Spiropyrans and spirooxazines
4.* Synthesis and spectral properties of 6´-halo-substituted spiro[indoline-2,2´-2*H*-pyrano[3,2-*h*]quinolines]

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The Duff formylation of 5-bromo- or 5-chloro-8-hydroxyquinoline leads to the corresponding 7-formyl derivatives, condensation of which with 2-methyleneindolines or 3*H*-indolium halides in the presence of a base afforded new photochromic 6´-halo-substituted spiro[indoline-2,2´-2*H*-pyrano[3,2-*h*]quinolines]. Thermal and photo-induced isomerization of compounds obtained have been investigated by ^{1}H NMR and UV spectroscopy.

Key words: formylquinolinols, spiroindolinepyranoquinolines, photochromism.

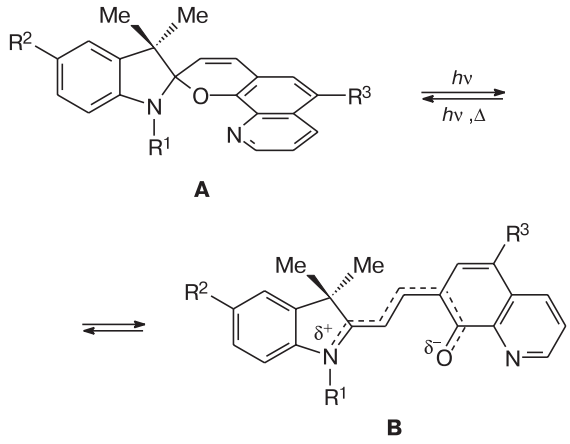
Elaboration and synthesis of polyfunctional molecular systems nowadays is under intensive research, this field is important for the development of molecular electronics and sensors.[2,3] Bistable photochromic compounds (spiropyrans, spirooxazines, chromenes), containing a cation-receptor center, are typical examples of such molecules.

Photochromism of spiropyrans of the type **A** (Scheme 1) is caused by thermally and photochemically reversible process of heterolytic cleavage of the C_{spiro}—O bond and subsequent *cis-trans*-isomerization to metastable merocyanine form **B**.[4,5]

The presence of partial negative charge on the oxygen atom of the merocyanine isomer makes it a potential ligand in the complex-forming reactions with metal ions,[6—8] as well as with a number of organic substrates.[9,10] Compounds of this class were first represented by spiroindolinepyranoquinolines.[11,12] In these compounds, both photochromic and coordination functions are integrated. Recently, it was shown[13—16] that spiroindolinepyranoquinolines are efficient photodynamic fluorescent chemosensors for a number of metal cations.

In the present work, in continuation of our research on fluorescent chemosensors on the basis of spiropyrans, we report the synthesis of 5-halo-substituted 7-formyl-8-hydroxyquinolines, as well as the synthesis and analysis of the photochromic properties of 6´-halo-substituted spiroindolinepyranoquinolines.

Scheme 1



Synthesis of 6´-halo-substituted spiroindolinepyranoquinolines. 6´-Halo-substituted spiroindolinepyranoquinolines were synthesized according to Scheme 2. The reaction of 2-methyleneindolines **5** and **6** or 3*H*-indolium halides **7—10** with 5-halo-substituted formylquinolinols **3** and **4** in the presence of a base afforded unsubstituted spiroindolinepyranoquinolines **11**[11] and **12**[15] and new spiroindolinepyranoquinolines **13—22**, containing various substituents in the indoline fragment of the molecule.

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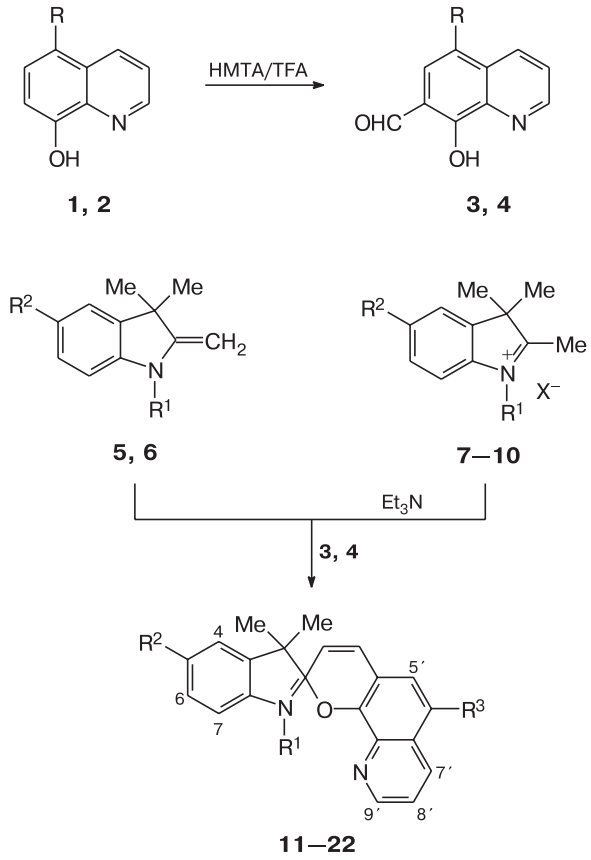
Scheme 2



Compound	R^1	R^2	X
7	Me	$OC_{16}H_{33}$	I
8	CH_2Ph	H	I
9	CH_2CH_2COOH	H	I
10	CH_2CH_2OH	H	Br

Compound	R^1	R^2	R^3
11	Me	H	Br
12	Me	H	Cl
13	Me	Cl	Br
14	Me	Cl	Cl
15	Me	$OC_{16}H_{33}$	Br
16	Me	$OC_{16}H_{33}$	Cl
17	CH_2Ph	H	Br
18	CH_2Ph	H	Cl
19	CH_2CH_2OH	H	Br
20	CH_2CH_2OH	H	Cl
21	CH_2CH_2COOH	H	Br
22	CH_2CH_2COOH	H	Cl

In contrast to the multi-step synthesis of 7-formyl-8-hydroxyquinoline described in the literature[13] (direct formylation of 8-hydroxyquinoline leads to 5-formyl derivative[17]), 5-halo-substituted formylquinolinols **3** and **4** were obtained by the Duff formylation of the corresponding quinolinols **1** and **2**.

The structures of compounds obtained were established by ^{1}H NMR spectroscopy and confirmed by elemental analysis data.

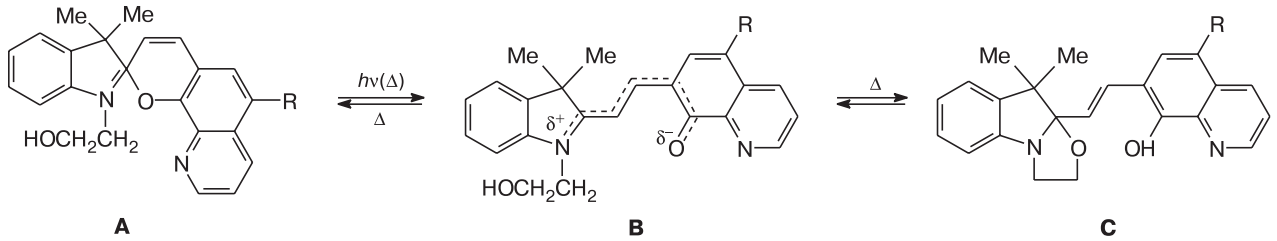
Spectral and photochemical investigations. Solutions of spiropyrans **11—18**, **21**, and **22** in polar solvents, in contrast to their solutions in nonpolar solvents, have a noticeable violet color, caused by the presence of merocyanine isomers **B**, which are in equilibrium with cyclic isomers **A** (see Scheme 1). ^{1}H NMR spectroscopy is one of the most convenient methods for the study of the ring-chain equilibrium spiropyran-merocyanine (**A** ⇌ **B**). Analysis of the ^{1}H NMR spectra allows one to establish the geometrical structure of the open-chain and cyclic forms of the spiro compound. When the open-chain form and the cyclic one are both presented in a solution, the method allows one to determine their ratio, since signals of such characteristic (indicator) fragments, as *gem*-dimethyl group, *N*-alkyl substituent, and protons of the double C(3)=C(4) bond usually can be easily identified and they have different chemical shifts for the cyclic (**A**) and open-chain (**B**) forms.[18—21]

According to ^{1}H NMR spectroscopy, spiropyrans **11—18** and **21**, **22** exist in the solution ($CDCl_3$ for compounds **11—18** and DMSO-d_6 for compounds **21** and **22**) as a mixture of isomeric spirocyclic (**A**) and merocyanine (**B**) forms, the ratio of which depends on the nature of substituents in the indoline fragment of the molecule. Signals of 3′-H and 4′-H protons of the spirocyclic form reveal themselves as two doublets at 5.76—5.84 ppm (5.91—5.94 ppm for compounds **21** and **22**) and 6.81—6.89 ppm (7.13—7.15 ppm for compounds **21** and **22**), respectively (J = 10.2 Hz). Signals of the corresponding vinyl 4′-H and 3′-H protons of the merocyanine form of compounds **15** and **16** (ratio of the spirocyclic and merocyanine forms for them is ~1 : 1) are located at 6.69—6.70 and 6.87—6.89 ppm, respectively (J = 14.0 Hz). Signals of the *gem*-dimethyl group of the spirocyclic form reveal themselves as two three-proton singlets at 1.18—1.30, 1.31—1.38 ppm for compounds **11—18** and at 1.06—1.09, 1.17—1.19 ppm for compounds **21** and **22**. Signals of the *gem*-dimethyl group of the merocyanine form of the spiropyrans **15** and **16** reveal themselves as six-proton singlet at 1.71—1.73 ppm. Signal of the *N*-methyl substituent of compounds **11—16** is located in the interval 2.72—2.79 ppm (spirocyclic form) and at 3.53—3.55 ppm in case of merocyanine form of spiropyrans **15** and **16**.

According to ^{1}H NMR spectroscopy, compounds **19** and **20**, in contrast to spiropyrans **11—18**, **21** and **22**, exist as a mixture of (hydroxystyryl)oxazolidinoindolines, presented in the *trans*-form (**C**), spirocyclic form (**A**), and insignificant amount of **B**-form (Scheme 3).

Signals of 3′-H and 4′-H of the spirocyclic form of compounds **19** and **20** are located at 5.75 and 6.86 ppm (J = 10.2 Hz), signals of the corresponding vinyl protons

Scheme 3



19, 20

of the oxazolidine form are located at 6.50 and 7.29 ppm (J = 16.0 Hz), which is in agreement with the data for similar oxazolidine derivatives.[22] Signals of the *gem*-dimethyl group of compounds **19** and **20** reveal themselves as two three-proton singlets at 1.18—1.20 and 1.33—1.34 ppm (spirocyclic form) and at 1.20—1.22 and 1.47—1.49 ppm in case of the oxazolidine form.

Table 1. Absorption spectra characteristics (λ/nm, ε/L mol^{-1} cm^{-1}) and observed times (τ/s) of thermal relaxation processes of spiropyrans **11—22** at 293 K

Compound	Toluene				Chloroform	
	λ_{max}^{abs} (**A**)	ε	λ_{max}^{abs} (**B**)	τ	λ_{max}^{abs} (**B**)	ε
11	343	4740	560	2.8	566	48700
			598		605	50750
12	343	4600	559	3.1	566	52700
			598		605	52600
13	342	4900	561	3.6	568	—[a]
			597		607	—[a]
14	341	4740	560	2.4	567	—[a]
			597		607	—[a]
15	342	4870	570	2.7	573	50400
			607		616	64200
16	343	4930	567	3.1	573	52000
			607		614	64300
17	343	4590	561	6.0	567	—[a]
			598		607	—[a]
18	342	4490	561	3.6	567	—[a]
			598		607	—[a]
19	337[b]	6370[b]	—[c]	—	569	—[a]
					603	—[a]
20	336[a]	7070[b]	—[c]	—	569	—[a]
					606	—[a]
21	—[d]	—	—	—	568	—
					607	—
22	—[d]	—	—	—	568	—
					608	—

[a] The equilibrium concentration of form **B** is insufficient for the determination of ε value. [b] Oxazolidine form (**C**). [c] Spiropyrans do not show photochromic properties at room temperature. [d] The substance is insoluble in toluene.

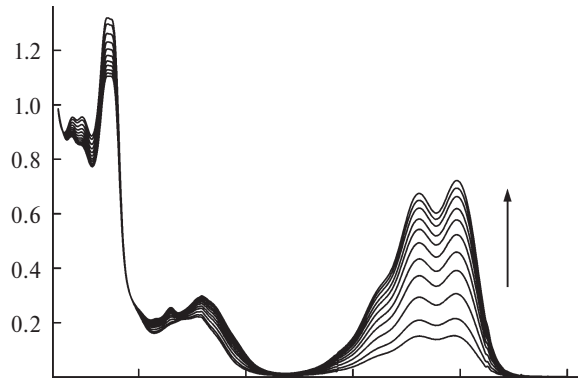


Fig. 1. Photo-induced changes of the absorption spectrum of spiropyran **11** in acetonitrile ($C_{\mathbf{11}} = 4.9 \cdot 10^{-5}$ mol L^{-1}, T = 293 K; irradiation with light of λ = 365 nm, the interval between the spectra is 0.5 s).

Signals of the ring protons of the indoline and quinoline fragments of the spirocyclic and merocyanine forms and of the ring protons of the quinoline fragment of the spirocyclic and oxazolidine forms of these compounds also differ in values of their chemical shifts.

Cyclic isomers **A** of spiropyrans **11—18**, **21**, and **22** are characterized by the long-wave absorption bands with maxima at 341—343 nm and their molar absorption coefficient values (ε) of 4490—4930 mol L^{-1} cm^{-1}, position and intensity of which virtually are independent of substituents R^1, R^2, and R^3 (Table 1, Fig. 1).

According to the ^{1}H NMR data, compounds **19** and **20** exist in solutions as an equilibrium mixture of spirocyclic, merocyanine, and oxazolidine (**C**) forms with the latter being a predominant component. Therefore, positions and intensities of the long-wave absorption of oxazolidine isomers can be estimated from the absorption characteristics of spiropyrans **19** and **20** solutions: the absorption maxima are located at 336 nm with the molar absorption coefficient ε = 6370 (**19**) and 7060 mol L^{-1} cm^{-1} (**20**) (see Table 2).

In polar solvents, such as acetonitrile or chloroform, an increase in intensities of the structured long-wave absorption bands of spiropyrans **11—18**, **21**, and **22** solutions, characteristic of acyclic merocyanine isomers **B**

Table 2. Chemical shifts (δ) of the protons in positions 7′, 8′, and 9′ of the indolinepyranoquinoline fragment of spiropyrans **11—22** for different isomeric form and the content of acyclic isomers of spiropyrans at 293 K

Compound	Solvent	Cyclic form (**A**)			Open-chain form (**B**)			C_B (%)
		H(7′)	H(8′)	H(9′)	H(7′)	H8′	H(9′)	
11	$CDCl_3$	8.35	7.37	8.77	8.15	7.46	8.74	24.6
12	$CDCl_3$	8.39	7.43	8.80	8.18	7.48	8.78	23.7
13	$CDCl_3$	8.36	7.39	8.80	8.16	7.48	8.75	9.3
14	$CDCl_3$	8.40	7.39	8.82	8.18	7.49	8.78	9.0
15	$CDCl_3$	8.35	7.37	8.76	8.15	7.45	8.74	49.2
16	$CDCl_3$	8.41	7.40	8.82	8.21	7.49	8.79	49.5
17	$CDCl_3$	8.36	7.39	8.79	8.13	7.45	8.73	16.4
18	$CDCl_3$	8.40	7.39	8.81	8.16	7.47	8.76	13.7
20	$CDCl_3$	8.39	7.39	8.78	8.46*	7.51*	8.79*	84.3*
19	$CDCl_3$	8.37	7.41	8.76	8.43*	7.52*	8.79*	84.4[a]
21	DMSO-d_6	8.33	7.57	8.75	8.14	7.60	8.66	15.2
22	DMSO-d_6	8.41	7.60	8.80	8.20	7.60	8.72	15.3

* Oxazolidine form (**C**).

is observed in the spectral region 522—620 nm (see Table 1). This indicates an increase in concentration of acyclic isomers **B** due to the shift of equilibrium in the ground state between spirocyclic and merocyanine forms. The intensity of the long-wave absorption bands of the merocyanine forms of spiropyrans in chloroform, calculated from the equilibrium composition, is characterized by ε values equal to 50750—64300 L mol^{-1} cm^{-1} in the maxima.

Introduction of an alkoxy substituent in position 5 of the indoline fragment of spiropyrans causes the most significant changes in the spectral characteristics of merocyanine isomers **B** out of all the R^1, R^2, and R^3 substituents. Such an introduction results in the bathochromic shift of the long-wave absorption maxima for the solutions of compounds **15** and **16**, as well as in the increase of molar absorption coefficient as compared with unsubstituted spiropyrans **11** and **12** (see Table 1).

Position of the spiropyran—merocyanine equilibrium depends only slightly on the nature of halogen atom in position 6′ (Table 2). At the same time, substituents in the indoline part of the molecule significantly shift position of the equilibrium. Thus, π-donor alkoxy substituent in position 5 assists in delocalization of the partial positive charge in the indoline fragment, thus increasing relative stability of the merocyanine form, in contrast to 5-chloro- and 1-benzyl-substituted spiropyrans, which show significantly lower equilibrium content of the open-chain form (see Table 2). In case of 1-(2-hydroxyethyl) derivatives, the basicity of the hydroxy oxygen atom, obviously, is higher than that of oxygen atom of the quinolone fragment of the merocyanine form, therefore, the cyclization of the latter proceeds with predominant formation of the oxazolidine ring and, to a lesser extent, of the pyran one, which leads to the observed shift of equilibrium in the ground state toward oxazolidine form **C**.

Table 3. Thermodynamic parameters (ΔH, ΔG/kJ mol^{-1} and ΔS/J mol^{-1} L^{-1}) of thermal equilibrium **A** ⇄ **B** in solutions of spiropyrans **11** and **12** at 293 K

Compound	Solvent	$K \cdot 10^2$	ΔH°	ΔG°	ΔS°
11	Toluene	1.7	—*	—*	—*
	Acetonitrile	8.4	6.2	6.0	0.7
	Chloroform	33.0			
12	Toluene	1.1	—*	—*	—*
	Acetonitrile	6.6	5.4	4.2	4.1
	Chloroform	31.0			

*The relationship of observed equilibrium constant K versus temperature does not obey the Vant Hoff law.

In polar solvents, the equilibrium in solutions of spiropyrans under study is shifted toward merocyanine form **B**. The equilibrium constants K for the solutions of

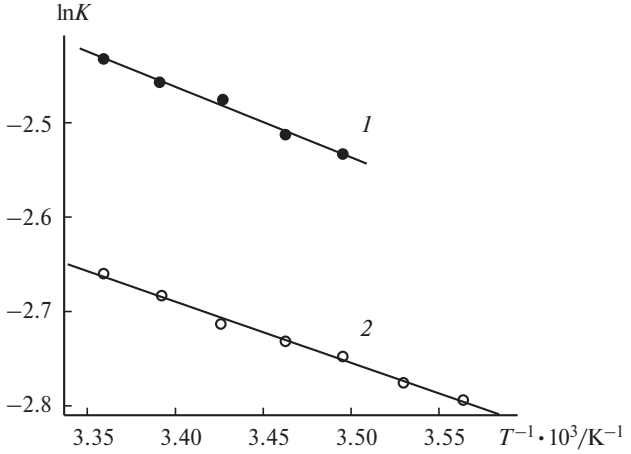


Fig. 2. Logarithm of equilibrium constant (K) of cyclic (**A**) and merocyanine (**B**) forms of spirocpyrans **11** (*1*) and **12** (*2*) in acetonitrile versus reciprocal temperature.

spiropyrans **11** and **12** in acetonitrile and chloroform are higher than in toluene (Table 3).

The equilibrium constant **A** ⇄ **B** increases with the increase of polarity of the solvents (see Table 3).

A linear plot of the logarithms of the equilibrium constants of the cyclic and merocyanine forms of spiropyrans **11** and **12** versus reciprocal temperature is presented in Figure 2. Analysis of the relationship of the equilibrium constants versus temperature in acetonitrile applying the Vant Hoff equation allowed us to determine thermo dynamic parameters of the equilibrium **A** ⇄ **B** and on the basis of the standard enthalpy ΔH° values to estimate the difference between the ground state levels of the cyclic and merocyanine isomers, which are equal to 6.2 and 5.4 kJ mol^{-1} for spiropyrans **11** and **12**, respectively (see Table 3).

When the spiropyran solutions are irradiated in the long-wave absorption bands, they acquire a color, which is caused by the increase of intensities of absorption bands of acyclic forms **B** (see Table 1, Fig. 1). After the irradiation is discontinued, a thermal discoloration is observed, resulting in the restoration of the initial equilibrium. The thermal relaxation processes are satisfactory described by the monoexponential function with the observed time constants being in the range τ = 2.4—6.0 s at 293 K (see Table 1).

On the basis of the equilibrium constants K and the thermal relaxation time constants τ values for spiropyrans **11** and **12**, the rate constants for the forward **A** → **B** ($k_{\mathbf{AB}}$) and the reverse **B** → **A** ($k_{\mathbf{BA}}$) thermal reactions were determined. It should be noted that going from toluene to acetonitrile, the rate constants of the thermal ring opening increase, whereas the rate constants of the thermal cyclization decrease (Table 4). For the rate constants of the thermal processes in acetonitrile $k_{\mathbf{BA}}$ and $k_{\mathbf{AB}}$, the Arrhenius type relationship versus temperature is observed (Fig. 3), which allowed us to determine the activation energy for the thermal reactions of coloration and discoloration (see Table 4).

Table 4. Kinetic parameters of the forward and reverse thermal reactions of spiropyrans **11** and **12**: the rate constant values ($k_{\mathbf{AB}}$, $k_{\mathbf{BA}}$) at 292 K and activation energy values ($E_a^{\mathbf{AB}}$, $E_a^{\mathbf{BA}}$)

Compound	Solvent	$k_{\mathbf{AB}} \cdot 10^2$	$k_{\mathbf{BA}} \cdot 10^2$	$E_a^{\mathbf{AB}}$	$E_a^{\mathbf{BA}}$
		s^{-1}		kJ mol^{-1}	
11	Toluene	0.6	35.5	—*	—*
	Acetonitrile	1.4	16.4	90.6	86.4
12	Toluene	0.3	31.7	—*	—*
	Acetonitrile	1.4	20.4	92.2	87.2

* The relationship of $k_{\mathbf{AB}}$ and $k_{\mathbf{BA}}$ for spiropyrans in toluene versus temperature does not obey the Arrhenius law.

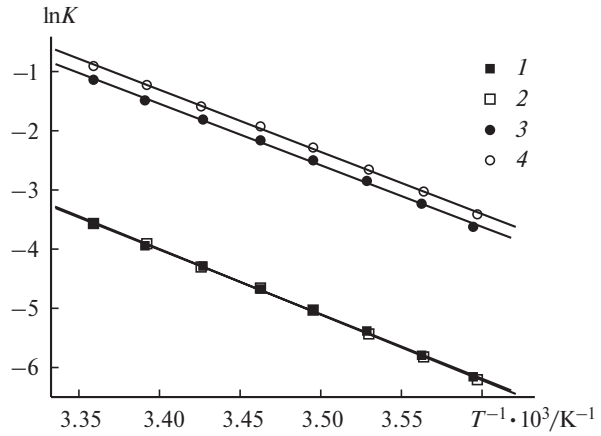


Fig. 3. Logarithms of the rate constant of the forward ($k_{\mathbf{AB}}$) (*1*, *2*) and reverse ($k_{\mathbf{BA}}$) (*3*, *4*) reactions of thermal isomerization of spiropyrans **11** (*1*, *3*) and **12** (*2*, *4*) in acetonitrile versus reciprocal temperature.

In toluene, spiropyrans **11** and **12** are found to deviate from the Vant Hoff and Arrhenius laws. In our opinion, most likely this caused by the fact that in toluene a decrease in temperature creates conditions for the stabilization of more than one transoid isomer of the merocyanine form.[20,21] Since absorption spectra of the transoid isomers differ only slightly,[23] a mistake occurs during the kinetic analysis of the overlapped absorption bands on the analytical wave lengths, which leads to the aforementioned deviations.

In conclusion, a one-step synthesis of 5-halo-substituted 7-formyl-8-hydroxyquinolines by the Duff formylation of 5-bromo- or 5-chloro-8-hydroxyquinolines has been proposed, on the basis of which new photochromic 6′-halo-substituted spiroindolinepyranoquinolines have been synthesized. Thermochromic and photochromic properties of the synthesized compounds have been studied. *N*-(2-Hydroxyethyl)-substituted spiropyrans, in contrast to the other spiropyrans, were found to exist in solutions as an equilibrium mixture of three isomeric forms: spirocyclic, merocyanine, and oxazolidine ones.

Experimental

^{1}H NMR spectra were recorded on a Varian Unity-300 spectrometer (300 MHz) at 20 °C, δ values were determined to within 0.01 ppm, spin-spin coupling constants, within 0.1 Hz. Electronic absorption spectra were recorded on a Varian Cary-100 spectrometer. Irradiation of the samples was carried out by the high-pressure mercury lamp DRSh-250, supplied with a set of interferential light filters for the selection of the mercury spectrum lines. Time constants of the processes of thermal discoloration τ were calculated using the equation

$$\ln(A_t - A_e) = -t/\tau + \ln(A_0 - A_e),$$

where A_0, A_t, and A_e are the initial, current, and equilibrium absorbance values. Rate constants of the forward and reverse pro-

cesses were calculated using the correlations

$$K = k_{AB}/k_{BA}$$

$$1/\tau = k_{AB} + k_{BA}.$$

Thermodynamic parameters of the equilibrium between cyclic and merocyanine forms were determined from the Vant Hoff equation:

$$\ln K = -\Delta H^{\circ}/RT + \Delta S^{\circ}/R.$$

Activation energy values of the thermal processes were obtained from the Arrhenius equation

$$\ln k = -E_a/RT + \ln A.$$

Toluene from Fluka was used for the preparation of solutions. All the measurements were performed at 20 °C.

Compounds **2** (Fluka), **5** (Lancaster), and **6** (Aldrich) were used as purchased, compounds **1**,[24] **7**,[25] **8**,[26] **9**,[27] and **10** (see Ref. 28) were obtained according to procedures described earlier.

Synthesis of formylquinolinols 3 and 4 (general procedure). A mixture of 5-haloquinolinol **1** or **2** (15 mmol), hexamethylenetetramine (4.2 g, 30 mmol), and trifluoroacetic acid (25 mL) was refluxed for 6 h under argon atmosphere, cooled, poured in a mixture of concentrated HCl (20 mL) and water (220 mL), and neutralized to pH ~5. A precipitate formed was filtered off, washed with water, and dried in air. The precipitate was extracted with hot benzene (3×20 mL), the solvent was evaporated, and the residue was crystallized from ethanol.

5-Bromo-8-hydroxyquinoline-7-carbaldehyde (3). The yield was 14%, m.p. 209—210 °C. Found (%): C, 47.80; H, 2.49; N, 5.43. $C_{10}H_6BrNO_2$. Calculated (%): C, 47.65; H, 2.40; N, 5.56. ^{1}H NMR, δ: 7.68 (dd, 1 H, H(3), J = 4.3 Hz, J = 8.6 Hz); 8.06 (s, 1 H, H(6)); 8.51 (dd, 1 H, H(4), J = 1.5 Hz, J = 8.6 Hz); 8.93 (dd, 1 H, H(2), J = 1.5 Hz, J = 4.3 Hz); 10.38 (s, 1 H, 7-CHO).

5-Chloro-8-hydroxyquinoline-7-carbaldehyde (4). The yield was 15%, m.p. 211—212 °C. Found (%): C, 57.97; H, 3.15; N, 6.86. $C_{10}H_6ClNO_2$. Calculated (%): C, 57.85; H, 2.91; N, 6.75. ^{1}H NMR, δ: 7.69 (dd, 1 H, H(3), J = 4.2 Hz, J = 8.5 Hz); 7.85 (s, 1 H, H(6)); 8.54 (dd, 1 H, H(4), J = 1.4 Hz, J = 8.5 Hz); 8.92 (dd, 1 H, H(2), J = 1.4 Hz, J = 4.2 Hz); 10.37 (s, 1 H, 7-CHO).

Synthesis of spiropyrans 11—14 (general procedure). A solution of 2-methyleneindoline **5** or **6** (1 mmol) in butan-2-one (2 mL) was added to a boiling solution of formylquinolinol **3** or **4** (1.05 mmol) in 2-butanone (15 mL) under argon atmosphere for 30 min. The mixture was refluxed for 16 h, the solvent was evaporated, the residue was purified by column chromatography on Al_2O_3 (eluent, $CHCl_3$) and recrystallized.

6′-Bromo-1,3,3-trimethylspiro[indoline-2,2′-2*H*-pyrano[3,2-*h*]quinoline] (11). The yield was 67%, m.p. 186—187.5 °C (from heptane) (*cf.* Ref. 12: m.p. 195 °C). Found (%): C, 65.05; H, 4.62; N, 7.03. $C_{22}H_{19}BrN_2O$. Calculated (%): C, 64.87; H, 4.70; N, 6.88. ^{1}H NMR ($CDCl_3$), δ: 1.19 (s, 3 H, C(3)Me); 1.34 (s, 3 H, C(3)Me); 2.79 (s, 3 H, NMe); 5.78 (d, 1 H, H(3′), J = 10.2 Hz); 6.52 (d, 1 H, H(7), J = 7.7 Hz); 6.82 (dt, 1 H, H(5), J = 7.4 Hz, J = 0.9 Hz); 6.87 (d, 1 H, H(4′), J = 10.2 Hz); 7.06 (dd, 1 H, H(4), J = 7.3 Hz, J = 1.1 Hz); 7.15 (dt, 1 H, H(6), J = 7.7 Hz, J = 1.2 Hz); 7.37 (dd, 1 H, H(8′), J = 8.6 Hz, J = 4.2 Hz); 7.52 (s, 1 H, H(5′)); 8.35 (dd, 1 H, H(7′), J = 8.6 Hz, J = 1.6 Hz); 8.77 (dd, 1 H, H(9′), J = 4.2 Hz, J = 1.7 Hz).

6′-Chloro-1,3,3-trimethylspiro[indoline-2,2′-2*H*-pyrano[3,2-*h*]quinoline] (12). The yield was 72%, m.p. 177—178 °C (from heptane) (*cf.* Ref. 16: m.p. 137—141 °C). Found (%): C, 72.90; H, 5.45; N, 7.83. $C_{22}H_{19}ClN_2O$. Calculated (%): C, 72.82; H, 5.28; N, 7.72. ^{1}H NMR ($CDCl_3$), δ: 1.19 (s, 3 H, C(3)Me); 1.34 (s, 3 H, C(3)Me); 2.79 (s, 3 H, 1-Me); 5.79 (d, 1 H, H(3′), J = 10.2 Hz); 6.52 (d, 1 H, H(7), J = 7.7 Hz); 6.82 (dt, 1 H, H(5), J = 7.4 Hz, J = 0.9 Hz); 6.87 (d, 1 H, H(4′), J = 10.2 Hz); 7.06 (dd, 1 H, H(4), J = 7.3 Hz, J = 0.9 Hz); 7.15 (dt, 1 H, H(6), J = 7.7 Hz, J = 1.2 Hz); 7.33 (s, 1 H, H(5′)); 7.43 (dd, 1 H, H(8′), J = 8.6 Hz, J = 4.2 Hz); 8.39 (dd, 1 H, H(7′), J = 8.6 Hz, J = 1.7 Hz); 8.80 (dd, 1 H, H(9′), J = 4.2 Hz, J = 1.7 Hz).

6′-Bromo-5-chloro-1,3,3-trimethylspiro[indoline-2*H*-pyrano-2,2′-[3,2-*h*]quinoline] (13). The yield was 47%, m.p. 209—210 °C (from heptane). Found (%): C, 60.00; H, 4.25; N, 6.43. $C_{22}H_{18}BrClN_2O$. Calculated (%): C, 59.82; H, 4.11; N, 6.34. ^{1}H NMR ($CDCl_3$), δ: 1.18 (s, 3 H, 3-Me); 1.31 (s, 3 H, 3-Me); 2.77 (s, 3 H, 1-Me); 5.76 (d, 1 H, H(3′), J = 10.2 Hz); 6.42 (d, 1 H, H(7), J = 8.2 Hz); 6.89 (d, 1 H, H(4′), J = 10.2 Hz); 7.00 (d, 1 H, H(4), J = 2.1 Hz); 7.09 (dd, 1 H, H(6), J = 8.2 Hz, J = 2.1 Hz); 7.39 (dd, 1 H, H(8′), J = 8.6 Hz, J = 4.2 Hz); 7.52 (s, 1 H, H(5′)); 8.36 (dd, 1 H, H(7′), J = 8.6 Hz, J = 1.6 Hz); 8.80 (dd, 1 H, H(9′), J = 4.2 Hz, J = 1.6 Hz).

5,6′-Dichloro-1,3,3-trimethylspiro[indoline-2,2′-2*H*-pyrano[3,2-*h*]quinoline] (14). The yield was 55%, m.p. 186—187 °C (from heptane). Found (%): C, 66.37; H, 4.48; N, 7.16. $C_{22}H_{18}Cl_2N_2O$. Calculated (%): C, 66.51; H, 4.57; N, 7.05. ^{1}H NMR ($CDCl_3$), δ: 1.18 (s, 3 H, 3-Me); 1.31 (s, 3 H, 3-Me); 2.76 (s, 3 H, 1-Me); 5.76 (d, 1 H, H(3′), J = 10.2 Hz); 6.42 (d, 1 H, H(7), J = 8.2 Hz); 6.88 (d, 1 H, H(4′), J = 10.2 Hz); 7.00 (d, 1 H, H(4), J = 2.1 Hz); 7.09 (dd, 1 H, H(6), J = 8.2 Hz, J = 2.1 Hz); 7.33 (s, 1 H, H(5′)); 7.39 (dd, 1 H, H(8′), J = 8.6 Hz, J = 4.2 Hz); 8.40 (dd, 1 H, H(7′), J = 8.6 Hz, J = 1.6 Hz); 8.82 (dd, 1 H, H(9′), J = 4.2 Hz, J = 1.6 Hz).

Synthesis of spiropyrans 15—22 (general procedure). A solution of Et_3N (1 mmol) in butan-2-one (2 mL) was added to a boiling mixture of the corresponding 3*H*-indolium halide **7—10** (1 mmol), formylquinolinol **3** or **4** (1.05 mmol), and 2-butanone (15 mL) under argon atmosphere for 30 min. The mixture was refluxed for 16 h and cooled, the solvent was evaporated. The residue was purified by column chromatography on Al_2O_3, eluent was $CHCl_3$ (compounds **15—18**), or on SiO_2 with benzene—acetone (4 : 1) as the eluent (compounds **19** and **20**) followed by recrystallization. In case of compounds **21** and **22**, the residue was triturated with a small amount of acetone, filtered off, washed with acetone, and recrystallized.

6′-Bromo-1-hexadecyloxy-3,3-dimethylspiro[indoline-2,2′-2*H*-pyrano[3,2-*h*]quinoline] (15). The yield was 46%, m.p. 87—88 °C (from heptane). Found (%): C, 70.61; H, 8.03; N, 4.48. $C_{38}H_{51}BrN_2O_2$. Calculated (%): C, 70.46; H, 7.94; N, 4.32. ^{1}H NMR ($CDCl_3$), δ, **A-form**: 0.86 (t, 3 H, 5-$OC_{16}H_{33}$, J = 6.9 Hz); 1.19 (s, 3 H, 3-Me); 1.22—1.28 (m, 24 H, 5-$OC_{16}H_{33}$); 1.31 (s, 3 H, 3-Me); 1.44 (m, 2 H, 5-$OC_{16}H_{33}$); 1.76 (m, 2 H, 5-$OC_{16}H_{33}$); 2.72 (s, 3 H, 1-Me); 3.90 (t, 2 H, 5-$OC_{16}H_{33}$, J = 6.6 Hz); 5.77 (d, 1 H, H(3′), J = 10.2 Hz); 6.41 (d, 1 H, H(7), J = 8.2 Hz); 6.67 (dd, 1 H, H(6), J = 8.2 Hz, J = 2.5 Hz); 6.71 (d, 1 H, H(4), J = 2.5 Hz); 6.86 (d, 1 H, H(4′), J = 10.2 Hz); 7.37 (dd, 1 H, H(8′), J = 8.6 Hz, J = 4.2 Hz); 7.51 (s, 1 H, H(5′)); 8.35 (dd, 1 H, H(7′), J = 8.6 Hz, J = 1.7 Hz); 8.76 (dd, 1 H, H(9′), J = 4.2 Hz,

J = 1.7 Hz); **B-form**: 0.86 (t, 3 H, 5-$OC_{16}H_{33}$, *J* = 6.9 Hz); 1.22—1.28 (m, 24 H, 5-$OC_{16}H_{33}$); 1.44 (m, 2 H, 5-$OC_{16}H_{33}$); 1.71 (s, 6 H, 3-Me); 1.76 (m, 2 H, 5-$OC_{16}H_{33}$); 3.53 (s, 3 H, 1-Me); 3.95 (t, 2 H, 5-$OC_{16}H_{33}$, *J* = 6.6 Hz); 6.69 (d, 1 H, H(4´), *J* = 14.0 Hz); 6.83 (dd, 1 H, H(6), *J* = 8.8 Hz, *J* = 2.2 Hz); 6.87 (d, 1 H, H(3´), *J* = 14.0 Hz); 6.89 (d, 1 H, H(4), *J* = 2.2 Hz); 6.90 (d, 1 H, H(7), *J* = 8.8 Hz); 7.45 (dd, 1 H, H(8´), *J* = 8.2 Hz, *J* = 4.4 Hz); 7.51 (s, 1 H, H(5´)); 8.15 (dd, 1 H, H(7´), *J* = 8.2 Hz, *J* = 1.5 Hz); 8.74 (dd, 1 H, H(9´), *J* = 4.4 Hz, *J* = 1.5 Hz).

6´-Chloro-1-hexadecyloxy-3,3-dimethylspiro[indoline-2,2´-2*H*-pyrano[3,2-*h*]quinoline] (16). The yield was 53%, m.p. 74—75 °C (from hexane). Found (%): C, 75.76; H, 8.63; N, 4.70. $C_{38}H_{51}ClN_2O_2$. Calculated (%): C, 75.66; H, 8.52; N, 4.64. ^{1}H NMR ($CDCl_3$), δ, **A-form**: 0.88 (t, 3 H, 5-$OC_{16}H_{33}$, *J* = 6.9 Hz); 1.21 (s, 3 H, 3-Me); 1.22—1.31 (m, 24 H, 5-$OC_{16}H_{33}$); 1.33 (s, 3 H, 3-Me); 1.47 (m, 2 H, 5-$OC_{16}H_{33}$); 1.76 (m, 2 H, 5-$OC_{16}H_{33}$); 2.74 (s, 3 H, 1-Me); 3.91 (t, 2 H, 5-$OC_{16}H_{33}$, *J* = 6.6 Hz); 5.80 (d, 1 H, H(3´), *J* = 10.2 Hz); 6.43 (d, 1 H, H(7), *J* = 8.2 Hz); 6.70 (dd, 1 H, H(6), *J* = 8.2 Hz, *J* = 2.5 Hz); 6.73 (d, 1 H, H(4), *J* = 2.5 Hz); 6.88 (d, 1 H, H(4´), *J* = 10.2 Hz); 7.34 (s, 1 H, H(5´)); 7.40 (dd, 1 H, H(8´), *J* = 8.5 Hz, *J* = 4.2 Hz); 8.41 (dd, 1 H, H(7´), *J* = 8.6 Hz, *J* = 1.7 Hz); 8.82 (dd, 1 H, H(9´), *J* = 4.2 Hz, *J* = 1.7 Hz); **B-form**: 0.88 (t, 3 H, 5-$OC_{16}H_{33}$, *J* = 6.9 Hz); 1.22—1.31 (m, 24 H, 5-$OC_{16}H_{33}$); 1.47 (m, 2 H, 5-$OC_{16}H_{33}$); 1.73 (s, 6 H, 3-Me); 1.76 (m, 2 H, 5-$OC_{16}H_{33}$); 3.55 (s, 3 H, 1-Me); 3.97 (t, 2 H, 5-$OC_{16}H_{33}$, *J* = 6.6 Hz); 6.70 (d, 1 H, H(4´), *J* = 14.0 Hz); 6.85 (dd, 1 H, H(6), *J* = 8.8 Hz, *J* = 2.2 Hz); 6.89 (d, 1 H, H(3´), *J* = 14.0 Hz); 6.91 (d, 1 H, H(4), *J* = 2.2 Hz); 6.92 (d, 1 H, H(7), *J* = 8.8 Hz); 7.34 (s, 1 H, H(5´)); 7.49 (dd, 1 H, H(8´), *J* = 8.2 Hz, *J* = 4.4 Hz); 8.21 (dd, 1 H, H(7´), *J* = 8.2 Hz, *J* = 1.5 Hz); 8.79 (dd, 1 H, H(9´), *J* = 4.4 Hz, *J* = 1.5 Hz).

1-Benzyl-6´-bromo-3,3-dimethylspiro[indoline-2,2´-2*H*-pyrano[3,2-*h*]quinoline] (17). The yield was 48%, m.p. 176—177 °C (from heptane). Found (%): C, 69.50; H, 4.95; N, 5.91. $C_{28}H_{23}BrN_2O$. Calculated (%): C, 69.57; H, 4.80; N, 5.79. ^{1}H NMR ($CDCl_3$), δ: 1.30 (s, 3 H, C(3)Me); 1.38 (s, 3 H, C(3)Me); 4.36 (d, 1 H, 1-CH_2Ph, *J* = 16.8 Hz); 4.63 (d, 1 H, 1-CH_2Ph, *J* = 16.8 Hz); 5.84 (d, 1 H, H(3´), *J* = 10.2 Hz); 6.30 (d, 1 H, H(7), *J* = 7.7 Hz); 6.82 (d, 1 H, H(4´), *J* = 10.2 Hz); 6.83 (dt, 1 H, H(5), *J* = 7.4 Hz, *J* = 0.9 Hz); 7.02 (dt, 1 H, H(6), *J* = 7.7 Hz, *J* = 1.2 Hz); 7.10 (dd, 1 H, H(4), *J* = 7.3 Hz, *J* = 1.1 Hz); 7.17—7.29 (m, 5 H, 1-CH_2Ph); 7.39 (dd, 1 H, H(8´), *J* = 8.6 Hz, *J* = 4.2 Hz); 7.49 (s, 1 H, H(5´)); 8.36 (dd, 1 H, H(7´), *J* = 8.6 Hz, *J* = 1.6 Hz); 8.80 (dd, 1 H, H(9´), *J* = 4.2 Hz, *J* = 1.6 Hz).

1-Benzyl-6´-chloro-3,3-dimethylspiro[indoline-2,2´-2*H*-pyrano[3,2-*h*]quinoline] (18). The yield was 51%, m.p. 156—157 °C (from heptane). Found (%): C, 76.72; H, 5.43; N, 6.29. $C_{28}H_{23}ClN_2O$. Calculated (%): C, 76.62; H, 5.28; N, 6.38. ^{1}H NMR ($CDCl_3$), δ: 1.30 (s, 3 H, C(3)Me); 1.38 (s, 3 H, C(3)Me); 4.35 (d, 1 H, 1-CH_2Ph, *J* = 16.8 Hz); 4.62 (d, 1 H, 1-CH_2Ph, *J* = 16.8 Hz); 5.85 (d, 1 H, H(3´), *J* = 10.2 Hz); 6.30 (d, 1 H, H(7), *J* = 7.7 Hz); 6.82 (d, 1 H, H(4´), *J* = 10.2 Hz); 6.82 (dt, 1 H, H(5), *J* = 7.4 Hz, *J* = 0.9 Hz); 7.02 (dt, 1 H, H(6), *J* = 7.7 Hz, *J* = 1.2 Hz); 7.10 (dd, 1 H, H(4), *J* = 7.3 Hz, *J* = 1.0 Hz); 7.17—7.29 (m, 5 H, 1-CH_2Ph); 7.30 (s, 1 H, H(5´)); 7.39 (dd, 1 H, H(8´), *J* = 8.6 Hz, *J* = 4.2 Hz); 8.40 (dd, 1 H, H(7´), *J* = 8.6 Hz, *J* = 1.6 Hz); 8.81 (dd, 1 H, H(9´), *J* = 4.2 Hz, *J* = 1.6 Hz).

6´-Bromo-1-(2-hydroxyethyl)-3,3-dimethylspiro[indoline-2,2´-2*H*-[3,2-*h*]quinoline] (19). The yield was 52%, m.p. 171—172 °C (from heptane—toluene, 2.5 : 1). Found (%): C, 63.35; H, 4.67; N, 6.52. $C_{23}H_{21}BrN_2O_2$. Calculated (%): C, 63.17; H, 4.84; N, 6.41. ^{1}H NMR ($CDCl_3$), δ, **A-form**: 1.20 (s, 3 H, 3-Me); 1.34 (s, 3 H, 3-Me); 1.75 (s, 1 H, OH); 3.49—3.87 (m, 4 H, 1-CH_2CH_2OH); 5.77 (d, 1 H, H(3´) *J* = 10.2 Hz); 6.67 (d, 1 H, H(7), *J* = 7.9 Hz); 6.88 (d, 1 H, H(4´), *J* = 10.2 Hz); 6.96 (dt, 1 H, H(5), *J* = 7.4 Hz, *J* = 0.9 Hz); 7.08 (dd, 1 H, H(4), *J* = 7.3 Hz, *J* = 1.0 Hz); 7.17 (dt, 1 H, H(6), *J* = 7.7 Hz, *J* = 1.2 Hz); 7.41 (dd, 1 H, H(8´), *J* = 8.5 Hz, *J* = 4.2 Hz); 7.54 (s, 1 H, H(5´)); 8.37 (dd, 1 H, H(7´), *J* = 8.5 Hz, *J* = 1.6 Hz), 8.76 (dd, 1 H, H(9´), *J* = 4.2 Hz, *J* = 1.6 Hz); **C-form**: 1.22 (s, 3 H, 3-Me); 1.49 (s, 3 H, 3-Me); 3.49—3.87 (m, 4 H, 1-CH_2CH_2OH); 6.52 (d, 1 H, H(3´), *J* = 16.1 Hz); 6.83 (d, 1 H, H(7), *J* = 7.8 Hz); 6.96 (dt, 1 H, H(5), *J* = 7.4 Hz, *J* = 0.9 Hz); 7.10 (dd, 1 H, H(4), *J* = 7.4 Hz, *J* = 1.0 Hz); 7.18 (dt, 1 H, H(6), *J* = 7.7 Hz, *J* = 1.3 Hz); 7.30 (d, 1 H, H(4´), *J* = 16.1 Hz); 7.52 (dd, 1 H, H(8´), *J* = 8.5 Hz, *J* = 4.3 Hz); 7.93 (s, 1 H, H(5´)); 8.43 (dd, 1 H, H(7´), *J* = 8.5 Hz, *J* = 1.5 Hz); 8.64 (s, 1 H, OH); 8.79 (dd, 1 H, H(9´), *J* = 4.3 Hz, *J* = 1.5 Hz).

6´-Chloro-1-(2-hydroxyethyl)-3,3-dimethylspiro[indoline-2,2´-2*H*-pyrano[3,2-*h*]quinoline] (20). The yield was 57%, m.p. 159—160.5 °C (from heptane—toluene, 2.5 : 1). Found (%): C, 70.49; H, 5.50; N, 6.99. $C_{23}H_{21}ClN_2O_2$. Calculated (%): C, 70.31; H, 5.39; N, 7.13. ^{1}H NMR ($CDCl_3$), δ, **A-form**: 1.18 (s, 3 H, 3-Me); 1.33 (s, 3 H, 3-Me); 1.73 (s, 1 H, 1-CH_2CH_2OH); 3.40—3.88 (m, 4 H, 1-CH_2CH_2OH); 5.75 (d, 1 H, H(3´), *J* = 10.2 Hz); 6.64 (d, 1 H, H(7), *J* = 7.8 Hz); 6.86 (d, 1 H, H(4´), *J* = 10.2 Hz); 6.94 (dt, 1 H, H(5), *J* = 7.4 Hz, *J* = 0.9 Hz); 7.06 (dd, 1 H, H(4), *J* = 7.3 Hz, *J* = 0.9 Hz); 7.15 (dt, 1 H, H(6), *J* = 7.7 Hz, *J* = 1.2 Hz); 7.33 (s, 1 H, H(5´)); 7.39 (dd, 1 H, H(8´), *J* = 8.6 Hz, *J* = 4.2 Hz); 8.39 (dd, 1 H, H(7´), *J* = 8.6 Hz, *J* = 1.7 Hz); 8.78 (dd, 1 H, H(9´), *J* = 4.2 Hz, *J* = 1.6 Hz); **C-form**: 1.20 (s, 3 H, 3-Me); 1.47 (s, 3 H, 3-Me); 3.40—3.88 (m, 4 H, 1-CH_2CH_2OH); 6.50 (d, 1 H, H(3´), *J* = 16.1 Hz); 6.81 (d, 1 H, H(7), *J* = 7.9 Hz); 6.94 (dt, 1 H, H(5), *J* = 7.4 Hz, *J* = 0.9 Hz); 7.08 (dd, 1 H, H(4), *J* = 7.3 Hz, *J* = 0.9 Hz); 7.16 (dt, 1 H, H(6), *J* = 7.7 Hz, *J* = 1.2 Hz); 7.30 (d, 1 H, H(4´), *J* = 16.1 Hz); 7.51 (dd, 1 H, H(8´), *J* = 8.5 Hz, *J* = 4.3 Hz); 7.72 (s, 1 H, H(5´)); 8.46 (dd, 1 H, H(7´), *J* = 8.5 Hz, *J* = 1.5 Hz); 8.57 (s, 1 H, OH); 8.79 (dd, 1 H, H(9´), *J* = 4.3 Hz, *J* = 1.5 Hz).

6´-Bromo-1-(2-carboxyethyl)-3,3-dimethylspiro[indoline-2,2´-2*H*-[3,2-*h*]quinoline] (21). The yield was 50%, m.p. 206—207 °C (from diethyl ketone). Found (%): C, 62.10; H, 4.45; N, 6.11. $C_{24}H_{21}BrN_2O_3$. Calculated (%): C, 61.95; H, 4.55; N, 6.02. ^{1}H NMR (DMSO-d_6), δ: 1.06 (s, 3 H, 3-Me); 1.17 (s, 3 H, 3-Me); 2.49 (m, 2 H, 1-CH_2CH_2COOH); 4.39 (m, 2 H, 1-CH_2CH_2COOH); 5.91 (d, 1 H, H(3´), *J* = 10.2 Hz); 6.64 (d, 1 H, H(7), *J* = 7.7 Hz); 6.79 (dt, 1 H, H(5), 5-H, *J* = 7.3 Hz, *J* = 0.9 Hz); 7.09 (dd, 1 H, H(4), *J* = 7.3 Hz, *J* = 0.9 Hz); 7.12 (dt, 1 H, H(6), 6-H, *J* = 7.6 Hz, *J* = 1.2 Hz); 7.13 (d, 1 H, H(4´), *J* = 10.2 Hz); 7.57 (dd, 1 H, H(8´), *J* = 8.6 Hz, *J* = 4.2 Hz); 7.84 (s,1 H, H(5´)); 8.33 (dd, 1 H, H(7´), *J* = 8.6 Hz, *J* = 1.5 Hz); 8.75 (dd, 1 H, H(9´), *J* = 4.2 Hz, *J* = 1.5 Hz).

1-(2-Carboxyethyl)-6´-chloro-3,3-dimethylspiro[indoline-2,2´-2*H*-pyrano[3,2-*h*]quinoline] (22). The yield was 54%, m.p. 203—204 °C (from diethyl ketone). Found (%): C, 68.65; H, 4.92; N, 6.73. $C_{24}H_{21}ClN_2O_3$. Calculated (%): C, 68.49; H, 5.03; N, 6.66. ^{1}H NMR (DMSO-d_6), δ: 1.09 (s, 3 H, 3-Me); 1.19 (s, 3 H, 3-Me); 2.50 (m, 2 H, 1-CH_2CH_2COOH); 4.42 (m, 2 H, 1-CH_2CH_2COOH); 5.94 (d, 1 H, H(3´), *J* = 10.2 Hz); 6.66 (d, 1 H, H(7), *J* = 7.7 Hz); 6.81 (dt, 1 H, H(5), *J* = 7.3 Hz, *J* = 0.9 Hz); 7.12 (dd, 1 H, H(4), *J* = 7.3 Hz, *J* = 0.9 Hz); 7.14 (dt, 1 H, H(6), *J* = 7.6 Hz, *J* = 1.2 Hz); 7.15 (d, 1 H, H(4´), *J* = 10.2 Hz); 7.60 (dd, 1 H, H(8´), *J* = 8.6 Hz, *J* = 4.2 Hz); 7.69 (s, 1 H, H(5´)); 8.41 (dd, 1 H,

H(7′), J = 8.6 Hz, J = 1.6 Hz); 8.80 (dd, 1 H, H(9′), J = 4.2 Hz, J = 1.6 Hz).

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