# Synthesis and studies of new photochromic spiropyrans containing a formylcoumarin fragment

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A computer search for new photoactive compounds among indoline spiropyrans of coumarin series was carried out using DFT B3LYP/6-31G(d,p) method. Based on the data obtained, the spiropyrans containing a formylcoumarin fragment annulated to the 2*H*-pyran ring and possessing photochromic properties were synthesized. The structure and photochromism of these compounds were studied by $^1$H NMR, IR, and UV/Vis spectroscopy. The introduction of a formyl group into the coumarin moiety of spiropyrans led to a bathochromic shift of the long wavelength absorption maxima of merocyanine isomers, as well as to a considerable increase in their lifetime.

**Key words:** spiropyrans, coumarin, quantum chemical calculations, photochromism.

Photochromic spiropyrans and spirooxazines are of significant interest for development of materials for recording and storage of optical information, molecular switches and chemosensors; their wide application is substantiated by a combination of photo-, thermo-, and solvatochromic properties.[1—6] Photochromic transformations of spiropyrans include the processes of a reversible cleavage of the $C_{spiro}$—O bond in the cyclic form and subsequent *Z*/*E*-isomerization to the metastable colored merocyanine isomer, which can be converted to the initial form thermally or upon exposure to visible light. There are reported studies of a number of spiropyrans containing a coumarin fragment in the 2*H*-pyran part of the molecule.[7—12]

The present work is directed on the development of new photochromic systems possessing properties of molecular switches based on spiropyrans containing a formylcoumarin fragment annulated to the 2*H*-pyran ring. The choice of formylspiropyrans as the objects of our studies is substantiated, on the one hand, by a possibility of the preparation of various derivatives on their basis (imines, hydrazones, thiosemicarbazones), whereas on the other hand, by the expected influence of the electron-withdrawing formyl group on the spectro-kinetic characteristics. Such an influence in the case of spirocyclic compounds (spiropyrans and spirooxazines) leads, as a rule, to a bathochromic shift of the long-wavelength absorption maximum of merocyanine isomers, as well as to the increase in their thermal stability, that is very important for the practical application of photochromic spiropyrans.[13]

## Results and Discussion

In the search of new molecular switches based on spiropyrans with annulated coumarin fragment, compounds **1**—**4** containing a formyl and/or hydroxy group in the benzene fragment of the 2*H*-pyran part of the molecule have been chosen for a preliminary quantum chemical studies (Scheme 1).

For spiropyrans **1** and **2**, the calculations showed a similarity of their geometric characteristics (Fig. 1) and total energies (Table 1) in both the spirocyclic (**S**) and the merocyanine (**M**) forms.

The position of the hydroxyaldehyde fragment stabilized by an intramolecular hydrogen bond practically does not affect the structure of the spiro center. The $C_{spiro}$—O bond distances in structures **1S** and **2S** are 1.501 and 1.503 Å, respectively. The calculations in the gas phase predict that the merocyanine forms **1M** and **2M** are more favorable than the cyclic forms **1S** and **2S** by 2.9 and 5.0 kJ mol$^{-1}$, this allows us to suggest a possibility of existence of a tautomeric equilibrium between spirocyclic and merocyanine forms.

Figure 2 shows an equilibrium geometries of the most stable isomers of spiropyrans **3** and **4**, in which, in contrast to structures **1** and **2** considered above, the hydrogen

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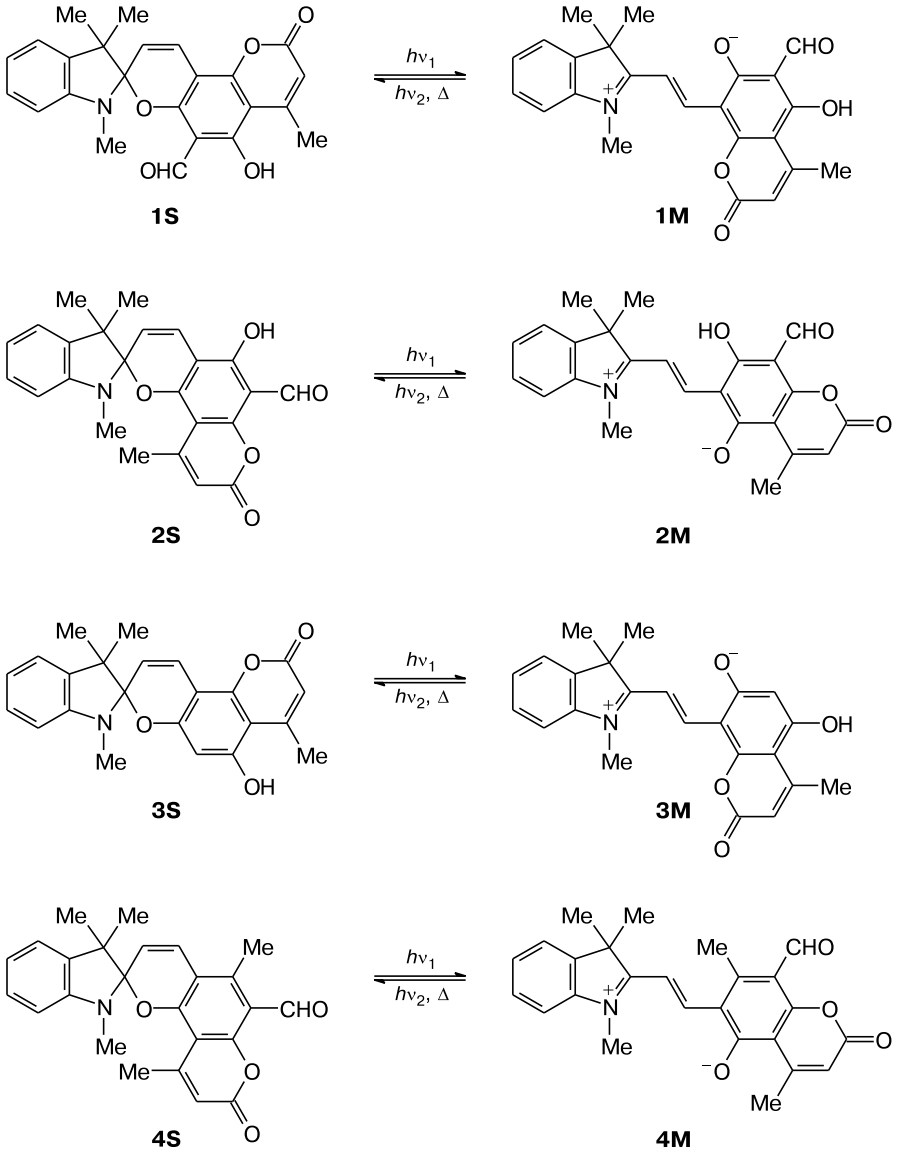
**Scheme 1**




bonds are absent. As it follows from the data given in Table 1, compounds **3** and **4** are stabilized in the spiroform **S**, the energy differences are 36.8 and 16.3 kJ mol$^{-1}$, respectively. The structure **4** is characterized by the elongation of the C—C bond, which is shared with the annulated coumarin fragment, to the value of 1.408 Å, that agrees with the found earlier dependence between this parameter and stability of different forms of coumarin spiropyrans.[14]

**Table 1.** Total energy ($E_{total}$) and relative energy ($\Delta E$) in the structures **1**—**4** calculated by DFT B3LYP/6-31G(d,p)

| Compound | $E_{total}$/a.u. | $\Delta E$/kJ mol$^{-1}$ |
|---|---|---|
| **1S** | −1358.120522 | 2.9 |
| **1M** | −1358.121693 | 0.0 |
| **2S** | −1358.119336 | 5.0 |
| **2M** | −1358.121323 | 0.0 |
| **3S** | −1244.779448 | −36.8 |
| **3M** | −1244.765426 | 0.0 |
| **4S** | −1322.193675 | −16.3 |
| **4M** | −1322.187489 | 0.0 |

In summary, the quantum chemical studies of structure and relative stabilities of coumarin spiropyrans **1**—**4** showed that a thermal equilibrium between forms **S** and **M** can exist for compounds **1** and **2**, while systems **3** and **4** are most stable in spiroform **S**. System **4**, the indoline fragment of which was modified by substituents of different nature, was chosen for conducting experimental studies.

Spiropyrans **4a**—**g** were obtained by the condensation of 5-hydroxy-4,7-dimethyl-2-oxo-2*H*-chromene-6,8-dicarbaldehyde (**5**) with the corresponding 3*H*-indolium perchlorates **6a**—**g** in the presence of triethylamine (Scheme 2).

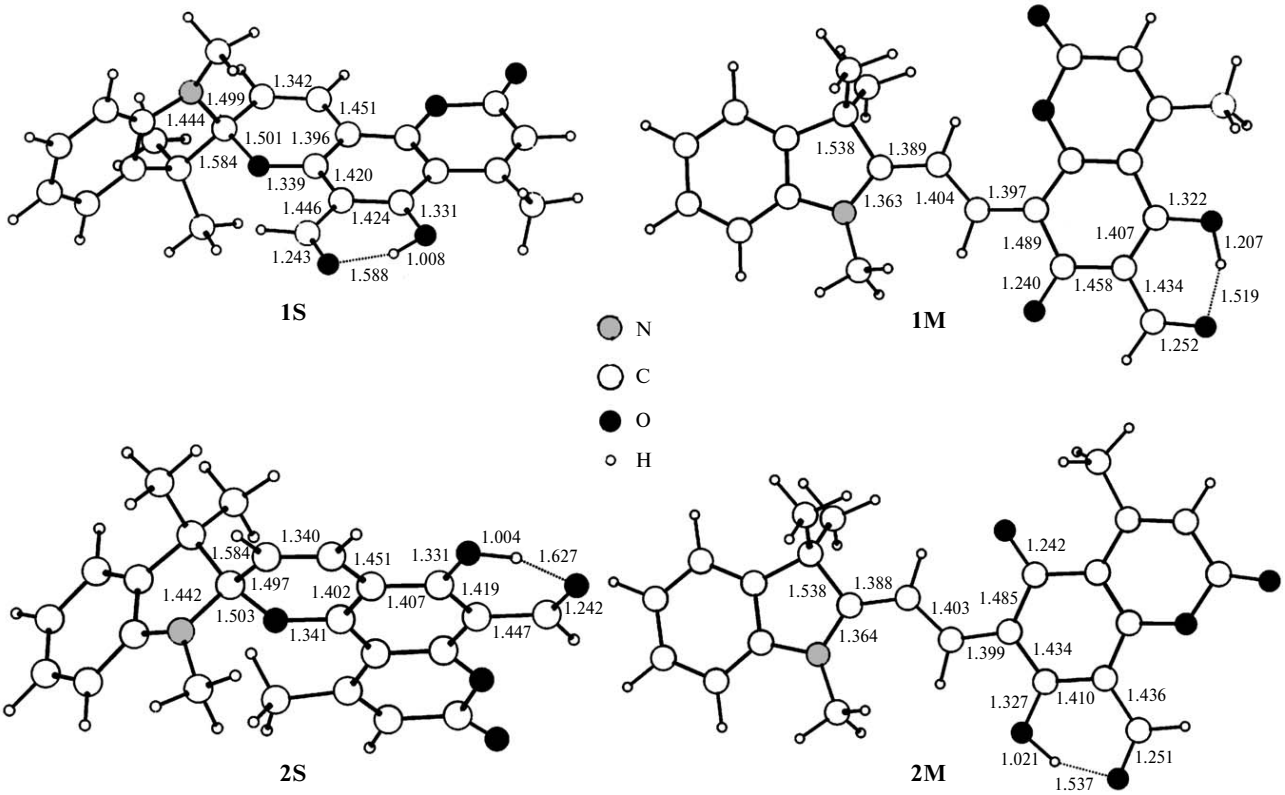



**FIg. 1.** Geometric characteristics of structures **1** and **2** calculated by DFT B3LYP/6-31G(d,p). Here and further the bond distances are given in Angströms.

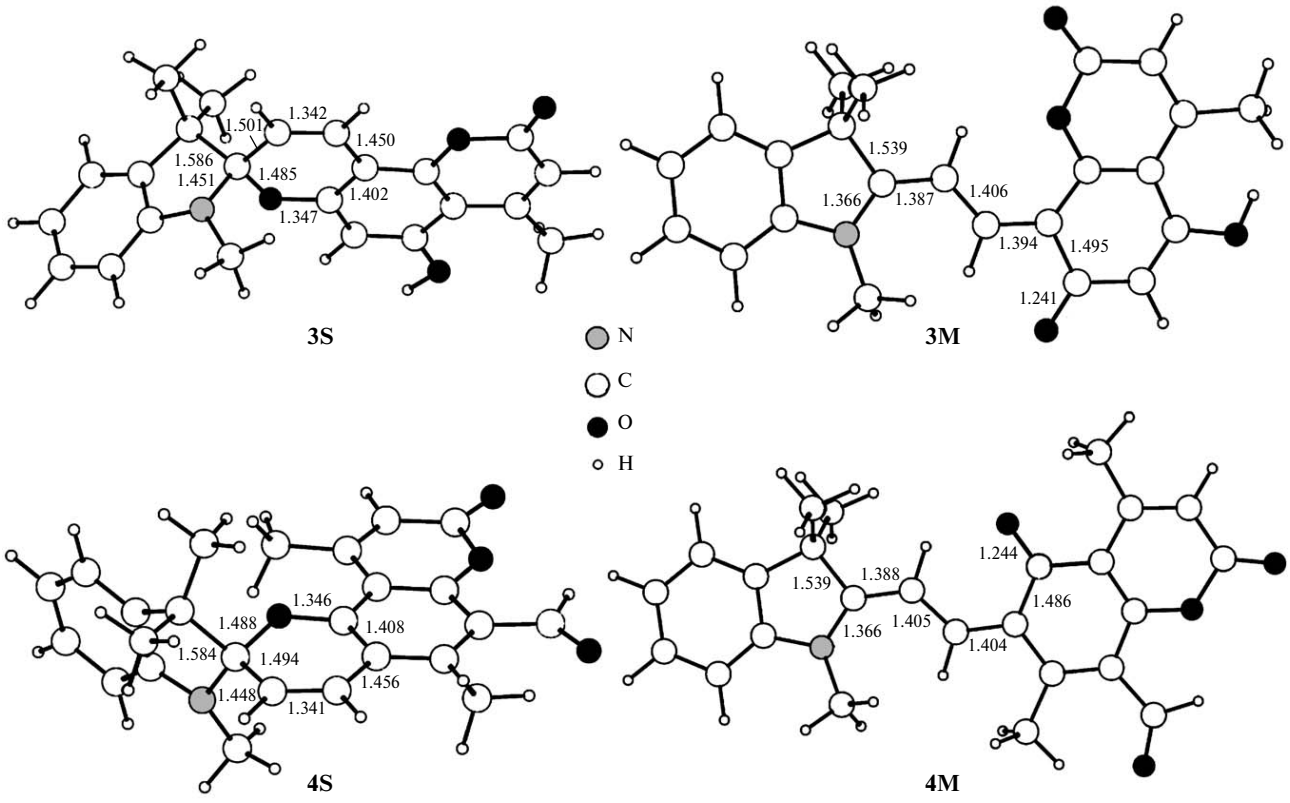
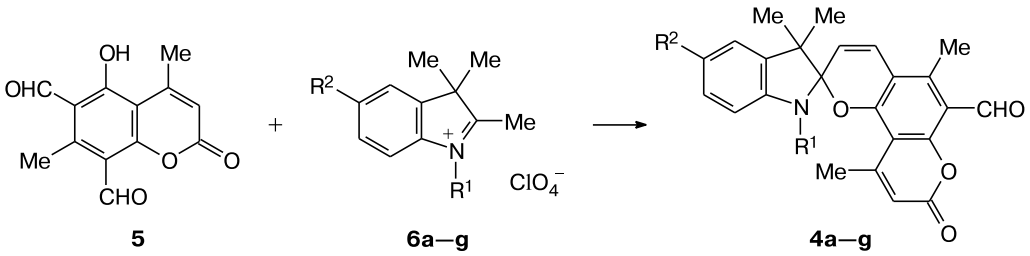



**FIg. 2.** Geometric characteristics of structures **3** and **4** calculated by DFT B3LYP/6-31G(d,p).

**Scheme 2**




| | a | b | c | d | e | f | g | |
|---|---|---|---|---|---|---|---|---|
| $R^1$ | Me | Me | Me | Me | Me | Me | Bn | $Pr^i$ |
| $R^2$ | H | Me | OMe | Cl | $NO_2$ | H | H | |

**Reagents and conditions:** $Et_3N$, $Pr^iOH$, Δ, 5 h, 31—45%.

The IR spectra of spiropyrans **4a**—**g** exhibit vibrational bands of the carbonyl groups of the coumarin fragment in the region of 1725—1747 $cm^{-1}$, vibrational bands of the C=C bond of the pyran ring in the region of 1606—1610 $cm^{-1}$, and the $C_{spiro}$—O bond in the region 908—920 $cm^{-1}$. Apart from that, vibrational bands of the 6′-formyl group are observed in the region of 1676—1681 $cm^{-1}$.

The $^1H$ NMR spectra exhibit two singlet signal for the magnetically nonequivalent geminal $CH_3$ group in the region of δ 1.14—1.34, the singlet signals corresponding to the 6′-formyl group are present in the low-field region of the spectrum at δ 10.71—10.74. The signals for the diastereotopic protons of the methylene group of the *N*-benzyl substituent of spiropyran **4f** are observed as two doublets at δ 4.05 and 4.50, The signals for the diastereotopic protons of the methyl groups in the *N*-isopropyl substituent of spiropyran **4g** are found as two doublets at δ 1.37 and 1.40. The position and splitting patterns of these signals correspond to the cyclic isomer **S** of compounds **4a**—**g**.

In the initial (before irradiation) solutions in toluene, spiropyrans **4a**—**g** also exist in the cyclic form **S**. Their electron absorption spectra are characterized by the bands of the long-wavelength absorption in the region of 345—363 nm with the molar extinction coefficients in the maxima of 2950—4770 L $mol^{-1}$ $cm^{-1}$ corresponding to the $S_0 \rightarrow S_1$ transition and more strong bands of the $S_0 \rightarrow S_2$ transition in the short-wavelength region of the spectrum with maxima at 292—293 nm and molar extinction coefficients of 24700—26700 L $mol^{-1}$ $cm^{-1}$ (Table 2).

As it is seen from the data in Table 2, the substituents in the indoline part of spiropyrans **4a**—**d**,**f**,**g** do not noticeably influence the position and form of the long-wavelength absorption bands. This is in accordance with the suggestion on the additive character of the absorption spectra of the acoplanar fragments of spiropyrans and the localization of the electron transition responsible for the most long-wavelength absorption band on the benzopyran part of the molecule. The structural modeling method showed that the electron absorption spectra of spiropyrans can be represented as a linear combination of absorption spectra of the composing fragments.[15] This is possible because of the weak interactions of mutually orthogonal fragments. At the same time, in the case of 5-nitro-substituted spiropyran **4e** the long-wavelength absorption band considerably differs in both the shape and intensity. This is probably due to the hyperconjugation effect caused by the presence of a strong electron-withdrawing group and supporting the interaction of the π-systems of indoline and coumarin fragments of spiropyran.

The irradiation of solutions of spiropyrans **4a**—**g** in toluene causes their coloring related to the photoinduced 2*H*-pyran ring opening in the course of the reaction **S**→**M**, which is accompanied by the appearance of absorption bands in the long-wavelength region of the spectrum (Scheme 3, Fig. 3).

**Scheme 3**

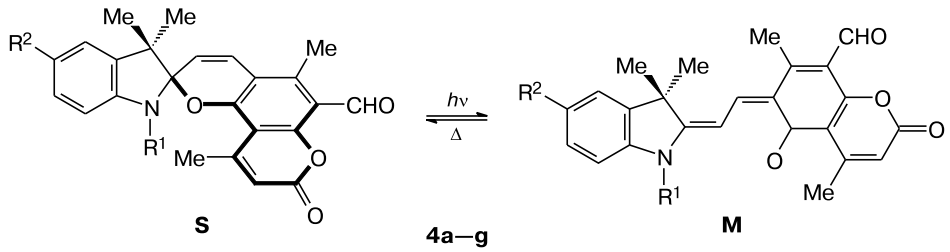


**Table 2.** Spectro-kinetic characteristics of spiropyrans **4a**—**g** in toluene at 293 K

| Compound | Spirocyclic form **S** | | Merocyanine form **M** | | |
|---|---|---|---|---|---|
| | $\lambda_{max}^{abs}$/nm | $\varepsilon_{max}$/L mol$^{-1}$ cm$^{-1}$ | $\lambda_{max}^{abs}$/nm | $\tau_{\mathbf{M}}$/s | $E_{\mathbf{MS}}^{a}$/kJ mol$^{-1}$ |
| **4a** | 293 | 24800 | 420 sh | 6.3 | 79.7 |
| | 345 sh | 4280 | 437 | | |
| | 362 sh | 2990 | 580 sh | | |
| | | | 597 | | |
| **4b** | 293 | 24710 | 417 sh | 10.8 | 88.1 |
| | 345 sh | 4700 | 438 | | |
| | 363 sh | 3170 | 576 sh | | |
| | | | 600 | | |
| **4c** | 293 | 26710 | 421 sh | 16.7 | 90.9 |
| | 345 sh | 4770 | 436 | | |
| | 362 sh | 3390 | 576 sh | | |
| | | | 598 | | |
| **4d** | 292 | 26460 | 423 sh | 2.7 | 85.4 |
| | 346 sh | 4280 | 443 | | |
| | 362 sh | 2950 | 580 sh | | |
| | | | 602 | | |
| **4e** | 356 | 19540 | 456 | 0.1 | 71.0 |
| | | | 550 sh | | |
| | | | 586 | | |
| | | | 634 sh | | |
| **4f** | 292 | 26890 | 421 sh | 1.3 | 76.3 |
| | 345 sh | 4380 | 441 | | |
| | 362 sh | 3180 | 582 sh | | |
| | | | 601 | | |
| **4g** | 293 | 26710 | 421 sh | 7.8 | 86.0 |
| | 345 sh | 4770 | 436 | | |
| | 362 sh | 3390 | 576 sh | | |
| | | | 598 | | |

*Note*. *$\tau_{\mathbf{M}}$ is the lifetime of merocyanine form **M**, $E_{\mathbf{MS}}^{a}$ is the activation energy of thermal relaxation process of spiropyran recyclization.

The long-wavelength absorption maxima of merocyanine isomers **M of** compounds **4a**—**d**,**f**,**g** related to the $S_0 \rightarrow S_1$-transitions lie in the region 586—602 nm (see Table 2), that is in accordance with the data on the absorption of merocyanine structures of spiropyrans described earlier.[7,16] The shape of the long-wavelength absorption bands is unsymmetrical with the shoulders on short-wavelength slopes (see FIg. 3). The $S_0 \rightarrow S_2$ transition bands of forms **M** are characterized by the maxima at 437—443 nm. The influence of structural factors on spectro-absorption characteristics of merocyanine isomers is exhibited in the case of 5-nitro-substituted spiropyran **4e**. The presence of a strong electron-withdrawing group in its indoline part leads to a hypsochromic shift of the long-wavelength absorption maximum (see Table 2). Note that the presence of 6′-formyl group in the coumarin fragment of the molecule leads to a considerable bathochromic shift of the long-wavelength absorption maximum of the merocyanine isomers **M** of compounds **4a**—**g**, which reaches 24—40 nm in comparison with the structurally similar spiropyran containing no aldehyde group.[17]

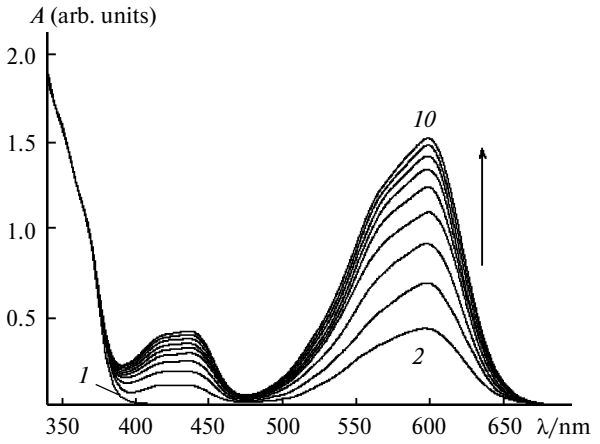



**Fig. 3.** Electron absorption spectra of compound **4b** ($C$ = $= 8.2 \cdot 10^{-5}$ mol L$^{-1}$) in toluene before (*1*) and after irradiation (*2*—*10*) ($\lambda_{irr}$ = 360 nm, $\Delta t$ = 30 s).

After stopping the irradiation, the solutions of spiropyrans **4a**—**g** lose their color, which can be attributed to the proceeding the recyclization reactions **M**→**S** in the ground

state (see Scheme 3). That means that all the coumarin spiropyrans obtained exhibit photochromic properties.

The kinetics of the reverse dark reactions obey the monoexponential law, that makes it possible to determine lifetimes of merocyanine isomers **M**. The lifetimes of the colored forms lie within 0.1—16.7 s and essentially depend on the nature of substituents in the indoline fragment (see Table 2). The electron-donating groups in the indoline part of spiropyrans lead to the increase in the lifetimes of merocyanine isomers, for example, compound **4c** with 5-methoxy group is characterized by a longest lifetime, which is 16.7 s. Conversely, the introduction of electron-withdrawing substituents decreases the thermal stability of merocyanine forms, which is seen, for example, for 5-nitro-substituted spiropyran **4e** characterized by the lifetime of 0.1 s. A comparison of the properties of spiropyrans **4a—g** with those of spiropyran containing no aldehyde group[17] demonstrates the stabilizing effect of the formyl substituent in the coumarin fragment on the thermal stability of merocyanine isomers. The correlations noted bear a general character for spirocyclic systems, spiropyrans and spirooxazines, and are determined by the influence of electron-withdrawing and electron-donating properties of the substituting groups in different parts of the molecule on the stabilization of the bipolar merocyanine structure.[18] Electron-donating groups in the indoline fragment lead to the delocalization of the positive charge on the nitrogen atom, whereas electron-withdrawing substituents in the benzopyran part lead to the delocalization of the negative charge on the oxygen atom and, therefore, to the stabilization of the bipolar structure of the merocyanine form.[19,20] In contrast to this, the introduction of electron-withdrawing substituents in the indoline part of spiropyrans destabilizes the bipolar merocyanine structure.[18]

The rate constants of thermal recyclization reaction of spiropyrans **4a—g** increase with the raising temperature. The character of the temperature dependence of the rate constants obeys the Arrhenius law. The dependence of the rate constants on the reciprocal temperature is used to determine activation energies ($E_{MS}$[a]) of the reverse dark processes, which are given in Table 2. As it is seen from the table data, the activation energies correlate with the lifetimes, reaching the highest value in the case of methyl-substituted spiropyran **4b** and the lowest for 5-nitro-substituted spiropyran **4e**.

In conclusion, design of coumarin spiropyrans containing a formyl group was accomplished based on quantum chemical modeling. Synthetic procedures were developed and used for obtaining a number of photochromic spiropyrans containing a formylcoumarin fragment with various substituents in the indoline part annulated to the 2*H*-pyran ring. It was found that the introduction of the formyl group into the coumarin part of the molecule of spiropyrans leads to considerable changes of spectral and kinetic characteristics: a bathochromic shift of the long-wavelength absorption band of merocyanine isomers and an increase in their lifetime.

## Experimental

Quantum chemical calculations of structures and relative stabilities of spirocyclic and merocyanine forms of spiropyrans **1—4** were performed using the Gaussian 03[21] program by density functional theory (DFT) with the B3LYP[22] functional and a standard 6-31G(d,p) basis. The search for the stationary points on the potential energy surface was carried out by the complete optimization of molecular geometry. All the stationary points found are characterized by the stable wave function.

$^1$H NMR spectra were recorded on Unity-300 spectrometer (Varian Medical Systems, USA, 300 MHz) in $CDCl_3$. Residual signals of $CHCl_3$ (δ 7.24) were used as a reference, the δ values were measured with an accuracy to 0.01 ppm, spin-spin coupling constants with an accuracy to 0.1 Hz. Vibrational spectra were recorded on an Excalibur 3100 FT-IR spectrometer (Varian Medical Systems) by frustrated total internal reflection, using a ZnSe crystal. Mass spectra were recorded on a GCMS-QP2010SE gas chromato-mass spectrometer (Shimadzu, Japan) with the system of the direct injection of the sample (ionization energy 70 eV). Electron absorption spectra and kinetic curves of thermal recyclization reactions of compounds under study were recorded on a Cary-50 spectrophotometer (Varian Medical Systems) with a console for thermostation of the samples. Photolysis of solutions was performed using a Newport 66902 radiator (Newport Corp., USA) based on a xenon lamp (300 W) with a Newport 77250 monochromator for the emission at a required wavelength in the range 240—800 nm. Solutions were prepared in toluene (Sigma-Aldrich Corp., USA) of spectroscopic grade. Elemental analysis was performed using a CHN-analyzer (KOVO, ChSSR). Melting points were measured in a glass capillary on a PTP-M device (Labtekh, Russia) without additional correction.

**Synthesis of indoline spiropyrans 4a—g (general procedure).** Triethylamine (0.1 mL, 0.7 mmol) was added to a solution of 5-hydroxy-4,7-dimethyl-2-oxo-2*H*-chromene-6,8-dicarbaldehyde (**5**)[23] (1.1 mmol) and substituted 2,3,3-trimethyl-3*H*-indolium perchlorate **6a—g**[24] (1 mmol) in propan-2-ol (20 mL) with reflux. The reaction mixture was refluxed for 5 h and cooled, then poured into water (50 mL) and extracted with chloroform (2×25 mL). The chloroform layer was dried with calcium chloride and concentrated to 10—15 mL. The residue was separated by column chromatography (sorbent $Al_2O_3$, eluent benzene) and recrystallized from benzene.

1,3,3,5′,10′-Pentamethyl-8′-oxo-8′H-spiro[indoline-2,2′-pyrano[2,3-*f*]chromene]-6′-carbaldehyde (**4a**) and 1,3,3,5,5′,10′-hexamethyl-8′-oxo-8′H-spiro[indoline-2,2′-pyrano[2,3-*f*]chromene]-6′-carbaldehyde (**4b**) were obtained earlier.[17]

**5-Methoxy-1,3,3,5′,10′-pentamethyl-8′-oxo-8′*H*-spiro-[indoline-2,2′-pyrano[2,3-*f*]chromene]-6′-carbaldehyde (4c)** was obtained according to the general procedure from aldehyde **5** and 5-methoxy-1,2,3,3-tetramethyl-3*H*-indolium perchlorate (**6c**) (0.30 g, 1 mmol). The yield was 0.13 g (31%). Lilac crystals, m.p. 205—207 °C. IR, ν/cm$^{-1}$: 1745, 1680, 1610, 912. $^1$H NMR ($CDCl_3$), δ: 1.26 (s, 3 H, 3-Me); 1.29 (s, 3 H, 3-Me); 1.92 (s, 3 H, 5′-Me); 2.69 (s, 3 H, 10′-Me); 2.75 (s, 3 H, NMe); 3.82 (s, 3 H,

5-OMe); 5.90 (d, 1 H, 3′-H, $J$ = 10.80 Hz); 6.00 (s, 1 H, 9′-H); 6.49 (d, 1 H, 7-H, $J$ = 7.70 Hz); 6.73 (d, 1 H, 4′-H, $J$ = 10.80 Hz); 6.74 (d, 1 H, 6-H, $J$ = 7.70 Hz); 7.25 (s, 1 H, 4-H); 10.74 (s, 1 H, CHO). MS (EI, 70 eV), $m/z$ ($I_{rel}$ (%)): 431 $[M]^+$ (100), 416 (40), 403 (7), 388 (10). Found (%): C, 72.66; H, 5.60; N, 3.53. $C_{26}H_{25}NO_5$. Calculated (%): C, 72.37; H, 5.84; N, 3.25.

**5-Chloro-1,3,3,5′,10′-pentamethyl-8′-oxo-8′*H*-spiro[indoline-2,2′-pyrano[2,3-*f*]chromene]-6′-carbaldehyde (4d)** was obtained according to the general procedure from aldehyde **5** and 5-chloro-1,2,3,3-tetramethyl-3*H*-indolium perchlorate (**6d**) (0.31 g, 1 mmol). The yield was 0.14 g (32%). Pale pink crystals, m.p. 220—222 °C. IR, ν/cm$^{-1}$: 1741, 1676, 1606, 908. $^1$H NMR ($CDCl_3$), δ: 1.21 (s, 3 H, 3-Me); 1.25 (s, 3 H, 3-Me); 1.90 (s, 3 H, 5′-Me); 2.67 (s, 3 H, 10′-Me); 2.70 (s, 3 H, NMe); 5.83 (d, 1 H, 3′-H, $J$ = 10.80 Hz); 5.97 (s, 1 H, 9′-H); 6.42 (d, 1 H, 7-H, $J$ = 8.20 Hz); 7.03 (d, 1 H, 4-H, $J$ = 1.90 Hz); 7.13 (dd, 1 H, 6-H, $J$ = 8.20 Hz, $J$ =1.90 Hz); 7.23 (d, 1 H, 4′-H, $J$ = 10.80 Hz); 10.71 (s, 1 H, CHO). MS (EI, 70 eV), $m/z$ ($I_{rel}$ (%)): 435 $[M]^+$ (80), 420 (30), 392 (9), 235 (23), 193 (100). Found (%): C, 69.06; H, 5.22; N, 3.31. $C_{25}H_{22}ClNO_4$. Calculated (%): C, 68.89; H, 5.09; N, 3.21.

**3,3,5′,10′-Pentamethyl-5-nitro-8′-oxo-8′*H*-spiro[indoline-2,2′-pyrano[2,3-*f*]chromene]-6′-carbaldehyde (4e)** was obtained according to the general procedure from aldehyde **5** and 1,2,3,3-tetramethyl-5-nitro-3*H*-indolium perchlorate (**6e**) (0.32 g, 1 mmol). The yield was 0.18 g (41%). Yellow crystals, m.p. 238—240 °C. IR, ν/cm$^{-1}$: 1744, 1677, 1606, 912. $^1$H NMR ($CDCl_3$), δ: 1.24 (s, 3 H, 3-Me); 1.33 (s, 3 H, 3-Me); 1.91 (s, 3 H, 5′-Me); 2.71 (s, 3 H, 10′-Me); 2.84 (s, 3 H, NMe); 5.84 (d, 1 H, 3′-H, $J$ = 10.80 Hz); 5.99 (s, 1 H, 9′-H); 6.55 (d, 1 H, 7-H, $J$ = 8.70 Hz); 7.33 (d, 1 H, 4′-H, $J$ = 10.80 Hz); 7.97 (d, 1 H, 4-H, $J$ = 2.20 Hz); 8.19 (dd, 1 H, H-6, $J$ = 8.20 Hz, $J$ = 2.20 Hz); 10.74 (s, 1 H, CHO). MS (EI, 70 eV), $m/z$ ($I_{rel}$ (%)): 446 $[M]^+$ (88), 431 (53), 375 (8), 204 (100). Found (%): C, 67.46; H, 5.10; N, 6.37. $C_{25}H_{22}N_2O_6$. Calculated (%): C, 67.26; H, 4.97; N, 6.27.

**1-Benzyl-3,3,5′,10′-tetramethyl-8′-oxo-8′*H*-spiro[indoline-2,2′-pyrano[2,3-*f*]chromene]-6′-carbaldehyde (4f)** was obtained according to the general procedure from aldehyde **5** and 1-benzyl-1,2,3,3-tetramethyl-3*H*-indolium perchlorate (**6f**) (0.35 g, 1 mmol). The yield was 0.18 g (41%). flesh-colored crystals, m.p. 232—234 °C. IR, ν/cm$^{-1}$: 1730, 1676, 1610, 909. $^1$H NMR ($CDCl_3$), δ: 1.31 (s, 3 H, 3-Me); 1.34 (s, 3 H, 3-Me); 1.90 (s, 3 H, 5′-Me); 2.68 (s, 3 H, 10′-Me); 4.05 (d, 1 H, $NCH_2$, $J$ = 16.19 Hz); 4.50 (d, 1 H, $NCH_2$, $J$ = 16.19 Hz); 5.90 (s, 1 H, 9′-H); 5.98 (d, 1 H, 3′-H, $J$ = 10.80 Hz); 6.33 (d, 1 H, 7-H, $J$ = 7.70 Hz); 6.85 (t, 1 H, 5-H, $J$ = 7.34 Hz, $J$ = 7.34 Hz); 7.05—7.20 (m, 8 H, ArH, 6-H, 4-H, 4′-H); 10.72 (s, 1 H, CHO). MS (EI, 70 eV), $m/z$ ($I_{rel}$ (%)): 477 $[M]^+$ (35), 386 (11), 235 (23), 144 (16), 91 (100). Found (%): C, 77.70; H, 5.92; N, 3.08. $C_{31}H_{27}NO_4$. Calculated (%): C, 77.97; H, 5.70; N, 2.93.

**1-Isopropyl-3,3,5′,10′-tetramethyl-8′-oxo-8′*H*-spiro[indoline-2,2′-pyrano[2,3-*f*]chromene]-6′-carbaldehyde (4g)** was obtained according to the general procedure from aldehyde **5** and 1-isopropyl-1,2,3,3-tetramethyl-3*H*-indolium perchlorate (**6g**) (0.30 g, 1 mmol). The yield was 0.15 g (35%). Pale pink crystals, m.p. 188—190 °C. IR, ν/cm$^{-1}$: 1740, 1678, 1610, 910. $^1$H NMR ($CDCl_3$), δ: 1.14 (s, 3 H, 3-Me); 1.23 (s, 3 H, 3-Me), 1.24 (d, 3 H, $CHMe_2$, $J$ = 8.70 Hz); 1.37 (d, 3 H, $CHMe_2$, $J$ = 8.70 Hz); 1.97 (s, 3 H, 5′-Me); 2.70 (s, 3 H, 10′-Me); 3.28 (m, 1 H, NCH); 5.80 (d, 1 H, 3′-H, $J$ = 10.80 Hz); 5.98 (s, 1 H, 9′-H); 6.72 (d, 1 H, 7-H, $J$ = 7.84 Hz); 6.85 (t, 1 H, 5-H, $J$ = 7.39 Hz); 7.01—7.12 (m, 2 H, 6-H, 4-H); 7.18 (d, 1 H, 4′-H, $J$ = 10.80 Hz); 10.72 (s, 1 H, CHO). MS (EI, 70 eV), $m/z$ ($I_{rel}$ (%)): 429 $[M]^+$ (100), 414 (62), 386 (11), 372 (10). Found (%): C, 75.66; H, 6.50; N, 3.43. $C_{27}H_{27}NO_4$. Calculated (%): C, 75.50; H, 6.34; N, 3.26.

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