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CHEMISTRY

New Photochromic Salt Spiropyran with Benzyl Substituent

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Abstract—A new salt spiropyran of indoline series containing benzyl substituent in the 8'-position of the [2H]-chromene moiety of the molecule has been synthesized and studied. The structure of the obtained compound has been confirmed by methods ^{1}H NMR and IR spectroscopy. The study of spectral characteristics and photochromic behavior of the target compound has shown that growing of its single crystal resulted in destruction on account of hydrolysis in acetonitrile. The ^{1}H NMR spectra of the initial salt spiropyran and product of hydrolysis have been compared.

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Spiropyrans are representatives of organic photochromic compounds [1]. Due to photochromic properties they can be used to create smart materials as photosensitive switches of various properties [2]. Nonvolatile memory cells were designed on the basis of photochromic spiropyran salts [3]. Two factors are necessary to use spiropyrans in optical memory devices: the long lifetime of photoinduced isomer and the maximal proximity of long-wavelength absorption maximum to the IR range. It is known that bulky substituents in the 2*H*-chromene moiety of molecule and at the nitrogen atom of the hetarene fragment provide a possibility to increase lifetime of photoinduced isomer for the spiropyrans of indoline series [4].

For the previously synthesized spiropyrans with a cationic substituent [5, 6] the merocyanine isomer has an absorption band in the near-IR region (λ_{max} = 728 nm).

In this work, with the aim to combine two these factors in one molecule, we synthesized 1,3,3-trimethyl-6'-[(E)-2-(1",3",3"-trimethylindolium-2"-yl)vinyl]-8'-benzyl-spiro[indolino-2,2'-2*H*-chromene] perchlorate (**3**) according to Scheme 1.

The structure of the obtained compound **3** was proved by the data of elemental analysis, IR and ^{1}H NMR spectroscopy.

The IR spectrum of salt spiropyran **3** has typical absorption bands corresponding to the stretching vibrations of C_{spiro}–O bond (923 cm^{-1}), ClO_4^- group (1095 cm^{-1}), the C=C bond of the 2H-pyrane ring (1607 cm^{-1}), and the C=C bond of the vinyl fragment (1302 cm^{-1}).

The ^{1}H NMR spectrum of compound **3** has a characteristic signal of proton in the 3'-position at 5.93 ppm as a doublet with spin-spin coupling constant 10.3 Hz, which indicates the *cis* configuration of the vinyl fragment C(3')=C(4'). The proton signals of CH_2 group appear as a two-proton doublet of doublets at 3.62 ppm. The signals of *trans* vinyl protons of the salt fragment as two one-proton doublets are observed at 7.53 and 8.36 ppm with spin-spin coupling constant 16.2 Hz. Three-proton singlet signal at 4.12 ppm corresponds to the N^+–CH_3 fragment of cationic substituent.

Single crystals of compound **3** were grown from acetonitrile solution to study details of molecular structure. X-ray diffraction study revealed that the obtained crystals are those of spiropyran of indoline series **4** with formyl group in the 6'-position of the 2*H*-chromene portion of molecule.

Figure 1 displays the molecular structure of spiropyran **4** containing formyl substituent in the 6'-position and benzyl group in the 8'-position.

Atoms N(1), C(3)–C(9) occupy the same plane with deviation not larger 0.15 Å, producing angle 24.9° with the plane of N(1), C(3), and C(2'2) atoms, the

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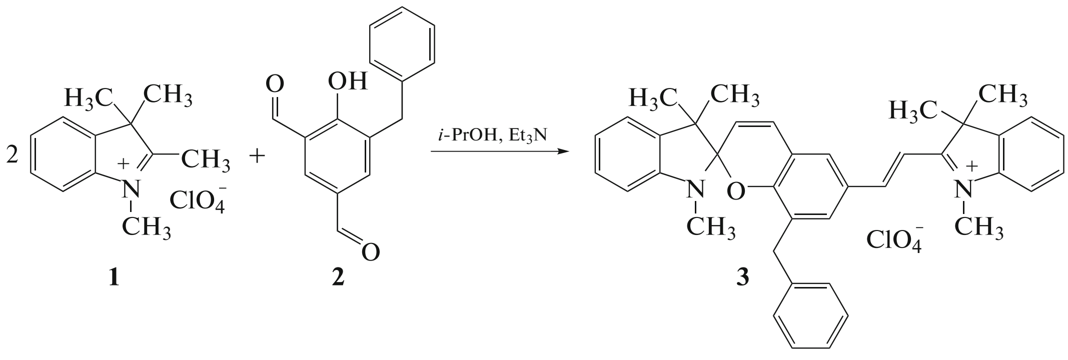


Scheme 1.

sum of the angles at the nitrogen atom is 345.6°. The right fragment relative to the C(2'2) spiro atom (atoms O(1'), O(2'), C(3')–C(12')) is out of "its own" plane by not more than 0.024 Å, producing angle 15.3° with the plane of atoms O(1'), C(2'2), and C(3'). The consideration of C(11') atom environment using Newman projection along the C(11')–C(8') bond displays that the right-hand portion of spiropyran lays in the plane close to the plane of atoms C(11'), C(8'), and H(11b). Phenyl ring C(13')–C(18') is oriented similarly relative to the plane of atoms C(11'), C(8'), and H(11a). Molecules are packed in single crystal in such a manner that intermolecular contacts of 2.57 and 2.69 Å are realized between the O(2') atom of one molecule and the hydrogen atoms of *gem* dimethyl group of other molecule.

This took place most likely because of hydrolysis of the cationic spiropyran in acetonitrile during crystal growing followed by formation of 1,3,3-trimethyl-6'-formyl-8'-benzylspiro[indolino-2,2'-2H-chromene] **4** and tetramethylindolium perchlorate **1** by Scheme 2.

We studied the spectral and photochemical properties of compound **3** in acetonitrile solution. The obtained compound was in equilibrium between spirocyclic and merocyanine forms. The UV spectrum of cyclic isomer showed two bands with maxima at 249 and 303 nm. It is important to note that, in comparison with the majority of previously studied spirocyclic

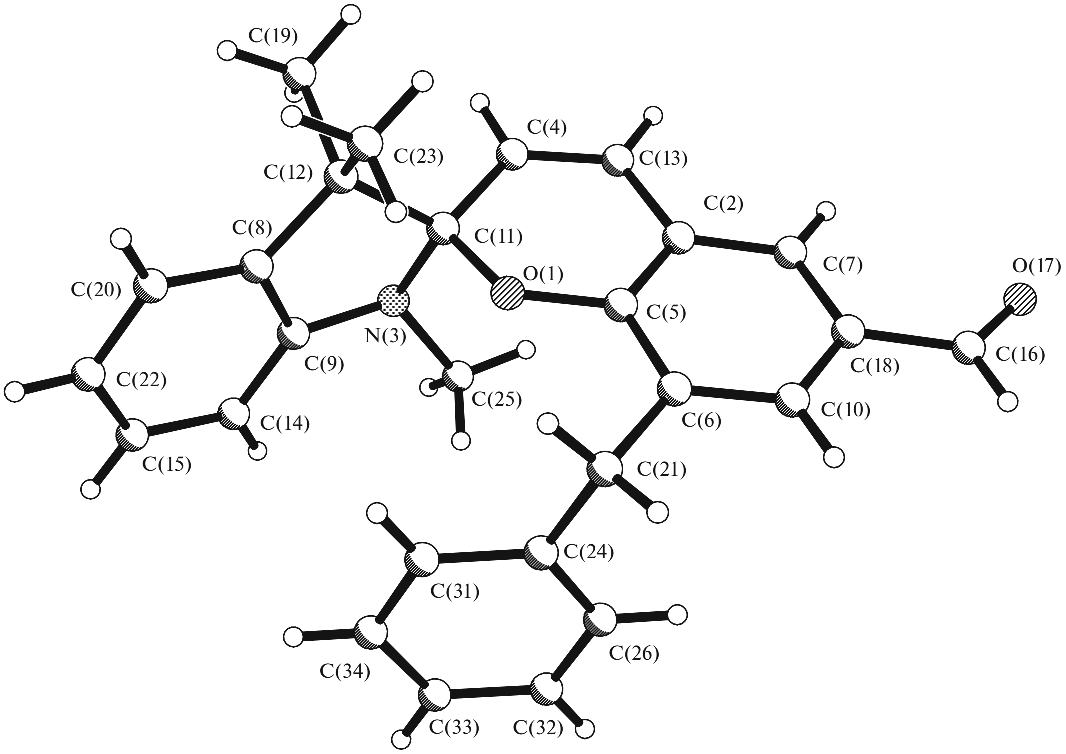
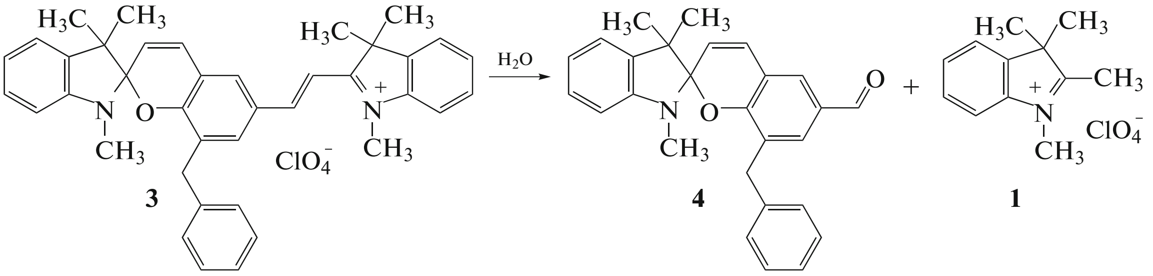


Fig. 1. Molecular structure of compound **4** according to X-ray diffraction study.



Scheme 2.

compounds, the closed form of salt spiropyrans also exhibited a wide strong absorption band in the visible region with maximum at 457 nm, which is explained by the length of conjugation chain. The maximum of absorption band for photoinduced isomer was 648 nm. Exposure to UV light with wavelength 365 nm led to increase in the intensity of absorption band at 648 nm. Figure 2 represents the changes in the absorption spectra upon irradiation in acetonitrile.

After termination of irradiation, we observed spectrum restoration. Compound **3** had relatively long lifetime of the photoinduced isomer (264.5 s). This is explained by the presence of the benzyl substituent in the 8' position of the 2*H*-chromene fragment, which causes steric hindrances for recyclization reaction.

Thus, we synthesized new salt spiropyran. Its structure was confirmed by IR and ^{1}H NMR spectroscopy. The compound showed photochromic properties in acetonitrile. The colored photoinduced from was characterized by long-wavelength absorption band with maximum at 648 nm and long lifetime of 264.5 s. We established by X-ray diffraction study that the target spiropyran undergoes hydrolysis upon crystal growth in acetonitrile solution.

EXPERIMENTAL

^{1}H NMR spectra in DMSO and deuteriochloroform solutions were recorded on a Bruker DPX-250 spectrometer operating at 250 MHz in the Training and Research Laboratory of Resonance Spectroscopy,

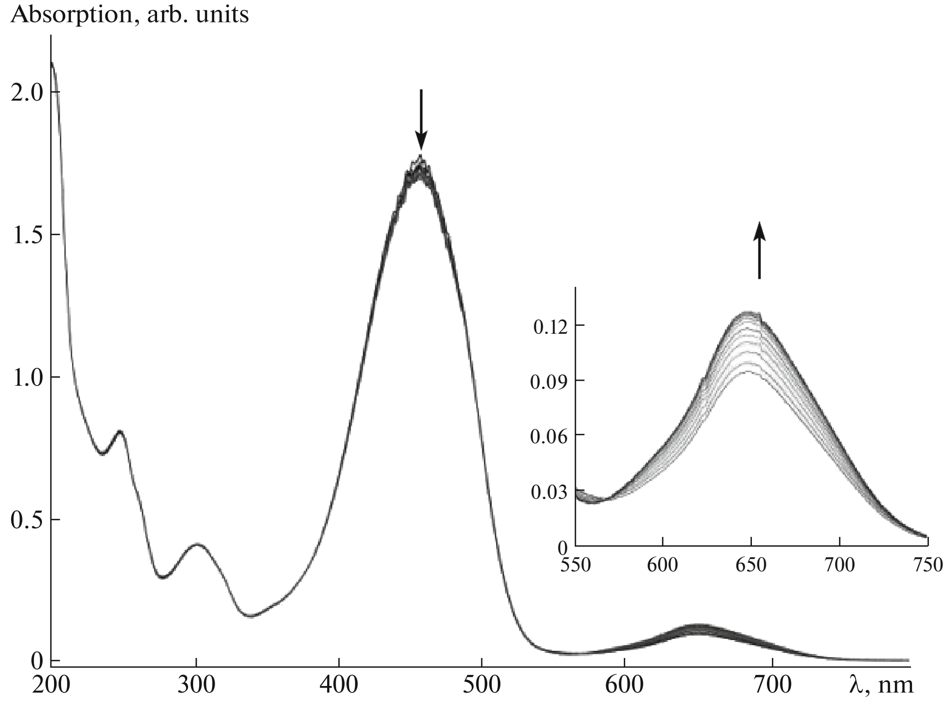


Fig. 2. Changes in the absorption spectra of compound **3** upon exposure to UV light (λ_{irr} = 365 nm, irradiation time 10 s) in acetonitrile, T = 293 K. Inset shows change in absorption spectra in the region corresponding to the photoinduced isomer.

Chair of Natural and Macromolecular Compounds, Chemistry Department, Southern Federal University. Signal position was determined in the δ scale, assignments were made relative to the signals of residual protons of the deuterated solvent $CDCl_3$ (δ = 7.26 ppm) and DMSO-d_6 (δ = 2.50 ppm).

IR spectra were recorded on a Varian Excalibur 3100 FT-iR spectrometer by attenuated total reflection. Electronic absorption spectra before and after irradiation in acetonitrile solutions were obtained on an Agilent 8453 spectrophotometer equipped with an adapter for sample thermostating.

Solution photolysis was performed with the use of a Newport system equipped with a 200-W mercury lamp with a set of interference light filters.

Elemental analysis was carried out by classical microanalysis method [7]. Melting points were determined on a ThermoFisher Scientific Fisher-Johns melting point apparatus.

X-ray diffraction analysis. Unit cell parameters of crystal and 3D set of intensities were obtained at 150 K on an Agilent Technologies Excalibur Eos automated diffractometer (MoK_α radiation, graphite monochromator). Single crystals of $C_{27}H_{25}NO_2$ are monoclinic: $a = 28.544(3)$ Å, $b = 9.5450(6)$ Å, $c = 16.011(1)$ Å, $\beta = 105.503(8)$ Å, $V = 4203.6(6)$ Å^3, $M = 395.48$, $Z = 8$, ρ(calcd.) = 1.250 g/cm^3, μ(MoK_α) = 0.078 mm^{-1}, space group $C2/c$. Intensities of 23 136 reflections were measured in the range ($2\theta \le 58.10°$) by ω-scanning of a single crystal with dimensions 0.30 × 0.27 × 0.26 mm. An empirical absorption correction was made by using Multiscan procedure. After exclusion of systematic absences and averaging of equivalent reflection intensities, working array of measured F^2(hkl) and $\sigma(F^2)$ included 5549 independent reflections, 3945 of which were with $F^2 > 2\sigma(F^2)$. The structure was solved by direct methods and refined in full-matrix least squares on F^2 by SHELXTL software in anisotropic approximation for non-hydrogen atoms. The majority of H atoms in the crystal structure were located in difference Fourier synthesis. Next, coordinates and isotropic thermal parameters of all hydrogen atoms were refined by least squares procedure with an idealized riding model [8]. The absolute shifts of all 282 variables in the last cycle of full-matrix refinement were less 0.001 σ, final value $R_1 = 0.074$.

1,3,3-Trimethyl-6'-[(*E*)-2-(1",3",3"-trimethylindolium-2"-yl)vinyl]-8'-benzyl-spiro[indolino-2,2'-2*H*-chromene] perchlorate (**3**). 2-Hydroxy-3-benxyl-5-formylbenzaldehyde **2** (0.48 g, 2 mmol) was dissolved on heating in 15 mL of isopropanol. Next, a solution of 1.094 g (4 mmol) of 1,2,3,3-tetramethyl-3*H*-indolium perchlorate **1** was added and 0.28 mL of (one molar equivalent) of triethylamine was added dropwise with stirring. The mixture was refluxed with stirring for about 60 min. The resultant precipitate was separated by filtration and recrystallized from acetonitrile. The precipitate (orange crystals) was separated by filtration and washed with cold ethanol. Mp = 265°C (from acetonitrile). Yield 26.8%. ^{1}H NMR (250 MHz, DMSO-d_6, δ, ppm, *J*, Hz): 1.06 (3H, s, *gem*-$C(CH_3)_2$), 1.10 (3H, s, *gem*-$C(CH_3)_2$), 1.76 (6H, s, *gem*-$C(CH_3)_2$), 2.41 (3H, s, N–CH_3), 3.62 (2H, dd, *J* = 13.5, 46.1 Hz,), 4.12 (3H, s, N^+–CH_3), 5.93 (1H, d, *J* = 10.3 Hz, H-3'), 6.63 (1H, d, *J* = 7.6 Hz, H-7), 6.76 (2H, m, arom. protons), 6.90 (1H, t, *J* = 7.3 Hz, H-5), 7.08 (4H, m, arom. protons), 7.14 (1H, m, arom. proton), 7.23 (1H, t, *J* = 7.5 Hz, arom. proton), 7.53 (1H, d, *J* = 16.2 Hz, *trans*-vinyl proton), 7.62 (2H, m, arom. protons), 7.86 (2H, m, arom. protons), 7.99 (1H, s, arom. proton), 8.20 (1H, s, arom. proton), 8.36 (1H, d, *J* = 16.2 Hz, *trans*-vinyl proton). IR (ν, cm^{-1}): 923 ν(C_{spiro}–O), 1095 ν (ClO_4^-), 1607 ν(C=C 2H-pyran ring), 1302 ν(C=C vinyl fragment).

For $C_{39}H_{40}N_2O_5Cl$ anal. calcd. (%): C, 71.82; H, 6.18; N, 4.30; Cl, 5.44.

Found (%): C, 71.86; H, 6.15; N, 4.34; Cl 5.42.

1,3,3-Trimethyl-6'-formyl-8'-benzyl-spiro[indolino-2,2'-2H-chromene] (**4**). 2-Hydroxy-3-benzyl-5-formylbenzaldehyde **2** (0.48 g, 2 mmol) was dissolved on heating in 15 mL of isopropanol. Next, a solution of 0.547 g (2 mmol) of 1,2,3,3-tetramethyl-3H-indolium perchlorate **1** was added and 0.28 mL of (one molar equivalent) triethylamine was added dropwise with stirring. The mixture was refluxed with stirring for about 30 min. The resultant precipitate was filtered off and recrystallized from ethanol. The precipitate (white crystals) was separated by filtration and washed with cold ethanol. Mp = 98°C (from ethanol). Yield 61.4%. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm, *J*, Hz): 1.11 (3H, s, *gem*-$C(CH_3)_2$), 1.16 (3H, s, *gem*-$C(CH_3)_2$), 2.42 (3H, s, N–CH_3), 3.60 (2H, dd, *J* = 14.1, 29.7 Hz,–CH_2–), 5.75 (1H, d, *J* = 10.3 Hz, H-3'), 6.49 (1H, d, *J* = 7.7 Hz, H-7), 6.77 (2H, m, arom. protons), 6.91 (2H, m, arom. protons), 7.08 (4H, m, arom. protons), 7.23 (1H, m, arom. proton), 7.51 (1H, s, arom. proton), 7.64 (1H, s, arom. proton), 9.83 (1H, s, –CHO). IR (ν, cm^{-1}): 926 ν(C_{spiro}–O), 1593 ν(C=C 2H-pyran ring), 1687 ν(C=O formyl group).

For $C_{27}H_{25}NO_2$ anal. calcd. (%): C, 82.00; H, 6.37; N, 3.54.

Found (%): C, 82.03; H, 6.36; N, 3.51.

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