Synthesis and structure of indoline spiropyrans of the coumarin series

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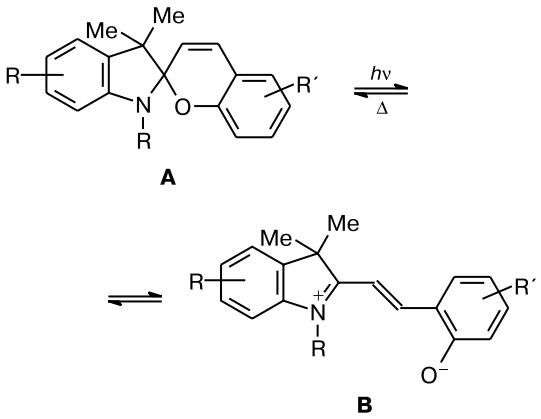
New indoline spiropyrans of the coumarin series were synthesized by the condensation of indoline and hydroxyformylcoumarin derivatives. Spiropyrans, *viz.*, derivatives of 8-formyl-7-hydroxy-4-methylcoumarin and 5-formyl-6-hydroxy-4-methylcoumarin, under irradiation are transformed into open forms, which are recyclized in the dark. The compounds formed by the condensation of the indoline derivatives with 3-formyl-4-hydroxycoumarin have an open structure of the merocyanine dyes and are transformed into spiro forms neither in the dark nor under irradiation with the visible light.

Key words: spiropyrans, indole and coumarin derivatives, photochromic properties, merocyanine derivatives.

Indoline spiropyrans and their heteroanalogs are known as intensely studied photochromic compounds.[1—9] Interest in them is caused by prospects of their use in different areas of molecular electronics: optical systems of information recording and storage, dynamic chemo- and biosensors, in systems of solar energy accumulation, transportation systems, catalysis, *etc*.

The photochromic properties of indoline spiropyrans are based on the photoinduced reaction of pyran ring opening followed by the thermal *cis—trans* isomerization of the open form with the formation of colored merocyanine and the subsequent thermal or photochemical recyclization of the open form to the starting colorless spiro compound. The mutual transformations of the spiro (**A**) and open (**B**) forms are shown in Scheme 1 for substituted spiro[2*H*-1-benzopyran-2,2′-indoline].

Scheme 1



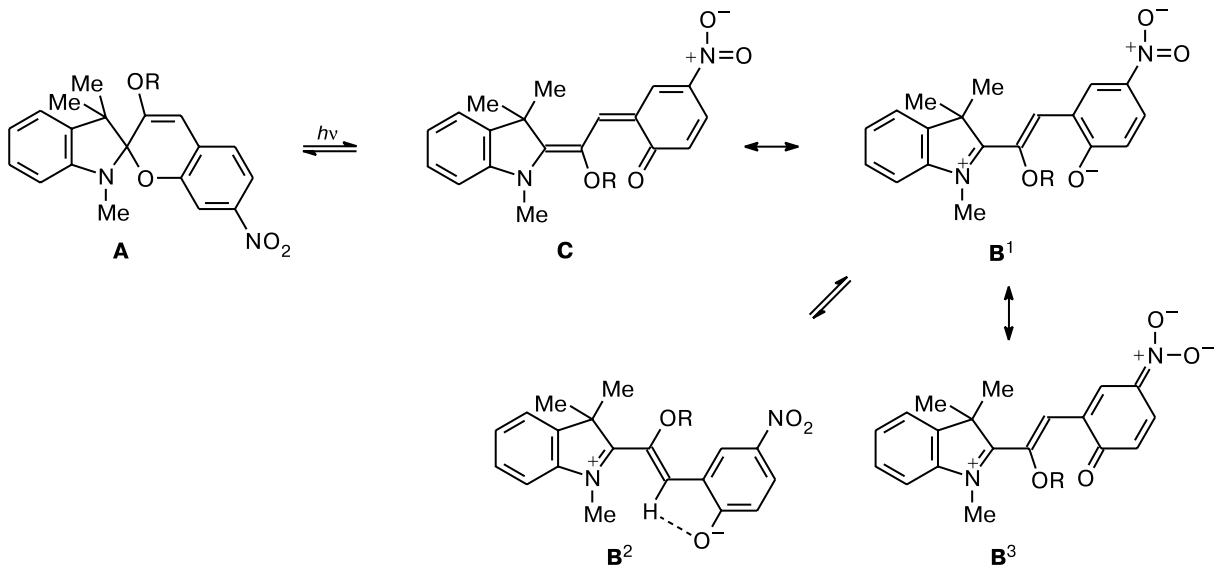
The important parameters of the photochromic properties are the absorption wavelength of the open form, the lifetime of this form, and the quantum yield of the photoreaction. A change in the structure of the spiro derivative exerts a substantial effect on these parameters. The role of one of the structural factors is shown in Scheme 2: the nature of the substituent in the benzopyran moiety of spiro[2*H*-1-benzopyran-2,2′-indoline]. The introduction of a strong electron-acceptor (nitro group) into the benzopyran fragment leads to the resonance delocalization of a negative charge, which is formed upon pyran ring opening and, thus, to an increase in the lifetime of the open form of spiropyran. Structure **B**[2], which contains a hydrogen bond, and quinoid structure **B**[3] introduce, most likely, the maximum contribution to the stabilization of the open form of merocyanine.

Numerous published data are available on the influence of both substituents in the fused benzene rings and different heteroatoms in the indoline and benzopyran moieties on the photochromic properties. In particular, spiro compounds containing benzoxazine or naphthoxazine fragments instead of the benzopyran fragment were synthesized and studied.[1,5,6]

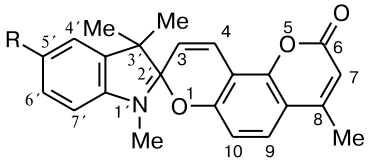
The syntheses of some representatives of indoline spiropyrans of the coumarin series have previously been reported.[10—13] However, details of the syntheses and methods for identification of the corresponding compounds are not presented in the literature. We planned to prepare a series of spiropyrans **1**—**3** for the systematic study of the

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2342—2349, October, 2005.

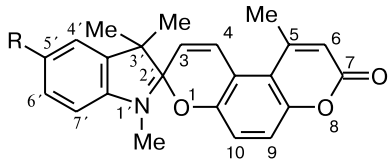
Scheme 2



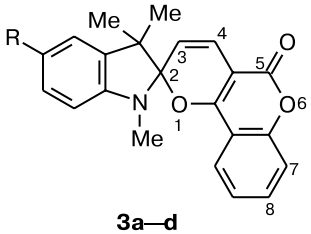
influence of the coumarin component on the photochromic properties of indoline spiropyrans of this type. 8-Formyl-7-hydroxy-4-methylcoumarin, 5-formyl-6-hydroxy-4-methylcoumarin, and 3-formyl-4-hydroxycoumarin were used as coumarin components in the synthesis of spiropyrans **1a**—**e** and **2a**—**c** and expected spirans **3a**—**d**, respectively.



1a—e



2a—c



3a—d

R = H(**a**), Me (**b**), Br (**c**), NO_2 (**d**), MeO (**e**)

Results and Discussion

Spiropyrans **1**, **2**, and **3** were synthesized by the Wizinger—Wennig method[14], which includes the condensation of Fischer´s base (or its heterocyclic analog) with formylhydroxycoumarin. Despite structural differences of the coumarin derivatives used, spiropyrans **1** and **2** are formed *via* the general scheme of nucleophilic addition of heterocyclic enamine to the formyl group of formylhydroxycoumarin. This reaction occurs during reflux of equimolar amounts of substituted indolenine and coumarin derivative in ethanol (Scheme 3) (the spirocyclization mechanism is discussed in detail below).

Indolenines, which are necessary for the synthesis of spiropyrans **1**—**3**, were prepared from aniline and its *p*-substituted derivatives[15—18] similarly to the method shown in Scheme 4.

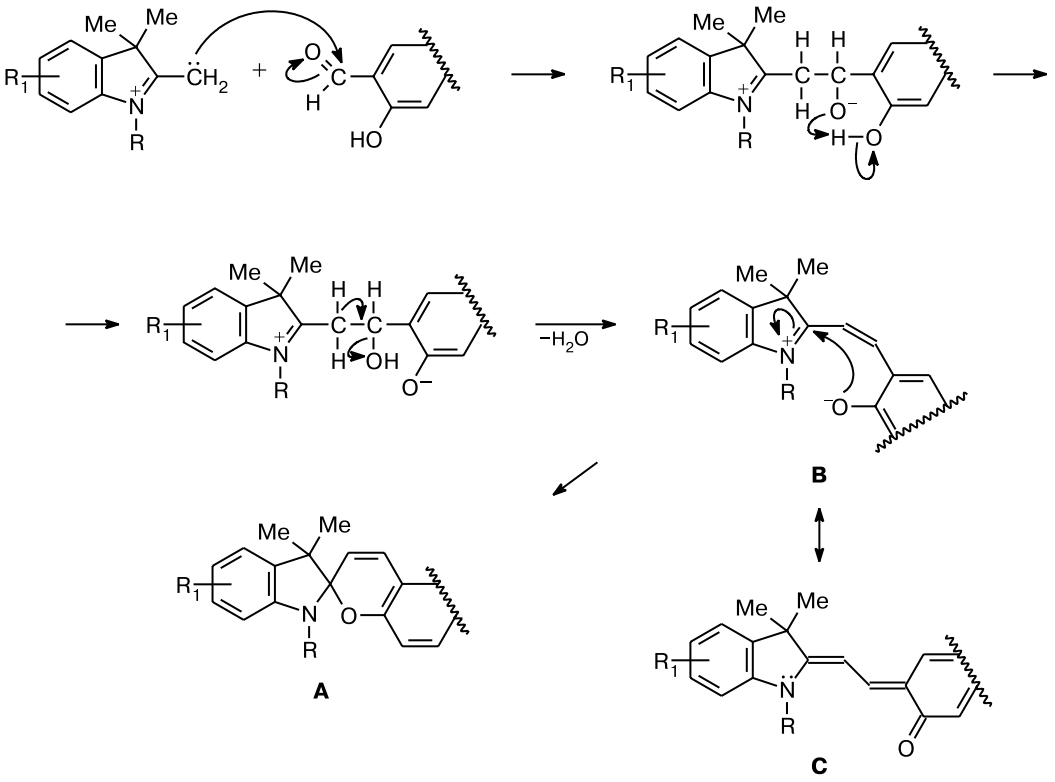
The formylhydroxycoumarins were synthesized by the formylation of 7-hydroxy-4-methyl-, 6-hydroxy-4-methyl-, and 4-hydroxycoumarins, respectively.[19—21]

As a rule, the Wizinger—Wennig condensation is carried out in ethanol, methanol, dimethylformamide, or methyl ethyl ketone. We used anhydrous ethanol, because both methylene bases and formylhydroxycoumarins are highly soluble and indoline spiropyrans that formed are easily precipitated in this alcohol.

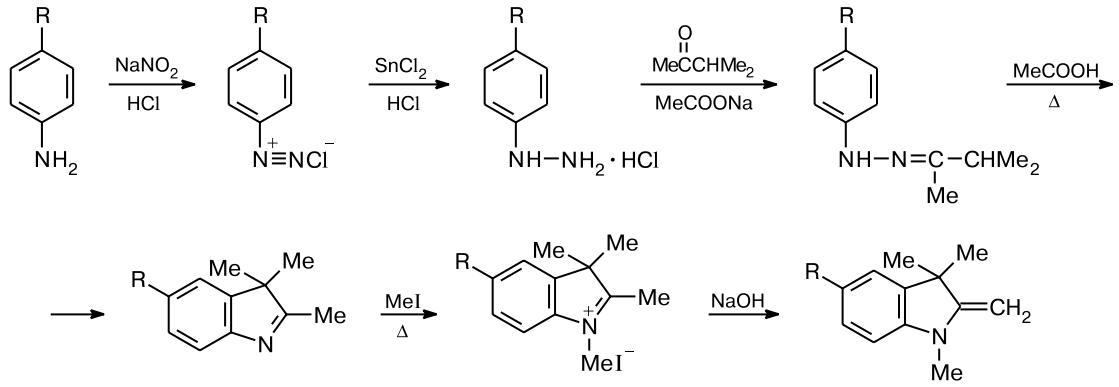
The structures of compounds **1**, **2**, and **4** were studied by ^{1}H NMR and electronic absorption spectroscopy, taking into account that they can exist in both the cyclic (spiro) and open forms. The data of their ^{1}H NMR spectra, which are characteristic of the spiro and open forms, are given in Table 1.

The high-field region of the ^{1}H NMR spectra of spiropyrans **1** and **2** exhibits two signals from the magnetically nonequivalent (due to the nonsymmetric spiro atom) geminal Me groups, which indicates the cyclic structure of these compounds. The methyl groups in position 3´ of

Scheme 3



Scheme 4



R = H, Me, Br, NO_2, MeO

the indoline moiety of spiropyrans **1** and **2** give two three-proton singlets at 1.18—1.35 ppm. Differences in chemical shifts Δδ of these singlet signals depend on the position and nature of the substituent, being 0.05—0.08 ppm. This signal of the *N*-methyl substituent of spiropyrans **1** and **2** is observed at 2.68—2.87 ppm.

The low-field region of the spectrum of spiropyrans **1** contains three groups of signals. One group of four or three protons is assigned to the benzene ring of the indoline fragment (containing no substituent or containing one substituent, respectively). There are two groups of two interacting nuclei, one of which corresponds to the methine protons of the C(3)H=C(4)H double bond, and the second group is attributed to the H(9) and H(10) aromatic protons of the benzene ring in the coumarin fragment.

The signals of the H(4′), H(5′), H(6′), and H(7′) protons of the indoline fragment in spiropyran **1a** have

Table 1. Parameters of the ^{1}H NMR spectra of compounds **1**, **2**, and **4**, which are specific for the spiro and open forms

Compound	δ (*J*/Hz)		
	CMe_2, s	NMe, s	H(3), H(4)*, H(2), H(1)**; d
1a	1.20, 1.30	2.75	5.81, 7.48 (*J* = 10.7)
1b	1.20, 1.28	2.72	5.81, 7.48 (*J* = 10.4)
1c	1.18, 1.27	2.71	5.78, 7.48 (*J* = 10.4)
1d	1.23, 1.35	2.87	5.80, 7.54 (*J* = 10.4)
1e	1.18, 1.28	2.68	5.79, 7.46 (*J* = 10.7)
2a	1.18, 1.32	2.70	5.85, 7.60 (*J* = 10.7)
2b	1.20, 1.30	2.70	5.85, 7.59 (*J* = 10.7)
2c	1.18, 1.25	2.68	5.78, 7.48 (*J* = 10.4)
4a	1.78	3.62	7.64, 9.03 (*J* = 14.7); 8.24, 8.82 (*J* = 14.7)
4b	1.75	3.62	7.64, 9.03 (*J* = 14.7); 8.22, 8.80 (*J* = 14.7)
4c	1.78	3.58	7.60, 9.01 (*J* = 14.7); 8.16, 8.80 (*J* = 14.7)
4d	1.82	3.63	7.65, 9.03 (*J* = 14.3); 8.05, 8.85 (*J* = 14.3)

* H(3) and H(4) for compounds **1a**—**e** and **2a**—**c**.
** H(2) and H(1) for compounds **4a**—**d**.

splittings characteristic of the ABCD system and are observed as a multiplet at 6.54—7.20 ppm.

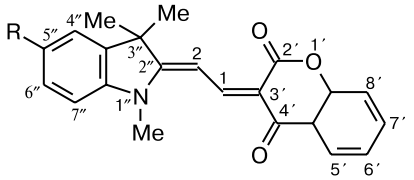
The H(4′), H(6′), and H(7′) protons of the benzene ring in the indoline moiety of 5′-substituted spiropyrans **1** are observed as a singlet and two doublets. For instance, in the spectrum of compound **1b**, the signals of these protons are detected at 6.88, 6.98, and 6.43 ppm, respectively. The signals of the H(3) and H(4) protons of the double bond in the pyran ring of **1** are detected as two doublets at 5.78—5.81 and 7.46—7.54 ppm, respectively. In the spectrum of spiropyrans **1**, the signals of the H(9) and H(10) protons of the benzene ring in the coumarin fragment are observed as two doublets at 7.33—7.38 and 6.53—6.68 ppm, respectively.

The ^{1}H NMR spectra of spiropyrans **2** are similar to those of spiropyrans **1**. The signals of the H(4′), H(5′), H(6′), and H(7′) protons of the indoline fragment in spiropyran **2a** have splittings characteristic of the ABCD system and are observed as a multiplet at 6.52—7.08 ppm.

The H(4′) and H(6′) protons in the indoline moiety of 5′-substituted spiropyrans **2** are observed as a multiplet at 6.92—7.22 ppm, and the H(7′) proton appears as a doublet at 6.38—6.43 ppm.

The signals of the H(3) and H(4) protons of the double bond in the pyran ring are detected as two doublets at 5.78—5.85 and 7.48—7.60 ppm, respectively. The signals of the H(9) and H(10) protons of the benzene ring of the coumarin moiety in the spectra of spiropyrans **2** are observed as two doublets at 7.22—7.36 and 6.67—6.92 ppm, respectively.

An analysis of the ^{1}H NMR spectra of compounds, which were synthesized from 3-formyl-4-hydroxycoumarin and 5-substituted 1,3,3-trimethyl-2-methyleneindolines, showed that these compounds exist in the open form **4a**—**d** rather than in the spiro form **3**.

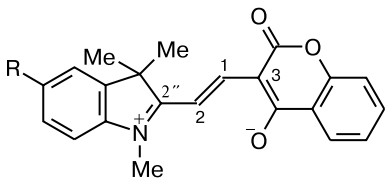


4a—d

R = H(**a**), Me (**b**), Br (**c**), NO_2 (**d**)

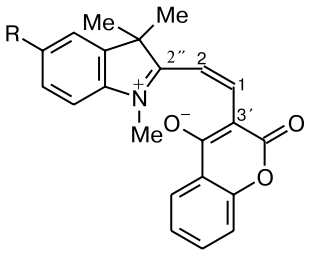
It turned out that the methyl groups in position 3″ of the indoline fragment of compounds **4** give one six-proton singlet at 1.75—1.82 ppm. The character of the signal of these protons indicate unambiguously in favor of the open form in which these compounds exist in solution. The low-field part of the spectrum of compounds **4** exhibits two groups of mutually related signals. One group of four or three protons is assigned to the benzene ring of the indoline fragment (containing no substituents or containing one substituent). One of the two other groups of interacting protons corresponds to the H(1) and H(2) methine protons (see Table 1), and the second group corresponds to the H(5′), H(6′), H(7′), and H(8′) protons attributed to the coumarin moiety.

It was unexpected that the analysis of the ^{1}H NMR spectra of compounds **4** revealed four doublets of the H(2) and H(1) protons (that correspond to the H(3) and H(4) methine protons of the expected structure **3**) with a relative intensity of signals of 1.3 : 1. A possibility that merocyanines **5** exist in the *trans*- and *cis*-forms can be



trans-**5**

ΔH_f = –8.79 kcal mol^{-1}



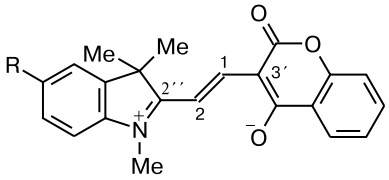
cis-**5**

ΔH_f = –1.45 kcal mol^{-1}

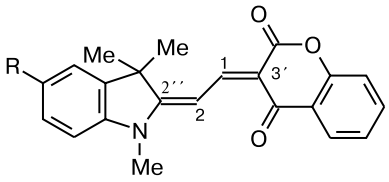
assumed as a reason for this fact. However, as shown by quantum chemical calculations by the standard AM1 procedure, the energy of formation of the *cis*-isomer is much higher than that of the *trans*-isomer and, therefore, a considerable predomination of the *trans*-isomer could be expected in the step of formation of the central double bond.

In addition, the *trans*- and *cis*-isomers of the merocyanine form should differ noticeably by spin-spin coupling constants of the *trans*- and *cis*-protons. However, no difference is observed in the spectra of compounds **4** synthesized: both groups of doublets have the same constants, for instance, $J = 14.7$ Hz for **4a**,**b**.

By analogy to other merocyanines,[22] compounds **4** can exist in both bipolar **B** and quinoid **C** forms.



B



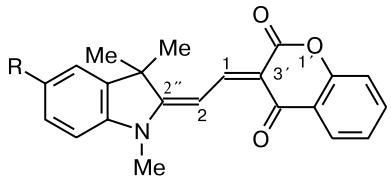
C

According to the positive charge on the cyclic nitrogen atom, bipolar form **B** should differ by a considerable downfield shift of signals of the protons of the indolenine fragment. However, this shift is not observed in the ^{1}H NMR spectra. For example, in the spectrum of **1a**, signals of the benzene protons of the indolenine fragment are observed at 6.54—7.20 ppm, while they are at 6.92—7.29 ppm in the spectrum of compound **4a**. The downfield shift of signals of the protons of the *N*-methyl groups is not so high: in the spectra of compounds **4**, the shift is observed at 3.58—3.63 ppm instead of 2.68—2.87 ppm, *e.g.*, in the spectra of spiropyrans **1**.

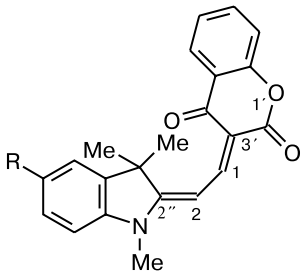
It seems rather probable that the quinoid structure of the synthesized merocyanines exists as two isomers relative to the C(1)—C(2) central ordinary bond.

However, the spin-spin coupling constants of the H(2) and H(1) protons should differ considerably for these isomers. In addition, they have substantially different values of the standard energies of formation calculated by the AM1 method.

In our opinion, the most adequate explanation of the existence of two doublets attributed to the H(1) and H(2) methine protons in the spectra of compounds **4** is a possibility of the merocyanine form to exist in different configurations relative not to the C(1)—C(2) central bond



(*S*)-*trans*



(*S*)-*cis*

but to two C(2′′)—C(2) and C(1)—C(3′) double bonds (Scheme 5).

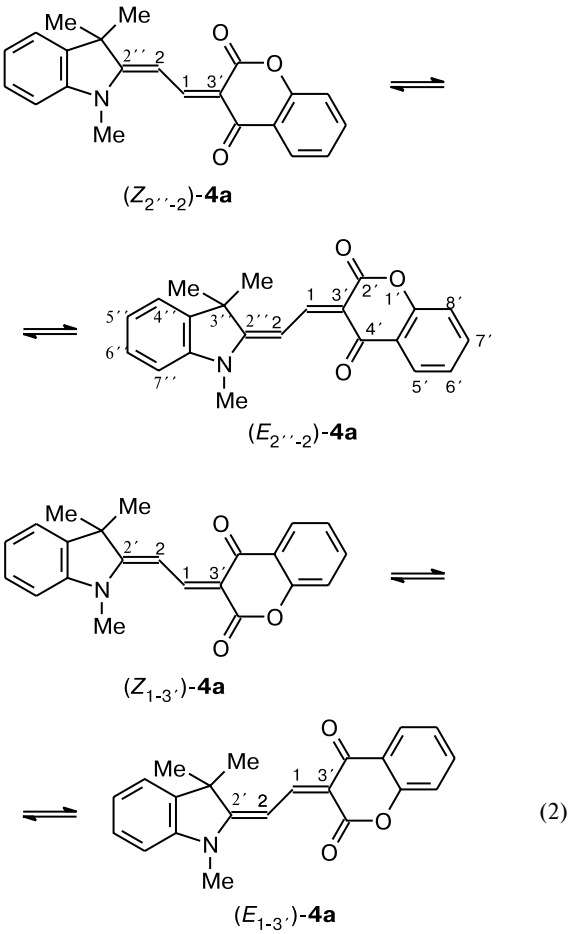
All of the four configurations should have similar spin-spin coupling constants of the H(1)—H(2) protons (in each of the structures shown, they are in the *trans*-position toward each other) and differ insignificantly by the calculated values of the standard energies of formation. The $Z_{2''\text{-}2}$-**4a** and $Z_{1\text{-}3'}$-**4a** configurations are the most stable and similar in ΔH_f values.

It should be mentioned that in a series of experiments in different solvents ($CDCl_3$, DMSO-d_6, and $CDCl_3$—DMSO-d_6 (1 : 1) mixture) at different temperatures (293, 303, 313, and 323 K) the character of the ^{1}H NMR spectra of compounds **4** undergo no substantial changes, and the relative intensity of signals of doublets depends only insignificantly on the substituent in position 5′′ of the indoline fragment.

The data on the electronic absorption spectra agree with the data of the ^{1}H NMR spectra and indicate unambiguously that compounds **1** and **2** exist in solution in the cyclic spiran form before irradiation, whereas compounds **4** exist in the open (merocyanine) form. The absorption spectra of compounds **1a**, **2a**, and **4a** are shown in Fig. 1 (curves *a*—*c*, respectively). In the complete agreement with the cyclic structure of compounds **1a** and **2a**, their solutions absorb predominantly in the near-UV region. By contrast, compound **4a** has an absorption maximum in the visible region of the electronic spectrum, which is characteristic of absorption of merocyanine dyes. All compounds **1**, **2**, and **4** possess pronounced fluorescence properties. Their fluorescence spectra are compared to the electronic absorption spectra in Fig. 1.

Let us consider the spirocyclization mechanism (see Scheme 3) to understand reasons for the formation of different reaction products of the Wizinger—Wennig condensation using 7- and 6-hydroxyformylcoumarins.

Scheme 5



Note. In the case of equilibrium (1), the *E*/*Z*-isomers relative to the C(2″)—C(2) bond are formed, $\Delta H°_f$ = –9.68 ($Z_{2''\text{-}2}$-**4a**), –8.79 kcal mol^{-1} ($E_{2''\text{-}2}$-**4a**); in the case of equilibrium (2), the *E*/*Z*-isomers relative to the C(1)—C(3) bond are formed, $\Delta H°_f$ = –9.66 ($Z_{1\text{-}3'}$-**4a**), ΔH_f = –9.54 kcal mol^{-1} ($E_{1\text{-}3'}$-**4a**).

The first and second steps of Scheme 3, namely, nucleophilic addition of enamine to the formyl group of coumarin and dehydration of the adduct that formed to merocyanine **B**, proceed, most likely, with the same easiness for each coumarin aldehyde.

Success of the final step of spirocyclization, *viz.*, intramolecular nucleophilic addition of the hydroxy group of the coumarin fragment to the immonium ion (structure **B**), depends, most likely, on the degree of negative charge delocalization on the oxygen atom of the hydroxy group. In the 7- and 6-hydroxycoumarin derivatives, this hydroxy group is sufficiently nucleophilic for an efficient attack of the α-C atom of the immonium fragment leading to the formation of spiro compound **A**.

In the derivatives of 4-hydroxycoumarin (which is a much stronger OH acid), the negative charge of the hydroxy group is substantially lower (a high contribution of resonance structure **C**) and insufficient for the completion of spirocyclization. According to this, the process

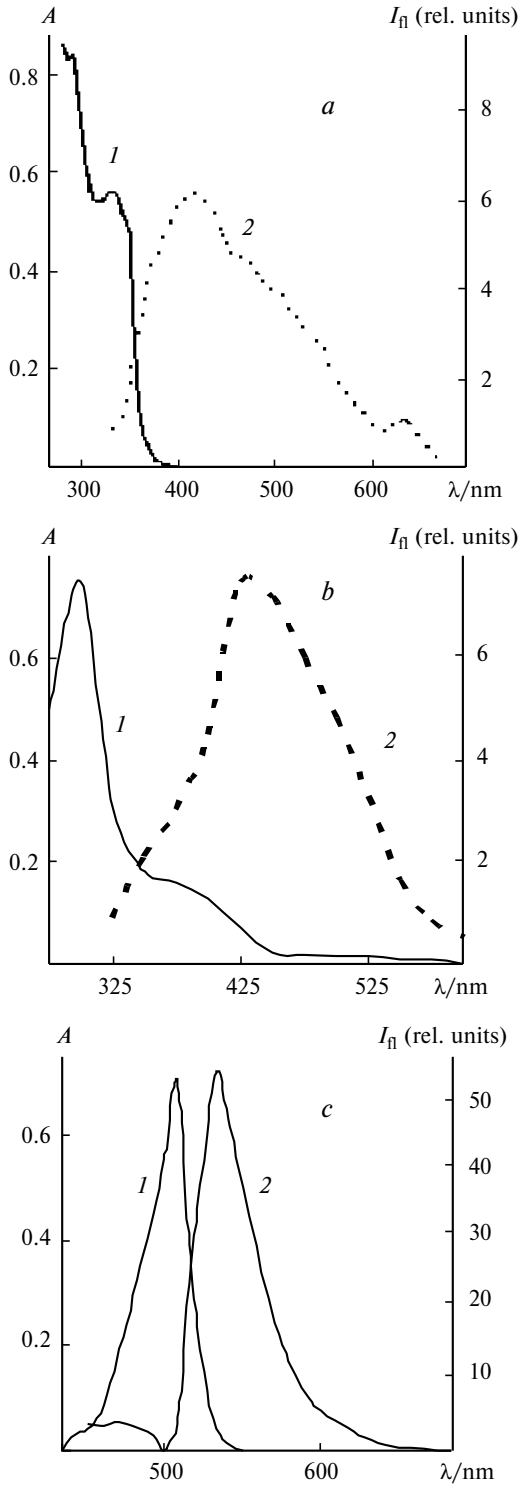


Fig. 1. Absorption (*1*) and fluorescence (*2*) spectra (C = $0.5 \cdot 10^{-4}$ mol L^{-1}) of compound **1a** in toluene (*a*), compound **2a** in toluene (*b*), and compound **4a** in benzene (*c*).

ceases at the step of formation of the corresponding merocyanine **C**.

Experimental

^{1}H NMR spectra were recorded in $CDCl_3$, DMSO-d_6, and a $CDCl_3$—DMSO-d_6 (1 : 1) mixture on a Bruker WP-200-SY spectrometer with a working frequency of 200 MHz at different temperatures of 293, 303, 313, and 323 K. IR spectra were measured on a Specord M-80 spectrophotometer in KBr pellets. Electron absorption spectra were obtained on a Specord M-400 spectrophotometer in ethanol in a 1-cm cell. Mass spectra were recorded on a GCQ mass spectrometer at an energy of ionizing electrons of 70 eV and a temperature of the source of 200 °C.

Synthesis of indoline spiropyrans 1a—e and 2a—c (general procedure). A mixture of 8-formyl-7-hydroxy-4-methylcoumarin[19] (or 5-formyl-6-hydroxy-4-methylcoumarin[20]) (0.56 g, 0.0027 mol) and anhydrous ethanol (10 mL) was heated until the coumarin derivative dissolved completely. 1,3,3-Trimethyl-2-methyleneindoline[15] (0.44 g, 0.0027 mol) was added to the resulting solution, and the mixture was refluxed for 5.5 h, cooled, and left for 18 h at 20 °C. Then water was added to the reaction mixture until a precipitate was formed. The precipitate was filtered off, dried, and recrystallized from dilute ethanol.

8,1′,3′,3′-Tetramethylspiro[indoline-2,2′-[2*H*,6*H*]pyrano[6,5-*f*][1]-benzopyran-6-one] (1a). The yield was 85%, m.p. 123—124 °C. ^{1}H NMR ($CDCl_3$), δ: 2.75 (s, 3 H, NMe); 1.20, 1.30 (both s, 6 H, C(3′)Me_2); 6.54—7.20 (m, 4 H, H(4′), H(5′), H(6′), H(7′)); 5.81 (d, 1 H, H(3), $J_{3,4}$ = 10.7 Hz); 7.48 (d, 1 H, H(4), $J_{4,3}$ = 10.7 Hz); 6.12 (s, 1 H, H(7)); 2.35 (s, 3 H, C(8)Me); 7.34 (d, 1 H, H(9), $J_{9,10}$ = 8.9 Hz); 6.68 (d, 1 H, H(10), $J_{10,9}$ = 8.9 Hz). IR, ν/cm^{-1}: 1735 (α-pyron), 1646 (C=C), 951 (C—O). Absorption spectrum, λ_{max}/nm (logε): 555 (2.65). Mass spectrum, *m*/*z* (I_{rel} (%)): 359 (10). Found (%): C, 76.17; H, 5.98; N, 3.88. $C_{23}H_{21}NO_3$. Calculated (%): C, 76.88; H, 5.85; N, 3.90.

8,1′,3′,3′,5′′-Pentamethylspiro[indoline-2,2′-[2*H*,6*H*]pyrano[6,5-*f*][1]-benzopyran-6-one] (1b). The yield was 55%, m.p. 112—113 °C. ^{1}H NMR ($CDCl_3$), δ: 2.72 (s, 3 H, NMe); 1.20, 1.28 (both s, 6 H, C(3′)Me_2); 6.88 (s, 1 H, H(4′)); 2.33 (s, 1 H, C(5′)Me); 6.98 (d, 1 H, H(6′), $J_{6',7'}$ = 7.9 Hz); 6.43 (d, 1 H, H(7′), $J_{7',6'}$ = 7.9 Hz); 5.81 (d, 1 H, H(3), $J_{3,4}$ = 10.4 Hz); 7.48 (d, 1 H, H(4), $J_{4,3}$ = 10.4 Hz); 6.15 (s, 1 H, H(7)); 2.39 (s, 3 H, C(8)Me); 7.34 (d, 1 H, H(9), $J_{9,10}$ = 8.9 Hz); 6.68 (d, 1 H, H(10), $J_{10,9}$ = 8.9 Hz). IR, ν/cm^{-1}: 1733 (α-pyron), 1646 (C=C), 951 (CO). Absorption spectrum, λ_{max}/nm (logε): 560 (3.07). Mass spectrum, *m*/*z* (I_{rel} (%)): 373 (14). Found (%): C, 76.39; H, 6.32; N, 3.92. $C_{24}H_{23}NO_3$. Calculated (%): C, 77.21; H, 6.17; N, 3.75.

5′-Bromo-8,1′,3′,3′-tetramethylspiro[indoline-2,2′-[2*H*,6*H*]pyrano[6,5-*f*][1]-benzopyran-6-one] (1c). The yield was 78%, m.p. 196—197 °C. ^{1}H NMR ($CDCl_3$), δ: 2.71 (s, 3 H, NMe); 1.18, 1.27 (both s, 6 H, C(3′)Me_2); 7.16 (d, 1 H, H(4′), $J_{4',6'}$ = 1.8 Hz); 7.29 (d, 1 H, H(6′), $J_{6',7'}$ = 8.2 Hz); 6.41 (d, 1 H, H(7′), $J_{7',6'}$ = 8.2 Hz); 5.78 (d, 1 H, H(3), $J_{3,4}$ = 10.4 Hz); 7.48 (d, 1 H, H(4), $J_{4,3}$ = 10.4 Hz); 6.13 (s, 1 H, H(7)); 2.38 (s, 3 H, C(8)Me); 7.35 (d, 1 H, H(9), $J_{9,10}$ = 8.8 Hz); 6.67 (d, 1 H, H(10), $J_{10,9}$ = 8.8 Hz). IR, ν/cm^{-1}: 1733 (α-pyron), 1647 (C=C), 952 (C—O). Absorption spectrum, λ_{max}/nm (logε): 557 (2.63). Mass spectrum, *m*/*z* (I_{rel} (%)): 437/439 (44/24). Found (%): C, 62.97; H, 4.56; N, 3.30. $C_{23}H_{20}NO_3Br$. Calculated (%): C, 63.01; H, 4.57; N, 3.20.

8,1′,3′,3′-Tetramethyl-5′-nitrospiro[indoline-2,2′-[2*H*,6*H*]pyrano[6,5-*f*][1]-benzopyran-6-one] (1d). The yield was 61%, m.p. 191—192 °C. ^{1}H NMR ($CDCl_3$), δ: 2.87 (s, 3 H, NMe); 1.23, 1.35 (both s, 6 H, C(3′)Me_2); 6.89 (s, 1 H, H(4′)); 8.20 (d, 1 H, H(6′), $J_{6',7'}$ = 8.5 Hz); 6.70 (d, 1 H, H(7′), $J_{7',6'}$ = 8.5 Hz); 5.80 (d, 1 H, H(3), $J_{3,4}$ = 10.4 Hz); 7.54 (d, 1 H, H(4), $J_{4,3}$ = 10.4 Hz); 6.15 (s, 1 H, H(7)); 2.38 (s, 3 H, C(8)Me); 7.38 (d, 1 H, H(9) $J_{9,10}$ = 8.9 Hz); 6.53 (d, 1 H, H(10), $J_{10,9}$ = 8.9 Hz). IR, ν/cm^{-1}: 1735 (α-pyron), 1647 (C=C), 949 (C—O). Absorption spectrum, λ_{max}/nm (logε): 350 (4.34). Mass spectrum, *m*/*z* (I_{rel} (%)): 404 (26). Found (%): C, 67.35; H, 4.96; N, 6.78. $C_{23}H_{20}N_2O_5$. Calculated (%): C, 68.32; H, 4.95; N, 6.93.

8,1′,3′,3′-Tetramethyl-5′-methoxyspiro[indoline-2,2′-[2*H*,6*H*]pyrano[6,5-*f*][1]benzopyran-6-one] (1e). The yield was 92%, m.p. 198—199 °C. ^{1}H NMR ($CDCl_3$), δ: 2.68 (s, 3 H, NMe); 1.18, 1.28 (both s, 6 H, C(3′)Me_2); 3.80 (s, 1 H, 5′-OMe); 6.45 (d, 1 H, H(7′), $J_{7',6'}$ = 9.1 Hz); 5.79 (d, 1 H, H(3), $J_{3,4}$ = 10.7 Hz); 7.46 (d, 1 H, H(4), $J_{4,3}$ = 10.7 Hz); 6.12 (s, 1 H, H(7)); 2.35 (s, 3 H, C(8)Me); 7.33 (d, 1 H, H(9), $J_{9,10}$ = 8.5 Hz); 6.65—6.78 (m, H(4′), H(6′), H(10)). IR, ν/cm^{-1}: 1730 (α-pyron), 1646 (C=C), 952 (CO). Absorption spectrum, λ_{max}/nm (logε): 558 (3.22). Mass spectrum, *m*/*z* (I_{rel} (%)): 389 (20). Found (%): C, 73.99; H, 5.90; N, 3.82. $C_{24}H_{23}NO_4$. Calculated (%): C, 74.04; H, 5.91; N, 3.60.

5,1′,3′,3′-Tetramethylspiro[indoline-2,2′-[2*H*,7*H*]pyrano[5,6-*f*][1]benzopyran-7-one] (2a). The yield was 88%, m.p. 224—225 °C. ^{1}H NMR ($CDCl_3$), δ: 2.70 (s, 3 H, NMe); 1.20, 1.32 (both s, 6 H, C(3′)Me_2); 6.52—7.08 (m, 4 H, H(4′); H(5′), H(6′), H(7′)); 5.85 (d, 1 H, H(3), $J_{3,4}$ = 10.7 Hz); 7.60 (d, 1 H, H(4), $J_{4,3}$ = 10.7 Hz); 2.65 (s, 3 H, C(5)Me); 6.28 (s, 1 H, H(6)); 7.02—7.18 (m, 2 H, H(9), H(10)). IR, ν/cm^{-1}: 1728 (α-pyron), 1646 (C=C), 975 (CO). Absorption spectrum, λ_{max}/nm (logε): 552 (3.04). Mass spectrum, *m*/*z* (I_{rel} (%)): 359 (10). Found (%): C, 76.87; H, 5.90; N, 3.87. $C_{23}H_{21}NO_3$. Calculated (%): C, 76.88; H, 5.85; N, 3.90.

5,1′,3′,3′,5′-Pentamethylspiro[indoline-2,2′-[2*H*,7*H*]pyrano[5,6-*f*][1]benzopyran-7-one] (2b). The yield was 93%, m.p. 213—214 °C. ^{1}H NMR ($CDCl_3$), δ: 2.70 (s, 3 H, NMe); 1.20, 1.30 (both s, 6 H, C(3′)Me_2); 2.33 (s, 1 H, C(5′)Me); 5.85 (d, 1 H, H(3), $J_{3,4}$ = 10.7 Hz); 7.59 (d, 1 H, H(4), $J_{4,3}$ = 10.7 Hz); 6.28 (s, 1 H, H(6)); 2.48 (s, 3 H, C(5)Me); 6.43 (d, 1 H, H(7′), $J_{7',6'}$ = 7.6 Hz); 6.92—7.22 (m, 4 H, H(4′), H(6′), H(9), H(10)). IR, ν/cm^{-1}: 1725 (α-pyron), 1616 (C=C), 974 (CO). Absorption spectrum, λ_{max}/nm (logε): 560 (3.53). Mass spectrum, *m*/*z* (I_{rel} (%)): 373 (14). Found (%): C, 77.16; H, 6.01; N, 3.85. $C_{24}H_{23}NO_3$. Calculated (%): C, 77.21; H, 6.17; N, 3.75.

5′-Bromo-5,1′,3′,3′-tetramethylspiro[indoline-2,2′-[2*H*,7*H*]pyrano[5,6-*f*][1]benzopyran-7-one] (2c). The yield was 65%, m.p. 197—198 °C. ^{1}H NMR ($CDCl_3$), δ: 2.68 (s, 3 H, NMe); 1.18, 1.25 (s, 6 H, C(3′)Me_2); 7.12—7.17 (m, 2 H, H(4′), H(6′)); 6.38 (d, 1 H, H(7′), $J_{7',6'}$ = 8.5 Hz); 5.78 (d, 1 H, H(3), $J_{3,4}$ = 10.4 Hz); 7.48 (d, 1 H, H(4), $J_{4,3}$ = 10.4 Hz); 6.12 (s, 1 H, H(6)); 2.35 (s, 3 H, C(5)Me); 7.36 (d, 1 H, H(9), $J_{9,10}$ = 8.8 Hz); 6.67 (d, 1 H, H(10), $J_{10,9}$ = 8.8 Hz). IR, ν/cm^{-1}: 1727 (α-pyron), 1647 (C=C), 953 (CO). Absorption spectrum, λ_{max}/nm (logε): 557 (3.12). Mass spectrum, *m*/*z* (I_{rel} (%)):

437/439 (24/15). Found (%): C, 62.96; H, 4.61; N, 3.28. $C_{23}H_{20}NO_3Br$. Calculated (%): C, 63.01; H, 4.57; N, 3.20.

Synthesis of compounds 4a—c (general procedure). A mixture of 3-formyl-4-hydroxycoumarin[21] (0.56 g, 0.0029 mol) and anhydrous ethanol (10 mL) was heated until the coumarin dissolved completely. 1,3,3-Trimethyl-2-methyleneindoline[15] or its 5-substituted derivative (0.51 g, 0.0029 mol) was added to the solution that formed, and the mixture was heated with boiling for 5.5 h. Then the reaction mixture was cooled and left for 18 h at 20 °C. Then a precipitate that formed was filtered off, recrystallized from dilute ethanol, and dried in air.

2-(2,4-Dioxochromanylidene)-1-(1,3,3-trimethylindolinylidene)ethane (4a). The yield was 67%, m.p. 281—282 °C. ^{1}H NMR ($CDCl_3$), δ: 3.62 (s, 3 H, NMe); 1.78 (s, 6 H, C(3′)Me_2); 6.92 (d, 1 H, H(7′′), $J_{7'',6''}$ = 8.5 Hz); 7.64, 8.24 (both d, 1 H each, H(2), *E*-isomer, *Z*-isomer, J_{trans} = 14.7 Hz); 8.82, 9.03 (both d, 1 H each, H(1), *E*-isomer, *Z*-isomer, J_{trans} = 14.7 Hz); 8.10 (m, 1 H, H(6′)); 7.20—7.29 (m, 3 H, H(4′′), H(5′′), H(6′′)); 7.36—7.43 (m, 2 H, H(8′), H(5′)); 7.48—7.57 (m, 1 H, H(7′)). IR, ν/cm^{-1}: 1735 (α-pyron), 1646 (C=C), 950 (C—O). Absorption spectrum, λ_{max}/nm (logε): 490 (4.90). Mass spectrum, m/z (I_{rel} (%)): 345 (10). Found (%): C, 76.04; H, 5.72; N, 4.01. $C_{22}H_{19}NO_3$. Calculated (%): C, 76.52; H, 5.51; N, 4.06.

2-(2,4-Dioxochromanylidene)-1-(1,3,3,5-tetramethylindolinylidene)ethane (4b). The yield was 51%, m.p. 188—189 °C. ^{1}H NMR ($CDCl_3$), δ: 3.62 (s, 3 H, NMe); 1.75 (s, 6 H, C(3′′)Me_2); 2.92 (s, 3 H, C(5′′)Me); 6.98 (d, 1 H, H(7′′), $J_{7'',6''}$ = 8.5 Hz); 7.64, 8.22 (both d, 1 H each, H(2), *E*-isomer, *Z*-isomer, J_{trans} = 14.7 Hz); 8.80, 9.03 (both d, 1 H each, H(1), *E*-isomer, *Z*-isomer, J_{trans} = 14.7 Hz); 8.10 (m, 1 H, H(6′)); 7.15—7.25 (m, 4 H, H(4′′), H(6′′), H(8′), H(5′)); 7.46—7.56 (m, 1 H, H(7′)). IR, ν/cm^{-1}: 1701 (α-pyron), 1619 (C=C), 943 (C—O). Absorption spectrum, λ_{max}/nm (logε): 494 (4.79). Mass spectrum, m/z (I_{rel} (%)): 359 (15). Found (%): C, 76.78; H, 5.95; N, 3.93. $C_{23}H_{21}NO_3$. Calculated (%):C, 76.88; H, 5.85; N, 3.90.

2-(2,4-Dioxochromanylidene)-1-(5-bromo-1,3,3-trimethylindolinylidene)ethane (4c). The yield was 87%, m.p. 308—309 °C. ^{1}H NMR ($CDCl_3$), δ: 3.58 (s, 3 H, NMe); 1.78 (s, 6 H, C(3′′)Me); 6.91 (d, 1 H, H(7′′), $J_{7'',6''}$ = 8.9 Hz); 7.60, 8.16 (both d, 1 H each, H(2), *E*-isomer, *Z*-isomer, J_{trans} = 14.7 Hz); 8.80, 9.01 (both d, 1 H each, H(1), *E*-isomer, *Z*-isomer, J_{trans} = 14.7 Hz); 8.10 (m, 1 H, H(6′)); 7.50—7.58 (m, 2 H, H(4′′), H(6′′)); 7.19—7.23 (m, 2 H, H(8′), H(5′)); 7.48—7.57 (m, 1 H, H(7′)). IR, ν/cm^{-1}: 1699 (α-pyron), 1617 (C=C), 984 (CO). Absorption spectrum, λ_{max}/nm (logε): 493 (4.96). Mass spectrum, m/z (I_{rel} (%)): 423/425 (17/10). Found (%): C, 62.17; H, 4.11; N, 3.30. $C_{22}H_{18}NO_3Br$. Calculated (%): C, 62.26; H, 4.25; N, 3.30.

2-(2,4-Dioxochromanylidene)-1-(1,3,3-trimethyl-5-nitroindolinylidene)ethane (4d). The yield was 94%, m.p. 273—275 °C. ^{1}H NMR ($CDCl_3$), δ: 3.63 (s, 3 H, NMe); 1.82 (s, 6 H, C(3′′)Me); 8.24 (s, 1 H, H(4′′)); 8.32 (d, 1 H, H(6′′), $J_{6'',7''}$ = 8.5 Hz); 7.09 (d, 1 H, H(7′′), $J_{7'',6''}$ = 8.5 Hz); 7.65, 8.05 (both d, 1 H each, H(2), *E*-isomer, *Z*-isomer, J_{trans} = 14.3 Hz); 8.85, 9.03 (both d, 1 H each, H(1), *E*-isomer, *Z*-isomer, J_{trans} = 14.3 Hz); 7.52—7.59 (m, 1 H, H(8′)); 7.20—7.29 (m, 2 H, H(7′), H(6′)); 7.58 (dd, 1 H, H(5′), $J_{5',6'}$ = 7.92 Hz, $J_{5',7'}$ = 1.5 Hz). IR, ν/cm^{-1}: 1701 (α-pyron), 1636 (C=C), 938 (C—O). Absorption spectrum, λ_{max}/nm (logε): 500 (4.97). Mass spectrum, m/z (I_{rel} (%)): 390 (10). Found (%): C, 67.42; H, 4.96; N, 7.23. $C_{22}H_{18}N_2O_5$. Calculated (%): C, 67.69; H, 4.62; N, 7.18.

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Received December 29, 2004;
in revised form June 29, 2005