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Photochromic properties of indoline spiropyrans of the coumarin series

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The photochromic properties and aggregation processes of merocyanine forms of indoline spiropyrans of the coumarin series in solutions were studied by spectral and kinetic methods. Photochromism of the compounds synthesized depends on their structure. The efficient formation of J-aggregates was found for indoline spiropyrans **1a,b** under UV irradiation and merocyanines **3a,b**, which is indicated by the appearance of absorption and fluorescence bands in the visible spectral region and the resonance character of fluorescence.

Key words: spiropyrans, indole and coumarin derivatives, photochromic transformations, spiran form, merocyanine form.

Among organic photochromes, indoline spiropyrans and their heteroanalogs are known as efficient compounds, whose photochromic properties are based on photo- and thermoreversible reactions of pyran ring opening to form isomeric quinoid and betaine structures.[1—5]

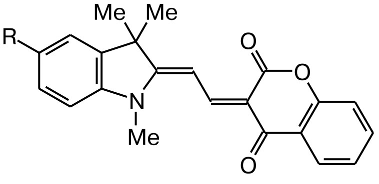
The studies of the spectral kinetic properties of the earlier synthesized photochromic spiropyrans in glassy solutions in an isopentane—isopropanol (4 : 1) mixture at 77—250 K found that the absorption spectra and efficiency of the photoreactions depend substantially on the nature of heterocycles in the spiropyran structures and polarity of the solvent.[6]

Spiropyrans of the coumarin series are poorly studied as compared to other indoline spiropyrans. Only few reports on the photochromic properties of some spiropyrans synthesized from 8-formyl-7-hydroxy-4-methylcoumarin and 3-formyl-4-hydroxycoumarin are available.[5,6]

For the systematic study of the effect of the coumarin moiety on the photochromic properties of indoline spiropyrans, we synthesized a series of coumarin-containing indoline spiropyrans **1Aa—e** and **2Aa—c** [7] (Scheme 1).

The photochromic transformations of spiropyrans are related to the reversible photodissociation of the C(2,2´)—O bond in the pyran ring of colorless cyclic form **A** followed by thermal *cis—trans*-isomerization to form merocyanine form **B**. The merocyanine form can be recyclized both *via* thermal relaxation and under visible light, which is absorbed by the merocyanine form (see Scheme 1).

An attempt[7] to synthesize indoline spiropyrans from 4-hydroxy-3-formylcoumarin gave merocyanine **3Ba—d**.



3Ba—d

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

In this article, we report the photochromic properties of indoline spiropyrans of the coumarin series **1A** and **2A**. In addition, we considered reasons for the existence of compounds **3B** in the merocyanine form.

Results and Discussion

All compounds **1a—e** in toluene solutions ($C = 2 \cdot 10^{-4}$ mol L^{-1}) at room temperature exhibit the photochromic properties, which are observed as reversible changes in the absorption spectra. For instance, when colorless solutions of spiro compound **1Aa** are UV-irradiated, a maximum at 584 nm and a shoulder at 620 nm appear in the long-wave spectral region (Fig. 1, curve *1*).

The highest values of the photoinduced absorbance were observed for the substances containing electron-releasing substituents in the indoline heterocycle (**1a—c**) (Table 1). In particular, the presence of the methoxy group

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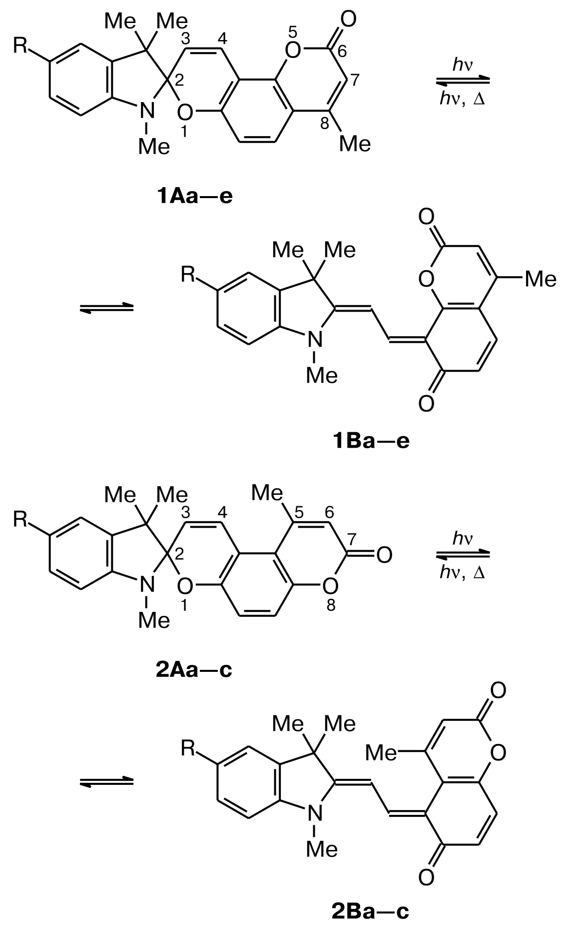
Scheme 1



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

in the indoline moiety (compound **1c**) results in the greatest increase in the absorption intensity in the long-wave maximum of the absorption band (see Table 1 and Fig. 1, curve *2*).

Less efficient photochromic transformations are observed for the compounds with the electron-withdrawing substituents R in the indoline moiety: **1d** (R = Br) and **1e** (R = NO_2). In this case, already the initial absorption spectrum, *i.e.*, before the solution was irradiated, exhibits a partial shift of equilibrium toward the formation of merocyanine forms **1Bd,e**.

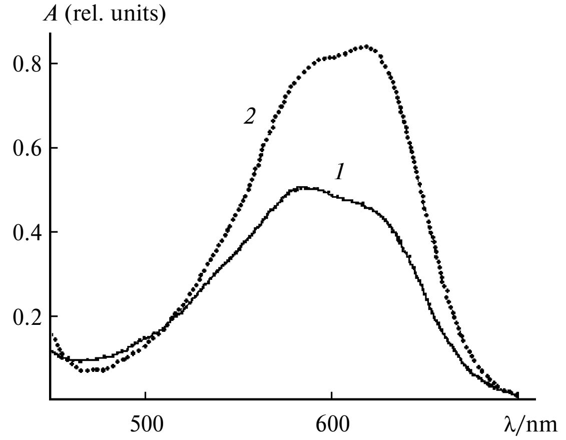


Fig. 1. Absorption spectra of photoinduced merocyanine form **B** in solutions of compounds **1a** (*1*) and **1c** (*2*) in toluene ($C = 2 \cdot 10^{-4}$ mol L^{-1}).

The efficiency of photochromic transformations of compounds **1a—e** can be suggested from a comparison of the kinetic curves of photocolorization and spontaneous decolorization (Fig. 2). The differences observed in their photochromic properties can be explained from the dependence of the kinetics of spontaneous relaxation of the photoinduced merocyanine form on the nature of the substituent in the indoline fragment (see Table 1). The introduction of electron-releasing substituents elongates the lifetime of the photoinduced form, while its lifetime shortens with an enhancement of the electron-withdrawing properties of the substituents. This agrees with the earlier revealed dependences of the properties of indoline spiropyrans on their structure.[2,3] Electron-releasing substituents in the indoline moiety favor the positive charge delocalization on the nitrogen atom, and the stability of compounds in the merocyanine form increases. It should be mentioned that for nitrosubstituted spiropyran **1Ae** the kinetics of thermal relaxation of the photoinduced form manifests an unusual biexponential dependence. This compound decomposes irreversibly under UV irradiation.

Table 1. Spectral and kinetic characteristics of spirocoumarinopyrans **1a—e** and **2a—c** and merocyanines **3a—d**

Compound	λ_{max}/nm		A_{max}	A	k /s^{-1}
	initial form	photoinduced form			
1a	293	584	1.0	0.98	0.052
1b	293	589	1.2	1.12	0.031
1c	293	620	2.0	1.79	0.021
1d	293	570	0.38	0.32	0.180
1e	350	600	0.1	0.07	0.240
2a	296	563	—	—	—
2b	290	569	—	—	—
2c	290	572	0.3	0.23	0.148
3a	492	—	—	—	—
3b	498	—	—	—	—
3c	496	—	—	—	—
3d	499	—	—	—	—

Note: λ_{max} are the maxima in the absorption spectra, A_{max} is the photoinduced absorbance in the absorption band maximum in the visible spectral region, A is the pre-exponential factor, and k is the rate constant of dark decolorization. $C = 2 \cdot 10^{-4}$ mol L^{-1} for compounds **1a—e**, **2a—c** (toluene), and **3a—d** ($CHCl_3$).

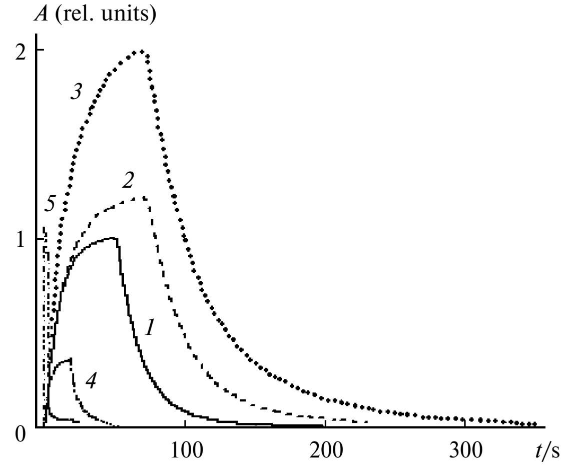


Fig. 2. Kinetic curves of photocolorization and spontaneous decolorization in solutions of compounds **1a** (*1*), **1b** (*2*), **1c** (*3*), **1d** (*4*), and **1e** (*5*) in toluene ($C = 2 \cdot 10^{-4}$ mol L^{-1}).

An important property of compounds **1a—e** is the fluorescence of their solutions before and after irradiation. A comparison of the fluorescence spectra of compound **1a** before and after irradiation (Fig. 3) shows that the initial colorless cyclic form of compound **1Aa** is characterized by the fluorescence band at 475 nm (see Fig. 3, curve *1*). Upon UV irradiation of the solution, the intensity of this band decreases with the simultaneous appearance of a new long-wave fluorescence band with a maximum at 668 nm (see Fig. 3, curve *2*), which is caused, as follows from a comparison of the absorption and fluorescence spectra, by the formation of photoinduced colored merocyanine form **1Ba** (see Scheme 1).

Spiropyrans **2Aa—c** are characterized by less pronounced photochromic transformations in solutions at room temperature compared to those of compounds **1Aa—e**, which is, probably, related to a sharp shortening of the lifetime of their photoinduced merocyanine form **B**.

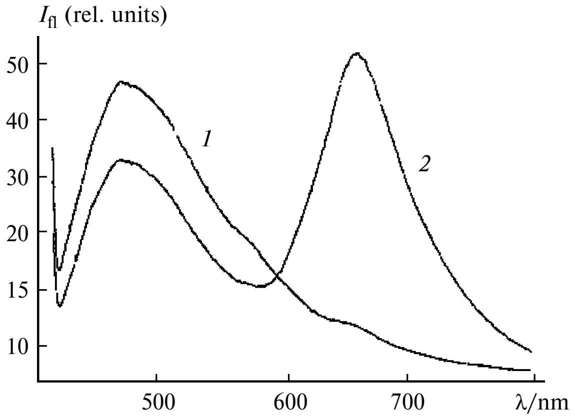


Fig. 3. Fluorescence spectra of a solution of spiropyran **1a** in benzene ($C = 1 \cdot 10^{-3}$ mol L^{-1}) before (*1*) and after (*2*) UV irradiation.

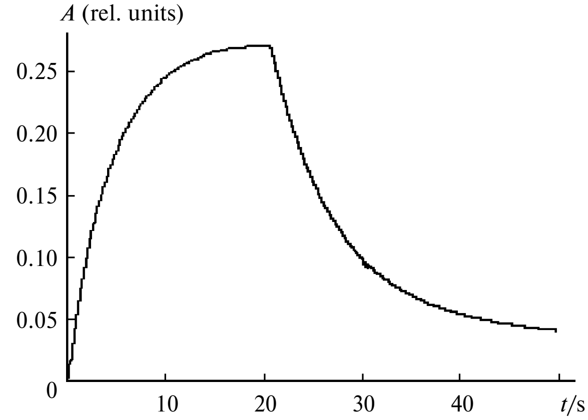


Fig. 4. Kinetic curve of photocolorization and spontaneous decolorization in a solution of compound **2Ac** in toluene ($C = 2 \cdot 10^{-4}$ mol L^{-1}).

Distinct photochromic transformations were detected only for compound **2Ac** (Fig. 4). As compared with compounds **1a—e**, the absorption maxima of the open forms of compounds **2a—c** are noticeably shifted to the short-wave spectral region (see Table 1).

Unlike spiropyrans **1** and **2**, already in the initial state compounds **3** exist in merocyanine form **B**. The narrow shape of the absorption bands in the electronic absorption spectra of compounds **3a—d** with a maximum at 498—500 nm (Fig. 5) is remarkable. The spectral curves contain a shoulder in the short-wave region along with the maximum. The ratio of the intensities of these bands depends on the nature of substituents. The intensity of the short-wave band increases upon the introduction of the electron-releasing substituents into the molecule (see Fig. 5, curve *2*) and decreases for the electron-withdrawing substituents (see Fig. 5, curves *3* and *4*) compared to unsubstituted compound **3a** (see Fig. 5, curve *1* and

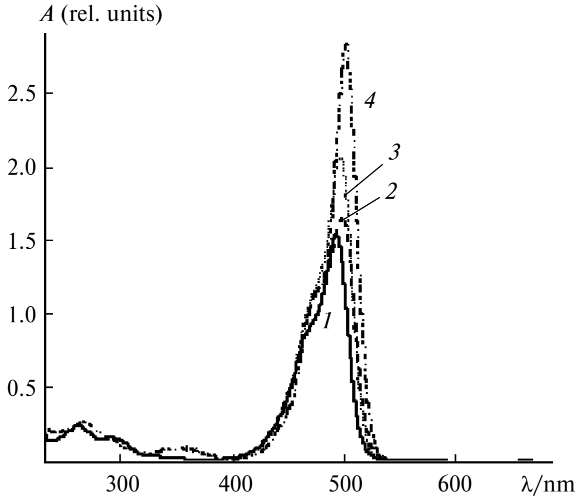


Fig. 5. Absorption spectra of solutions of merocyanines **3a** (*1*), **3b** (*2*), **3c** (*3*), and **3d** (*4*) in chloroform ($C = 1 \cdot 10^{-4}$ mol L^{-1}).

Table 1). On the contrary, the introduction of electron-acceptors into position 5´ of the indoline fragment increases the intensity of the long-wave absorption band. These experimental data indicate, probably, the presence of both monomeric and J-aggregated structures of the merocyanine forms of compounds **3a—d**.

An analysis of the obtained spectral data for compounds **1a,b** suggests that UV irradiation results in the J-aggregation of molecules of the merocyanine form, which is indicated by an increase in the intensities of absorption and fluorescence bands due to the photoinduced increase in the number of molecules in the merocyanine form. The absorption and fluorescence spectra of a more concentrated solution of compound **1a** in benzene (C = 10^{-3} mol L^{-1}) are shown in Fig. 6. The electronic absorption spectrum of compound **1a** before irradiation (see Fig. 6, curve *1*) contains the absorption band of the initial spiran form **A** in the UV spectral region and also a band in the visible region with a maximum at 565 nm, which belongs, most likely, to merocyanine form **B** of this compound. The appearance of the latter band is caused by the partial shift of equilibrium in concentrated solutions toward the formation of an insignificant amount of the merocyanine form. UV irradiation of the solution increases the concentration and, hence, the intensity of the absorption band of merocyanine form **B** (see Fig. 6, curve *2*). In this case, the absorption band becomes broad and has two maxima at 575 and 618 nm. The former is close to the absorption maximum of the merocyanine form before irradiation, while the second maximum is shifted toward the long-wave region by approximately 40 nm. As followed from the photoinduced absorption spectra, monomeric compounds and, possibly, dimeric aggregates are present in the solution along with the J-aggregates. The spectral interval between the long-wave absorption maximum and photoinduced fluorescence maximum (668 nm) (see Fig. 6, curve *3*) is 50 nm.

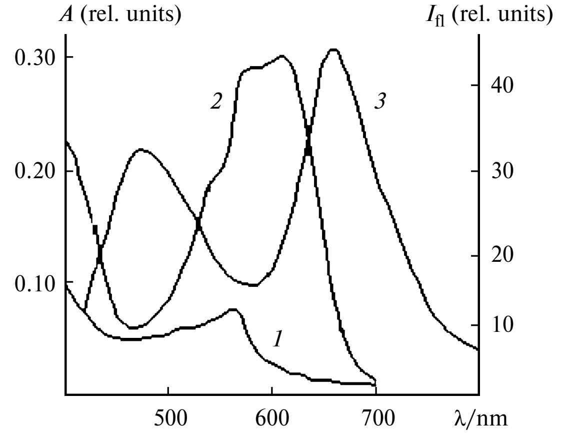


Fig. 6. Absorption (*1*, *2*) and fluorescence spectra at λ_{exc} = 400 nm (*3*) before (*1*) and after (*2*, *3*) UV irradiation of a solution of compound **1a** in benzene ($C = 1 \cdot 10^{-3}$ mol L^{-1}).

Similar spectral changes are also observed for concentrated solutions of compound **1b** in benzene.

It should be mentioned that the efficiency of aggregation in **1a** depends on the polarity of the solvent and decreases with an increase in the solvent polarity, for instance, as a result of the replacement of benzene (ε = 2.25) by acetone (ε = 20.7). In addition, the aggregation decreases in the presence of the 5´-methyl substituent in the indoline moiety compared to that for the unsubstituted compound.

Unlike solutions, a polymolecular layer of compound **1a** is characterized by a spectral interval between the maxima of the absorption and fluorescence bands, which is equal to 100 nm (Fig. 7). The spectral characteristics of the initial and photoinduced forms of compounds **1a,b** in polymolecular layers and a large spectral interval between maxima of the absorption and fluorescence bands indicate that the J-aggregation process does not occur. Probably, the molecular packing prevents the aggregation of molecules in the polymolecular layer.

Unlike the above-considered indoline spiropyrans, compounds **3a,b** manifest the photochromic properties in neither solutions nor polymolecular layers. The prolong UV or visible irradiation of these compounds and heating of their solutions to 65 °C did not result in any noticeable spectral changes. The data of electronic absorption spectroscopy and fluorescence spectra of compound **3a**, *viz.*, narrow absorption bands at 490 nm and fluorescence bands at 515 nm and an insignificant spectral interval between the maxima of the absorption and fluorescence bands (about 25 nm), indicate that the starting solution of this compound contains J-aggregates. Efficient aggregation is also observed for merocyanine molecules of compound **3b**. The replacement of nonpolar benzene by more polar acetone broadens the absorption and fluorescence bands due to the appearance of monomeric and dimeric molecules.

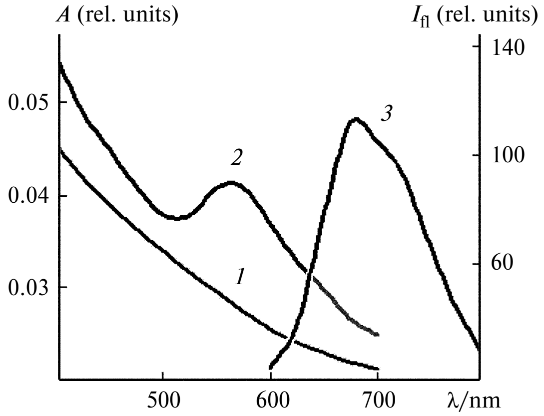


Fig. 7. Absorption (*1*, *2*) and fluorescence spectra at λ_{exc} = 550 nm (*3*) before (*1*) and after (*2*, *3*) UV irradiation of the one-component polymolecular layer (nine monolayers) based on compound **1a**.

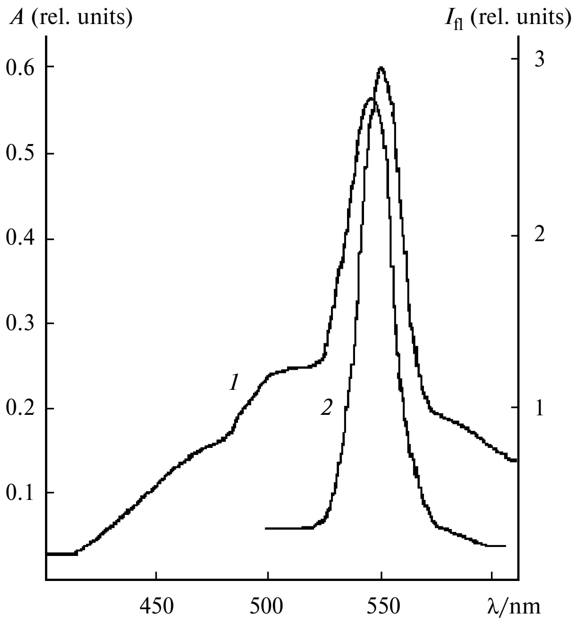


Fig. 8. Absorption (*1*) and fluorescence (*2*) spectra of compound **3a** in the polymolecular layer (nine monolayers).

The polymolecular layers based on compound **3a** manifest the best spectral characteristics (Fig. 8). In this case, the maxima of the absorption and fluorescence bands of this compound virtually coincide, *i.e.*, resonance fluorescence is observed, which is a convincing proof for the formation of J-aggregates of molecules of the merocyanine form. The absorption and fluorescence spectra measured for the polymolecular layers based on compound **3b** show that the monomeric molecules are also present.

The prepared polymolecular layers based on compound **3a** containing J-aggregates were used for studying their nonlinear optical properties.[8] The dependence of the intensity of second harmonic generation on the change in the angle of incidence of the exciting light was measured (Fig. 9). Laser pumping during experiment was carried out in the plane of radiation incidence (the plane that passes through the normal to the plate and the wave vector), and the analyzer was turned in the plane of beam incidence. The total dipolar moment of the molecules is predominantly perpendicular to the plate surface and, therefore, the molecules are oriented in the same direction. The nature of the signal observed was checked. When the analyzer is turned by 90°, the generation of the harmonic disappears to confirm the conclusion about the generation of the second harmonic of laser radiation. This signal cannot be polarized fluorescence, because this process requires a high ordering of the system, which is hardly achieved when polymolecular layers are prepared by the Langmuir—Schaeffer method.

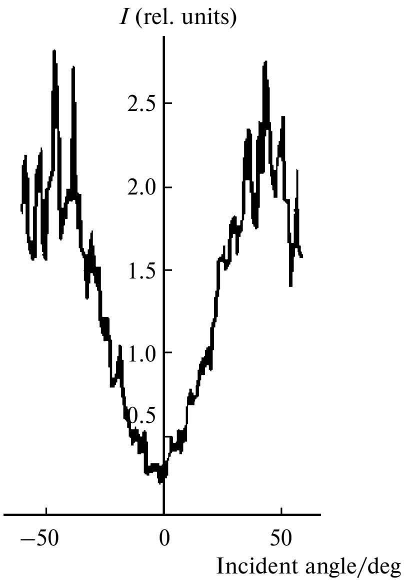


Fig. 9. Intensity of the second harmonic generation of laser radiation *vs.* angle of incidence of the exciting light.

Reasons for differences in the properties of the open forms of compounds **1—3** should be searched, most likely, for conditions of the negative charge delocalization in the coumarin fragments of different structures, because the indoline moiety on which the positive charge is localized is the same in all compounds.

As follows from analysis of the resonance structures of merocyanines **1B—3B** (the most stable of them, according to the data of semiempirical quantum chemical AM1 calculations, are shown in Scheme 2), the conditions for negative charge delocalization differ in the fragments of 7-, 6-, and 4-hydroxycoumarins. Each open form of compounds **1a—e** and **3a—d** has three stable resonance structures, and only two of them can be presented for compounds **2Ba—c**.

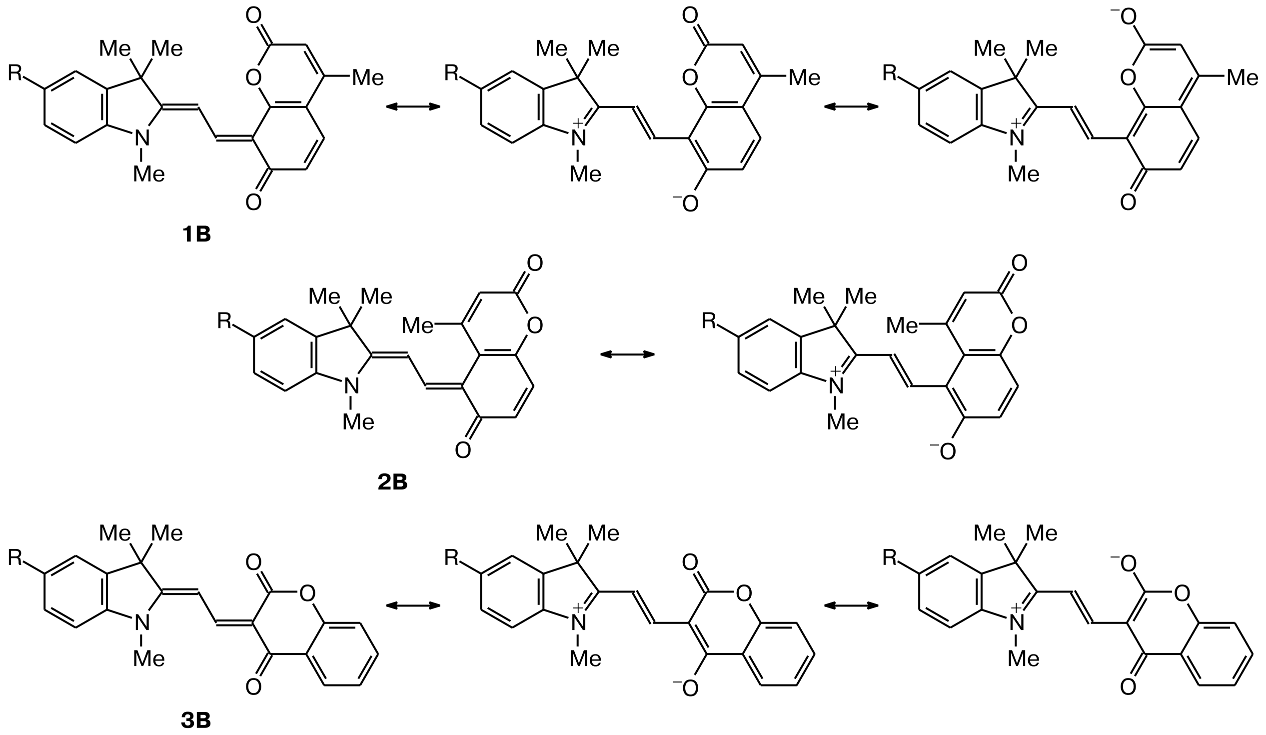
The heats of formation ΔH° for the cyclic (spiro) and open forms of compounds **1a** and **2a** (see Scheme 1) and merocyanine **3Ba** (Scheme 3), which were calculated by the standard procedure of AM1 calculations, are given in Table 2.

The results of the calculations show that the 1,3-diketo form (compound **3Ba**) is the most stable. It is most likely that the spiro compounds of structure **3A** are not

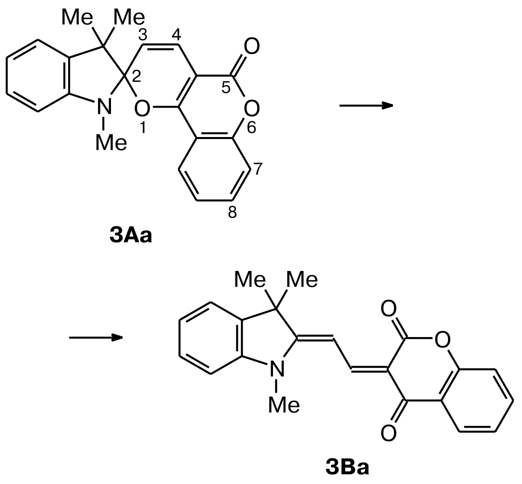
Table 2. Heats of formation ($\Delta H°_f$/kcal mol^{-1}) for the spiro (**A**) and merocyanine (**B**) forms of unsubstituted indoline spirocoumarins

Compound	$\Delta H°_f$		$\Delta\Delta H°_f$ ($\Delta H°_f$(**B**) − $\Delta H°_f$(**A**))
	A	**B**	
1a	−4.4676	−2.2853	+2.1823
2a	+2.0103	+6.0439	+4.0336
3a	+0.9123	−8.6327	−9.5450

Scheme 2



Scheme 3



formed in the studied temperature interval just for this reason.[7]

The most closest are the heats of formation of the spiro and open forms in the series of compounds **1a—e**. Evidently, due to this compounds **1a—e** are most prone to reversible phototransformations.

Finally, according to the results of calculations, open form **B** of spiropyrans **2a—c** is the least stable one. The heat of formation of open form **B** of spiro compound **2a** is much higher than the heat of formation of cyclic form **A** of this compound. This fact is the main reason, most likely, for high rates of the thermal decolorization of compounds **2a—c**.

Thus, the comparative study of the photochromic properties of the synthesized indoline spiropyrans with different structures of the coumarin moiety showed that compounds **1a—e** synthesized from 8-formyl-7-hydroxy-4-methylcoumarin have the most pronounced photochromic properties. As in the case of other indoline spiropyrans, the electron-releasing substituents in the indoline fragment of **1a—e** increase and the electron-withdrawing substituents decrease the lifetime of the photoinduced form. Spiropyrans **2a—c** synthesized using 5-formyl-6-hydroxy-4-methylcoumarin are characterized by a shorter lifetime of the photoinduced merocyanine form at room temperature. Under normal conditions, compounds **3a—d** based on 3-formyl-4-hydroxycoumarin are not photochromic and exist in the merocyanine form. According to the quantum chemical calculations, the experimental data can be explained by differences in the negative charge delocalization in the coumarin fragments of the corresponding merocyanines.

The appearance of absorption and fluorescence bands in the visible spectral region and the resonance character of fluorescence of indoline spiropyrans **1a,b** under UV irradiation and merocyanines **3a,b** indicate the efficient formation of J-aggregates.

Experimental

Photochromic transformations of spiropyrans **1A** and **2A** and compound **3B** were studied in solutions. Toluene, chloroform, and benzene (analytically pure grade) were used as solvents. The concentrations of the photochromic substances in solutions were $C = 2 \cdot 10^{-4}$—$1 \cdot 10^{-3}$ mol L^{-1}.

Absorption spectra were recorded on Cary 50 (Varian) and Hitachi 330 spectrophotometers. Fluorescence spectra were obtained on Shimadzu RF-500 and Cary Eclipce (Varian) spectrofluorimeters. The kinetics of reactions of photocolorization and thermal decolorization of the photoinduced form was measured on a special kinetic setup including photoactivation and probing sources, a monochromator, a radiation receiver, and a signal amplifier. Experimental data were delivered to a personal computer, which processed the results. For the photoactivation of solutions of the compounds under study, a DRSh-250 high-pressure mercury lamp was used, whose radiation was filtered by glass light filters from a standard set of colored glasses to isolate the UV and visible radiations that coincide with the absorption bands of the starting and photoinduced forms of spiropyrans, respectively.

An MDT-LB 5 setup for molecular lamination (Russian Federation) was used to prepare polymolecular layers. Distilled water was used as the subphase. Monolayers of the compounds under study were formed from a solution in chloroform on the aqueous subphase surface, compressed to 7 mN m^{-1}, and deposited on quartz supports $40 \times 10 \times 1$ mm in size according to the Langmuir—Blodgett method. For the preparation of two-component polymolecular layers, potassium stearate served as the matrix substance. Potassium stearate was dissolved in chloroform, and the resulting solution was mixed with spiropyrans solutions in different ratios. As a rule, nine monolayers were deposited on a support.

Thus prepared solutions and polymolecular layers were studied by absorption and fluorescence spectroscopies. A cell filled with the corresponding solvent was used as a reference for measuring absorption and fluorescence spectra. In the case of photochromic spiropyrans, the photoinduced form was obtained under UV irradiation with the light from a SVD-120 lamp, which was passed through the UFS-8 light filter.

The nonlinear optical properties of polymolecular layers were studied measuring the dependence of the second harmonic generation of the laser radiation on the angle of incidence of the exciting light using a setup based on a laser with the radiation wavelength $\lambda = 1064$ nm, pulse duration $\tau = 30$ ns, and radiation power $P = 5$ mJ.[9]

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