

PHOTO- AND THERMOCHROMIC SPIRANS

36.* SYNTHESIS, STRUCTURE AND PHOTOCHROMIC PROPERTIES OF 7',7''-{1,4-PHENYLENEDI(METHYLENE)-BIS(5-CHLORO-1,3,3-TRIMETHYL-1,3-DIHYDROSPIRO-[INDOLE-2,3'-PYRANO[3,2-*f*]QUINOLINIUM])} DIODIDE

K. N. Khalanskiy¹, Yu. S. Alekseenko², B. S. Lukyanov^{1**},
G. S. Borodkin¹, and S. O. Bezuglyi²

A synthesis is reported for a new photochromic indoline bisspiropyran salt containing a quinoline fragment. This compound exists as a racemic mixture. The photochromic properties of this symmetrical bisspiropyran were studied.

Keywords: indoline bisspiropyran, quinoline, 2*H*-chromene fragment, photochrome.

The photochromic properties of spiropyrans are defined by the structure and substituents of the heterene part of the molecule and the 2*H*-chromene fragment [2]. In previous work [3], we studied the structure and photochemical properties of a series of synthesized spiropyrans and their salt analogs containing a quinoline fragment.

Spirocyclic compounds containing two 2*H*-chromene fragments in their structure have attracted particular interest. Irradiation of solutions of these compounds with unfiltered light leads to opening of both pyran rings [4]. Spiropyran salts [3], containing a chromoxalate complex as the anion, have photomagnetic properties in the crystalline form [5].

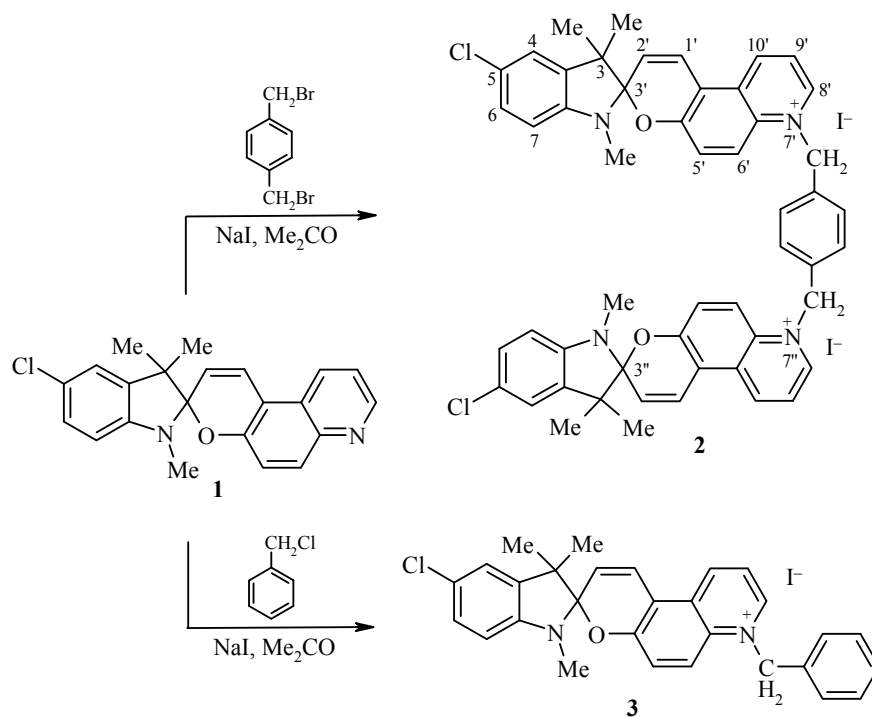
We have synthesized a new symmetrical bisspiropyran salt **2** from previously prepared indoline spiropyran **1** [6], containing a chlorine atom at C-5 of the indoline part of the molecule and a quinoline fragment fused with the 2*H*-pyran ring, by introducing a *para*-xylene bridge connecting two spiropyran molecules through the quinoline nitrogen atoms.

*For Communication 35, see [1].

**To whom correspondence should be addressed, e-mail: bluk@ipoc.sfedu.ru.

¹Research Institute of Physical and Organic Chemistry, Southern Federal University, 194/2 Stachki Ave., 344006 Rostov-on-the-Don, Russia.

²Southern Scientific Center, Russian Academy of Sciences, 41 Chekhov St., 344006 Rostov-on-the-Don, Russia, e-mail: labs811@ipoc.sfedu.ru.



The IR spectrum of iodide **2** has aromatic carbon bond stretching bands at 1580, 1603, and 1645 cm^{-1} , as well as $\nu_{\text{C}=\text{N}}$ bands for the *2H*-pyran fragment at 1481 and 1537 cm^{-1} , characteristic for indoline spiropyrans [7]. The $\nu_{\text{C}-\text{N}}$ stretching bands of the indoline fragment appear at 1261 and 933 ($\text{C}-\text{O}$), while the $\nu_{\text{C}-\text{O}}$ bands of the *2H*-pyran ring appear at 1049 cm^{-1} and 1109 cm^{-1} ($\text{C}_{\text{Ar}}-\text{O}$), respectively.

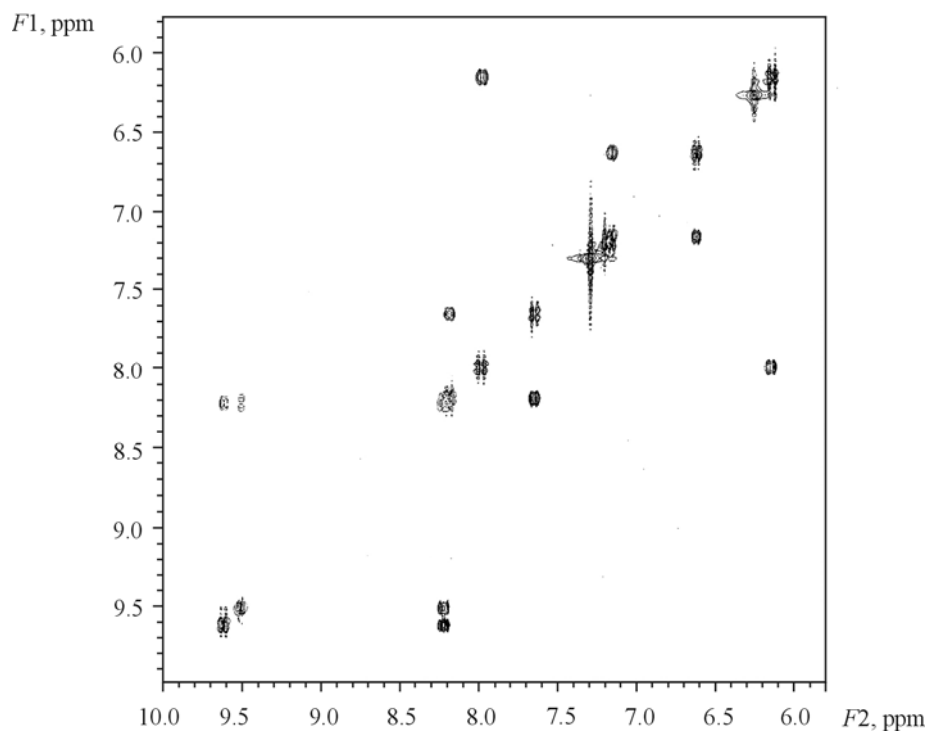


Fig. 1. Two-dimensional $^1\text{H}-^1\text{H}$ COSY correlation spectrum of spiropyran **2**.

The ^1H NMR signals for the two 3-Me groups of the indoline fragment in iodide **2** are seen at 1.16 and 1.21 ppm, which confirms the presence of an asymmetric carbon atom and, therefore, a spirocyclic structure for this molecule. The obtained spiropyran **2**, which contains an asymmetric spirocarbon atom, exists as a racemic mixture. This fact was supported by an X-ray diffraction structural investigation of a previously prepared spiro[1,1,3-trimethylbenzo[*e*]indolino-2,3'-[3*H*]pyrano[3,2-*f*]quinoline], which contains two asymmetric spiropyran molecules in the crystal, according to X-ray structural analysis [8].

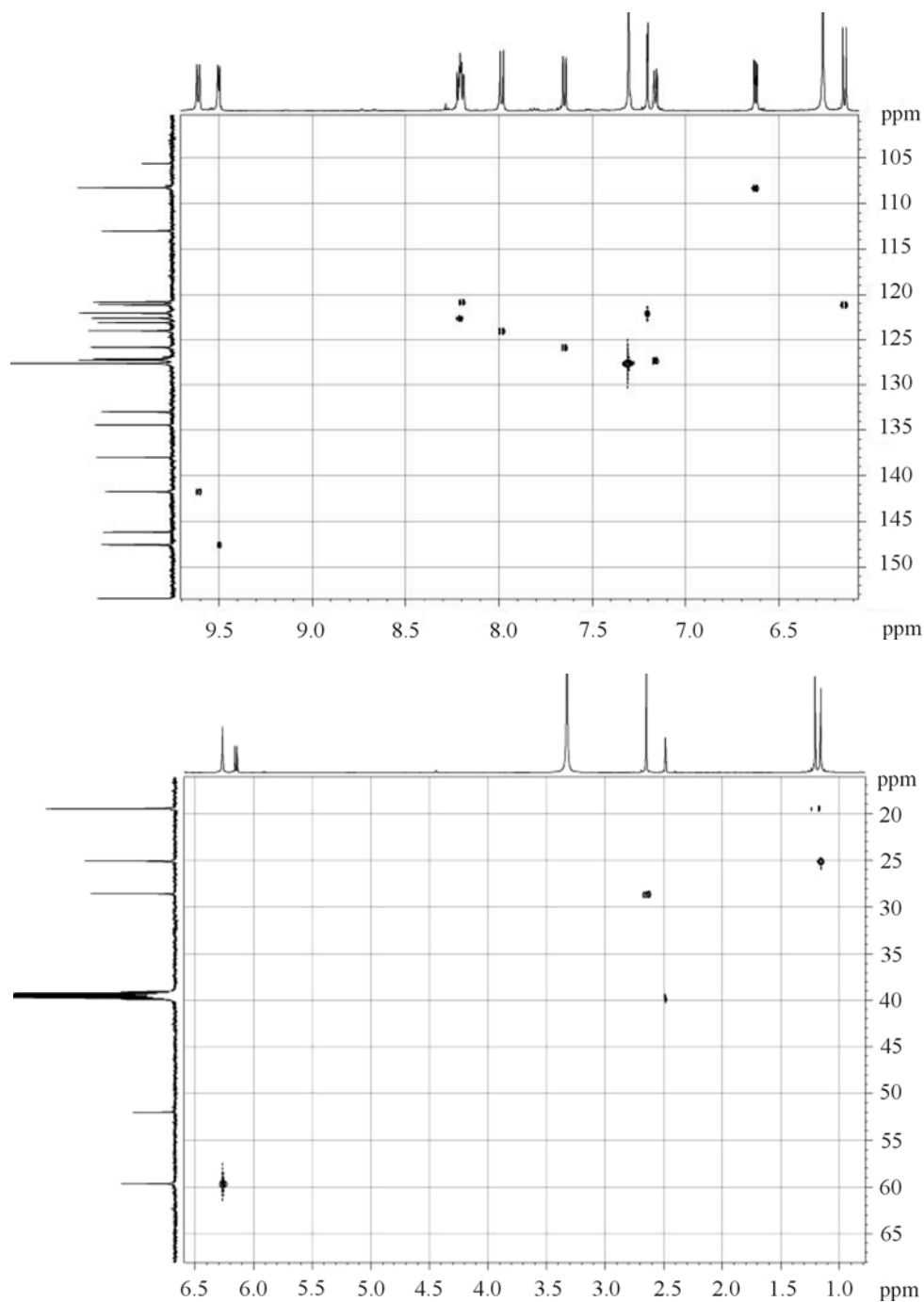


Fig. 2. Heteronuclear single-quantum ^1H - ^{13}C HSQC correlation spectrum of spiropyran **2**.

The six-proton singlet of the 1-CH₃ methyl groups is seen at 2.65 ppm, while the four-proton singlet for the methylene groups at the quinoline N-7' nitrogen atom is found at 6.27 ppm, which indicates a salt component in the molecule. The signals for the H-1' and H-2' protons appear as one-proton doublets at 8.00 and 6.15 ppm, respectively ($J = 10.7$ Hz), which indicates a *cis* structure for this vinyl fragment of the 2*H*-pyran ring. The singlet of the four aromatic protons of the *para*-xylene bridge at 7.30 ppm confirms the symmetrical arrangement of the two spirocyclic components in the molecular structure.

Two-dimensional ¹H-¹H COSY correlation spectrum was recorded (Fig. 1) to confirm the assignment of the signals in the one-dimensional ¹H NMR spectrum.

The one-dimensional ¹³C NMR spectrum was also recorded, and its signals were assigned on the basis of the single-quantum ¹H-¹³C heteronuclear HSQC correlation spectrum (Fig. 2). The ¹³C signals of the methyl groups at C-3 are seen in the ¹³C NMR spectrum at 19.5 and 25.1 ppm, the signals for the C-1' and C-2' atoms are seen at 124.0 and 121.1 ppm, while the signals for the carbon atoms of the methylene bridges at the charged nitrogen atom and benzene ring connecting the spiropyran fragments are seen at 59.6 and 127.6 ppm, respectively. These signals perfectly match the signals of the corresponding protons upon their extrapolation in the ¹H-¹³C HSQC spectrum.

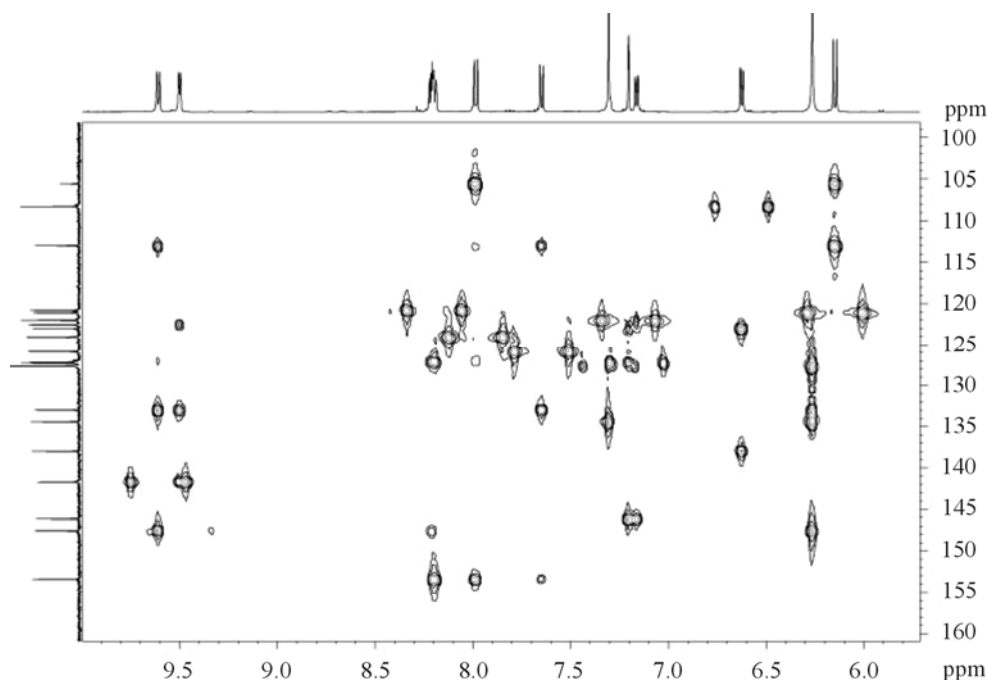


Fig. 3. Distant bond ¹H-¹³C HMBC heteronuclear correlation spectrum of spiropyran **2**.

¹H-¹³C HMBC (Fig. 3) and ¹H-¹⁵N HMBC spectra (Fig. 4) for the heteronuclear correlation of distant bonds were used to determine the chemical shifts of the carbon atoms not bound to hydrogen atoms and the nitrogen atoms. The distant bond correlation spectra completely confirmed the structure of the bis-compound obtained. All the spiropyran atoms not bound to hydrogen atoms were assigned using these spectra. Thus, we found that the C-2,3' spiroatom appearing in the ¹³C NMR spectrum at 105.6 ppm has a two-bond correlation with H-2' and a three-bond correlation with H-1'.

The nitrogen atoms of the indoline and quinoline fragments in the ¹⁵N NMR spectrum give signals at 95.6 and 198.2 ppm, respectively. The following picture is observed upon extrapolation of the ¹H and ¹⁵N NMR spectra of spiropyran **2** in the distant bond heteronuclear ¹H-¹⁵N HMBC correlation spectrum (Fig. 4): nitrogen atom N-1 has three-bond correlation with protons H-7 and H-2' and a two-bond correlation with protons of the 1-CH₃

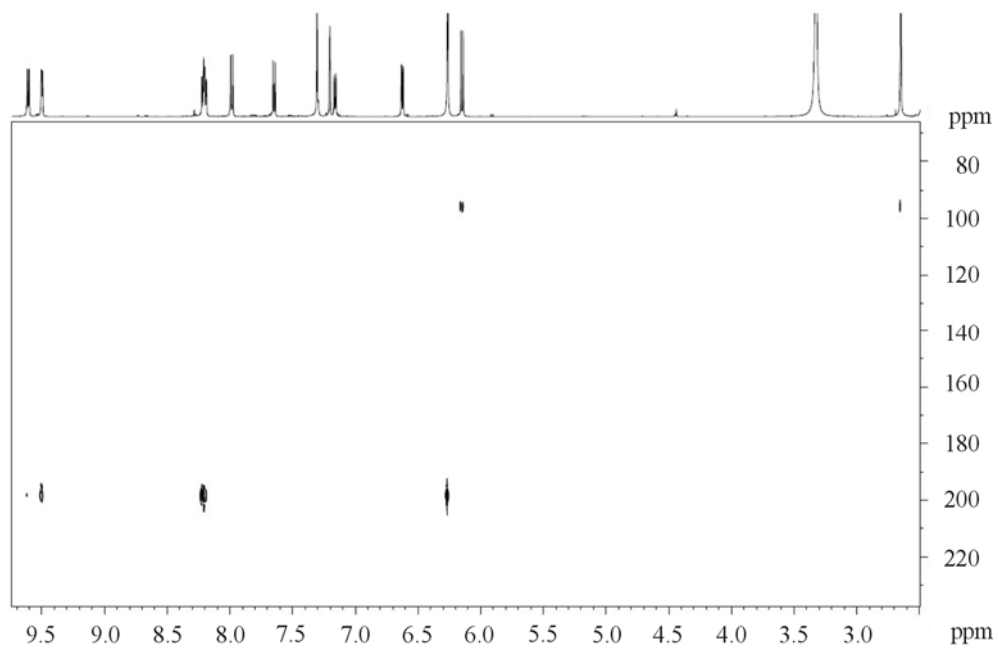


Fig. 4. Distant bond ^1H - ^{15}N HMBC heteronuclear correlation spectrum of spiropyran **2**.

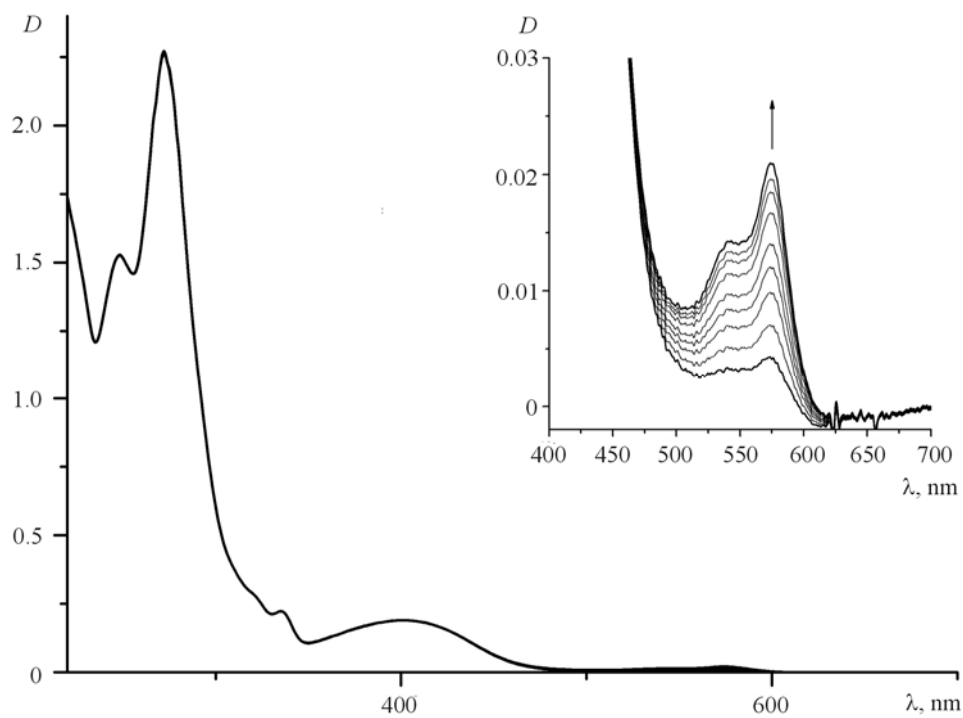


Fig. 5. Photoinduced spectral changes of a solution of spiropyran **2** in acetonitrile upon irradiation with Σ -light using a UFS-1 light filter (1.5 sec interval). The insert gives an enlargement of the part of the spectrum undergoing change upon irradiation.

methyl group; the nitrogen atom N-7' has a three-bond correlation with protons H-6' and H-9' as well as two-bond correlations with proton H-8' and the protons of the methylene bridge $-\text{CH}_2-$. The correlations of these atoms confirm the assignment of the signals in the spectra both for the nitrogen and hydrogen atoms. Thus, the ^1H - ^{15}N HMBC spectrum completely confirmed the upfield position of the indoline nitrogen atom signal and the downfield position of the quinoline nitrogen atom, which, in turn, confirms the salt structure of spiroopyran **2** with positive charge on the N-7' nitrogen atom.

Thus, all the employed NMR methods allowed a precise establishment of the molecular structure of the product through a complete assignment of all the carbon, nitrogen, and hydrogen atoms and their extrapolation relative to each other.

The photochemical data obtained for the bisSpiropyran **2** (Fig. 5) differ significantly from such data for its precursor, Spiropyran **1** (Table 1).

The maximum of the long-wavelength absorption band of the open form of Spiropyran **2** is shifted bathochromically, and its lifetime exceeds that of the Spiropyran **1** by an order of magnitude. Similar, although less pronounced behavior is observed when comparing the UV spectra of Spiropyran **2** with those of the alkyl-substituted analog **4** [8] and the benzyl-substituted Spiropyran salt **3** (Table 1).

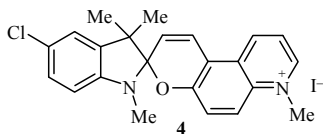
The results of the conducted studies allow to suggest that the symmetrical charged bisSpiropyran synthesized from an indoline Spiropyran may be used as a component of photocontrolled salt-forming magnetics by analogy to 1,3,3,7'-tetramethyl-1,3-dihydrospiro[indole-2,3'-pyrano[3,2-*f*]quinolinium] iodide [5], which makes this system worthy of further investigation.

EXPERIMENTAL

The IR spectra were recorded on a Varian Excalibur 3100 FT-IR spectrometer by the frustrated total internal reflection method. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 600 spectrometer (600 and 150 MHz, respectively) relative to the solvent residual proton signals. The elemental analysis was carried out by classical microanalysis [9]. The melting points were determined on a Fisher Scientific Fisher-Johns instrument. The electronic absorption spectra were recorded on an Agilent 8453 spectrophotometer. The irradiation source was a Newport 200 W mercury lamp using an UFS-1 optical filter.

TABLE 1. Spectral and Kinetic Properties of Compounds **1-4**

Compound	λ_{max}^A , nm	$\epsilon \cdot \lambda_{\text{max}}^A$, $\text{M}^{-1}\text{cm}^{-1}$	λ_{max}^B , nm	τ_{24}^B , sec
1	289	10140		
	301	9650	~530	~0.2
	350	4480	564	
2	272	88250		
	335	8640	574	6.5
	401	7340		
3	247	32430		
	272	28130	573	5.9
	335	2480		
	401	2120		
	270	46430		
4	334	4520	~538	
	397	3810	570	5.3



7',7''-{1,4-Phenylenedi(methylene)bis(5-chloro-1,3,3-trimethyl-1,3-dihydrospiro[indole-2,3'-pyrano[3,2-f]quinolinium])} Diiodide (2). Spiropyran **1** [8] (0.300 g, 0.827 mmol) and 1,4-di(bromomethyl)benzene (0.109 g, 0.413 mmol) was dissolved in absolute acetone (15 ml) in the presence of sodium iodide (1.24 g, 8.26 mmol), heated at reflux for 4.5 h, and then cooled. The precipitate formed was filtered off and recrystallized from chloroform. Yield 0.127 g (28%); mp 233-235°C. IR spectrum, ν , cm^{-1} : 933 (C–O); 1049, 1109 ($\text{C}_{\text{Ar}}\text{--O}$); 1261 (C–N); 1481, 1537 (C=N); 1580, 1603, 1645 (C=C). ^1H NMR spectrum (DMSO- d_6), δ , ppm (J , Hz): 1.16 (6H, s, 2(3- CH_3)); 1.21 (6H, s, 2(3- CH_3)); 2.65 (6H, s, 2(1- CH_3)); 6.15 (2H, d, $J = 10.7$, H-2'); 6.27 (4H, s, 2 CH_2); 6.63 (2H, d, $J = 8.2$, H-7); 7.17 (2H, dd, $J = 8.2$, $J = 2.0$, H-6); 7.22 (2H, s, H-4); 7.30 (4H, s, H Ar); 7.66 (2H, d, $J = 9.1$, H-10'); 8.00 (2H, d, $J = 10.7$, H-1'); 8.20 (2H, dd, $J = 6.3$, $J = 9.1$, H-9'); 8.23 (2H, d, $J = 10.0$, H-6'); 9.51 (2H, d, $J = 6.3$, H-8'); 9.62 (2H, d, $J = 10.0$, H-5'). ^{13}C NMR spectrum (DMSO- d_6), δ , ppm: 19.5 (3- CH_3); 25.1 (3- CH_3); 28.6 (1- CH_3); 52.0 (C-3); 59.6 (CH_2); 105.6 (C-2,3'); 108.2 (C-7); 113.0 (C-10b'); 120.8 (C-9'); 121.1 (C-2'); 122.0 (C-4); 122.6 (C-6'); 123.1 (C-3a); 124.0 (C-1'); 125.9 (C-10'); 127.2 (C-10a'); 127.3 (C-6); 127.6 (C-12'); 133.0 (C-6a'); 134.4 (C-11'); 138.0 (C-5); 141.7 (C-5'); 146.1 (C-7a); 147.5 (C-8'); 153.4 (C-4a'). ^{15}N NMR spectrum, δ , ppm: 95.6 (N-1); 198.2 (N-7'). Found, %: C 57.68; H 4.28; N 5.26. $\text{C}_{52}\text{H}_{46}\text{Cl}_2\text{I}_2\text{N}_4\text{O}_2$. Calculated, %: C 57.63; H 4.28; N 5.17.

7'-Benzyl-5-chloro-1,3,3-trimethyl-1,3-dihydrospiro[indole-2,3'-pyrano[3,2-f]quinolinium] Iodide (3). A solution of the spiropyran **1** [8] (0.06 g, 0.165 mmol) and benzyl chloride (0.02 ml, 0.174 mmol) in absolute acetone (15 ml) in the presence of sodium iodide (0.52 g, 3.48 mmol) was heated at reflux for 3.5 h with protection from atmospheric moisture. The reaction mixture was left for 48 h, and the precipitate formed was filtered off. The desired spiropyran salt **3** was then extracted from the precipitate with acetone (5×10 ml). The extract was evaporated, and the residue was recrystallized from chloroform. Yield 0.063 g (35%); mp 202-205°C. IR spectrum, ν , cm^{-1} : 1100 ($\text{C}_{\text{Ar}}\text{--O}$); 1620, 1600, 1576 (C=C). ^1H NMR spectrum (CDCl_3), δ , ppm (J , Hz): 1.20 (3H, s, 3- CH_3); 1.25 (3H, s, 3- CH_3); 2.67 (3H, s, 1- CH_3); 6.04 (1H, d, $J = 10.7$, H-2'); 6.44 (2H, s, CH_2); 7.02 (1H, d, $J = 2.1$, H-7); 7.14 (1H, d, $J = 2.1$, H-6); 7.24 (1H, s, H-4); 7.33 (5H, m, H Ph); 7.46 (1H, d, $J = 9.6$, H-6'); 7.75 (1H, d, $J = 10.7$, H-1'); 8.12 (1H, d, $J = 9.6$, H-5'); 8.22 (1H, dd, $J = 5.7$, $J = 8.9$, H-9'); 9.44 (1H, d, $J = 8.9$, H-10'); 10.12 (1H, d, $J = 5.7$, H-8'). Found, %: C 60.07; H 4.40; N 4.73. $\text{C}_{29}\text{H}_{26}\text{ClIN}_2\text{O}$. Calculated, %: C 59.96; H 4.51; N 4.82.

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