatochromism. Similar examples of negative solvatochromism were described in [11].

The data obtained provide evidence that the photochemical and spectral properties of the investigated bisspiropyrans differ little from the properties of the corresponding monospiropyrans. However, it is important to note that an appreciable decrease in Φ_B (by a factor of ~ 2-2.5) as compared with the corresponding monospiropyrans is observed for maximum drawing together of the spiropyran fragments (bisspiropyrans X and XI), i.e., the photosensitivity of the photochromic system in this case decreases appreciably as compared with the photosensitivity of the photochromic system based on monospiropyrans.

EXPERIMENTAL

5,5'-Methylenedisalicylaldehyde. This compound was synthesized by E. G. Rukhadze and co-workers and kindly given to us. It melted at 142-143° [12].

5,5'-Methylenebis(3-nitrosalicylaldehyde). A 1.2-ml (18 mmole) sample of nitric acid (d 1.49) was added by drops at 0° in the course of 10 min to a suspension of 1.28 g (5 mmole) of 5,5'-methylenedisalicylaldehyde in 35 ml of acetic acid–tetrahydrofuran (6 : 1), and the mixture was heated at 35° until the solid had dissolved completely. It was then cooled to 20° and stirred for another 30 min at this temperature. After 2 h, the dinitro derivative was separated, washed with glacial acetic acid, and recrystallized from 40 ml of dioxane to give 0.83 g (48%) of a product with mp 229.5-230.5° (yellow crystals). Found: C 52.0; H 3.0; N 8.0%. $C_{15}H_{10}N_2O_8$. Calculated: C 52.0; H 2.9; N 8.1%.

5,5''-Methylenebis(1,3,3-trimethyl-6'-nitrospiro[indoline-2,2'-(2H-1)benzopyran]) (XI). This compound, with mp 125° (dec.) (mp 120-122° [6]), was obtained from 5,5'-methylenebis(1,2,3,3-tetramethylindoleninium iodide) and 5-nitrosalicylaldehyde by the method in [6]. Found: N 14.9%. $C_{39}H_{36}N_4O_6$. Calculated: N 14.9%.

1,1''-Ethylenebis(3,3-dimethyl-6'-nitrospiro[indoline-2,2'-(2H-1)benzopyran]) (I). A mixture of 19.08 g (0.12 mole) of 2,3,3-trimethylindolenine and 3.76 g (0.02 mole) of dibromoethane was heated at 135-140° for 22 h. The resulting 1,1'-ethylenebis(2,3,3-trimethylindoleninium bromide) (IV) was dissolved in 100 ml of water containing activated charcoal, and the solution was evaporated to dryness in vacuo to give 3.53 g (34.8%) of IV. A mixture of 2.53 g (5 mmole) of IV, 1.67 g (10 mmole) of 5-nitrosalicylaldehyde, and 2 ml (20 mmole) of piperidine was refluxed for 20 min in 20 ml of methanol. The resulting precipitate was separated and refluxed with alcohol–benzene (3 : 2) to give 2.38 g (74.1%) of I as a green powder without a definite melting point. Found: C 71.0; H 5.5; N 8.6%. $C_{38}H_{34}N_4O_6$. Calculated: C 71.0; H 5.6; N 8.7%.

1,1'-Tetramethylenebis(2,3,3-trimethylindoleninium iodide) (V). A mixture of 19.08 g (0.12 mole) of 2,3,3-trimethylindolenine and 9.3 g (0.03 mole) of 1,4-diiodobutane was heated at 140° for 24 h. The resulting V was separated, washed with acetone and ether, and crystallized from water to give 14.58 g (77.5%) of V with mp 265° (dec.). Found: C 48.6; H 6.2; N 4.2%. $C_{26}H_{34}I_2N_2$. Calculated: C 49.7; H 5.4; N 4.5%.

1,1'-Tetramethylenebis(2-methylene-3,3-dimethylindoline). A 5.66-g sample of V was dissolved in 700 ml of water, and the solution was refluxed with activated charcoal and neutralized to pH 7 with sodium bicarbonate. The rose-colored oil was extracted with ether, and the extract was dried over anhydrous sodium sulfate. The solvent was evaporated to give 2.57 g (77%) of the free base as rose-colored crystals with mp 101-102.5° (from hexane). Found: C 83.8; H 8.6; N 7.4%. $C_{26}H_{32}N_2$. Calculated: C 83.8; H 8.7; N 7.5%.

1,1''-Tetramethylenebis(3,3-dimethyl-6'-nitrospiro[indoline-2,2'-(2H-1)benzopyran]) (II). A mixture of 3.14 g (5 mmole) of V, 1.67 g (10 mmole) of 5-nitrosalicylaldehyde, and 1 ml (10 mmole) of piperidine in 20 ml of methanol was refluxed for 30 min. The precipitate was removed by filtration, washed with benzene, and refluxed with methanol to give 3.20 g (96%) of II with mp 195-197° (dec.) as green crystals. Found: C 71.6; H 5.7; N 8.4%. $C_{40}H_{38}N_4O_6$. Calculated: C 71.6; H 5.7; N 8.4%.

1-(ω-Iodotetramethylene)-2,3,3-trimethylindoleninium Iodide. A mixture of 13.99 g (0.088 mole) of 2,3,3-trimethylindolenine and 110 g (0.355 mole) of 1,4-diiodobutane was heated at 85° for 20 h in 90 ml of absolute benzene. The quaternary salt was separated and washed successively with acetone and ether to give 29.80 g (72.2%) of product. A sample for analysis was recrystallized twice from water to give white needles with mp 168-169°. Found: C 38.5; H 4.5; I 54.3%. $C_{15}H_{21}I_2N$. Calculated: C 38.4; H 4.5; I 54.1%.

1-(ω-Iodotetramethylene)-3,3-dimethyl-6'-nitrospiro[indoline-2,2'-(2H-1)benzopyran] (VII). A mixture of 4.69 g (10 mmole) of unpurified 1-(ω-iodotetramethylene)-3,3-dimethylindoleninium iodide, 1.67 g (10 mmole) of 5-nitrosalicylaldehyde, and 1 ml (10 mmole) of piperidine in 20 ml of absolute methanol was refluxed for 20 min and evaporated to half its original volume. The resulting precipitate was separated, extracted with boiling toluene–hexane (1 : 1), and recrystallized from alcohol–benzene (9 : 1) to give 3.57 g of a mixture of VII and II. A 0.5-g sample of this mixture was separated by preparative thin-layer chromatography (TLC) on hydrated silicic acid (25 g, 220-by-260-mm plate) in a benzene–hexane system (1 : 1) with elution with methanol to give 0.32 g of VII and 0.14 g of II. The overall yield of yellow crystals [from alcohol–benzene (9 : 1)] of VII, with mp 114-115° (mp 110° [7]) and R_f 0.54, was 2.28 g (46.5%). The overall yield of II, with mp 195-197° (dec.) and R_f 0.22, was 0.96°. Found for VII: N 5.6%. $C_{22}H_{23}IN_2O_3$. Calculated N 5.7%.

1,1'-Hexamethylenebis(2,3,3-trimethylindoleninium iodide) (VI). The method used to prepare V was used to obtain VI from 3.38 g (0.01 mole) of 1,6-diiodohexane and 4.77 g (0.03 mole) of 2,3,3-trimethylindolenine. The product was crystallized from alcohol–benzene (1 : 4) to give 5.06 g (77%) of yellow needles with mp 220-221°. Found: C 51.2; H 5.9; I 38.6; N 4.1%. $C_{28}H_{38}I_2N_2$. Calculated: C 51.2; H 5.8; I 38.7; N 4.3%. 1,1'-Hexamethylenebis(2-methylene-3,3-dimethylindoline) was isolated as described for the 1,1'-tetramethylene derivative as a red liquid, which was used without further purification.

1,1''-Hexamethylenebis(3,3-dimethyl-6'-nitrospiro[indoline-2,2'-(2H-1)benzopyran]) (III). A mixture of 3.01 g (7.5 mmole) of 1,1'-hexamethylenebis(2-methylene-3,3-dimethylindoline) and 2.50 g (15 mmole) of 5-nitrosalicylaldehyde was refluxed for 5 h in 38 ml of absolute methanol. The precipitate was separated and refluxed with alcohol to give 4.30 g (82%) of blue crystals with mp 180.2-181.2° (from benzene). Found: C 72.1; H 6.0; N 7.5%. $C_{42}H_{42}N_4O_6$. Calculated: C 72.2; H 6.1; N 8.0%.

1-(ω-Iodohexamethylene)-2,3,3-trimethylindoleninium Iodide. A mixture of 3.18 g (0.02 mole) of 2,3,3-trimethylindolenine and 20.28 g (0.06 mole) of 1,6-diiodohexane was heated at 85° for 24 h in 18 ml of absolute benzene. The resulting dark-brown oil was separated and dissolved in 200 ml of hot water. The solution was refluxed with activated charcoal, cooled, and filtered to give 4.25 g (44.5%) of quaternary salt. A sample for analysis was recrystallized from alcohol–ether (1 : 1) to give yellow needles with mp 128.6-129.6°. Found: C 41.2; H 5.0; I 51.0; N 2.8%. $C_{17}H_{25}I_2N$. Calculated: C 41.1; H 5.1; I 51.0; N 2.8%.

1-(ω-Iodohexamethylene)-3,3-dimethyl-6'-nitrospiro[indoline-2,2'-(2H-1)benzopyran] (VIII). A mixture of 3.65 g (7.3 mmole) of unpurified iodide, 1.22 g (7.3 mmole) of 5-nitrosalicylaldehyde, and 0.9 ml (9 mmole) of piperidine was refluxed for 10 min in 15 ml of absolute methanol. The solvent was removed by vacuum distillation, and the residue was recrystallized from alcohol–benzene (9 : 1) to give 2.36 g of a mixture of VIII and III. A 0.5-g sample of the mixture was separated by preparative TLC as described in the preparation of VII to give 0.41 g of VIII and 0.05 g of III. The overall yield of yellow needles of VIII, with mp 140.8-142° (from benzene) and R_f 0.80, was 1.81 g, while the overall yield of III, with mp 180.2-181.2° and R_f 0.40, was 0.21 g. Found for VIII: C 56.0; H 5.3; I 24.5; N 5.1%. $C_{24}H_{27}IN_2O_3$. Calculated: C 55.6; H 5.2; I 24.3; N 5.4%.

6',6'''-Methylenebis(1-propyl-3,3-dimethylspiro[indoline-2,2'-(2H-1)benzopyran]) (IX). A mixture of 1.65 g (5 mmole) of 1-propyl-2,3,3-trimethylindoleninium iodide [13], 0.64 g (2.5 mmole) of 5,5'-methylenedisalicylaldehyde, and 0.43 ml (43 mmole) of piperidine was refluxed for 5 h in 30 ml of methanol. Compound IX was separated and recrystallized from alcohol–benzene (1 : 1) to give 1.05 g (67.7%) of white crystals with mp 137.5-138.5°. Found: C 82.5; H 7.8; N 5.2%. $C_{43}H_{46}N_2O_2$. Calculated: C 82.9; H 7.4; N 4.5%.

6',6'''-Methylenebis(1-propyl-3,3-dimethyl-8'-nitrospiro[indoline-2,2'-(2H-1)benzopyran]) (X). A mixture of 1.55 g (4.7 mmole) of 1-propyl-2,3,3-trimethylindoleninium iodide, 0.81 g (2.35 mmole) of 5,5'-methylenebis(3-nitrosalicylaldehyde), and 0.6 ml (6 mmole) of piperidine was refluxed for 5 h in 150 ml of methanol. The solvent was removed by vacuum distillation, and X was extracted from the residue with boiling benzene–hexane (1 : 1) to give 1.1 g (65.3%) of dark-green product without a definite melting point. Found: C 72.9; H 6.7; N 7.4%. $C_{43}H_{44}N_4O_6$. Calculated: C 72.4; H 6.2; N 7.9%.

The photochemical experiments were carried out in the chamber of an SP-700 spectrophotometer in special quartz cuvettes (l' 0.5 cm, l 3 cm). The methods used in the spectral and kinetic measurements were presented in previous papers of this series.

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