Photo- and thermochromic spiropyrans
21.* 8´-Formyl-3,6´-dimethyl-4-oxospiro(3,4-dihydro-2*H*-1,3-benzoxazine-2,2´-[2*H*]chromene) possessing photochromic properties in the solid phase

B. B. Safoklov,[a]★ B. S. Luk´yanov,[b] A. O. Bulanov,[b] A. V. Metelitsa,[b] V. I. Minkin,[b] V. V. Tkachev,[a] and S. M. Aldoshin[a]

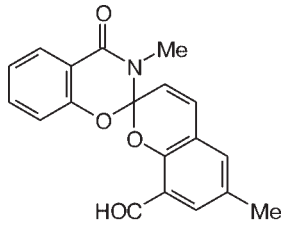
[a]*Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 (095) 515 3588. E-mail: vatka@icp.ac.ru*
[b]*Institute of Physical and Organic Chemistry, Rostov State University, 194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation*

Spiropyran of the chromene series, *viz.*, 8´-formyl-3,6´-dimethyl-4-oxospiro(3,4-dihydro-2*H*-1,3-benzoxazine-2,2´-[2*H*]chromene), was synthesized. In the solid phase, this compound exhibits photochromic properties. These properties were examined and the crystal structure of the compound was established by X-ray diffraction analysis. The compound is a convenient starting reagent for the synthesis of new spiropyrans containing functional groups at position 8´.

Key words: spiropyrans, photochromic materials, materials for optical data recording.

Spiropyrans (SP) are promising photochromic materials for data recording, storage, and transfer[2,3] among which are compounds of the indoline series containing simultaneously the nitro and methoxy substituents in the chromene fragments, for example, 5´-bromo-8´-methoxy-1,3,3-trimethyl-6´-nitrospiro(indolino-2,2´-[2*H*]chromene) and 5´-bromo-8´-methoxy-1,3,3-trimethyl-6´-nitro-7-phenylspiro(indolino-2,2´-[2*H*]chromene),[2,3] which exhibit photochromic properties in the solid phase. Photochromic materials based on these compounds are prepared by treating glass supports with a solution of a mixture of spiropyrans with obligatory conservation of the resulting amorphous layer upon subsequent drying because its photochromic properties disappear upon crystallization.[2] Another representative, *viz.*, 1-allyl-3,3-dimethyl-6´-nitrospiro(indolino-2,2´-[2*H*]chromene), exhibits photochromic activity in the crystalline state but possesses low sensitivity, whereas 1,3,3-trimethylspiro(indolino-2,2´-[2*H*]chromene) exhibits photochromic properties at 0 °C in a glassy film prepared by cooling a melt of spiropyran.[2]

In the present study, we synthesized 8´-formyl-3,6´-dimethyl-4-oxospiro(3,4-dihydro-2*H*-1,3-benzoxazine-2´,2-[2*H*]chromene) (**1**) based on 2,6-diformyl-4-methylphenol, examined its photochromic properties in solutions and in the solid state (in polydispersed films prepared by vacuum deposition on to glass or quartz supports), and established its crystal structure. The presence of the formyl substituent in compound **1** will allow one to prepare new SP bearing various π-acceptor substituents and study their influence on the photochromic properties.



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Experimental

The ^{1}H NMR spectra were recorded on a Varian Unity 300 radiospectrometer (300 MHz) in the pulse Fourier mode in $CDCl_3$.

The IR absorption spectra were measured on a two-beam Specord IR-75 prism spectrometer in Nujol mulls. The instrument was calibrated against polystyrene.

The electronic absorption spectra were recorded on a Specord UV Vis spectrophotometer equipped with a cryostat for low-temperature measurements. Samples were irradiated with a DRSh-250 mercury lamp using light filters to separate lines at λ_{max} = 313 and 365 nm.

Thin films of spiropyran **1**, which exhibits photochromic properties in the solid phase, were deposited on to degreased quartz and glass supports using a VUP-4 vacuum deposition apparatus (the residual pressure was ~$1.5 \cdot 10^{-5}$ Torr; the temperature of evaporation, which was chosen considering the quality of the films, was in the range of 250—400 °C). Homogeneity of the films was monitored based on the shifts of interference bands using an MPI-5 polarizing interference microscope (PZO Warsaw, Poland) by scanning along two coordinate axes. The IR absorption spectra of the films were recorded on a Specord M-40 spectrophotometer; irradiation was carried out on a

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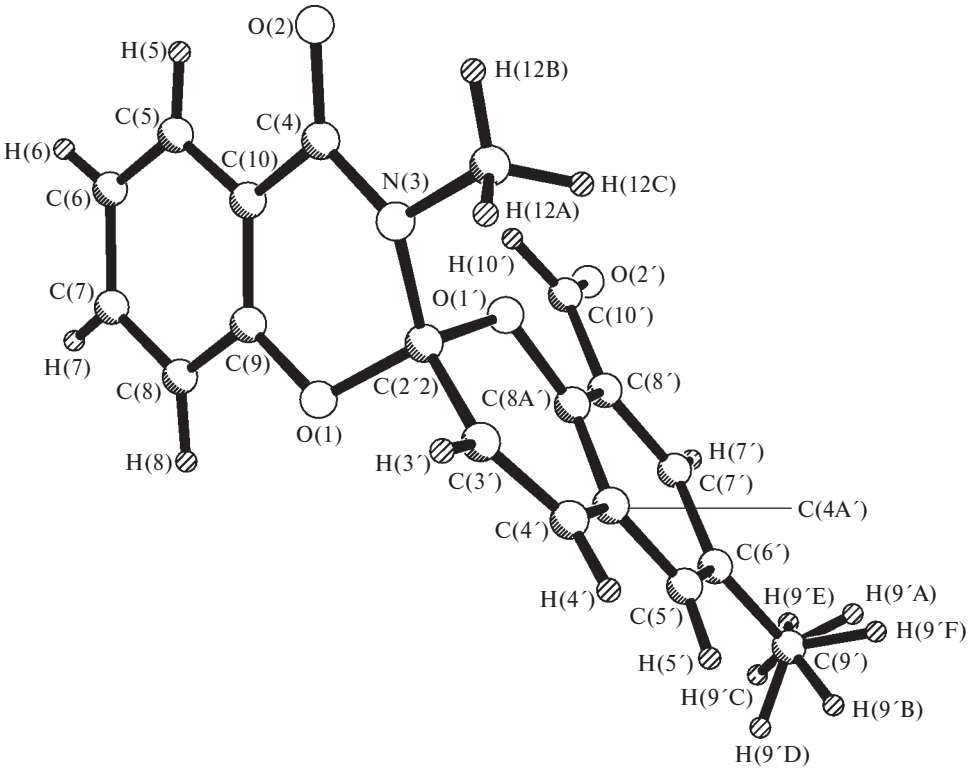

Fig. 1. Molecular structure of **1**.

Documator DDB-2 instrument (Carl Zeiss, Jena); the exposure time was varied from 30 to 360 s.

Compound **1** ($C_{19}H_{15}NO_4$) crystallized as yellow crystals belonging to the triclinic system with the unit cell parameters a = 8.320(2), b = 9.248(2), c = 11.536(3) Å, α = 71.30(2), β = 71.59(2), γ = 81.40(2)°, V = 796.6(3) Å^3, space group $\bar{P}1$, Z = 2, d_{calc} = 1.352 g cm^{-3}, $F(000)$ = 342, M = 321. A total of 3108 independent non-zero reflections were measured on an automated CAD-4 diffractometer (Mo-Kα radiation) at 293 K in the θ angle range of 1.94—25.45°. The structure was solved by direct methods and refined anisotropically by the least-squares method to R = 4.1% (R_w = 5.1%, Gof = 1.012) based on 2949 reflections with $I > 2\sigma(I)$ using the SHELXL-93 program package.[6] The positions of the hydrogen atoms were revealed from the difference Fourier synthesis and only their positional parameters were refined. The molecular structure is shown in Fig. 1. The principal bond lengths and bond angles are given in Tables 1 and 2, respectively. The energy of the crystal (E = −67 kcal mol^{-1}) was calculated by the atom-atom potential method with the use of the PCM program[7] involving parameters of 6-exp potentials proposed by A. N. Kitaigorodskii.

Spiropyran **1** was prepared from 2,6-diformyl-4-methylphenol[4] by a procedure described previously.[5] M.p. 146 °C (EtOH). Found (%): C, 71.07; H, 4.64; N, 4.54. $C_{19}H_{15}NO_3$. Calculated (%): C, 71.02; H, 4.70; N, 4.36.

IR (Nujol mulls), ν/cm^{-1}: 1670 (C=O); 1638, 1610, 1582 (C=C); 958, 936 (C—O). ^{1}H NMR ($CDCl_3$), δ: 2.33 (s, 3 H, 6′-Me); 3.04 (s, 3 H, N—Me); 6.00 (d, 1 H, 3′-H, J = 12.5 Hz); 6.30—8.13 (m, 7 H); 9.75 (s, 1 H, 8′-CHO).

UV (propan-2-ol, −80 °C), λ_{max} (log ε): 238 (4.52); 265 (4.14); 294 sh (3.55); 340 (3.58). For the photoinduced form, λ_{max} were 427 and 556 nm.

Table 1. Bond lengths (d) in molecule **1**

Bond	d/Å	Bond	d/Å
O(1′)—C(8A′)	1.367(2)	C(5′)—H(5′)	0.97(2)
O(1′)—C(2′2)	1.439(2)	C(4′)—H(4′)	0.97(2)
C(8′)—C(8A′)	1.384(2)	O(2′)—C(10′)	1.192(2)
C(8′)—C(7′)	1.395(2)	C(9)—C(8)	1.374(2)
C(8′)—C(10′)	1.468(2)	C(9)—C(10)	1.384(2)
C(4A′)—C(5′)	1.391(2)	C(10)—C(5)	1.389(2)
C(4A′)—C(8A′)	1.394(2)	C(10)—C(4)	1.472(2)
C(4A′)—C(4′)	1.444(2)	C(6′)—C(9′)	1.508(2)
N(3)—C(4)	1.368(2)	O(2)—C(4)	1.217(2)
N(3)—C(2′2)	1.438(2)	C(9′)—H(9′A)	1.05(2)
N(3)—C(12)	1.458(2)	C(9′)—H(9′B)	1.10(2)
O(1)—C(9)	1.370(2)	C(9′)—H(9′C)	1.01(2)
O(1)—C(2′2)	1.405(2)	C(9′)—H(9′D)	1.01(2)
C(7′)—C(6′)	1.379(2)	C(9′)—H(9′E)	0.97(2)
C(7′)—H(7′)	0.93(2)	C(9′)—H(9′F)	0.93(2)
C(3′)—C(4′)	1.322(2)	C(10′)—H(10′)	0.98(2)
C(3′)—C(2′2)	1.493(2)	C(12)—H(12A)	0.96(3)
C(3′)—H(3′)	0.97(2)	C(12)—H(12B)	0.97(3)
C(5′)—C(6′)	1.387(2)	C(12)—H(12C)	0.95(3)

Results and Discussion

Thin films of spiropyran **1**, which were prepared by thermal vacuum deposition on to glass and quartz supports, turned colored under UV irradiation at λ_{max} = 365 nm (~29397 cm^{-1}). The maximum spectral sensitivity

Table 2. Bond angles (ω) in molecule **1**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(8A′)—O(1′)—C(2′2)	118.55(9)	C(4A′)—C(4′)—H(4′)	120.2(1)	C(6′)—C(9′)—H(9′D)	113.0(3)
C(8A′)—C(8′)—C(7′)	118.46(1)	O(1)—C(9)—C(8)	118.24(1)	H(9′A)—C(9′)—H(9′D)	58.4(9)
C(8A′)—C(8′)—C(10′)	120.96(1)	O(1)—C(9)—C(10)	120.51(1)	H(9′B)—C(9′)—H(9′D)	56.8(9)
C(7′)—C(8′)—C(10′)	120.57(1)	C(8)—C(9)—C(10)	121.22(1)	H(9′C)—C(9′)—H(9′D)	166(3)
C(5′)—C(4A′)—C(8A′)	118.11(1)	C(9)—C(10)—C(5)	118.6(2)	C(6′)—C(9′)—H(9′E)	109(2)
C(5′)—C(4A′)—C(4′)	124.34(1)	C(9)—C(10)—C(4)	119.54(1)	H(9′A)—C(9′)—H(9′E)	139(3)
C(8A′)—C(4A′)—C(4′)	117.55(1)	C(5)—C(10)—C(4)	121.72(1)	H(9′B)—C(9′)—H(9′E)	57.5(9)
C(4)—N(3)—C(2′2)	119.23(1)	C(7′)—C(6′)—C(5′)	117.83(1)	H(9′C)—C(9′)—H(9′E)	60.8(9)
C(4)—N(3)—C(12)	118.78(1)	C(7′)—C(6′)—C(9′)	121.03(1)	H(9′D)—C(9′)—H(9′E)	109.0(3)
C(2′2)—N(3)—C(12)	117.16(1)	C(5′)—C(6′)—C(9′)	121.13(9)	C(6′)—C(9′)—H(9′F)	111.0(2)
O(1′)—C(8A′)—C(8′)	118.15(1)	O(1)—C(2′2)—O(1′)	107.84(9)	H(9′A)—C(9′)—H(9′F)	60.6(9)
O(1′)—C(8A′)—C(4A′)	120.45(1)	O(1)—C(2′2)—N(3)	112.21(9)	H(9′B)—C(9′)—H(9′F)	142.0(3)
C(8′)—C(8A′)—C(4A′)	121.28(2)	O(1′)—C(2′2)—N(3)	104.71(9)	H(9′C)—C(9′)—H(9′F)	62.3(9)
C(9)—O(1)—C(2′2)	116.08(1)	O(1)—C(2′2)—C(3′)	105.85(9)	H(9′D)—C(9′)—H(9′F)	114.0(2)
C(6′)—C(7′)—C(8′)	122.09(1)	O(1′)—C(2′2)—C(3′)	112.31(9)	H(9′E)—C(9′)—H(9′F)	101.0(3)
C(6′)—C(7′)—H(7′)	119.3(1)	N(3)—C(2′2)—C(3′)	113.90(9)	O(2′)—C(10′)—C(8′)	124.84(9)
C(8′)—C(7′)—H(7′)	118.5(1)	O(2)—C(4)—N(3)	122.1(9)	O(2′)—C(10′)—H(10′)	118.0(9)
C(4′)—C(3′)—C(2′2)	120.05(1)	O(2)—C(4)—C(10)	122.5(9)	C(8′)—C(10′)—H(10′)	117.2(9)
C(4′)—C(3′)—H(3′)	123.4(1)	N(3)—C(4)—C(10)	115.34(9)	N(3)—C(12)—H(12A)	112.0(2)
C(2′2)—C(3′)—H(3′)	116.4(1)	C(6′)—C(9′)—H(9′A)	111.9(9)	N(3)—C(12)—H(12B)	110.1(9)
C(6′)—C(5′)—C(4A′)	122.22(1)	C(6′)—C(9′)—H(9′B)	107.0(2)	H(12A)—C(12)—H(12B)	107.0(2)
C(6′)—C(5′)—H(5′)	121.2(9)	H(9′A)—C(9′)—H(9′B)	113.0(2)	N(3)—C(12)—H(12C)	112.2(9)
C(4A′)—C(5′)—H(5′)	116.6(1)	C(6′)—C(9′)—H(9′C)	80.0(2)	H(12A)—C(12)—H(12C)	101.0(2)
C(3′)—C(4′)—C(4A′)	121.44(1)	H(9′A)—C(9′)—H(9′C)	122.0(2)	H(12B)—C(12)—H(12C)	115.0(2)
C(3′)—C(4′)—H(4′)	118.3(1)	H(9′B)—C(9′)—H(9′C)	116.6(1)		

was observed in the wavelength region of the most intense mercury absorption line (λ = 365 nm), which allowed for using serial devices, in particular, a Documator DDB-2 instrument, as a source of activating radiation. The resulting colored form is characterized by absorption in the visible region with λ_{max} = 605 nm (Fig. 2) and the lifetime of ~1 h (Fig. 3). The broad absorption band of the colored form makes it possible to extract data using radiation of a helium-neon laser with λ = 632.8 nm. The recorded data were erased upon heating to 70 °C. The repeated data recording became possible after cooling of a film to ~20 °C (see Fig. 2). Presently, 1,3,3-trimethyl-6′-nitroindolinospiropyran (**2**) is considered as a reagent of choice. We compared the relative rates of the direct photocoloration reactions performed under identical conditions of irradiation of thin films of spiropyrans **1** and **2**, which were prepared by thermal vacuum deposition on to glass supports. The transmittance of the films thus prepared was ~1% at the wavelength of 365 nm, *i.e.*, virtually complete absorption of activating light was achieved thus providing the identity of the conditions of measurements. The overall rate constants of the direct photocoloration reaction were determined from a slope of the $\Delta D(t)$ plot with $t \to 0$ (Fig. 4). A comparison of the rate constants for spiropyrans **1** (0.06 s^{-1}) and **2** (0.002 s^{-1}) shows that the rate of photocoloration increases by a factor of 30 on going from **2** to **1**.

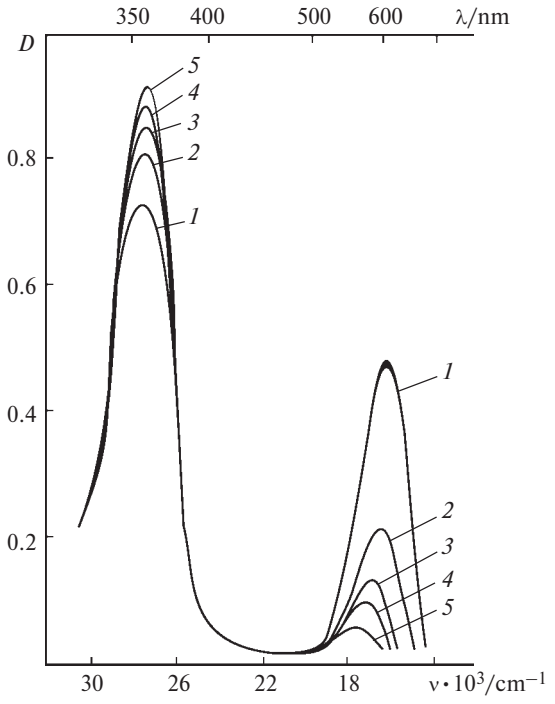

Fig. 2. Electronic absorption spectra of the irradiated film of spiropyran **1**: *1*, the irradiated form (reverse dark reaction). Time after irradiation/min: *2*, 5; *3*, 15; *4*, 30; *5*, 60.

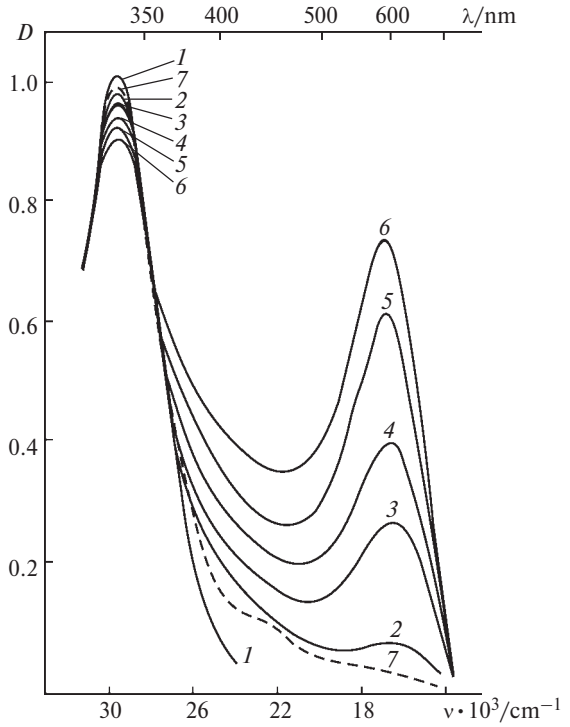

Fig. 3. Electronic absorption spectra of the polydispersed film of spiropyran **1** adsorbed on the quartz surface. Irradiation time/s: *1*, 0; *2*, 30, *3*, 120; *4*, 240; *5*, 270; *6*, 360; *7*, after heating of the film to 70 °C, data erasure.

According to the results of X-ray diffraction study, the molecular packing in the crystals of compound **1** is isotropic. The energy of intermolecular interactions between the adjacent molecules ranges from −7.2 to −8.3 kcal mol^{-1}. The molecules related by the translation along the *b* axis were found to be involved in specific intermolecular interactions between the oxygen atoms of the formyl group and the (H5′) atoms of the benzene fragment (C(5′)—H(5′)...O(2′), 2.45 Å; C(5′)...O(2′), 3.387 Å;

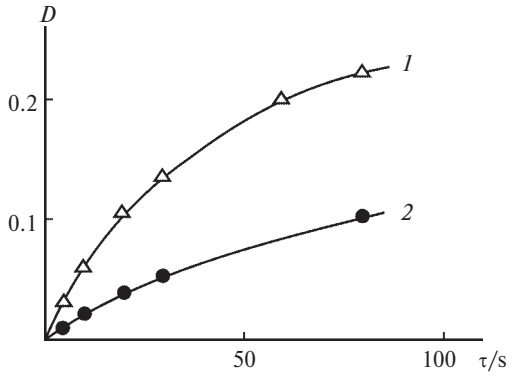

Fig. 4. Optical density (*D*) at the maximum of the absorption line of the photoinduced forms *vs.* the time of UV irradiation (λ_{max} = 365 nm) of 1,3,3-trimethyl-6′-nitroindolinospiropyran **2** (*1*) and spiropyran **1** (*2*).

the C(5′)—(H5′)—O(2′) bond angle, 172.5°). The equipotent symmetrical positions of the H(9′A), H(9′B), H(9′C) atoms and the H(9′D), H(9′E), H(9′F) atoms at the C(9′) atom relative to the plane of the benzene fragment C(5′)—C(6′)—C(7′)—C(8′)—C(8A′)—C(4A′) with the multiplicities of 0.5 indicate that there are two spatial orientations of the hydrogen atoms of the methyl fragment in the crystal of compound **1** (see Fig. 1).

For the crystal of **1**, the packing coefficient is 0.54. The free volume of the unit cell per each molecule is ~171 Å^3. This parameter characterizes the possibility of conformational changes of the molecules occurring in the crystal in the course of photoconversions. We plan to simulate the photoconversion process in the crystals with consideration for relaxation of the nearest environment.

In the starting molecule, the nonplanar benzopyran (BP) and benzoxazine (BO) fragments are approximately orthogonal to each other. The BO fragment is folded along the N(3)...O(1) line (the folding angle ϕ is 39.9°) and the BP fragment is folded along the C(3′)...O(1′) and C(4′)...O(1′) lines (α = 27.0° and β = 11.3°, respectively). The O(1), C(4), N(3), and O(2) atoms lie in the plane of the benzene ring. In molecule **1**, the C(2′2)—O(1′) bond length (1.439(2) Å in the BP fragment) is substantially larger than the analogous C(2′2)—O(1) bond length (1.405(2) Å) in the BO fragment. The N(3) atom deviates from the plane passing through the C(4), C(2′2), and C(12) atoms by 0.15 Å, and the sum of the bond angles at the N(3) atom is 345.2°. These values are in the range typical of spiropyrans of the indoline series studied previously[2] and are indicative of the pyramidal configuration of the nitrogen atom and of the noticeable sp^3 character of the lone electron pair of the N(3) atom. The orientations of the bonds at the N(3) atom correspond to the *trans* position of the lone electron pair of the nitrogen atom with respect to the C(2′2)—O(1′) bond. The angle between the vector of the C(2′2)—O(1) bond and the plane passing through the C(4), C(12), and C(2′2) atoms, which is the base of the pyramid of the N(3) atom, is 88.5°. This structure of the spiro unit indicates that the antibonding σ* orbital of the C(2′2)—O(1) bond is virtually parallel to the lone electron pair of the N(3) atom, which makes possible the orbital interaction between the n-lone electron pair of the N(3) atom and the antibonding σ* orbital of the C(2′2)—O(1) bond.[2] This interaction must cause strengthening of the C(2′2)—N(3) bond and weakening of the C(2′2)—O(1′) bond.[2]

The efficiency of this n—σ* interaction depends on the mutual orientation of the heteroatoms in the spiro unit and the electronic state of these heteroatoms. The mutual arrangement of the heteroatoms is responsible for the possible occurrence of the following interactions: the interactions of the antibonding σ* orbital of the C(2′2)—O(1′) bond with the lone electron pair of the N(3) atom and the π-lone pair of the O(1) atom and the

opposite interaction between the antibonding σ* orbital of the C(2´2)—O(1) bond and the π-lone pair of the O(1´) atom. The angle between the vector of the C(2´2)—O(1´) bond and the C(2´2), O(1), C(9) plane is 90.0° and the angle between the C(2´2)—O(1) bond and the C(2´2), O(1´), C(8A´) plane is 110.0°. However, the efficiency of these interactions depends on the electronic state of the heteroatoms. It is known that the energy of the π orbital of the lone electron pair of the nitrogen atom is higher than those of the π orbitals of the lone electron pairs of the oxygen atoms. The more substantial is the polarity of the C(2´2)—O(1´) and C(2´2)—O(1) bonds, the higher are the energies of their σ* orbitals. The electronic states of the O(1´) and O(1) atoms and the polarity of the C_{spiro}—O bond depend on the degree of involvement of the lone electron pair of the oxygen atom in π conjugation with the benzene rings. Considering that the O(1´)—C(8A´) and O(1)—C(9) bond lengths (1.367(2) and 1.370(2) Å, respectively) are identical to within the experimental error, the lone electron pairs of the oxygen atoms are involved in interactions with the π systems of the benzene rings to the same extent. Hence, the n—σ* orbital (C(2´2´)—O(1´)) interaction plays a decisive role in the spiro unit of molecule **1**. However, the activity of the lone electron pair of the nitrogen atom can be weakened through the competitive interaction between the sp^3-hybridized lone electron pair of the N(3) nitrogen atom and the adjacent C(4)=O(2) carbonyl group, which is known as the amide conjugation resulting in shortening of the C—N bond. For example, these bond lengths in the arylhydrazide derivatives studied by us previously are in the range of 1.350(3)—1.348(3) Å.[9,10] At the same time, this bond length in molecule **1** is 1.368 Å, which provides evidence for the possible involvement of the lone electron pair in two competitive interactions, *viz.*, with the σ* orbital of the C(2´2)—O(1´) bond and with the π bond of the carbonyl group. The N—C(sp^2) bond is elongated to 1.368 Å, suggesting the presence of weak amide conjugation. Besides, the C(4)—C(10) bond length (1.472(2) Å) is substantially smaller than those in arylhydrazide derivatives (1.501—1.503 Å),[8,9] *i.e.*, the carbonyl group in molecule **1** is involved in essential conjugation with the phenyl fragment. In molecule **1**, the N(3)—C(2´2) bond is shortened (1.438(2) Å) and its length is close to the analogous C_{spiro}—N bond lengths in SP of the indoline series (1.432—1.453 Å). Unlike the O(1´)—C(2´2) bond length, the O(1)—C(2´2) bond length (1.405(2) Å) is typical of six-membered heterocycles.[10]

In molecule **1**, the O(1´), C(8´), C(8A´), C(10´), and H(10´) atoms are approximately in a single plane (the C(10´) and H(10´) atoms deviate from this plane by 0.02 and 0.03 Å, respectively). However, the O(1´)—H(10´)—C(10´) angle is 99.1°, the O(1´)—...H(10´) distance is 2.437(1) Å, and the C(8´)—C(10´) bond length (1.468(2) Å) has the value typical of the C_{Ph}—CHO bonds (1.463—1.480 Å).[10] These geometric parameters are indicative of the absence of intramolecular hydrogen bonding, which could additionally influence the electronic state of the O(1´) atom.

To summarize, we synthesized the spiropyran of the benzoxazine series bearing the formyl group, which exhibits photochromic properties in the solid phase. These properties correlate with the characteristic features of the molecular and crystal structure of compound **1**. We plan to synthesize a series of spiropyran derivatives based on compound **1** and to examine the effect of the substituents on their structures and photochromic properties of the crystals.

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