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# Synthesis and Photochromic Properties of Spiropyrans Containing a Fused Benzopyranone Fragment

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**Abstract**—New spiro compounds of the indole, phthalazine, isobenzofuran, and benzopyran series, containing a fused benzopyranone fragment in the chromene moiety, were synthesized. Indole derivatives were found to exhibit photochromic properties under stationary conditions at 293 K. The thermal stability of merocyanine isomers sharply decreases upon introduction of electron-withdrawing nitro group into the indole fragment and fusion of a benzene ring to the chromene fragment.

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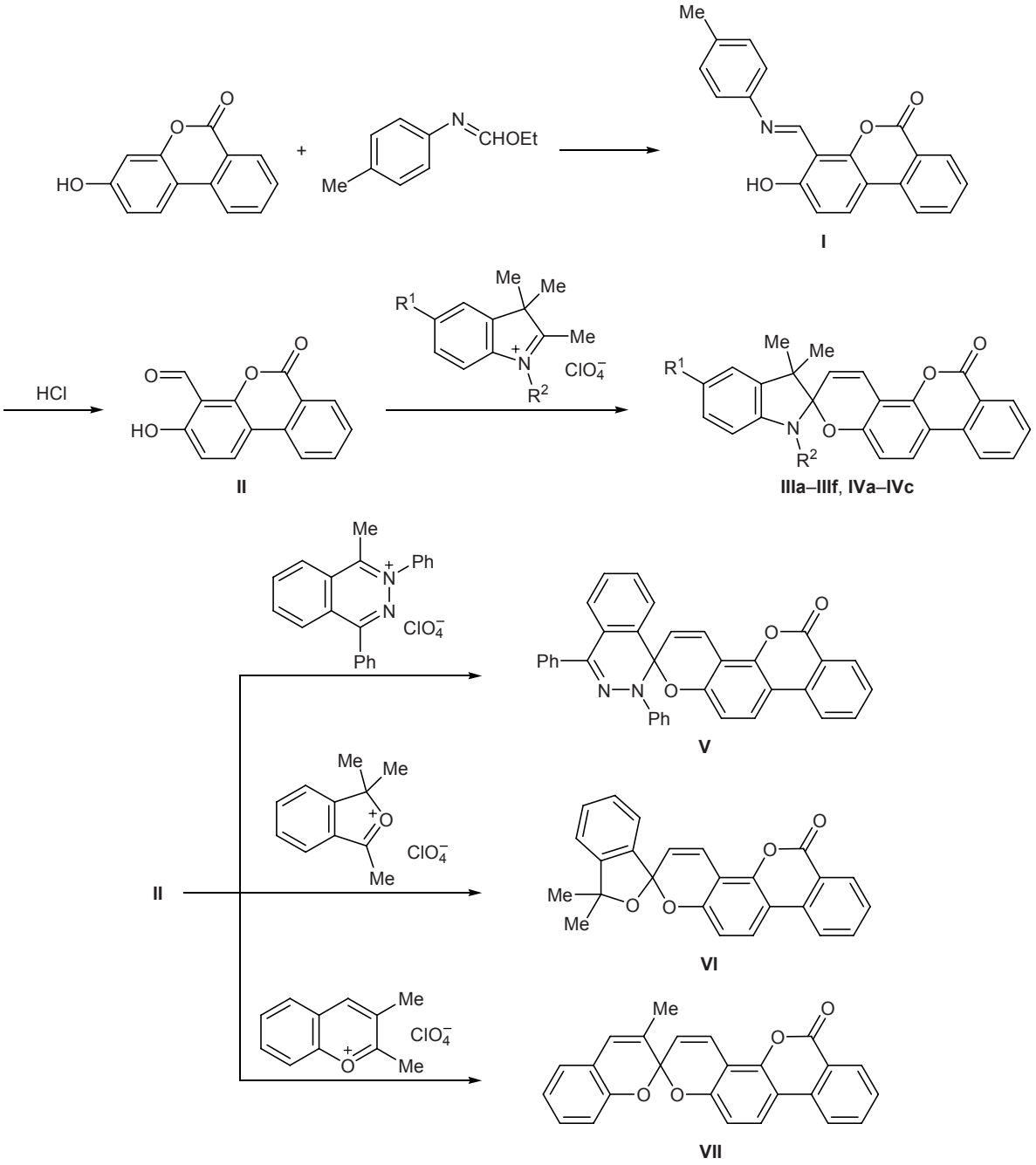
Photochromic compounds on the basis of spiropyrans and spirooxazines are promising as materials for optical data storage devices and photoswitches and are widely used in technics due to their photo-, thermo-, and solvatochromic properties [1–3]. Photodynamic parameters of spiropyrans depend on the structure of both chromene and hetarene fragments of their molecules [4]. The mechanism of photochromic transformations of spiropyrans involves reversible dissociation of the $C_{spiro}$–O bond in the cyclic isomer, followed by *Z*–*E* isomerization to colored merocyanine structure. The latter may be converted into the initial spiro isomer on heating or irradiation with visible light. Some spiropyrans of the indole series containing a benzopyranone fragment were reported previously [5, 6]. In the present work we synthesized new spiro compounds of the indole, phthalazine, isobenzofuran, and benzopyran series and examined their spectral and photochromic properties with a view to estimate the effects of benzene ring fusion in the pyranone fragment and structure of the hetarene fragment on the behavior of the spirocyclic isomers.

Condensation of 3-hydroxy-6*H*-benzo[*c*]chromen-6-one with ethyl *N*-(4-methylphenyl)formimidate generated *in situ* from *p*-toluidine and ethyl orthoformate gave 3-hydroxy-4-(4-methylphenyliminomethyl)-6*H*-benzo[*c*]chromen-6-one (**I**) which was subjected to hydrolysis with dilute hydrochloric acid to obtain 3-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-4-carbaldehyde (**II**). Spiro compounds **III**–**V** were synthesized by condensation of 3-hydroxy-6-oxo-6*H*-benzo[*c*]-chromene-4-carbaldehyde (**II**) with the corresponding 3*H*-indolium or 1-methyl-2,4-diphenylphthalazinium perchlorates in the presence of triethylamine. Compounds **VI** and **VII** were obtained by heating aldehyde **II** with an equimolar amount of 1,3,3-trimethylisobenzofuranium or 2,3-dimethylchromenylium perchlorate, respectively, in boiling acetic acid and subsequent treatment of the oxonium salt thus formed with anhydrous ammonia in benzene (Scheme 1).

The IR spectra of **III**–**VII** contained absorption bands at 1600–1630 $cm^{-1}$, typical of stretching vibrations of C=C bond in the pyran ring, and carbonyl absorption bands in the region 1720–1740 $cm^{-1}$. Compounds **III**–**VII** displayed in the $^1H$ NMR spectra two singlets at δ 1.15–1.75 ppm from nonequivalent geminal methyl groups, which indicated their cyclic structure. The doublet signal from 3′-H in the pyran ring was characterized by a coupling constant *J* of 9.7–10.7 Hz, which corresponds to *cis* configuration of the vinyl fragment.

In the electronic absorption spectra of spiropyrans **III**–**VII** in toluene the long-wave absorption maxima were located at λ 333–339 nm, i.e., in the region

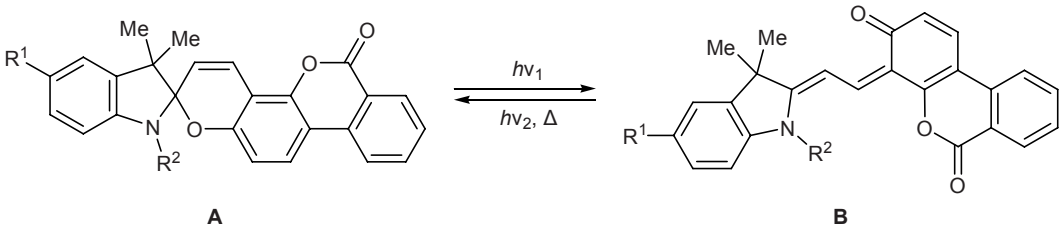
**Scheme 1.**




**III**, $R^1$ = H, $R^2$ = Me (**a**), Et (**b**), $C_8H_{17}$ (**c**), *i*-Pr (**d**), $PhCH_2$ (**e**), $HO(CH_2)_2$ (**f**); **IV**, $R^2$ = Me, $R^1$ = Me (**a**), Cl (**b**), $O_2N$ (**c**).

typical of cyclic isomers **A** [1, 2, 7] (Scheme 2, Fig. 1). The position of the long-wave absorption maximum depends only slightly on the nature of the heterocyclic fragment (compounds **III**–**VII**) and on the substituents ($R^1$, $R^2$) in the indole fragment (**IIIb**–**IIIf**, **IVa**–**IVc**). As shown previously, the reason is that structural components of molecules **III**–**VII** are not coplanar to each other, and the electron transition responsible for the long-wave absorption band is localized on the chromene fragment [8]. The lack of appreciable electronic interaction between the molecular fragments allows us to consider the electronic absorption spectra of **III**–**VII** to be linear combination of the spectra of the corresponding components. Structural modeling studies showed that the longwave maximum belongs to photochemically active chromene fragment and that

**Scheme 2.**




**A** **B**

the shortwave absorption maximum originates from the other heterocyclic fragment [8].

Acyclic merocyanine isomers **B** absorb at considerably longer wavelengths as compared to their cyclic isomers **A** [1, 2, 7]. The absence of absorption bands with $\lambda_{max} > 400$ nm in the spectra of spiro compounds **III**–**VII** in toluene suggests that the ring–chain equilibrium **A** ⇆ **B** in toluene at 293 K is completely displaced toward spiro isomer **A**.

Irradiation of solutions of **III** and **IV** at a wavelength corresponding to absorption maximum of the cyclic form is accompanied by appearance in the electronic absorption spectra of two structured bands in the visible region with their maxima at $\lambda_1$ 405–429 and $\lambda_2$ 572–663 nm (the solution turns colored) due to electronic transitions $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$, respectively, in merocyanine isomers **B** (see table, Fig. 1) [2, 7]. As follows from the data in table, the position of vibrational maxima on the long-wave absorption band of structure **B** depends on the nature of the $R^1$ and $R^2$ substituents. In going from $R^2$ = Alk to $R^2 = PhCH_2$ (**IIIe**) these maxima shift to longer wavelengths, whereas blue shift is observed for compound **IIIf** with $R^2 = HOCH_2CH_2$. Compound **IVb** ($R^1$ = Cl) absorbs at longer wavelength than does its 5′-methyl-substituted analog **IVa**. No fluorescence was observed at 293 K for both cyclic isomer **A** and merocyanine structure **B**.

After termination of UV irradiation, thermal relaxation processes **B** → **A** were observed for compounds **III** and **IV**, and the solutions turned colorless. The kinetics of thermal recyclization are well described by exponential function (Fig. 2). The lifetime of merocyanine form **B** of **III** and **IV** in toluene at 293 K ranges from 1.2 to 27.6 s. As shown previously, introduction of a nitro group into the chromene fragment of indole-based spiro compounds considerably increases the lifetime of their merocyanine isomers [9]. In contrast, the presence of a nitro group in position 5′ of the indole fragment (compound **IVc**) sharply shortens the lifetime of the colored form as compared to 5′-methyl analog **IVa**. A similar pattern was observed for spiro compounds derived from indole and naphthooxazines, where the substituents in the indole and naphthooxazine fragments affected the degree of quinoidization or dipolar character of the merocyanine form. Electron-donor substituents in the indole fragment and electron-withdrawing substituents in the naphthooxazine fragment of these compounds favored delocalization of the positive charge on the nitrogen atom, and of the negative charge, on the oxygen atom, thus stabilizing the dipolar structure. In contrast, electron-withdrawing substituents in the indole fragment and electron-donating groups in the naphthooxazine fragment favor localization of the positive charge on the nitrogen atom and of the negative charge on the oxygen; as a result, the dipolar structure becomes thermodynamically unfavorable, while quinoid merocyanine structure is stabilized [10]. Likewise, the presence of a nitro group in the indole fragment of molecule **IVa** reduces the degree of charge separation between the nitrogen and oxygen atoms in merocyanine structure **B** (its polarity decreases) and weakens stabilizing effect of the solvent.

The lifetime of the colored form also shortens upon replacement of methyl group on the nitrogen atom by benzyl (**IIIe**), as well as upon substitution of hydrogen

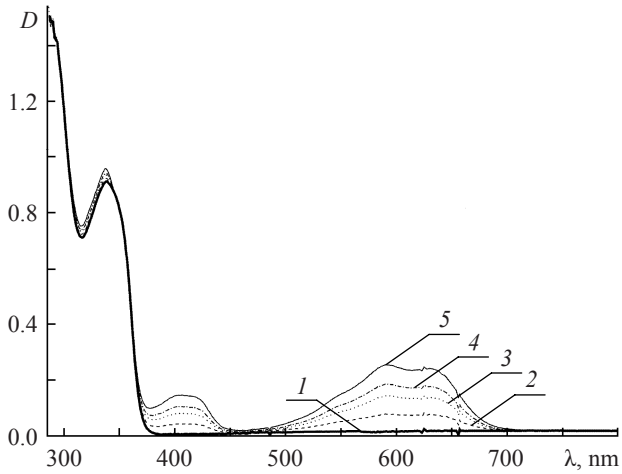



**Fig. 1.** Electronic absorption spectra of spiro compound **IIIb** in toluene (*1*) before irradiation and after irradiation with UV light (λ 365 nm; $c = 8.55 \times 10^{-5}$ M) for (2) 6, (3) 10, (4) 15, and (5) 45 s.

Spectral parameters of isomers **A** and **B** of compounds **III** and **IV** and lifetimes of merocyanine isomers **B**; solvent toluene, temperature 293 K

| Comp. no. | Cyclic isomer **A** | | Merocyanine isomer **B** | | |
|---|---|---|---|---|---|
| | $\lambda_{max}$, nm | $\varepsilon_{max}$, mol × $l^{-1}$ $cm^{-1}$ | $\lambda_{1max}$, nm | $\lambda_{2max}$, nm | τ, s |
| **IIIb** | 338 | 10600 | 405 | 592, 630 | 16.0 |
| **IIIc** | 339 | 10200 | 405 | 593, 630 | 16.1 |
| **IIId** | 339 | 10300 | 405 | 592, 628 | 17.7 |
| **IIIe** | 338 | 12700 | 406 | 595, 635 | 3.8 |
| **IIIf** | 335 | 9700 | 405 | 609 | 15.4 |
| **IVa** | 339 | 10100 | 405 | 592, 630 | 27.6 |
| **IVb** | 335 | 11400 | 408 | 595, 637 | 6.3 |
| **IVc** | 353 | 18800 | 429 | 572, 615, 663 | 1.2 |

in position 5′ of the indole fragment by chlorine (**IVc**). The lifetime of acyclic structure **B** is more sensitive to substitution at the 5′-position. Introduction of a methyl group into that position increases the lifetime by more than 40% relative to 5′-unsubstituted analog.

In order to estimate the effect of benzene ring fusion to the chromene fragment of spiropyrans on the thermal stability of their merocyanine isomers, we synthesized compounds **Xa** and **Xb** according to the procedure described previously [11].

The kinetics of dark relaxation processes following photoisomerization of compounds **Xa** and **Xb** were studied under the same conditions as for compounds **III** and **IV**. The lifetimes of the merocyanine forms of **Xa** and **Xb** were estimated at 112.0 and 1.4 s, respectively. Comparison of the lifetimes in couples **IVa**/**Xa** and **IVc**/**Xb** showed that fusion of a benzene ring to the chromene fragment destabilizes the corresponding merocyanine isomers. The ratio $\tau_B/\tau_B$ for 5′-methyl derivatives **IVa** and **Xa** is 1 : 4, whereas the corresponding difference for 5′-nitro analogs **IVc** and **Xb** is considerably smaller. Presumably, destabilizing effect of the 5′-nitro group predominates. This unobvious conclusion is supported by the data for other series of spiro compounds, in particular for 5′-(4,5-diphenyl-1,3-oxazol-2-yl)-substituted spiro[indole-benzo(or naphtho)pyrans] [12, 13].

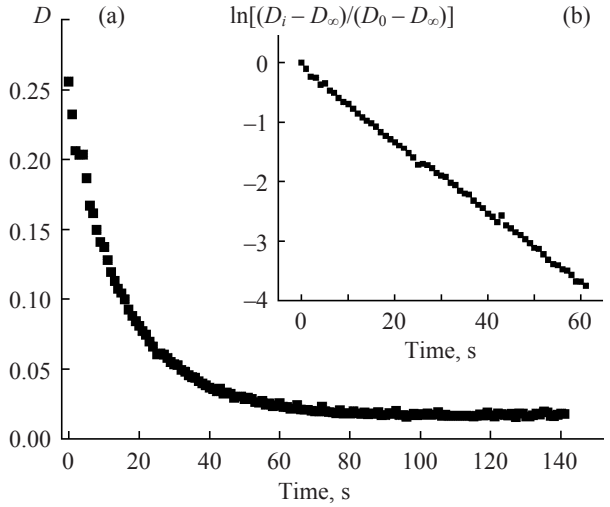
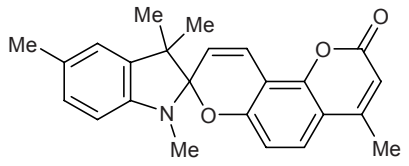
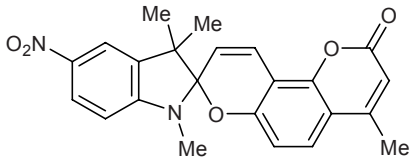



**Fig. 2.** Kinetic curves for thermal relaxation of compound **IIIb** in toluene ($c = 8.55 \times 10^{-5}$ M) in the coordinates (a) $D$–τ and (b) $\ln[(D_i - D_\infty)/(D_0 - D_\infty)]$–τ




**Xa**




**Xb**

Introduction of a nitro group into the chromene fragment reduces the stability of spiro compounds toward photodecomposition as a result of promotion of triplet deactivation channel of electronic excitation energy [14]. Analogous effect is observed for compound **IVc** having a nitro group in the indole fragment. Figure 3 illustrates variations in optical density at the absorption maximum of colored forms of compounds **IVa** and **IVc** under comparable irradiation conditions. It is seen that the photocoloration plot for compound **IVa** only approaches the maximal optical density in 70 s, while the optical density at the long-wave absorption maximum of isomer **B** of compound **IVc** attains its maximum value in 2 s and then decreases by a factor of 4, indicating low stability of the photoinduced structure.

Spiropyrans **V**–**VII** showed no photochromism at 293 K. Presumably, the reason is high rate of recyclization **B**→**A**, which hampers detection of isomer **B** under stationary irradiation conditions.

## EXPERIMENTAL

The electronic absorption spectra were measured on a Specord M40 spectrophotometer. The IR spectra were recorded from samples dispersed in mineral oil

on a Specord 75IR instrument. The $^1$H NMR spectra were obtained on a Varian Unity-300 spectrometer at 300 MHz using $CDCl_3$ as solvent and reference ($CHCl_3$, δ 7.25 ppm). Solutions of compounds **III**–**VII** were irradiated with a DRSh-250 mercury lamp using a set of light filters.

**3-Hydroxy-4-(4-methylphenyliminomethyl)-6*H*-benzo[*c*]chromen-6-one (I).** A mixture of 10 g (47 mmol) of 3-hydroxy-6*H*-benzo[*c*]chromen-6-one [15], 10 g (93 mmol) of *p*-toluidine, and 14 ml of triethyl orthoformate was heated for 12 h at 170°C. The bright orange precipitate was filtered off, washed with ethanol, and recrystallized from DMF. Yield 36%, mp 185–186°C. $^1$H NMR spectrum, δ, ppm: 2.41 s (3H, $CH_3$), 6.98–8.40 m (10H, $H_{arom}$), 9.41 s (1H, =CH), 15.17 s (1H, OH). Found, %: C 76.40; H 4.65; N 4.20. $C_{21}H_{15}NO_3$. Calculated, %: C 76.58; H 4.59; N 4.25.

**3-Hydroxy-6-oxo-6*H*-benzo[*c*]chromene-4-carbaldehyde (II).** Compound **I**, 5 g (15 mmol), was dissolved in 100 ml of dioxane, 100 ml of 15% hydrochloric acid was added on heating, and the mixture was heated for 10 min at the boiling point, cooled, and diluted with water (500 ml). The precipitate was filtered off, dried, and recrystallized from acetone. Yield 78%, mp 232–233°C. IR spectrum, ν, cm$^{-1}$: 1740, 1640, 1600. $^1$H NMR spectrum, δ, ppm: 6.96–8.40 m (6H, $H_{arom}$), 10.68 s (1H, CHO), 12.16 s (1H, OH). Found, %: C 70.13; H 3.40. $C_{14}H_8O_4$. Calculated, %: C 70.00; H 3.36.

**Spiro compounds IIIa–IIIf and IVa–IVc (*general procedure*).** Triethylamine, 0.1 ml (0.7 mmol), was added on heating to a solution of 1.1 mmol of compound **II** and 1 mmol of the corresponding 2,3,3-trimethyl-3*H*-indolium perchlorate in propan-2-ol. The mixture was heated for 2–3 h under reflux, cooled, poured into water, and extracted with several portions of chloroform. The extracts were combined, dried over calcium chloride, and evaporated to a volume of 10–15 ml. The residue was subjected to chromatography on aluminum oxide using chloroform as eluent, and the product was additionally purified by recrystallization from propan-2-ol.

**1′,3′,3′-Trimethyl-1′,3′-dihydro-6*H*-spiro[benzo[*c*]pyrano[2,3-*h*]chromene-2,2′-indol]-6-one (IIIa).** Yield 38%. IR spectrum, ν, cm$^{-1}$: 1730, 1610. $^1$H NMR spectrum, δ, ppm: 1.16 s and 1.28 s (3H each, $CH_3$), 2.62 s (3H, $NCH_3$), 5.83 d (1H, 3-H, $J$ = 10.3 Hz), 6.57–8.42 m (11H, $H_{arom}$, 4-H). Found, %: C 79.06; H 5.30; N 3.53. $C_{26}H_{21}NO_3$. Calculated, %: C 78.97; H 5.35; N 3.54.

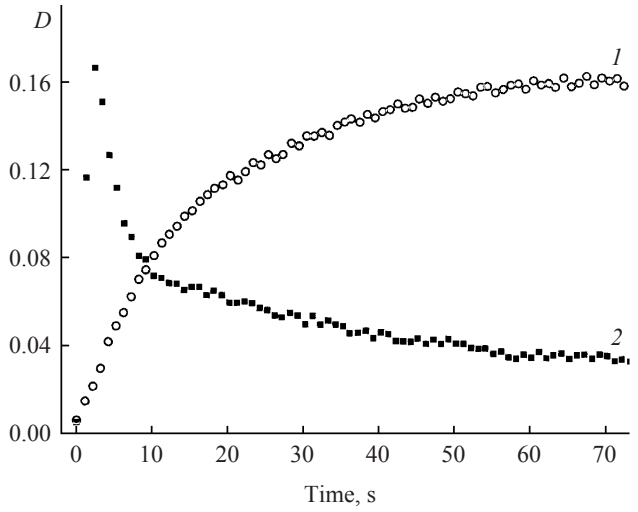



**Fig. 3.** Variation of optical density at the long-wave absorption maxima during irradiation of solutions of spiro compounds (*1*) **IVa** ($c = 7.33 \times 10^{-5}$ M) and (*2*) **IVc** ($c = 4.37 \times 10^{-5}$ M) in toluene with UV light (λ 365 nm).

**1′-Ethyl-3′,3′-dimethyl-1′,3′-dihydro-6*H*-spiro[benzo[*c*]pyrano[2,3-*h*]chromene-2,2′-indol]-6-one (IIIb).** Yield 38%, mp 146–147°C. IR spectrum, ν, cm$^{-1}$: 1730, 1620, 1610. $^1$H NMR spectrum, δ, ppm: 1.15–1.32 m (9H, $CH_3$), 3.21–3.41 m (2H, $CH_2$), 5.82 d (1H, 3-H, $J$ = 10.5 Hz), 6.56–8.38 m (11H, $H_{arom}$, 4-H). Found, %: C 79.11; H 5.65; N 3.57. $C_{27}H_{23}NO_3$. Calculated, %: C 79.20; H 5.66; N 3.42.

**3′,3′-Dimethyl-1′-octyl-1′,3′-dihydro-6*H*-spiro[benzo[*c*]pyrano[2,3-*h*]chromene-2,2′-indol]-6-one (IIIc).** Yield 51%, mp 105–106°C. IR spectrum, ν, cm$^{-1}$: 1720, 1600. $^1$H NMR spectrum, δ, ppm: 1.15–1.37 m (21H, $CH_3$, $CH_2$), 3.14–3.26 m (2H, $CH_2$), 5.83 d (1H, 3-H, $J$ = 10.6 Hz), 6.55–8.38 m (11H, $H_{arom}$, 4-H). Found, %: C 80.15; H 7.22; N 2.80. $C_{33}H_{35}NO_3$. Calculated, %: C 80.29; H 7.15; N 2.84.

**1′-Isopropyl-3′,3′-dimethyl-1′,3′-dihydro-6*H*-spiro[benzo[*c*]pyrano[2,3-*h*]chromene-2,2′-indol]-6-one (IIId).** Yield 6%, mp 255–256°C. IR spectrum, ν, cm$^{-1}$: 1720, 1620, 1600. $^1$H NMR spectrum, δ, ppm: 1.15–1.42 m (12H, $CH_3$), 3.83 m (1H, CH), 5.80 d (1H, 3-H, $J$ = 10.4 Hz), 6.71–8.39 m (11H, $H_{arom}$, 4-H). Found, %: C 79.51; H 6.06; N 3.28. $C_{28}H_{25}NO_3$. Calculated, %: C 79.41; H 5.95; N 3.31.

**1′-Benzyl-3′,3′-dimethyl-1′,3′-dihydro-6*H*-spiro[benzo[*c*]pyrano[2,3-*h*]chromene-2,2′-indol]-6-one (IIIe).** Yield 64%, mp 172–173°C. IR spectrum, ν,

$cm^{-1}$: 1740, 1630, 1600. $^1H$ NMR spectrum, δ, ppm: 1.32 s and 1.37 s (3H each, $CH_3$), 4.21 d (1H, $CH_2$, $J$ = 16.5 Hz), 4.59 d (1H, $CH_2$, $J$ = 16.5 Hz), 5.88 d (1H, 3-H, $J$ = 10.7 Hz), 6.32–8.38 m (16H, $H_{arom}$, 4-H). Found, %: C 81.42; H 5.30; N 3.08. $C_{32}H_{25}NO_3$. Calculated, %: C 81.51; H 5.34; N 2.97.

**1′-(2-Hydroxyethyl)-3′,3′-dimethyl-1′,3′-dihydro-6*H*-spiro[benzo[*c*]pyrano[2,3-*h*]chromene-2,2′-indol]-6-one (IIIf).** Yield 16%, mp 85–86°C. IR spectrum, ν, $cm^{-1}$: 1720, 1610. $^1H$ NMR spectrum, δ, ppm: 1.21 s and 1.33 s (3H each, $CH_3$), 1.83 t (1H, OH), 3.37–3.83 m (4H, $CH_2$), 5.84 d (1H, 3-H, $J$ = 10.5 Hz), 6.67–8.39 m (11H, $H_{arom}$, 4-H). Found, %: C 76.25; H 5.31; N 3.35. $C_{27}H_{23}NO_4$. Calculated, %: C 76.22; H 5.45; N 3.29.

**1′,3′,3′,5′-Tetramethyl-1′,3′-dihydro-6*H*-spiro-[benzo[*c*]pyrano[2,3-*h*]chromene-2,2′-indol]-6-one (IVa).** Yield 37%, mp 205–206°C. IR spectrum, ν, $cm^{-1}$: 1730, 1610. $^1H$ NMR spectrum, δ, ppm: 1.20 s and 1.32 s (3H each, $CH_3$), 2.34 s (3H, 5′-$CH_3$), 2.73 s (3H, $NCH_3$), 5.83 d (1H, 3-H, $J$ = 10.5 Hz), 6.45–8.38 m (10H, $H_{arom}$, 4-H). Found, %: C 79.05; H 5.64; N 3.51. $C_{27}H_{23}NO_3$. Calculated, %: C 79.20; H 5.66; N 3.42.

**5′-Chloro-1′,3′,3′-trimethyl-1′,3′-dihydro-6*H*-spiro[benzo[*c*]pyrano[2,3-*h*]chromene-2,2′-indol]-6-one (IVb).** Yield 42%, mp 160–161°C. IR spectrum, ν, $cm^{-1}$: 1720, 1610, 1600. $^1H$ NMR spectrum, δ, ppm: 1.20 s and 1.30 s (3H each, $CH_3$), 2.74 s (3H, $NCH_3$), 5.79 d (1H, 3-H, $J$ = 10.4 Hz), 6.44–8.39 m (10H, $H_{arom}$, 4-H). Found, %: C 72.68; H 4.75; N 3.17. $C_{26}H_{20}ClNO_3$. Calculated, %: C 72.64; H 4.69; N 3.26.

**1′,3′,3′-Trimethyl-5′-nitro-1′,3′-dihydro-6*H*-spiro[benzo[*c*]pyrano[2,3-*h*]chromene-2,2′-indol]-6-one (IVc).** Yield 6%, mp 255–256°C. IR spectrum, ν, $cm^{-1}$: 1730, 1610. $^1H$ NMR spectrum, δ, ppm: 1.22 s and 1.35 s (3H each, $CH_3$), 2.88 s (3H, $NCH_3$), 5.82 d (1H, 3-H, $J$ = 10.5 Hz), 6.54–8.40 m (10H, $H_{arom}$, 4-H). Found, %: C 70.91; H 4.45; N 6.40. $C_{26}H_{20}N_2O_5$. Calculated, %: C 70.90; H 4.58; N 6.36.

**2′,4′-Diphenyl-2′*H*,6*H*-spiro[benzo[*c*]pyrano-[2,3-*h*]chromene-2,1′-phthalazin]-6-one (V)** was synthesized as described above for compounds **III** and **IV** from 1-methyl-2,4-diphenylphthalazinium perchlorate. Yield 8%, mp 220–221°C. IR spectrum, ν, $cm^{-1}$: 1720, 1600. $^1H$ NMR spectrum, δ, ppm: 6.00 d (1H, 3-H, $J$ = 10.2 Hz), 6.69–8.37 m (21H, $H_{arom}$, 4-H). Found, %: C 81.03; H 4.35; N 5.32. $C_{35}H_{22}N_2O_3$. Calculated, %: C 81.07; H 4.28; N 5.40.

**3,3-Dimethyl-3*H*,6′*H*-spiro[2-benzofuran-1,2′-benzo[*c*]pyrano[2,3-*h*]chromen]-6′-one (VI).** A mixture of 1 mmol of 1,3,3-trimethyl-2-benzofuranium perchlorate and 1 mmol of compound **II** in 10 ml of acetic acid was heated for 15–20 min under reflux. The mixture was cooled, the precipitate was filtered off and dissolved in 50 ml of benzene, and dry ammonia was passed through the solution. The mixture was evaporated, and the residue was recrystallized from propan-2-ol. Yield 33%, mp 192–193°C. IR spectrum, ν, $cm^{-1}$: 1720, 1610. $^1H$ NMR spectrum, δ, ppm: 1.57 s and 1.70 s (3H each, $CH_3$), 5.98 d (1H, 3′-H, $J$ = 10.4 Hz), 6.91–8.40 m (11H, $H_{arom}$, 4′-H). Found, %: C 78.61; H 4.69. $C_{25}H_{18}O_4$. Calculated, %: C 78.52; H 4.74.

**3′-Methyl-6*H*-spiro[benzo[*c*]pyrano[2,3-*h*]chromene-2,2′-chromen]-6-one (VII)** was synthesized in a similar way from 2,3-dimethylchromenylium perchlorate. Yield 10%. IR spectrum, ν, $cm^{-1}$: 1730, 1610. $^1H$ NMR spectrum, δ, ppm: 2.00 s (3H, $CH_3$), 5.98 d (1H, 3-H, $J$ = 9.7 Hz), 6.91–8.40 m (12H, $H_{arom}$, 4-H). Found, %: C 79.05; H 4.20. $C_{25}H_{16}O_4$. Calculated, %: C 78.94; H 4.24.

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