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PHOTO- AND THERMOCHROMIC SPIRANES. 31.* PHOTOCHROMIC CATIONIC SPIROPYRANS WITH A PYRIDINIUM FRAGMENT IN THE ALIPHATIC SIDE CHAIN*[2]

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Syntheses are reported for cationic indoline spiropyrans with a quaternized pyridinium fragment in the aliphatic side chain, which display photochromic properties in solution. The major effect of introducing a quaternized pyridinium fragment into the benzopyran part of the spiropyran entails a significant decrease in the rate of thermal relaxation processes.

Keywords: cationic indolinospiropyrans, pyridinium fragment, photochromism, electronic absorption spectroscopy.

Photochromic organic molecules, some of which are spiropyrans and spirooxazines, have recently been the subject of intensive research due to the use of these compounds in optical recording and data transformation systems, sensors, optical electronics, optical bioelectronics, and transport systems [2-5].

However, the limit to improving the characteristics of monofunctional materials has now been reached and attention is being directed toward the development of hybrid polyfunctional materials holding promise for application in molecular electronics.

A possible solution of this problem lies in the creation of hybrid polyfunctional materials, which combine structural units responsible for different physicochemical properties such as photochromism and magnetism [6-9], photochromism and conductivity [10, 11], electrical and magnetic properties [12], and optical dichroism and magnetism [13]. A systematic study of both the structure and properties of such units and the feasibility of their combination into a single crystal lattice is required for the development of such materials from molecular units differing in their chemical nature, the investigation of the interaction of such units on each other, and methods for the modification of the properties of the separate units to impart desired properties to the hybrid materials.

* For Communication 30 see [1].

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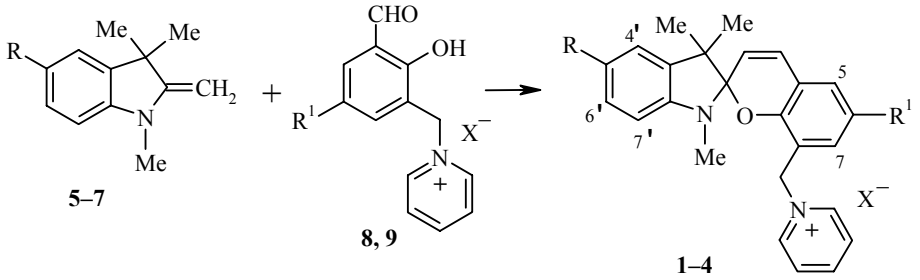
Cationic forms of photochromic systems are required for the development of hybrid polyfunctional materials containing photochromic cations in their structure [8, 9, 14,15]. Salts of spiropyrans (SP^+X^-) and spirooxazines (SO^+X^-) hold promise for the development of hybrid polyfunctional materials, combining photochromic and magnetic properties in a single crystal lattice [6-9, 16], in which the spiropyran or spirooxazine cations have photochromic properties. Thus, the synthesis, structure, and photochemical properties of cationic spiropyrans and spirooxazines have recently attracted considerable investigation [8, 9, 14-17]. A completely new class of hybrid polyfunctional compounds has recently been discovered. Such compounds combine a photochromic cationic spiropyran sublattice and a magnetic anionic bimetallic oxalate sublattice [18, 19], in which the spiropyran acts as a photochemical molecular switch perturbing the magnetic sublattice.

In a continuation of these studies, we investigated the synthesis and photochromic properties of a series of cationic spiropyrans containing a pyridinium fragment in the aliphatic side chain.

The synthesis of cationic spiropyrans (SPP) of type**1** and **2** by the condensation of a methylene base with 3-chloromethyl-2-hydroxy-5-nitrobenzaldehyde and the subsequent reaction of the resultant chloromethyl spiropyran derivative with pyridine has been described by Takagi [20] and Artemova [21]. In contrast to this method, spiropyrans **1-4** were obtained by the reaction of methyleneindolines **5-7** and pyridiniummethyl derivatives of aldehydes **8** and **9** in accord with our recently reported method [9]. (Scheme 1).

Scheme 1

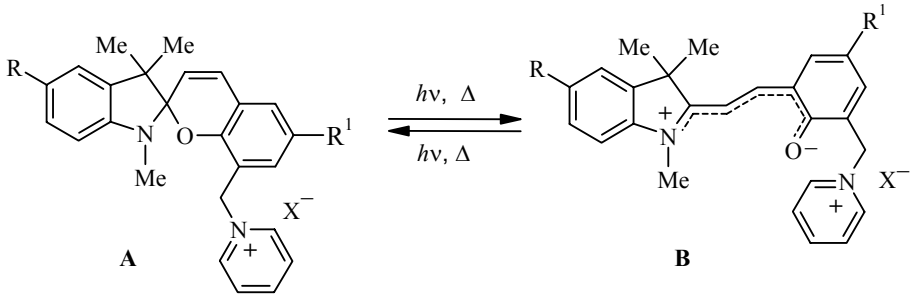


1 R = Cl, $R^1 = NO_2$, X = Cl; **2** R = OMe, $R^1 = NO_2$, X = Cl; **3** R = R^1 = H, X = Br; **4** R = Cl, R^1 = H, X = Br; **5** R = H; **6** R = Cl; **7** R = OMe; **8** $R^1 = NO_2$, X = Cl; **9** R^1 = H, X = Br

The ^{1}H NMR spectral data including signals from magnetically inequivalent geminal methyl groups, diastereotopic splitting of the signals of protons of the methylene group of the pyridiniummethyl substituent, chemical shifts and coupling constants of the protons of the pyran double bond and protons of the indoline fragment unequivocally support the structure of the spiropyrans obtained. However, the absence of signals for the N-methyl and *gem*-dimethyl groups, singlet of the methylene group of the pyridiniummethyl substituent, *trans*-vicinal protons and other protons of the indoline and pyran fragments in the spectral regions characteristic for opening of the merocyanine form indicates that the products exist in solution in $CDCl_3$ and DMSO-d_6 mainly in the spirocyclic form.

The mechanism for the photochromic transformation of spiropyrans, spirooxazines, and their salts (Scheme 2) involves the thermally and photochemically reversible heterolytic clevage of the C_{spiro}–O bond of cyclic isomer **A** with subsequent *cis-trans* isomerization to give metastable merocyanine form **B**, which converts to the starting spiroform either spontaneously or by the action of visible light [2, 3].

The electronic absorption spectra of the cyclic isomers of spiropyrans **1-4** in acetonitrile show long-wavelength bands at 290-345 nm with molar extinction coefficients at the maxima 3480-8180 $mol^{-1}\cdot liter\cdot cm^{-1}$ corresponding to an $S_0 \rightarrow S_1$ transition and stronger bands with maxima at 245-259 nm and molar extinction coefficient 16210-24190 $mol^{-1}\cdot liter\cdot cm^{-1}$ for the $S_0 \rightarrow S_2$ transition. There are



three groups of spiropyrans according shape and position of their UV bands: 1) SPP **1** and **2** with a nitro group in the benzopyran part of the molecule, having broad long-wavelength bands, 2) SPP **3** and **4**, which are unsubstituted in the benzopyran part and have much narrower bands, shifted hypsochromically relative to the absorption bands of SPP **1** and **2**, and 3) SPP **1** and **4** with a 5-chloro atom in the indoline part of the molecule, which have a pronounced $S_0 \rightarrow S_2$ transition with maxima at 257 and 253 nm (Fig. 1). Thus, in the general case, substitution in the benzopyran part of the SPP primarily affects the position and shape of the long-wavelength absorption band, while substituents in the indoline part lead to modification of the short-wavelength band for the $S_0 \rightarrow S_2$ transition. This corresponds to the assumption of additivity of the absorption spectra of the acoplanar fragments of the spiropyrans and localization of the electronic transition responsible for the longest-wavelength absorption band in the benzopyran part of the molecule. Structural modeling was used to show that the electronic absorption spectra of the spiropyrans may be represented as a linear combination of the absorption spectra of the component fragments [22]. This proves possible due to an only slight interaction of the orthogonal fragments. The long-wavelength absorption band is related to the photochemically-active benzopyran fragment, while the short-wavelength band is related to the heterocyclic part of the molecule.

We found that the cyclic forms of the SPP at 293 K do not possess fluorescence.

The maxima of the long-wavelength bands of the acyclic merocyanine isomers **B** of spiropyrans **1-4** lie in the range 540-586 nm, which corresponds to the absorption data of merocyanine isomers of previously described spiropyrans (Table 1) [2, 3].

The merocyanine forms of SPP **1** and **2** demonstrate fluorescence at 293 K. The fluorescence band maxima lie in the range 618-625 nm and the fluorescence excitation bands are in good accord with the long-wavelength absorption bands of merocyanine forms **B** (Table 1).

Spiropyrans **3** and **4** in the initial acetonitrile solutions prior to irradiation exist exclusively in cyclic form **A**. In contrast, an equilibrium of the cyclic and merocyanine forms is observed in the case of SPP **1** and SPP **2**, which gives rise to an additional long-wavelength absorption bands in the electronic absorption spectra with maxima at 540-544 nm relative to SPP **3** and **4** (see the spectra of SPP **3** and **4** in Fig. 1 and spectra *(1)* in Figs. 2 and 3). In this case, judging from the ratio of the absorption bands of the cyclic and merocyanine isomers for 5-methoxy SPP **2**, the equilibrium is more sharply shifted toward the merocyanine isomers relative to chloro-substituted SPP **1**. Thus, the introduction of the strongly electron-withdrawing NO_2 group into the benzopyran part of the SPP and, subsequently, the introduction of an electron-donor OCH_3 group into the indoline part of the SPP lead to a progressive increase in the thermodynamic stability of the merocyanine isomers, which is manifest in a further shift in the **A-B** equilibrium toward cyclic forms **B**.

The behavior of spiropyrans **1-4**, as in the case of spirooxazines [23, 24], is probably a function of the dependence of the molecular structure of the merocyanine form, namely, quinoidization or dipolarity, on the electron-withdrawing and electron-donor properties of the substituents in some part of the SPP. The strongly electron-withdrawing NO_2 group in the benzopyran fragment leads to delocalization of the negative charge on the oxygen atom and thereby to stabilization of the dipolar structure of the merocyanine form. An additional effect in this direction in the case of compound **2** is related to the introduction of the electron-donor OCH_3 group into the

TABLE 1. Spectral and Kinetic Properties* of Cationic Spiropyrans **1-4** in Acetonitrile at 293 K

Compound	λ_{max}, nm	ε, l•mol^{-1}•cm^{-1}	λ_{max}, nm	λ^{f}_{max}, nm	k_{obs}*^{2}•10^{-5}, sec^{-1}
	Cyclic form **A**		Merocyanine form **B**		
1	257	24190	544	625	8.9
	311	8500			
	340, sh.	7840			
2	259	19670	540	618	0.8
	317	9950			
	345, sh.	8180			
3	245, sh.	16210	579		6370
	298	5400			
	320, sh.	3480			
4	253	19470	586		4700
	306	5900			
	321, sh.	4050			

* Absorption: λ_{max}, ε; fluorescence, λ^{f}_{max}.

*^{2} In the case of SPP **1** and SPP **2**, the observed rate constant (k_{obs}) of the thermal relaxation process is the sum of the rate constants of thermal ring opening (k_{AB}) and thermal recyclization (k_{BA}). For SPP **3** and **4**, $k_{obs} = k_{BA}$.

indoline fragment of the SPP, which facilitates delocalization of positive charge on the nitrogen atom. In the case of a polar environment of the isomeric SPP forms by acetonitrile molecules, the transition from the weakly polar cyclic form to the dipolar merocyanine form is thermodynamically justified.

Irradiation of solutions of spiropyrans **3** and **4** in acetonitrile by UV light at the absorption bands of the cyclic isomers leads to coloration related to clevage of a C–O bond and subsequent *cis-trans* isomerization and the formation of a colored metastable product **B** (Table 1) [2, 3]. UV irradiation (365 nm) of SPP **1** and **2**, which exist in acetonitrile solution as equilibrium forms **A** and **B**, leads to excitation of both cyclic forms **A** due to the $S_0 \rightarrow S_1$ transition and merocyanine forms **B** due to the $S_0 \rightarrow S_2$ transition. Upon reaching the photostationary state, the resultant effect, which reflects the arrangement of the absorption levels of the merocyanine forms in the equilibrium and photostationary states, has a directly opposite value for SPP **1** and **2**: an increase in the amount of merocyanine isomers relative to the equilibrium content is observed in solutions of SPP **1** and, *vice versa*, the concentration of the merocyanine forms of SPP **2** in the photostationary state is much lower than in the equilibrium state (compare Figs. 2 and 3). The position of the equilibrium is determined by the ratio of the rate constants of the forward **A** → **B** thermal reactions and reverse **B** → **A** thermal reactions. The level of the photostationary state, in addition, depends on the molar extinction coefficients of the isomeric forms at the irradiation wavelength as well as the quantum yields of the photocoloration and photodecoloration reactions. The combination of these factors determines the resultant effect of UV irradiation.

Thermal relaxation processes are observed after the termination of irradiation at 365 nm. The relaxation process for SPP **3** and **4** involves the reverse thermal recyclization **B** → **A** and is characterized by rate constant k_{BA}. The establishment of equilibrium occurs in solutions of compounds **1** and **2** and, in this case, the observed rate constant (k_{obs}) is the sum of the rate constants of the thermal coloration reactions (k_{AB}) and thermal decoloration reaction (k_{BA}). We note that while the relaxation process for SPP **1**, which is dark decoloration of the solution, obeys exponential attenuation, the dark coloration for SPP **2** is described satisfactorily by an increasing exponential function.

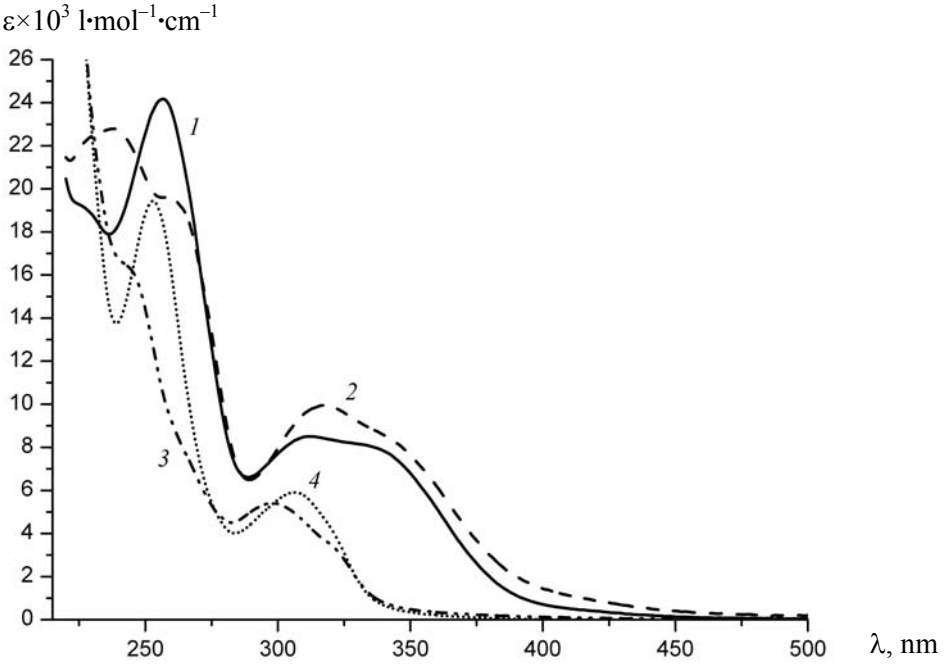


Fig. 1. Electronic absorption spectra of cyclic isomeric forms **A** of SPP **1-4** (*1-4*, respectively) in acetonitrile (the spectra of compounds **3** and **4** were taken immediately after dissolution; the solutions of compounds **1** and **2** were initially irradiated at 546 nm until the long-wavelength bands of merocyanine isomers **B** completely disappeared).

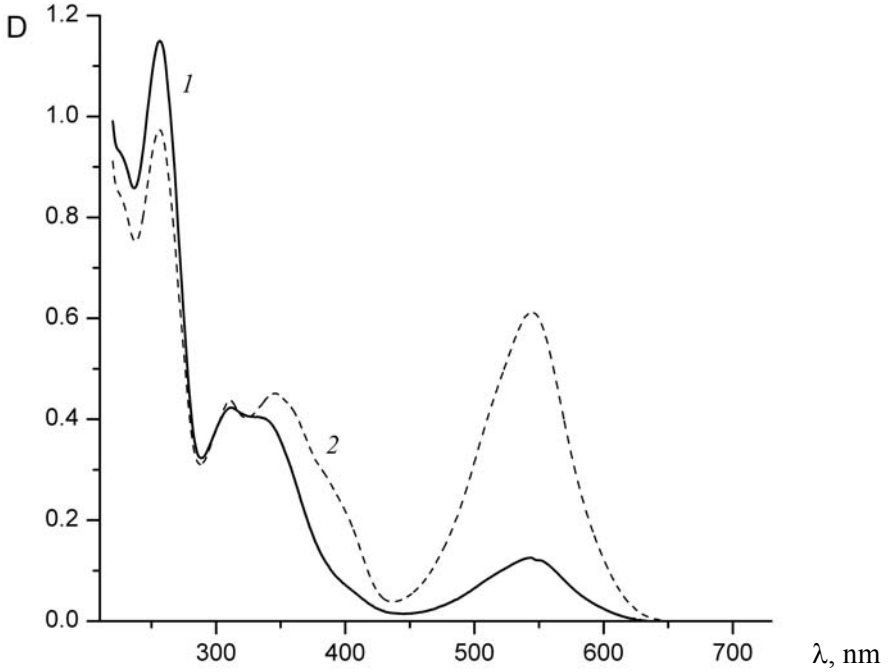


Fig. 2. Electronic absorption spectra of SPP **1** ($4.95 \cdot 10^{-5}$ mol/liter) in acetonitrile at 293K at thermodynamic equilibrium (*1*) and in the photostationary state (*2*) upon irradiation at 365 nm.

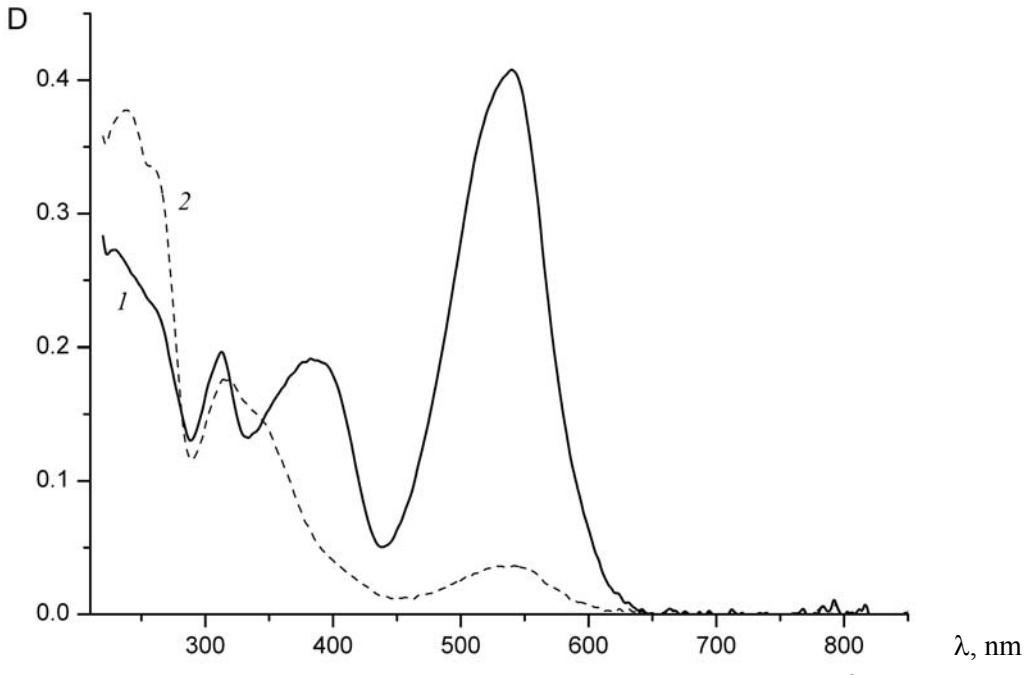


Fig. 3. Electronic absorption spectra of SPP **2** ($1.75 \cdot 10^{-3}$ mol/liter) in acetonitrile at 293 K at thermodynamic equilibrium (*1*) and in the photostationary state upon irradiation at 365 nm (*2*).

The observed rate constants of the thermal relaxation processes are given in Table 1. The rate constant of the dark decoloration for 6-NO_2-BIPS (1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline]) equal to $1.54 \cdot 10^{-3}$ sec^{-1}, which was obtained under the same conditions (acetonitrile, 293 K) as for compound **1-4**, is also given. On one hand, these data show that the introduction of a quaternized pyridine fragment into the benzopyran part of the spiropyran molecule leads to a decrease in the rate of the thermal recyclization by three orders of magnitude, while, on the other, the results support the conclusion that introduction of an electron-withdrawing group into the benzopyran part and the introduction of an electron-donor group into the indoline part of the SPP, as in the case of spirooxazines, which are structural analogs of SPP, also lead to stabilization of the merocyanine form in polar solvents [24].

The photochemical channel for $\mathbf{B} \rightarrow \mathbf{A}$ recyclization demonstrated above for the excitation of the merocyanine forms of compound **1** and **2** to the S_2 state was confirmed upon direct irradiation of acyclic isomers **B** in the long-wavelength bands. In contrast, an increase in the rate of decoloration for SPP **3** and **4** after prior photocoloration upon irradiation in the long-wavelength absorption bands of the merocyanine isomers of these spiropyrans could not be detected against the background of the thermal relaxation.

EXPERIMENTAL

The ^{1}H NMR spectra were taken on a Varian Unity-300 spectrometer at 300 MHz at 20°C. The signals were assigned relative to the signal of the residual protons of the deuterosolvent, $CDCl_3$ (δ 7.26 ppm) and DMSO-d_6 (δ 2.50 ppm). The error in the measurement of δ was 0.01 ppm and the error in the measurement of the coupling constants was 0.1 Hz.

The electronic absorption spectra and the kinetic curves for the thermal relaxation processes were recorded on an Agilent 8453 spectrophotometer with a thermal stabilization device. The photolysis of the solutions was carried out using a 200-W Lot Oriel mercury lamp with a set of interference light filters. The fluorescence spectra were taken using a Varian Cary Eclipse fluorimeter. The solutions were prepared using a spectral-grade acetonitrile sample obtained from Aldrich. Methyleneindoline **5** (obtained from Lancaster) and methyleneindoline **6** (obtained from Aldrich) were used without further purification. Methyleneindoline **7** was prepared according to Pottier [25], while aldehyde **8** was prepared according to our previous procedure [9].

1-(3-Formyl-2-hydroxybenzyl)pyridinium bromide (9) was obtained analogously to aldehyde **8** [9] in 53% yield; mp 169-171°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 5.84 (2H, s, 1-CH_2–Ar); 7.18 (1H, t, *J* = 7.6, H-5 Bn); 7.85 (1H, dd, *J* = 7.6, *J* = 1.7, H-6 Bn); 7. 87 (1H, dd, *J* = 7.7, *J* = 1.8, H-4 Bn); 8.08-8.13 (2H, m, H-3, H-5 Py); 8.58 (1H, tt, *J* = 7.8, *J* = 1.3, H-4 Py); 9.05-9.08 (2H, m, H-2, H-6 Py); 10.01 (1H, s, 3-CHO Bn); 11.38 (1H, s, 2-OH Bn). Found, %: C 53.32; H 4.30; N 4.61. $C_{13}H_{12}BrNO_2$. Calculated, %: C 53.08; H 4.11; N 4.76.

1-[(5'-Chloro-1',3,',3'-trimethyl-6-nitro-spiro[2H-1-benzopyran-2,2'-indolin-8-yl)methyl]pyridinium Chloride (1). A solution of 2-methylenindoline **6** (0.42 g, 2 mmol) in methanol (2 ml) was added dropwise to a mixture of aldehyde **8** (0.59 g, 2 mmol) and methanol (14 ml) at reflux over 30 min. The mixture was heated at reflux for 4 h. The solvent was evaporated off and the residue was recrystallized from acetonitrile to give compound **1** in 57% yield. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.83 (3H, s, 3'-CH_3); 1.11 (3H, s, 3'-CH_3); 2.61 (3H, s, 1'-CH_3); 5.82 (1H, d, *J* = 10.4, H-3); 6.08 (1H, d, *J* = 14.1, 8-CH_2–Py); 6.30 (1H, d, *J* = 14.1, 8-CH_2–Py); 6.54 (1H, d, *J* = 8.3, H-7'); 6.90 (1H, d, *J* = 2.1, H-4'); 6.95 (1H, d, *J* = 10.4, H-4); 7.26 (1H, dd, *J* = 8.2, *J* = 2.1, H-6'); 7.72 (2H, dd, *J* = 7.8, *J* = 6.7, H-3, H-5 Py); 8.04 (1H, d, *J* = 2.6, H-5); 8.37 (1H, tt, *J* = 7.8, *J* = 1.1, H-4 Py); 8.87-8.90 (3H, m, H-7, H-2,H-6 Py). Found, %: C 62.10; H 4.96; N 8.53. $C_{25}H_{23}Cl_2N_3O_3$. Calculated, %: C 61.99; H 4.79; N 8.67.

1-[(5'-Methoxy-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2H'-indolin]-8-yl)methyl]pyridinium chloride (2) was obtained in 55% yield analogously to spiropyran **1** from 2-methyleneindoline **7** and aldehyde **8** and recrystallized from ethanol. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.94 (3H, s, 3'-CH_3); 1.15 (3H, s, 3'-CH_3); 2.47 (3H, s, 1'-CH_3); 3.87 (3H, s, 5'-OCH_3); 5.86 (1H, d, *J* = 10.5, H-3); 5.97 (1H, d, *J* = 13.5, 8-CH_2-Py); 6.21 (1H, d, *J* = 13.5, 8-CH_2–Py); 6.49 (1H, d, *J* = 8.3, H-7'); 6.68 (1H, d, *J* = 2.4, H-4'); 6.83 (1H, dd, *J* = 8.3, *J* = 2.4, H-6'); 6.94 (1H, d, *J* = 10.5, H-4); 7.73 (2H, t, *J* = 6.6, H-3, H-5 Py); 8.06 (1H, d, *J* = 2.2, H-5); 8.38 (1H, t, *J* = 7.6, H-4 Py); 8.73 (2H, d, *J* = 5.1, H-2, H-6 Py); 8.93 (1H, d, *J* = 2.2, H-7). Found, %: C 65.21; H 5.38; N, 8.63. $C_{26}H_{26}ClN_3O_4$. Calculated, %: C 65.06; H 5.46; N 8.75.

1-[(1',3',3'-Trimethylspiro[2H-1-benzopyran-2,2'-indolin]-8-yl)methyl]pyridinium bromide (3) was obtained in 56% yield analogously to spiropyran **1** from 2-methyleneindoline **5** and aldehyde **9** and recrystallized from 1:1 acetonitrile–ethyl acetate, mp 143-145°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.01 (3H, s, 3'-CH_3); 1.14 (3H, s, 3'-CH_3); 2.42 (3H, s, 1'-CH_3); 5.69 (1H, d, *J* = 10.3, H-3); 5.70 (1H, d, *J* = 13.5, 8-CH_2–Py); 5.95 (1H, d, *J* = 13.5, 8-CH_2–Py); 6.49 (1H, d, *J* = 7.7, H-7'); 6.87 (1H, d, *J* = 10.3, H-4); 6.96 (1H, t, *J* = 7.6, H-6); 6.97 (1H, dt, *J* = 7.3, *J* = 0.9, H-5'); 7.09 (1H, dd, *J* = 7.3, *J* = 1.3, H-4'); 7.16 (1H, dd, *J* = 7.6, *J* = 1.6, H-5); 7.28 (1H, dt, *J* = 7.6, *J* = 1.3, H-6'); 7.63 (2H, dd, *J* = 7.8, *J* = 6.7, H-3, H-5 Py); 7.99 (1H, dd, *J* = 7.6, *J* = 1.6, H-7); 8.28 (1H, tt, *J* = 7.8, *J* = 1.4, H-4 Py); 8.55 (2H, dd, *J* = 6.7, *J* = 1.4, H-2, H-6 Py). Found, %: C 66.67; H 5.70; N 6.40. $C_{25}H_{25}BrN_2O$. Calculated, %: C 66.81; H 5.61; N 6.23.

1-[(5'-Chloro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indolin]-8-yl)methyl]pyridinium Bromide (4) was obtained analogously to spiropyran **1** in 51% yield from 2-methyleneindoline **6** and aldehyde **9** and recrystallized from 1:1 acetonitrile–ethyl acetate. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.88 (3H, s, 3'-CH_3); 1.12 (3H, s, 3'-CH_3); 2.50 (3H, s, 1'-CH_3); 5.66 (1H, d, *J* = 10.3, H-3); 5.85 (1H, d, *J* = 13.6, 8-CH_2–Py); 5.90 (1H, d, *J* = 13.6, 8-CH_2–Py); 6.46 (1H, d, *J* = 8.2, H-7'); 6.87 (1H, d, *J* = 10.3, H-4); 6.94 (1H, d, *J* = 2.1, H-4'); 6.98 (1H, t, *J* = 7.6, H-6); 7.16 (1H, dd, *J* = 7.6, *J* = 1.6, H-5); 7.24 (1H, dd, *J* = 8.2, *J* = 2.1, H-6');

7.65-7.70 (2H, m, H-3, H-5 Py); 8.00 (1H, dd, $J = 7.6$, $J = 1.6$, H-7); 8.32 (1H, tt, $J = 7.8$, $J = 1.4$, H-4 Py); 8.64-8.67 (2H, m, H-2, H-6 Py). Found, %: C 62.23; H 4.94; N 5.73. $C_{25}H_{24}BrClN_2O$. Calculated, %: C 62.06; H 5.00; N 5.79.

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REFERENCES

1. B. S. Lukyanov, A. N. Utenyshev, V. V. Tkachev, S. M. Aldoshin, V. I. Minkin, M. B. Lukyanova, and Yu. S. Alekseenko, *Khim. Geterotsikl. Soedin.*, 221 (2008). [*Chem. Heterocycl. Comp.*, **44**, 163 (2008)].
2. R. Guglielmetti, in: H. Dürr and H. Bouas-Laurent (editors), *Photochroism*, Elsevier, Amsterdam (1990), Ch. 8.
3. R. C. Bertelson, in: J. C. Crano and R. J. Guglielmetti (editors), *Organic Photochromic and Thermochromic Compounds*, vol. 1, Plenum Press, New York (1999), Ch. 1.
4. G. Bercovic, V. Krongauz, and V. Weiss, *Chem. Rev.*, **100**, 1741 (2000).
5. V. I. Minkin, *Chem. Rev.*, **104**, 2751 (2004).
6. S. Bénard and P. Yu, *Chem. Commun.*, 65 (2000).
7. S. Bérnard, E. Riviere, and P. Yu, *Chem. Mater.*, **13**, 159 (2001).
8. I. Kashima, M. Okubo, Y. Ono, M. Itoi, N. Kida, M. Hikita, M. Enomoto, and N. Kojima, *Synth. Meth.*, **153**, 473 (2005).
9. S. M. Aldoshin, N. A. Sanina, V. I. Minkin, V. A. Voloshin, V. N. Ikorskii, V. I. Ovcharenko, V. A. Smirnov, and N. K. Nagaeva, *J. Mol. Struct.*, **826**, 69 (2007).
10. I. Shevyakova, L. Buravov, V. Tkacheva, L. Zorina, S. Khasanov, S. Simonov, J. Yamada, E. Canadell, R. Shibaeva, and E. Yagubskii, *Adv. Funct. Mater.*, **14**, 660 (2004).
11. S. V. Simonov, I. Yu. Shevyakova, L. V. Zorina, S. S. Khasanov, L. I. Buravov, V. A. Emel'yanov, E. Canadell, R. P. Shibaeva, and E. B. Yagubskii, *J. Mater. Chem.*, **15**, 2476 (2005).
12. T. G. Prokhorova, S. S. Khasanov, L. V. Zorina, L. I. Buravov, V. A. Tkacheva, A. A. Baskakov, R. B. Morgunov, M. Gener, E. Canadell, R. P. Shibaeva, and E. B. Yagubskii, *Adv. Funct. Mater.*, **13**, 403 (2003).
13. N. S. Ovanesyan, V. D. Makhaev, S. M. Aldoshin, P. Gredin, K. Boubekeur, C. Train, and M. Gruselle, *J. Chem. Soc., Dalton Trans.*, 18, 3101 (2005).
14. S. Bénard and P. Yu, *Adv. Mater.*, **12**, 48 (2000).
15. S. M. Aldoshin, L. A. Nikonova, V. A. Smirnov, G. V. Shilov, and N. K. Nagaeva, *J. Mol. Struct.*, **750**, 158 (2005).
16. K. Nakatani and P. Yu, *Adv. Mater.*, **13**, 1411 (2001).
17. S. M. Aldoshin, L. A. Nikonova, V. A. Smirnov, G. V. Shilov, and N. K. Nagaeva, *Izv. Akad. Nauk, Ser. Khim.*, 2050 (2005).
18. S. Bénard, E. Riviere, P. Yu, K. Nakatani, and J. F. Delouis, *Chem. Mater.*, **13**, 159 (2001).
19. I. Kashima, M. Okubo, Y. Ono, M. Itoi, N. Kida, M. Hikita, M. Enomoto, and N. Kojima, *Synth. Meth.*, **155**, 703 (2005).
20. K. Takagi, T. Kurematsu, and Y. Sawaki, *J. Chem. Soc., Perkin Trans. 2*, 1667 (1995).

21. N. K. Artemova, V. A. Smirnov, B. G. Rogachev, G. V. Shilov, and S. M. Aldoshin, *Izv. Akad. Nauk, Ser. Khim.*, 1548 (2006).
22. N. W. Tyer, Jr. and R. S. Becker, *J. Am. Chem. Soc.*, **92**, 1289 (1970).
23. A. V. Metelitsa, V. Lokshin, J. C. Micheau, A. Samat, R. Guglielmetti, and V. I. Minkin, *Phys. Chem. Chem. Phys.*, **4**, 4340 (2002).
24. V. Lokshin, A. Samat, and A. V. Metelitsa, *Usp. Khim.*, **71**, 1015 (2002).
25. E. Pottier, M. Sergent, R. Phan Tan Luu, and R. Guglielmetti, *Bull. Soc. Chim. Belg.*, **101**, 719 (1992).