Structural studies of 1,3-oxazolidine-containing spiropyrans

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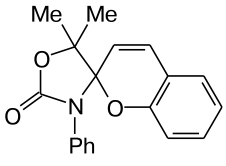
New 3´-(4-chlorophenyl)-5´,5´-dimethyl-2´-oxospiro[(2*H*)-chromene-2,4´-1,3-oxazolidine] was synthesized to study the donor influence of the chlorine atom at the *N*-phenyl substituent on the structure and photochromic properties of 1,3-oxazolidine-containing spiropyrans. Photochemical properties of synthesized 1,3-oxazolidine derivatives were studied at room temperature in toluene. The X-ray diffraction parameters for the new compound were compared with the data obtained earlier for similar spiropyrans.

Key words: spiropyran, 1,3-oxazolidine, photochromism, X-ray crystallography.

Earlier studies of photochromic properties of 5´,5´-dimethyl-2´-oxo-3´-phenyl- (**1**) and 5´,5´-dimethyl-2´-thioxo-3´-phenylspiro[(2*H*)-chromene-2,4´-1,3-oxazolidine] (**2**) in solutions showed that at reduced temperature under conditions of stationary irradiation they underwent valence isomerization with the formation of colored merocyanine forms.[1,2]



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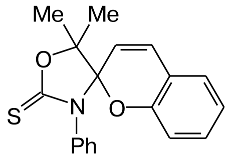

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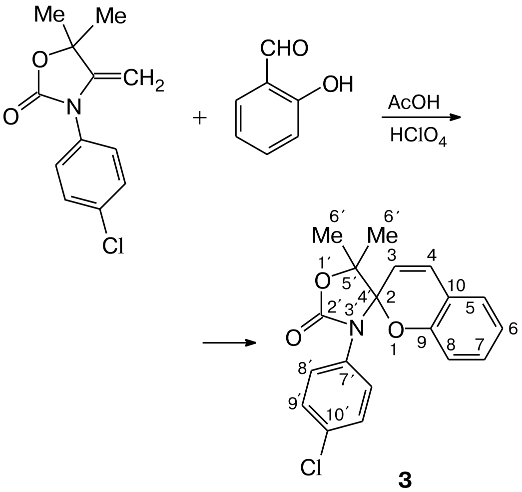
To study the influence of substituents on the stabilization of the spiropyran open form containing in the *N*-phenyl fragment such electron-donating substituent as a chlorine atom, as well as on the structure and properties of this type of spiropyrans, we synthesized a new spiropyran **3** (Scheme 1) in addition to the earlier[1,2] obtained spiropyrans **1** and **2** and carried out X-ray diffraction and photochemical studies.

In the ^{1}H NMR spectrum of spiropyran **3** despite the presence of diastereotopic *gem*-dimethyl groups at position 5 of the oxazolidinone fragment, the protons of the methyl group are found as a six-proton singlet at δ 1.46, *i.e.*, like in compounds **1** and **2**. Nonetheless, like in the spectra of compounds **1** and **2**, the signals for the carbon atoms of the *gem*-dimethyl groups manifest themselves separately, namely, at δ 20.83 and 23.07 (for compound **1**, at δ 19.50 and 21.7 (see Ref. 1); for compound **2**, at δ 19.31 and 21.93 (see Ref. 2)), which confirms a spirocyclic structure of compound **3**.

Scheme 1



The studies of the photochromic properties of compounds **1—3** at room temperature in toluene showed that under the stationary irradiation conditions, their absorption spectral characteristics in the ground state are virtually identical (Table 1). Upon the irradiation of toluene solutions of spiropyrans **1—3** by the light with λ = 365 nm,

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Table 1. Changes in the spectral characteristics of spiropyrans **1**—**3** upon irradiation by the light with λ = 365 nm in toluene at room temperature

Compound	λ^A_{max} /nm	$\varepsilon(\lambda^A_{max})$ /L mol^{-1} cm^{-1}	λ^B_{max} /nm
1	317	3020	—
	327 sh	2530	
2	317	3380	485
	327 sh	2830	
3	317	3030	—
	327 sh	2530	

only spiropyran **2** bearing a thioxo group at position 2´ of the oxazolidinone fragment is a photoactive compound (Fig. 1). Under similar conditions of the photochemical experiment, spiropyrans **1** and **3** containing a carbonyl group in the oxazolidine part of the molecule did not exhibit photochromic properties (see Table 1).

The results of the X-ray diffraction studies for compounds **2** and **3** considerably complemented the X-ray diffraction characteristics obtained earlier[3] for compound **1** and allowed one to make comparative structural analysis of the synthesized compounds.

The oxazolidinone ring of compound **1** molecule (Fig. 2) has a *twist* conformation.[3] The atoms C(2´) and C(5´) deviate from the plane formed by the atoms O(1´), N(3´), and C(4´) by 0.17 and –0.52 Å, respectively. The pyran fragment of the molecule is not perpendicular to the oxazolidinone ring, which is due to the folding along the line O(1)—C(3) by 27.6° with a considerable deviation of the spiro carbon atom C(4´) (by –0.38 Å) from the plane formed by the atoms O(1), C(3), C(4), C(9), and C(10). The angle formed by the phenyl fragment and the oxazolidine ring is 31.5°.

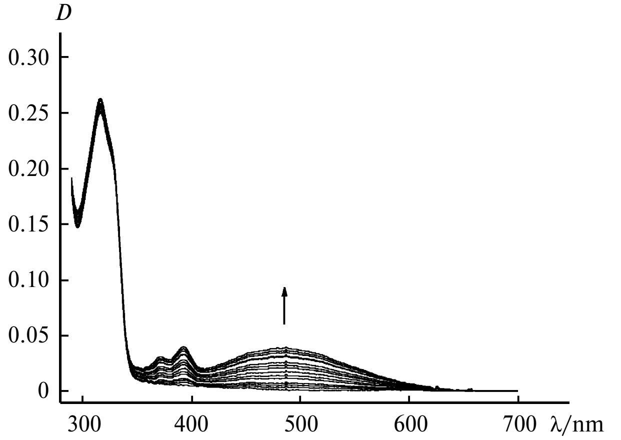

Fig. 1. Absorption spectrum of spiropyran **2** in toluene at 20 °C in the process of irradiation in the stationary regime by the light with λ = 365 nm (Δ*t* = 0.5 s).

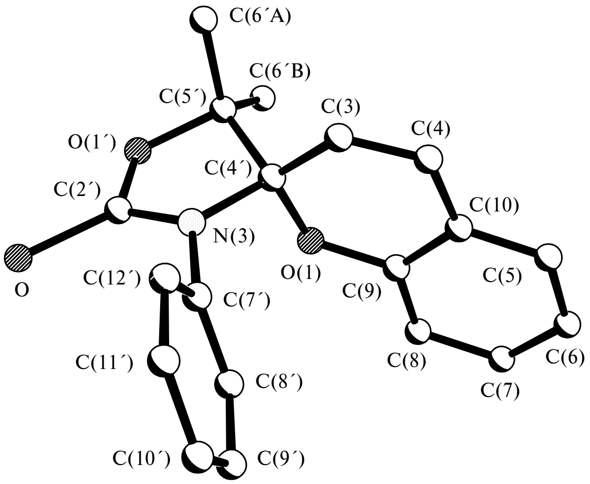

Fig. 2. General view of molecule **1**.

The C=O and N—C_{arom} bond distances are 1.198 Å and 1.426 Å, respectively. In the pyran ring, the C(3)—C(4) bond (1.321 Å) is a double one, whereas the C(4´)—C(3) (1.500 Å) and the C(4)—C(10) (1.47 Å) bonds are close to single bonds. The C(4´)—O(1) bond distance in the pyran moiety of the molecule equal to 1.439 Å is typical of heterocyclic compounds, the standard deviations of bond distances are 0.007—0.011 Å. Unfortunately, the cited work[3] does not have tables of geometric parameters with errors; the bond distances and bond angles are indicated in figures without errors, the text contains only the phrase "the standard deviations of bond distances are 0.007—0.011 Å".

A general view of molecule **2** is shown in Fig. 3. Like in the molecule **1**, the five-membered ring in the molecule of compound **2** has a *twist* conformation. The atoms C(2´) and C(5´) deviate from the plane formed by the atoms O(1´), N(3´), and C(4´) by –0.12 and 0.44 Å, respectively.

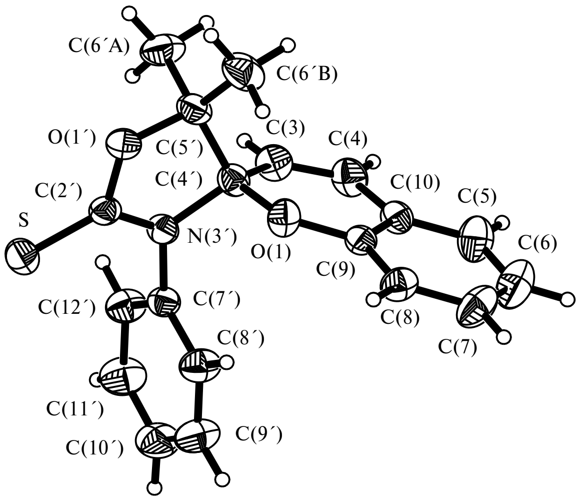

Fig. 3. General view of molecule **2**.

The fold of the pyran fragment along the line O(1)—C(3) is insignificant and is equal to 1.7°, the atom C(4′) deviates from the plane formed by the atoms O(1), C(3), C(4′), C(9), and C(10) by –0.008 Å, the S=C(2′) and N(3′)—C(8′) bond distances are 1.628(3) and 1.437(4) Å, respectively. In the pyran fragment of the molecule **2**, the C(3)—C(4) bond (1.310(4) Å) is a double bond, whereas the C(4′)—C(5′), C(4′)—C(3), and C(4′)—N(3′) bond lengths are 1.553(5), 1.483(5), and 1.470(4) Å, respectively. The C(4′)—O(1) (1.433(4) Å) bond is typical of heterocyclic compounds. The phenyl ring forms an angle with the oxazolidine fragment equal to 96.1°.

A general view of molecule **3** is shown in Fig. 4. In molecule **3**, the fold along the line O(1)—C(3) is equal to 20.2°, with considerable deviation of the spiro carbon atom C(4′) (–0.28 Å) from the plane formed by the atoms O(1), C(3), C(4), C(9), and C(10) of the pyran heterocycle. The $N—C_{arom}$ bond distance is 1.406(4) Å, in the pyran ring the C(3)—C(4) bond (1,303(5) Å) is a double bond, whereas the C(4′)—C(3) (1.480(6) Å) and C(4)—C(10) (1.433(6) Å) bonds are close to single ones, the bond distance between the spiro carbon atom C(4′) and the atom O(1) of the pyran moiety of the molecule is equal to 1.443(5) Å. The phenyl ring is turned relative to the oxazolidine fragment by 67.5°.

Let us consider specific features of the structures of oxazolidine and 2*H*-chromene fragments in compounds **2** and **3** upon superimposition (Fig. 5) the atoms of their five-membered oxazolidine rings.

First of all, it should be noted that the turn of the phenyl ring at the atom N(3′) around the N(3′)—C(7′) bond in spiropyran **2** is equal to 96.1°, while in compound **3** it is 67.5°. Apart from that, the peripheral atoms of the right part of the molecules, *i.e.*, the C(6) and C(6A), are remote from each other by 1.64 Å. More significant differences in the structures of molecules **2** and **3** are found comparing some distances.

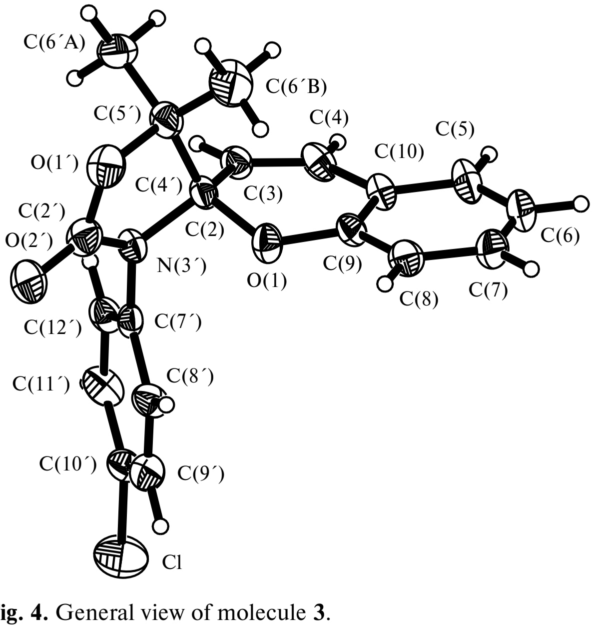

Fig. 4. General view of molecule **3**.

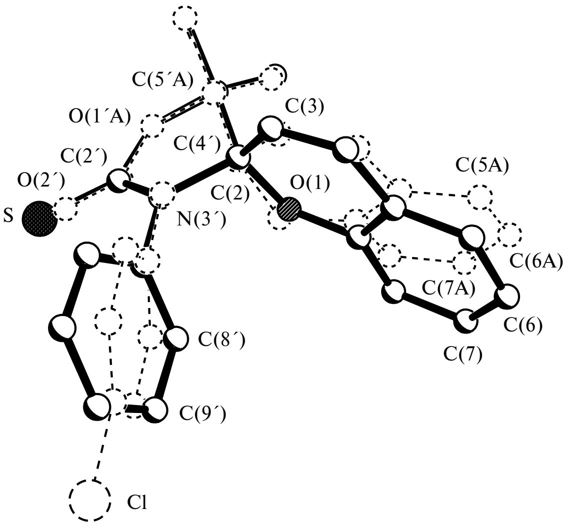

Fig. 5. Superimposition of structures **2** (solid lines) and **3** (dashed lines).

Thus, the distances between the atoms in spiropyran **2** are as follows: 1.470(4) Å (C(4′)—N(3′)), 1.437(4) Å (C(7′)—N(3′)), 1.628(3) Å (C(2′)—S), and 1.378(4) Å (O(1)—C(9)), which are noticeably longer than similar distances in molecule **3**, which, respectively, are equal to 1.376(5) Å, 1.405(5) Å, 1.164(5) Å, and 1.329(5) Å. The distance O(1)—C(4′) in 2*H*-chromene moiety of molecule **2** (1.433(4) Å) and in compound **3** (1.443(5) Å) are formally equal within 3σ.

To sum up, the introduction of a chlorine atom at *para*-position of the N-phenyl fragment did not lead to a fundamental change in the molecular structure. Bond distances, bond angles, and distances between planes in molecule **3** differ insignificantly from the corresponding values in molecule **1**.

However, analysis of bond distance and bond angle values showed that the appearance of a sulfur atom instead of the keto oxygen atom in the oxazolidine fragment of spiropyran had a significant effect on the structure and, consequently, on the photochemical properties of compound **2**.

The geometry of the pyran fragment in the molecular structure of compound **2** sharply differs from that in compounds **1** and **3**. The pyran fragment in compound **2** is virtually planar, the spiro carbon atom C(4′) deviates insignificantly from the plane formed by the atoms O(1), C(3), C(4), C(9), and C(10) (–0.008 Å, *cf.* –0.38 Å in **1** and –0.28 Å in **3**).

Taking into account a similar structure in the chromene part of compounds **1**—**3**, it becomes obvious that a key factor influencing photochromic properties is the presence of a sulfur atom in 1,3-oxazolidine fragment in compound **2**, the electron-withdrawing effect of which is considerably lower than a similar influence of the oxygen atom of the oxo group in compounds **1** and **3**. This influence results in the appearance of a merocyanine colored form of compound **2**, which is revealed in the absorption spectra upon irradiation of the toluene solution at room temperature. At the same time, the presence of such mesomeric donor as a chlorine atom in the *N*-phenyl substituent did not lead to the stabilization of the open form of compound **3** under conditions indicated above.

Experimental

^{1}H and ^{13} NMR spectra were recorded on a Varian Unity 300 spectrometer (300 MHz) in pulsed Fourier-regime in $CDCl_3$. Positions of signals of studied compounds were determined in the δ scale. Chemical shifts were assigned relative to the signals of residual protons of the deuterated solvent $CDCl_3$ ($\delta = 7.26$). Electronic absorption spectra of solutions of studied compounds before and after irradiation were recorded on an Agilent 5483 spectrophotometer, using a DRSh-250 mercury lamp as a source of photoactive UV radiation with a light filter singling out a 365-nm mercury line. Elemental analysis was carried out by traditional method of microanalysis.[4] Melting points were determined on a FisherScientific Fisher—Jones stage.

3´-(4-Chlorophenyl)-5´,5´-dimethyl-2´-oxospiro[(2*H*)-chromene-2,4´-[1,3]oxazolidine (3). A mixture of 3-(4-chlorophenyl)-5,5-dimethyl-4-methylidene-2-oxooxazolidine[5] (2.35 g, 0.01 mol) and salicylaldehyde (1.34 g, 1.16 mL, 0.011 mol) was refluxed for 1.5 h in acetic acid (20 mL) with three drops of 70% perchloric acid as a catalyst. After cooling, the reaction mixture was poured into water (80 mL) and extracted with benzene (4×5 mL). The combined extracts were sequentially washed with 5% aqueous solution of $NaHCO_3$ and water and dried with anhydrous Na_2SO_4. The residue obtained after evaporation of the solvent *in vacuo* was recrystallized from ethanol. The yield after crystallization was 1.23 g (36%). M.p. 171—172 °C. Found (%): C, 66.6; H, 4.8; Cl, 10.7; N, 3.9. $C_{19}H_{16}ClNO_3$. Calculated (%): C, 66.8; H, 4.7; Cl, 10.4; N, 4.1. ^{1}H NMR ($CDCl_3$), δ: 1.47, 1.49 (both s, 3 H each, gem. Me_2); 5.44 (d, 1 H, C(3)H, J = 10.1 Hz); 6.65 (d, 1 H, C(4)H, J = 10.1 Hz); 6.83—7.27 (m, 8 H, ArH). ^{13}C NMR ($CDCl_3$), δ: 21.28 (CH_3); 23.55 (CH_3); 85.56 (C(5´)); 95.36 (C(4´)); 111.23 (C(3´)); 115.90 (C(8)); 116.92 (C(10)); 120.43 (C(6)); 125.63 (C(5)); 125.87 (C(8´)); 127.31 (C(9´)); 128.46 (C(4)); 129.38 (C(7)); 129.98 (C(10´)); 134.12 (C(7´)); 150.64 (C(9)); 152.74 (C(2´)).

X-ray diffraction study. Compound **2** ($C_{19}H_{17}NO_2S$) crystallized in a monoclinic crystal system. Crystal parameters for compound **2**: a = 26.074(5), b = 11.249(2), c = 14.190(3) Å, β = 126.69(3)°, V = 3337.4(1) Å^3, d_{calc} = 1.287 g cm^{-3}, M_r = 323.4, space group $C2/c$, Z = 8. Compound **3** ($C_{19}H_{16}ClNO_3$) crystallized in a monoclinic crystal system. Crystal parameters for compound **3**: a = 20.000(4), b = 11.087(2), c = 7.326(1) Å, β = 97.27(3)°, V = 1611.4(5) Å^3, d_{calc} = 1.409 g cm^{-3}, M_r = 341.8, space group $P2_1/n$, Z = 4.

Intensities of 2966 (**2**) and 3204 (**3**) reflections were obtained on a KUMA four-circle diffractometer (Mo-Kα radiation) at T = 293(2) K in the 1.95—25.08° for **2** and 2.05—26.17° for **3** θ range. Both structures were solved by direct method and refined by the full-matrix least squares method in anisotropic approximation for nonhydrogen atoms using the SHELXTL program.[6] All the hydrogen atoms in both structures were localized from the difference Fourier synthesis and refined using a riding model. The final divergence factor values are as follows: R = 0.037, R_w = 0.1209, GOOF = 0.832 (**2**) and R = 0.052, R_w = 0.1336, GOOF = 0.729 (**3**)_with respect to all the observed reflections with $I > 2\sigma$.

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