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PHOTO- AND THERMOCHROMIC SPIROPYRANS 42.* THE EFFECT OF STRUCTURAL FACTORS ON THE PHOTOCHROMIC PROPERTIES OF INDOLINOSPIRO-PYRANS CONTAINING A CONDENSED FURAN FRAGMENT

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Syntheses are reported for a series of N-substituted indolinospiropyrans containing a fused furan fragment in the benzopyran part of the molecule. The structure of these compounds was established by IR and multinuclear NMR spectroscopy. A study was carried out on the effect of the fused benzene ring and bulky N-benzyl substituent on the photochromic properties of these compounds in solution and in a polymer matrix. Dynamic NMR spectroscopy was used to study the thermally induced isomerization of the N-benzyl derivative.

Keywords: furo[3,2-*f*]chromene, indolinospiropyrans, multinuclear NMR spectroscopy, photochromism, photoisomerization.

The major factors affecting the spectrokinetic behavior of photochromic compounds with an indoline spiro ring are the structure of the indoline segment and the nature of the substituent at the nitrogen atom. Both these factors affect the stability of the open form and, thereby, the photochromic properties such as the solution color intensity and lifetime of the open form [2].

In previous work [3], we obtained *N*-methylindolinospiropyrans **1a**,**b**. A spectrokinetic study showed that the equilibrium is shifted toward formation of the colored photoinduced form upon the irradiation of ethanolic solutions of spiropyrans **1a**,**b** at 365 nm at room temperature.

In this work, in the framework of systematic studies we investigated the effect of the steric effect of the bulky *N*-benzyl substituent as well as of isomeric benzo-fused *N*-methylindolinospiropyrans, which were thought capable of hindering the photochromic transformations.

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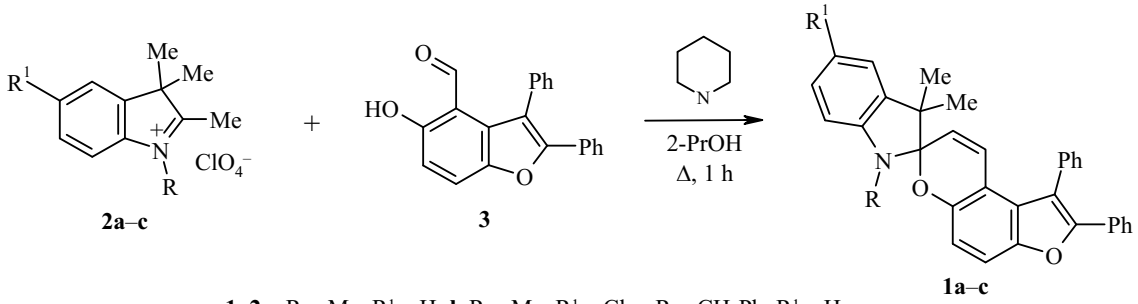
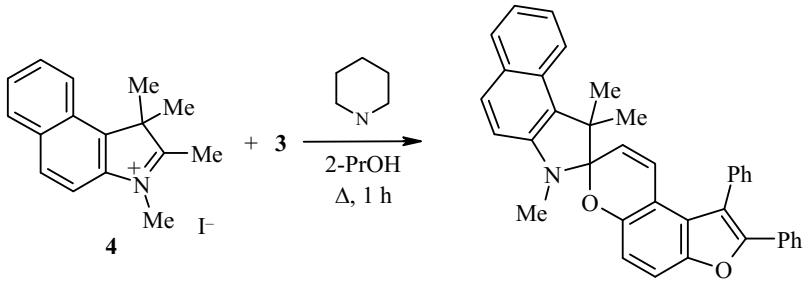
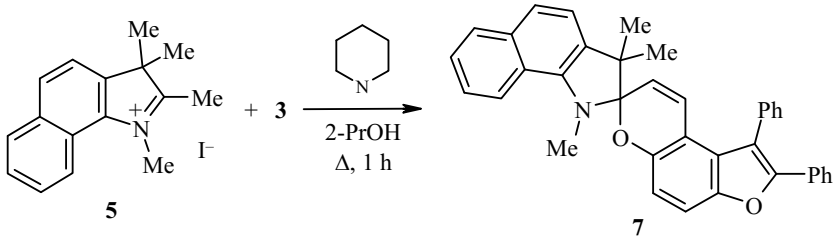
For this purpose, we obtained spiropyrans **1a-c** through brief heating of equimolar amounts of the corresponding *N*-substituted 2,3,3-trimethylindolenylium perchlorates **2a-c**, hydroxyaldehyde **3**, and piperidine in 2-propanol at reflux. Under analogous conditions, benzo-fused derivatives **6** and **7** were obtained from 1,2,3,3-tetramethylbenzo[*e*]indolinium (**4**) and 1,2,3,3-tetramethylbenzo[*g*]indolinium iodides (**5**).

The structures of products **1**, **6**, **7** were confirmed by elemental analysis, IR and ^{1}H NMR spectroscopy. In addition, the structure of spiropyran **1c** was further confirmed by ^{13}C and ^{15}N NMR spectroscopy. The IR spectra of these compounds have bands at 1600-1620 (*υ* C=C), 1250-1290 (*υ* C-N), and 930-950 cm^{-1} (*υ* C-O).



1, **2 a** R = Me, R^{1} = H; **b** R = Me, R^{1} = Cl; **c** R = CH_2Ph, R^{1} = H





The protons of the *gem*-dimethyl groups at position 3 of the indoline fragment in the ^{1}H NMR spectra of spiropyrans **1a-c**, **6**, **7** are seen at 1.08-1.26 and 1.32-1.65 ppm due to their magnetic inequivalence, which is evidence for the spirocyclic structure of these products. The ^{1}H NMR spectra of spiropyran **1c** shows two doublets for the benzyl substituent methylene group at 4.12 and 4.53 ppm in addition to the two three-proton singlets from the *gem*-dimethyl group. In order to refine the structure of these compounds, a series of two-dimensional NMR spectral experiments were carried out for spiropyran **1c** (Supplementary material to this article).

Our assignment of the signals in the ^{1}H NMR spectra of spiropyran **1c** was supported by the two-dimensional ^{1}H–^{1}H COSY correlation spectrum. The ^{1}H–^{13}C HSQC single-quantum heteronuclear correlation spectrum was used to identify the signals in the ^{13}C NMR spectrum of spiropyran **1c**. ^{1}H–^{13}C HMBC and ^{1}H–^{15}N HMBC techniques for long-range heteronuclear correlation were used for the assignment of the chemical shifts of the carbon atoms not attached to hydrogen atoms.

TABLE 1. Absorption Spectral and Kinetic Properties of Spiropyrans **1a-c**, **6** and **7** in Ethanol

Compound	λ_{max}^{abs} (SP), nm (ε, $M^{-1}\times cm^{-1}$)	λ_{max}^{abs} (MC), nm	$\tau_{1/2}^{20°C}$, s
1a	245, 320, 362 sh	476, 586	3.09
1b	252, 320, 361 sh	484, 598	1.16
1c	244 (22100), 323 (29300), 363 (4500) sh	482, 596	0.69
6	246 (52100), 320 (47850), 365 (7560) sh	487, 601	3.59
7	249 (55400), 324 (48300), 368 (9100) sh	481, 609	2.42

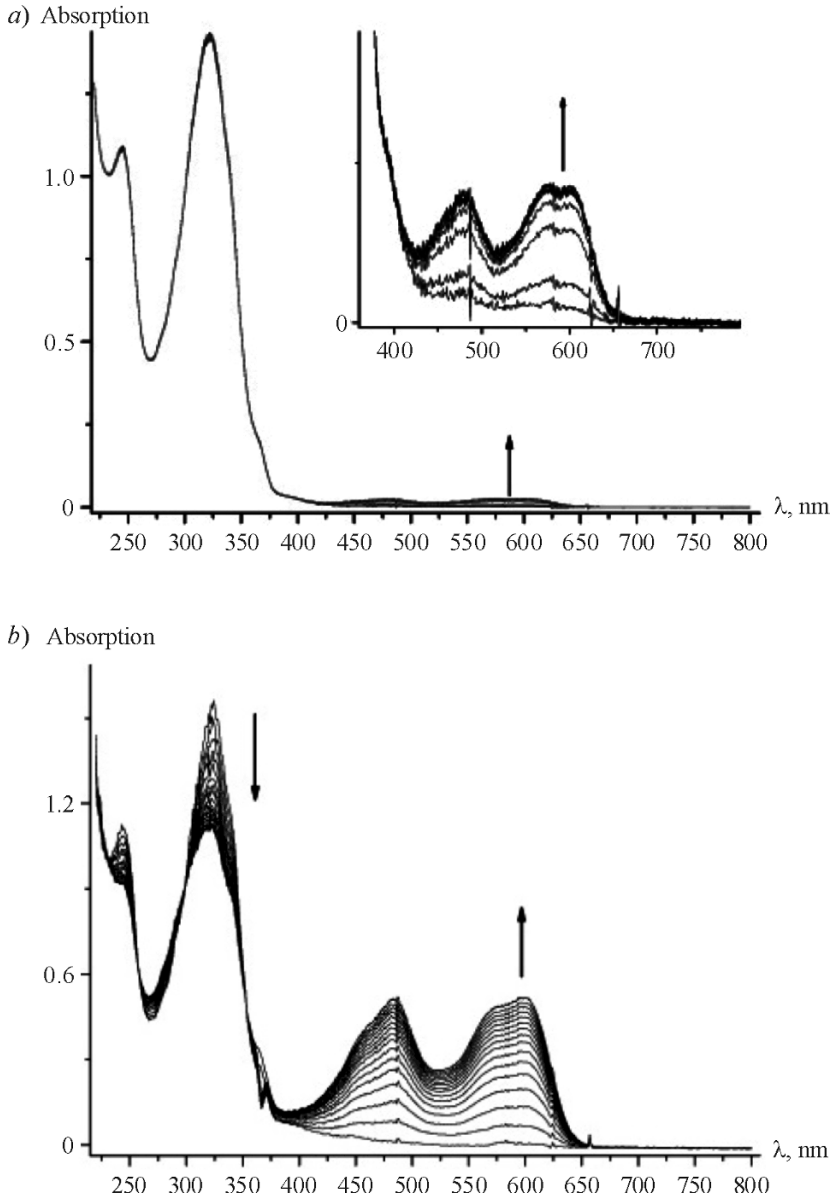


Fig. 1. Absorption spectra of spiropyran **1c** in ethanol upon steady-state irradiation at λ 365 nm at 20°C (the interval between the spectra was 1 s) (*a*) and at -70°C (the interval between the spectra was 10 s) (*b*).

The long-range correlation spectra permitted the unequivocal identification of the carbon atoms in spiropyran **1c** not attached to hydrogen atoms and fully confirmed the structure of this compound.

The signal at 104.2 ppm was reliably assigned to the spiro atom C-2(7'), which is in complete accord with second-order coupling constants reflecting coupling of the carbon atom with the proton H-8' and third-order coupling constants reflecting coupling of the carbon atom C-2(7') with the protons of the methyl groups at position 3' as well as with the methylene group at the nitrogen atom.

The results of the photochemical investigation of ethanolic solutions of photochromic spiropyrans **1a-c**, **6**, and **7** (Table 1) showed that the intensity of the absorption band of the open form of benzyl derivative **1c** is much lower than for the analogous parameter of spiropyrans **1a**,**b** after photoirradiation at 365 nm at room temperature (Fig. 1*a*). Careful examination of the kinetic curve for the absorption intensity when taking the spectra for spiropyrans **1a-c** at an interval of 1 s showed that they have a similar growth rate only in the first stage, while the absorption intensity of the solution of the benzyl derivative upon further irradiation almost stops increasing.

This finding may indicate either steric hindrance related to opening of the pyran heterocycle due to the bulky substituent or photodecomposition of the open form, whose accumulation in the irradiated solution would lead to steady enhancement of coloration. On the other hand, the parameter characterizing the lifetime of the open form ($\tau_{1/2}$) of benzyl derivative **1c** is 0.7 s, which is comparable to the analogous value for methyl derivatives **1a**,**b**. Similar time characteristics are also found for solutions of spiropyrans **1a-c** upon taking the spectra at -70°C (60, 60, and 45 s for compounds **1a**, **1b**, and **1c**, respectively). However, the rates of increase of the absorption intensity of the benzyl derivative are not discernible on the background of the other photochromic products, which is shown in the case of compound **1c** (Fig. 1*b*). These results indicate photodecomposition of the open form of compound **1c** at room temperature. In order to confirm this hypothesis, we irradiated a solution of compound **1c** with ultraviolet light at 365 nm for 2 h at 24°C. No decoloration of the solution was observed in this case. This finding indicated accumulation of a photodecomposition product having constant coloration. However, the presence of impurities in significant amounts was not observed using NMR spectroscopy, indicating that, despite formation of a colored photodecomposition product leading to a shift of the photoisomerization equilibrium toward formation of the open form, ring opening is slow and rate-determining for formation of the photodecomposition product of the merocyanine form.

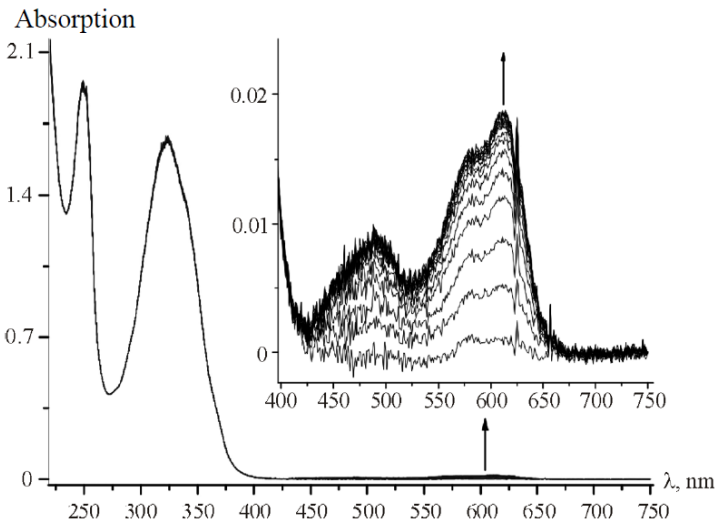


Fig. 2. Absorption spectra of a solution of spiropyran **7** in ethanol upon irradiation at λ 365 nm at 20°C (the interval between the spectra was 1 s). The insert shows visible spectrum on an enlarged scale.

A study of the photochromic properties of isomeric benzo-fused *n*-methylindolinospiropyrans **6** and **7** showed that the steric hindrance arising due to interaction of the *N*-methyl group of spiropyran **7** with the *peri* position of the naphthalene fragment of benzo[*g*]indole leads to deformation and change in electronic properties of the heterocyclic system. This finding is reflected in the spectrokinetic behavior of this compound **7**.

The absorption intensity of spiropyran **7** upon steady state irradiation at λ 365 nm is four times less than for isomer **6** (Figs. 2 and 3). The lifetime of the open form of spiropyran **7** ($\tau_{1/2}$) under these conditions is 2.42 s, which is 1.5 times less than the lifetime of the sterically unhindered isomer **6**. Hence, the structure of spiropyran **7** is less conducive to formation of the merocyanine form than the structure of isomer **6**. The steric hindrance due to the methyl group in the benzo[*g*]indoline skeleton leads to more rapid closing of the pyran heterocycle in spiropyran **7**.

The photochemical transformations of spiropyran **1c** were also studied in a polystyrene film obtained by evaporation of a dichloromethane solution of polystyrene and compound **1c** over 48 h in the dark.

The absorption spectra of the polystyrene film were recorded upon irradiation at 365 nm (Fig. 4). The intensity of the long-wavelength absorption band at 350 nm steadily decreased over 50 min and a slight increase in the optical density at 483 nm was observed. No significant absorption was observed at longer wavelengths (550-700 nm).

Photo- and thermochromic spiropyrans containing diastereotopic groups may be objects for study of thermally induced bond isomerization using dynamic NMR spectroscopy. Such groups in spiropyrans **1** are the *gem*-dimethyl groups at position 3 of the indoline fragment. The rate constants and activation parameters may be determined using the temperature dependence of the NMR spectra of exchanging diastereotopic groups. When there is no exchange, the spectra show two singlets of the inequivalent methyl groups at position 3 and two doublets for the methylene group (Fig. 5).

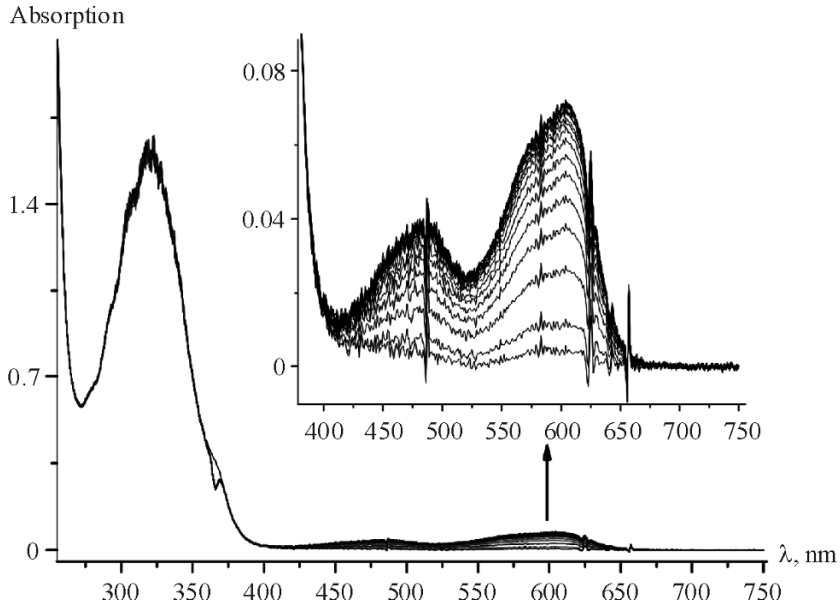


Fig. 3. Absorption spectra of a solution of spiropyran **6** in ethanol upon irradiation at λ 365 nm at 20°C. The intervals between the spectra were 1 s. The insert shows the visible portion of the spectrum on an enlarged scale.

The dynamics was studied in a solution of nitrobenzene-d_5 for spiropyran **1c** (Fig. 5). Upon heating, the peaks of the ^{1}H NMR signals for the protons characterizing spirocyclic form **1c** begin to broaden and coalesce but complete coalescence of both the methyl and methylene protons is not achieved under the experimental conditions. This finding suggests that the free energy for conversion of the closed form of the spiropyrans is rather high and a special calculation apparatus must be used to determine the theoretical coalescence temperature and, thus, the activation parameters of the thermally induced bond isomerization of spiropyran **1c**.

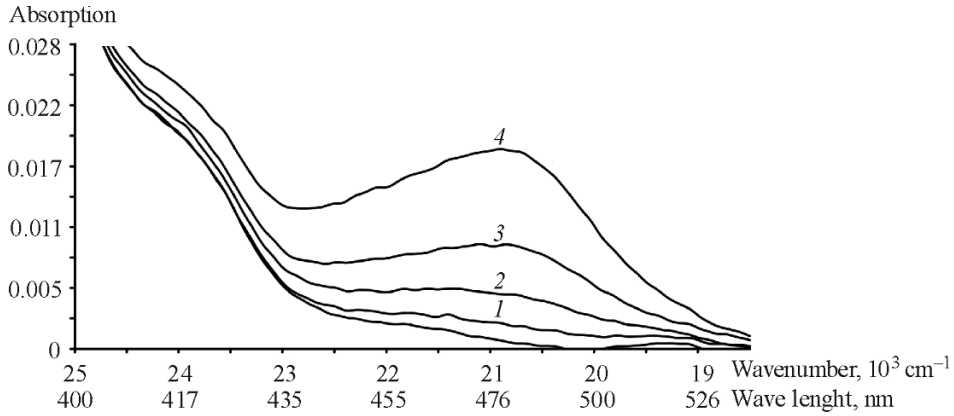


Fig. 4. Absorption spectra of a polystyrene film of compound **1c** upon irradiation at 365 nm in the absorption range of the photoproduct. Irradiation times: *1*) 180 s, *2*) 480 s, *3*) 1080 s, and *4*) 3000 s.

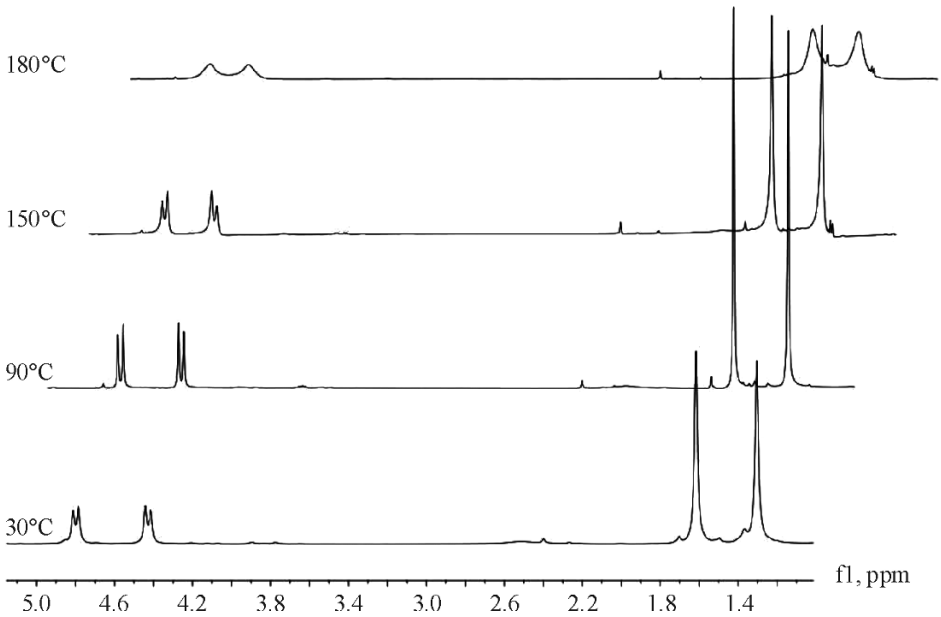


Fig. 5. Dynamics of the signals of the protons of the methyl and methylene groups in the ^{1}H NMR spectrum of compound **1c** at 30-180°C in nitrobenzene-d_5.

Thus, our study has shown that fusion of a benzene ring to the indoline fragment of the molecule in the case of *N*-substituted benzo[*e*]indoline system leads to a slight increase in absorption in the ultraviolet spectral region, while the steric hindrance due to the *N*-methyl substituent in the benzo[*g*]indoline derivative leads to poorer photochromic characteristics. We also discovered that the introduction of a bulky substituent at the nitrogen atom such as a benzyl group does not lead to marked change in the photochromic properties of the benzofuran derivatives of indolinospiropyrans at reduced temperature, while ultraviolet irradiation at room temperature leads to photodecomposition of the open form. This finding may be attributed to the high lability of the methylene group hydrogen atom.

EXPERIMENTAL

IR spectra were recorded on a Varian Excalibur 3100 FT-IR (frustrated total internal reflection). Electronic absorption spectra of solutions of the products before and after irradiation were recorded on an Agilent 5483 spectrophotometer. A DRSh-250 mercury lamp with a light filter separating out the mercury spectrum line at 365 nm was used as the source of photoactive UV light. ^{1}H NMR spectra were recorded on a Bruker Avance DPX 250 spectrometer at 250 MHz in a Fourier pulse mode in $CDCl_3$. The ^{13}C and two-dimensional ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded (600, 125, and 60 MHz, respectively) in $CDCl_3$ and also dynamic ^{1}H NMR spectra in nitrobenzene-d_5 were recorded on a Bruker Avance-600 spectrometer. The signals were assigned relative to the signals of the residual proton signals of the $CDCl_3$ and nitrobenzene-d_5 samples (7.24 and 8.22 ppm, respectively). Elemental analysis was carried out by the classical microanalysis method [4]. Melting points were determined on a Fisher–Jones instrument from Fisher Scientific.

1-Benzyl-3,3-dimethyl-1',2'-diphenylspiro[indoline-2,7'-furo[3,2-*f*]chromene] (1c). Piperidine (0.1 ml) was added to a suspension of indolinium salt **2c** (0.349 g, 1 mmol) in 2-propanol (10 ml) at 50°C, and then aldehyde **3** [5] (0.314 g, 1 mmol) was added to the resultant solution. The solution was maintained at reflux for 1 h. After cooling, the resultant colorless precipitate was filtered off, washed with ethanol, and dried. Yield 0.5 g (92.1%). Mp 179-183°C (EtOH). IR spectrum, ν, cm^{-1}: 1639, 1604 (υ C=C), 1286, 1252 (υ C–N), 952, 910 (υ C–O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.21 (3H, s, CH_3); 1.35 (3H, s, CH_3); 4.12 (1H, d, *J* = 16.6) and 4.53 (1H, d, *J* = 16.6, NCH_2); 5.49 (1H, d, *J* = 10.4, H-8'); 6.22 (1H, d, *J* = 7.7, *J* = 1.3, H-7); 6.42 (1H, d, *J* = 10.5, H-9'); 6.73 (1H, d, *J* = 7.6, H-5'); 6.80 (1H, td, *J* = 7.5, *J* = 1.3, H-5); 7.00 (1H, td, *J* = 7.6, *J* = 0.9, H-6); 7.08 (1H, dd, *J* = 7.2, *J* = 0.9, H-4); 7.13-7.25 (8H, m, H Ph); 7.24 (1H, d, *J* = 7.6, H-4'); 7.40-7.50 (7H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 20.2 (CH_3); 26.0 (CH_3); 47.7 ($\underline{C}H_2Ph$); 52.1 ($\underline{C}Me_2$); 104.2 (C-2(7')); 107.6 (C-7); 110.8 (C-9'b); 111.5 (C-4'); 113.0 (C-5); 117.8 (C-3a); 118.3 (C-8'); 119.2 (C-5); 121.5 (C-4); 125.4 (C-9'); 125.9 (C-9'a); 127.3 (C-6); 139.5 (C-1'); 147.5 (C-7a); 148.5 (C-5'a); 150.5 (C-3'a); 151.7 (C-2'). Found, %: C 85.82; H 5.74; N 2.59. $C_{39}H_{31}NO_2$. Calculated, %: C 85.84; H 5.73; N 2.57.

1,3,3-Trimethyl-1',2'-diphenylspiro[benzo[*e*]indoline-2,7'-furo[3,2-*f*]chromene] (6) was obtained analogously to spiropyran **1c** from indolinium salt **4** and aldehyde **3**. Yield 91%. Mp 225-227°C (EtOH). IR spectrum, ν, cm^{-1}: 1644, 1592 (υ C=C), 1270, 1259 (υ C–N), 952, 942 (υ C–O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.26 (3H, s, 3-CH_3); 1.65 (3H, s, 3-CH_3); 2.78 (3H, s, NCH_3); 5.49 (1H, d, *J* = 10.5, H-8'); 6.54 (1H, d, *J* = 10.5, H-9'); 6.66 (1H, d, *J* = 9.1, H Ar); 6.94 (1H, d, *J* = 8.6, H Ar); 7.18-7.27 (5H, m, H Ar); 7.38 (1H, td, *J* = 8.4, *J* = 1.3, H Ar); 7.43-7.62 (7H, m, H Ar); 7.72 (1H, d, *J* = 8.6, H Ar); 7.78 (1H, d, *J* = 7.9 H Ar); 7.92 (1H, d, *J* = 8.5, H Ar). Found, %: C 85.51; H 5.52; N 2.72. $C_{37}H_{29}NO_2$. Calculated, %: C 85.55; H 5.63; N 2.70.

1,3,3-Trimethyl-1',2'-diphenylspiro[benzo[*g*]indoline-2,7'-furo[3,2-*f*]chromene] (7) was obtained analogously to spiropyran **1c** from indolinium salt **5** and aldehyde **3**. Yield 74%. Mp 168-173°C (EtOH). IR spectrum, ν, cm^{-1}: 1642, 1606 (υ C=C), 1309, 1257 (υ C–N), 962, 937 (υ C–O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.08 (3H, s, 3-CH_3); 1.37 (3H, s, 3-CH_3); 3.30 (3H, s, NCH_3); 5.49 (1H, d, *J* = 10.5, H-8); 6.52 (1H, d, *J* = 10.5, H-9); 6.67 (1H, d, *J* = 8.8, H Ar); 7.27-7.62 (15H, m, H Ar); 7.79 (1H, m, H Ar); 8.30 (1H, d, *J* = 9.8, H Ar). Found, %: C 85.54; H 5.57; N 2.69. $C_{37}H_{29}NO_2$. Calculated, %: C 85.55; H 5.63; N 2.70.

A file with supplementary information is available on the site http://hgs.osi.lv and contains the two-dimensional NMR spectra of spiropyran **1c**.

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