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PHOTO- AND THERMOCHROMIC SPIRANES
31.* STRUCTURE AND PHOTOCHROMIC PROPERTIES OF FUNCTIONALIZED BENZOXAZINE SPIROPYRANS

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An X-ray diffraction study gave the structure of a 4-oxohydro-2H-1,3-benzoxazine spiropyran with molecular formula $C_{28}H_{25}N_3O_7$, in which the π-electron-withdrawing formyl group is replaced with a chelatophoric hydrazine fragment containing a methoxy group. The structural parameters of this spiropyran were determined and compared with the data for similar spiropyrans. The photochromic properties of this compound in acetonitrile were studied in the presence of zinc ions.

Keywords: benzoxazines, spiropyrans, X-ray diffraction structural analysis, photochromic properties.

In studying photochromic systems, the most interesting results have been obtained for indoline spiropyrans (ISP). In particular, analysis of the orbital interactions in the spiro site of this molecule has permitted us to elucidate the conditions favorable for photoinitiated conformational transformations in such molecules [2]. In light of the high stability of the open form of indoline spiropyrans, the use of reactions of functional substituents for their structural modification is limited [3]; such reactions often proceed with decomposition of the spiropyran system [4]. Hence, we undertook a study of the effect of π-electron-withdrawing substituents other than the nitro group. Data for such groups are presently extremely limited. We also studied the properties of nonindoline spiropyrans [5].

Benzoxazine spiropyrans were selected for study since the anionic localization energy L_a^- for the benzoxazine fragment with which the relative stability of the cyclic spiropyran forms correlates [6] is less than for indoline analogs (5.44 and 6.18 eV, respectively) [7]. Hence, we might expect that in going from indoline spiropyrans to benzoxazine spiropyrans, the relative stability of the spiropyran structures would increase and there would be less difficulty in obtaining cyclic derivatives with nonnitro group π-electron-withdrawing substituents.

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* For Communication 30, see [1].

Dedicated to Professor A. F. Prozharskii on the occasion of his 70th jubilee.

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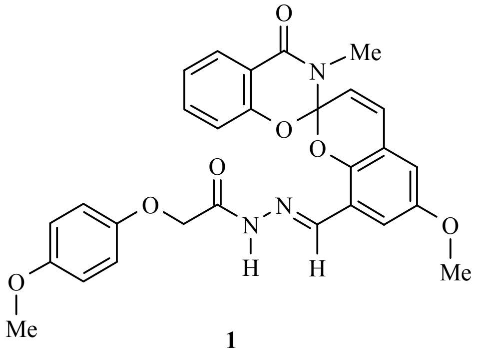
The existence of a chelate-forming hydrazine fragment in compounds **1** and **2** predisposes toward formation of mono- or binuclear transition metal complexes. The two methoxy groups in compound **1** presumably not only enhance solubility, which permits carrying out a detailed study of the properties of the complexes obtained, but also expands the possibilities of complexation due to participation of the unshared electron pairs of the methoxy group oxygen atom, including adjacent molecules.



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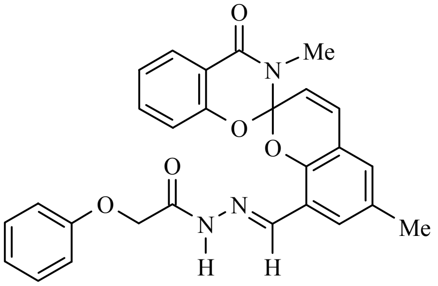

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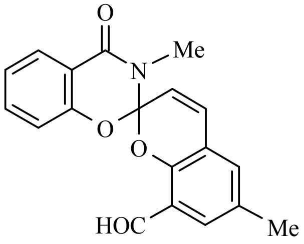

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As shown in our previous work, spiropyran **3** upon steady-state UV irradiation displays photochromic properties in solution at low temperatures and in the solid phase in thin films obtained by means of vacuum thermal spraying onto glass or quartz supporter [8]. Spiropyran **2** is nonphotoactive [1], while compound **1** in contrast to compound **3**, also does not show photochromic properties in the solid phase under steady-state UV irradiation. Upon irradiation under analogous conditions, a solution of compound **1** in acetonitrile undergoes efficient dehydration occurs and coloration is not observed (Fig. 1).

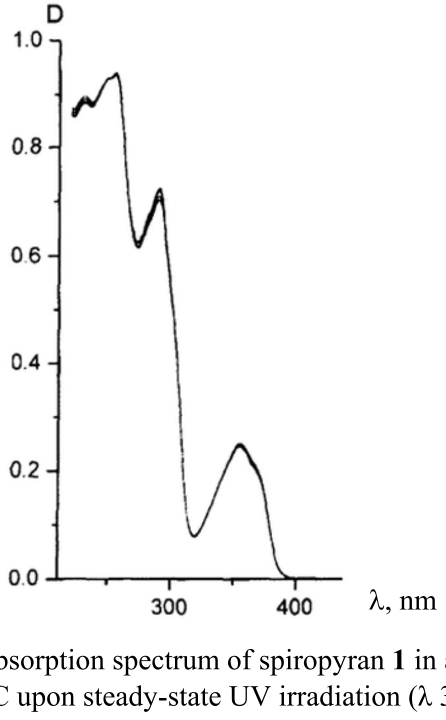

Fig. 1. Absorption spectrum of spiropyran **1** in acetonitrile at 25°C upon steady-state UV irradiation (λ 365 nm).

The addition of a zinc salt leads to the formation of complexes formed by merocyanine isomers, which results in the appearance of a long-wavelength absorption with λ_{max} ~ 580 nm (Fig. 2).

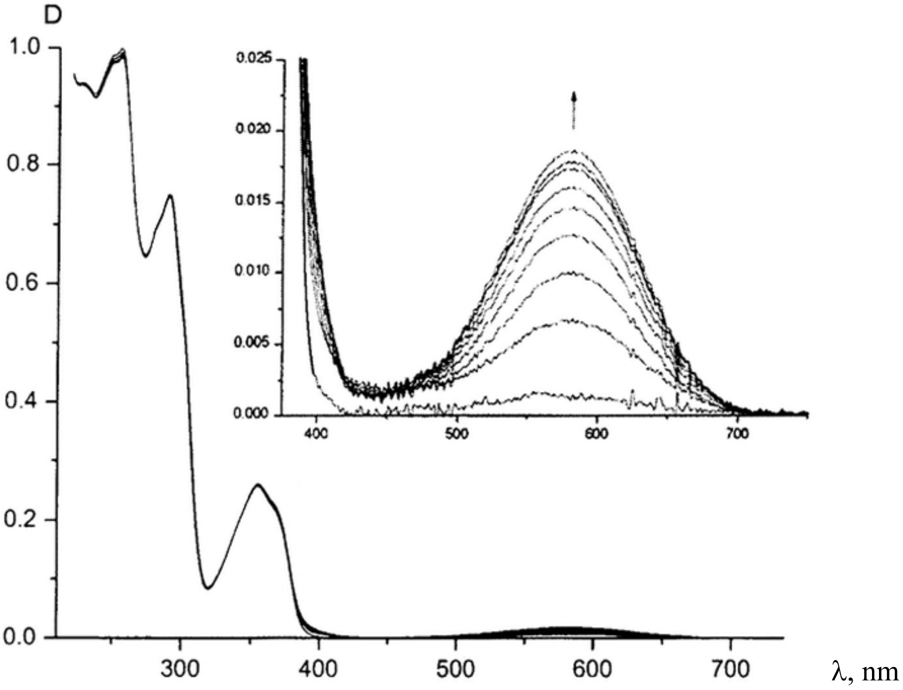

Fig. 2. Change in the absorption spectrum of spiropyran **1** upon the addition of a zinc salt in acetonitrile at 25°C; [**1**] = $3.29 \cdot 10^{-5}$ M, [Zn^{2+}] = $1.12 \cdot 10^{-3}$ M, *dt* = 10 sec.

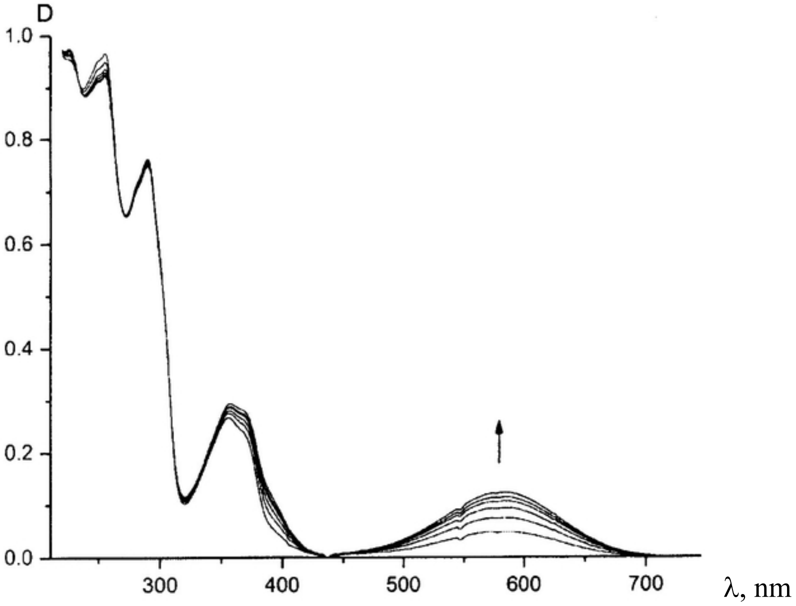

Fig. 3. Change in the absorption spectrum of the zinc complex of spiropyran **1** under following UV irradiation in acetonitrile at 25°C; [**1**] = $3.29 \cdot 10^{-5}$ M, [Zn^{2+}] = $1.12 \cdot 10^{-3}$ M, *dt* = 10 sec.

UV irradiation leads to the formation of an excess amount of complex in comparison with the thermal equilibrium state (Fig. 3). The molecular system involving the complex is photochromic with thermal reversibility; the optical density of the long-wavelength absorption band decreases also upon irradiation with visible light in the long-wavelength absorption band (Fig. 4).

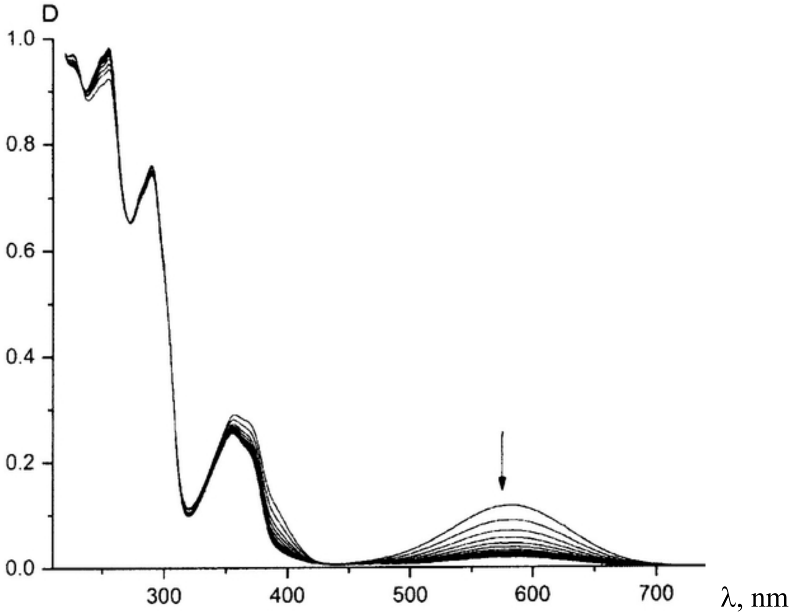

Fig. 4. Change in the absorption spectrum of the zinc complex of spiropyran **1** upon irradiation by light with λ_{max} 578 nm in acetonitrile at 25°C, *dt* = 10 sec.

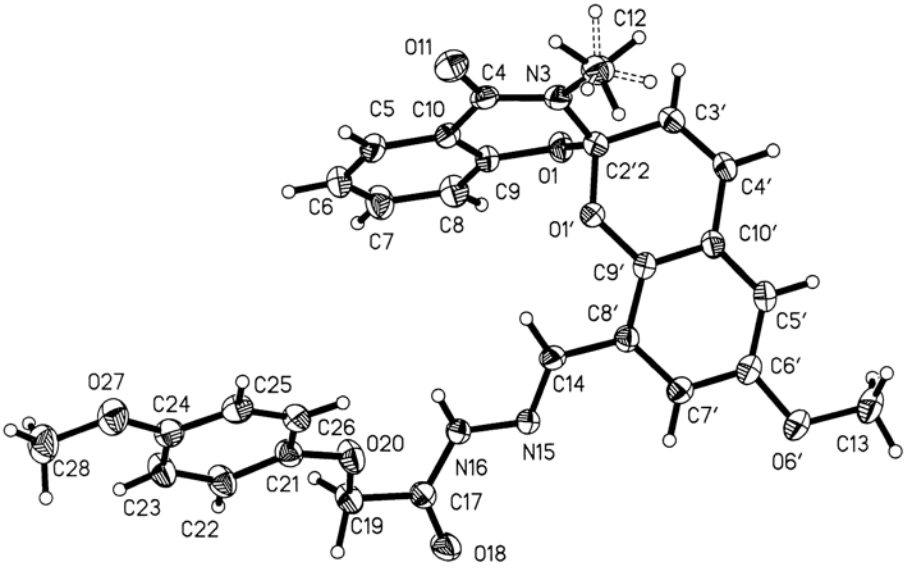

Fig. 5. Three-dimensional structure of spiropyran **1** according to X-ray diffraction data.

An X-ray diffraction structural analysis was carried out for a monocrystal of spiropyran **1** to elucidate the effect of the structure of this compound on its photochromic properties. A general view of spiropyran **1** is given in Fig. 5. The hydrogen atoms of the methyl group at N(3) are found in two equally probable positions differing in a 60° rotation relative to the N(3)–C(12) bond. Table 1 gives the bond lengths and bond angles in spiropyran **1**.

TABLE 1. Bond Lengths (l) and Bond Angles (ω) Derived from X-ray Diffraction Data

Bond	l, Å	Angle	ω, deg
O(1)–C(9)	1.373(2)	C(9)–O(1)–C(2'2)	115.6(2)
O(1)–C(2'2)	1.418(2)	O(1)–C(2'2)–O(1')	108.9(1)
C(2'2)–O(1')	1.423(2)	O(1)–C(2'2)–N(3)	111.2(1)
C(2'2)–N(3)	1.439(2)	O(1')–C(2'2)–N(3)	105.1(1)
C(2'2)–C(3')	1.488(2)	O(1)–C(2'2)–C(3')	105.7(1)
N(3)–C(4)	1.355(2)	O(1')–C(2'2)–C(3')	112.8(1)
N(3)–C(12)	1.460(2)	N(3)–C(2'2)–C(3')	113.2(1)
C(4)–O(11)	1.225(3)	C(4)–N(3)–C(2'2)	120.7(1)
C(4)–C(10)	1.467(2)	C(4)–N(3)–C(12)	118.3(2)
C(5)–C(6)	1.368(3)	C(2'2)–N(3)–C(12)	117.6(1)
C(5)–C(10)	1.385(2)	O(11)–C(4)–N(3)	121.5(2)
C(6)–C(7)	1.373(3)	O(11)–C(4)–C(10)	122.6(2)
C(7)–C(8)	1.378(3)	N(3)–C(4)–C(10)	115.9(1)
C(8)–C(9)	1.378(2)	C(6)–C(5)–C(10)	120.3(2)
C(9)–C(10)	1.382(2)		

The benzopyran (BP) and benzoxazine (BO) fragments in molecule **1**, as in molecules **2** and **3**, are approximately orthogonal to each other and, taken individually, not planar. The BO fragment has a flexure at the O(1)···N(3) line of 34.3° (compared to 38.1° in **2** and 39.9° in **3**), while the BP fragment has flexures at the O(1')···C(3') and O(1')···C(4') lines of 16.8°and 9.1°, respectively (20.2° and 11.4° in **2**, 29.0° and 11.3° in **3**).

The substituent at C(8') does not lie in the plane of the BP fragment due to twisting of the *o*-methoxyphenol fragment about the C(17)–C(19) bond at an angle of 32.7°, while the twist of the analogous substituent in molecule **2** about the C(17)–C(19) bond is 15.8°. The extrusion of N(3) atom from the plane traversing C(4), C(2'2), and C(12) is 0.15 Å (0.15 Å for **2** and 0.18 Å for **3**), which is close to the lower limit for the range of such values (0.34-0.12 Å) for previously studied ISP with a methyl substituent at the nitrogen atom. The sum of the bond angles at N(3) is 356.6° for **1**, 356.8° for **2**, and 355.8° for **3**. These values reflect the only slight pyramidalization of the nitrogen atom configuration and less sp^3 nature of its unshared electron pair (UEP) than in the case of ISP. The unshared electron pair has *syn* orientation relative to the σ*-orbital of the C(2'2)–O(1') bond.

Atom N(3) in spiropyran **1** participates in amide conjugation with the C(4)=O(11) carbonyl group, which leads to shortening of the N(3)–C(4) bond to 1.355(2) Å (1.370(4) Å for compounds **2** and **3**) and to a diminished π-σ* interaction of the nitrogen UEP and the σ*-orbital of the C(2'2)–O(1) bond in molecule **1** in comparison with indoline analogs. Atom N(15) in spiropyran molecule **1** also may participate in amide conjugation with the C(17)=O(18) carbonyl group. The sum of the bond angles at atom N(16) in molecule **1** is 360° as in the case of molecule **2**, while the N(16)–C(17) bond length is 1.339(2) Å and the C(17)=O(18) bond length is 1.214(2) Å (in spiropyran **2**, the N(16)–C(17) bond length is 1.348(3) Å and the C(17)=O(18) bond length is 1.220(3) Å).

Judging from the O(1)–C(9) bond length equal to 1.373(2) Å (1.385(4) Å in **2** and 1.370(3) Å in **3**) and the O(1')–C(9') bond length equal to 1.379(2) Å (1.391(4) Å in **2** and 1.375(3) Å in **3**), the participation of the UEP of atoms O(1) and O(1') in conjugation with the benzene rings is identical and, thus, the polarity of these bonds is identical. The O(1)–C(2'2) and O(1')–C(2'2) bond lengths are equal to 1.418(2) and 1.423(2) Å, respectively (1.423(4) and 1.433(4) Å in **2**), and identical within the 3σ range but fall outside the range of analogous values for C_{spiro}–O bond lengths in ISP (1.485-1.492 Å). The N(3)–C(2'2) bond length is 1.439(2) Å

(1.455(4) Å in **2**), which is in the range for analogous values in ISP. These results are attributed to the absence of the photochromic properties of compound **1** in the solid phase (as for compound **2**) in contrast to compound **3**, in which there is a formyl substituent at C(8').

Dimeric aggregates are formed in the crystal structure of spiropyran **1** analogously to compound **2** (Fig. 6) due to N–H···O=C intermolecular hydrogen bonding (IMHB) with the following parameters: O(11a)···N(16), 2.945(2) Å (2.961(4) Å in **2**); O(11a)···H(16), 2.11(3) Å (2.13(4) Å in **2**); O(11a)H(16)N(16), 160.9° (146.4 in **2**).

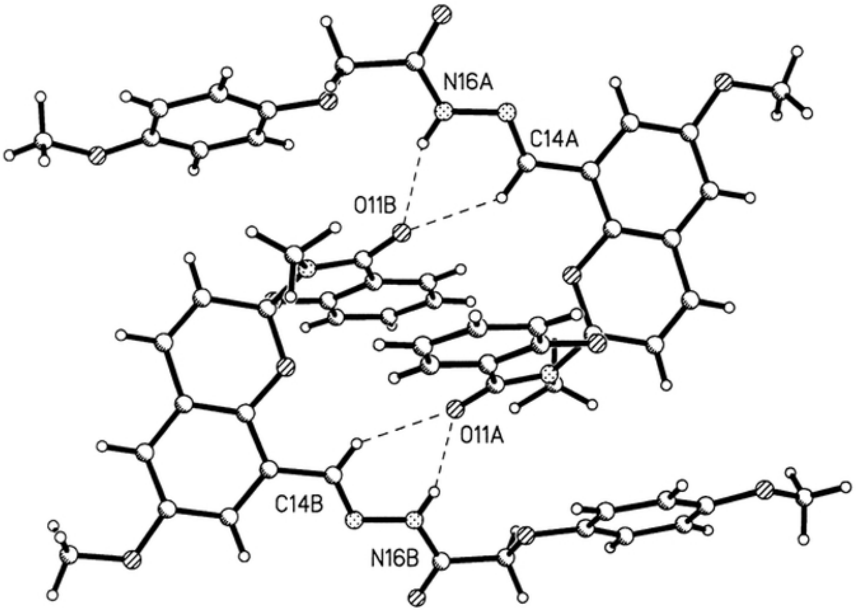

Fig. 6. Molecules of spiropyran **1** linked by IMHB (the disordering of the hydrogen atom is not shown).

The distances between the O(11) oxygen atom of the methoxy group in the benzo system of the [2H]-chromene fragment of one molecule and the hydrogen atoms at C(14) and N(16) of an adjacent molecule are 2.10 and 2.34 Å, respectively, which suggests the participation of the methoxy group oxygen atoms in complexation.

Thus, the introduction of methoxy groups into spiropyran **1** does not lead to a significant change in molecular structure, which is similar to the structure of spiropyran **2**.

EXPERIMENTAL

Spiropyran 1 ($C_{28}H_{25}N_3O_7$) was obtained from methanol solution as colorless, transparent monoclinic crystals: $M = 515.51$, $a = 10.602(2)$, $b = 15.628(3)$, $c = 13.733(3)$ Å, $\beta = 91.96(2)°$, $V = 2488.7(9)$ Å^3, $Z = 4$, $\rho_{calc} = 1.376$ g/cm^3, μ(MoKα) = 0.10 mm^{-1}, space group $P2_1/c$. The unit cell parameters of the crystal and the three-dimensional set of intensities were obtained on a KUMA automatic diffractometer using Mo$K\alpha$ radiation and a graphite monochromator. The intensities of 3658 reflections were measured in an inverse space quadrant ($2\theta \leq 50°$) by $\omega/2\theta$ scanning using an 0.5×0.5×0.4-mm monocrystal.

After exclusion of the systematically extinguished reflections and averaging of the intensities of equivalent reflections, the working set of measured F^2_{hkl} and $\sigma(F^2)$ contained 4288 independent reflections, of which 2833 reflections with $F^2 > 4\sigma(F^2)$ were used in the calculations. The structure was solved by the direct method and refined by the full matrix method of least squares relative to F^2 using the SHELX-97 program [9] anisotropically for the non-hydrogen atoms. All the hydrogen atoms in the crystal structure were localized in the Fourier electron density difference map. The coordinates and isotropic temperature parameters of all the hydrogen atoms were then calculated in the method of least squares procedure using the "rider model" [9]. The absolute displacements in the last cycle of the full matrix refinement of all 343 varied parameters of the structure were less than 0.001 σ. The final refinement parameters were as follows: $R_1 = 0.035$, $wR_2 = 0.089$ using 2823 observed reflections with $I \geq 2\sigma(I)$; $R_1 = 0.089$, $wR_2 = 0.97$ using all the measured reflections. The *GOOF* was 0.96. After completion of the refinement, the maximum and minimum electron density difference values were 0.203 and -0.177 eÅ^3.

The electronic spectra were taken on an Agilent 5483 manufactured in the United States using a DRSh-250 mercury lamp with light filters emitting light with λ_{max} 360 and 578 nm as the excitation source.

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