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PHOTO- AND THERMOCHROMIC SPIRANES

32*. SYNTHESIS AND PHOTOCHROMISM OF 3-METHYL-4-OXOSPIRO(2,3-DIHYDRONAPHTHO-[2,1-*e*]-1,3-OXAZINE-2,2'-[2H]-CHROMENES)

E. L. Mukhanov[1], Yu. S. Alekseenko[2], B. S. Lukyanov[1], V. I. Minkin[1,2], S. O. Bezuglyi[2], A. N. Utenyshev[3], V. V. Tkachev[3], and S. M. Aldoshin[3]**

Spiropyrans of the naphthoxazinone series have been obtained containing various substituents in the [2H]-chromene portion of the molecule. The spatial structure of a spiropyran containing ortho-positioned hydroxyl and formyl groups was established by X-ray structural analysis. The photochromic properties of the obtained compounds have been studied.

Keywords: naphthoxazinone, spiropyran, photochromism.

The phenomenon of photochromism, the ability of a substance to undergo a reversible change of absorption spectrum under the action of activating radiation of various spectral composition, is widely used in contemporary molecular electronics for the design of optical switches and devices for three-dimensional molecular memory. Of the organic photochromic materials the spiropyrans attract special attention, and undergo photoinitiated valence isomerization under the action of UV radiation. This is accompanied by cleavage of the C_{spiro}–O bond with the formation of colored quinonoid–betaine structures, the reversible rearrangement of which into the initial spiro form occurs under the action of visible light or spontaneously [2-4].

One of the most widespread routes for the regulation of spectral and photochemical properties of compounds of this class is the variation of the substituents in the [2H]-chromene portion [5]. Another direction for the modification of properties of photochromic spiropyrans, to which the current investigation is devoted, consists of varying the hetarene component and studying the effect of its structure on the photodynamic characteristics of spiropyrans. The present work is a continuation of our investigations in [6].

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* For Communication 31 see [1].

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

[1]Institute of Physical and Organic Chemistry, Southern Federal University, Rostov-on-Don 344090, Russia.
[2]Southern Scientific Center, Russian Academy of Sciences, Rostov-on-Don 344090, Russia.
[3]Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432, Moscow region, Russia.

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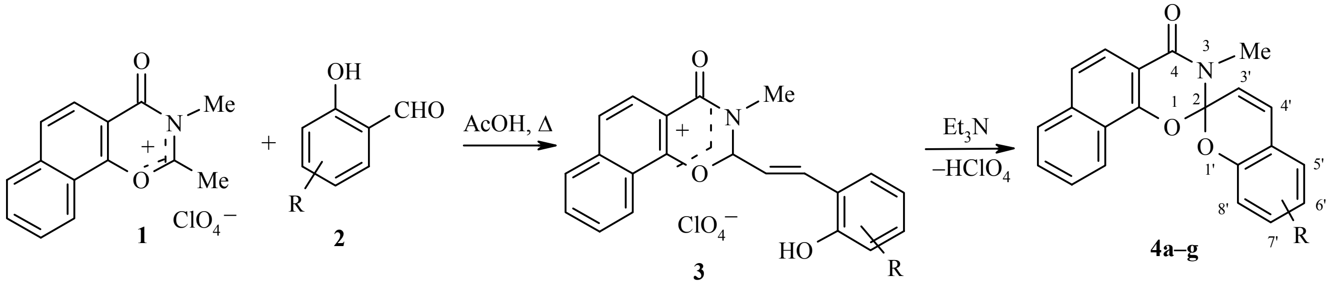
3-Methyl-4-oxospiro(2,3-dihydronaphtho[2,1-*e*]-1,3-oxazine-2,2'-[2H]-chromenes) **4** were obtained by a two-step synthesis. In the first step 2-[β-(2-hydroxyaryl)vinyl]-3-methyl-4-oxodihydronaphtho[2,1-*e*]-1,3-oxazinium perchlorates **3** were obtained in 25-45% yield by boiling 2,3-dimethyl-4-oxodihydronaphtho-[2,1-*e*]oxazinium perchlorate (**1**) and the appropriate *o*-hydroxyaromatic aldehyde in acidic medium. These



a R = 6'-Me, **b** R = 6'-Me, 8'-CHO; **c** R = 7'-OH, 8'-CHO; **d** R = 6'-NO_2; **e** R = 8'-NO_2; **f** R = 6'-OMe; **g** R = 6'-Cl

TABLE 1. 3-Methyl-4-oxospiro(2,3-dihydronaphtho[2,1-*e*]-1,3-oxazine-2,2'-[2H]-chromenes) **4**

Compound	Empirical formula	Found, % / Calculated, % C	H	N	mp, °C	Yield, %
4a	$C_{22}H_{17}NO_3$	$\frac{76.89}{76.97}$	$\frac{5.03}{4.97}$	$\frac{4.01}{4.08}$	162	45
4b	$C_{23}H_{17}NO_4$	$\frac{74.51}{74.39}$	$\frac{4.46}{4.58}$	$\frac{3.89}{3.77}$	201	42
4c	$C_{22}H_{15}NO_5$	$\frac{70.76}{70.78}$	$\frac{4.01}{4.02}$	$\frac{3.71}{3.75}$	191	45
4d	$C_{21}H_{14}N_2O_5$	$\frac{67.41}{67.38}$	$\frac{3.72}{3.74}$	$\frac{7.56}{7.49}$	205	35
4e	$C_{21}H_{14}N_2O_5$	$\frac{67.45}{67.38}$	$\frac{3.73}{3.74}$	$\frac{7.48}{7.49}$	177	33
4f	$C_{22}H_{17}NO_4$	$\frac{73.61}{73.54}$	$\frac{4.72}{4.74}$	$\frac{3.89}{3.90}$	201	36
4g*	$C_{21}H_{14}ClNO_3$	$\frac{69.34}{69.33}$	$\frac{3.93}{3.86}$	$\frac{3.91}{3.86}$	154	49

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* Found, %: Cl 9.10. Calculated, %: Cl 9.21

TABLE 2. Spectral Characteristics of Spiropyrans **4**

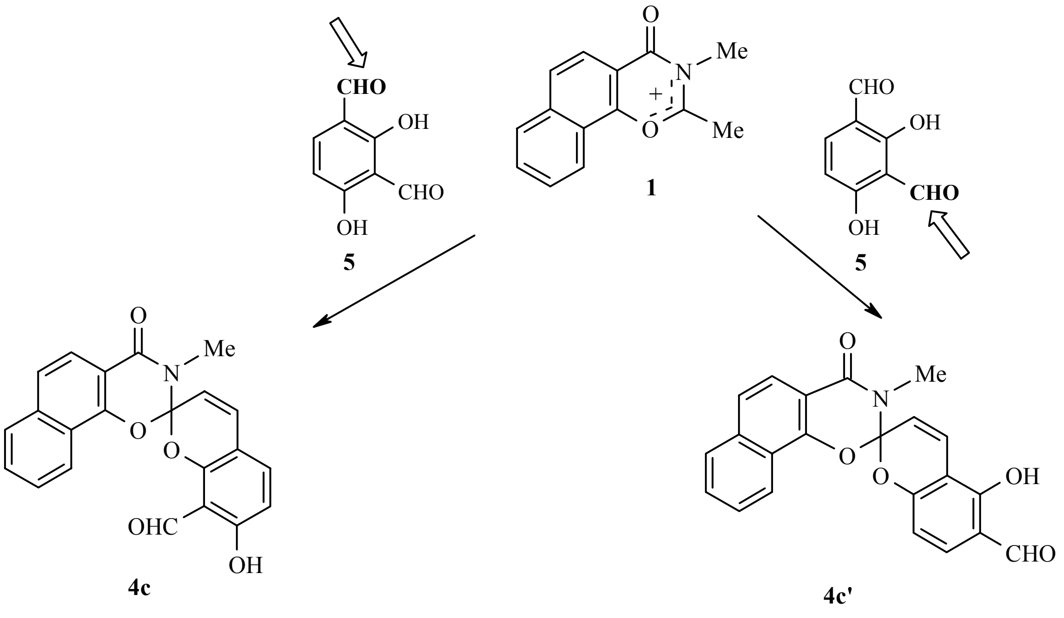
Compound	IR spectrum, ν, cm^{-1}			^1H NMR spectrum, δ, ppm (*J*, Hz)			
	C=O	C=C	C_{spiro}–O	N–CH_3 (3H, s)	H-3' (1H, d)	H-4' and arom. protons	Other protons (s)
4a	1662	1634	972	3.20	6.12 (*J* = 9.7)	6.64-8.06	2.30 (3H, 6'-CH_3)
4b	1673	1660, 1633	986	3.22	6.23 (*J* = 10.0)	7.07-8.02	2.32 (3H, 6'-CH_3); 9.88 (1H, 8'-CHO)
4c	1673	1647	973	3.20	6.07 (*J* = 10.0)	6.60-8.03	9.78 (1H, 8'-CHO); 11.64 (1H, 7'-OH)
4d	1679	1629	970, 940	3.00	6.32 (*J* = 9.9)	7.10-8.40	
4e	1673	1647, 1620	971	3.22	6.32 (*J* = 9.6)	7.06-8.03	
4f	1680	1639	927	3.20	6.15 (*J* = 9.7)	6.60-8.05	3.80 (3H, OCH_3)
4g	1660	1640	972	3.18	6.19 (*J* = 9.7)	6.67-8.03	

compounds are intensely colored orange-red crystalline substances which were later used without intermediate purification. Perchlorates **3** suspended in absolute ether were treated with triethylamine, which led to removal of $HClO_4$ and cyclization with the formation of spiropyrans **4**.

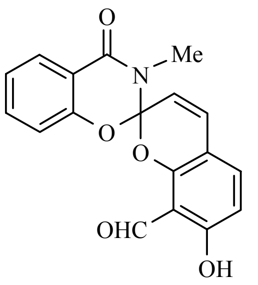
Characteristic bands were present in the IR spectra of the obtained spiropyrans (Table 2) for the stretching vibrations in the 1660-1680 region (C=O oxazinone fragment), at 1620-1660 (C=C bond of the pyran fragment), and also bands characteristic of the C_{spiro}–O bond in the 925-990 cm^{-1} range.

In the ^{1}H NMR spectra of spiropyrans **4** (Table 2) signals were present in the 3.18-3.22 ppm region for the N–CH_3 group protons. In the spectrum there were also doublet signals for protons in position 3' of the benzopyran fragment in the 6.12-6.32 ppm region (J = 9.6-10.0 Hz), which is characteristic of all spiropyran structures.

The formation of spiropyran **4c** may also theoretically proceed at each of the two formyl groups of the initial 2,4-dihydroxyisophthalic aldehyde **5**. The spiropyran structure of compound **4c** was demonstrated with the aid of data of ^{1}H NMR spectroscopy. Characteristic of its ^{1}H NMR spectrum is the presence of a doublet signal for the H-3' proton (J = 10.0 Hz) at 6.07 ppm of the [2H]-chromene fragment and also singlet signals of the protons of the formyl and hydroxyl groups at 9.78 and 11.64 ppm respectively. The significant displacement of the signals of the OH group protons towards low field is explained by the presence of intramolecular hydrogen bonds.



The mutual disposition of OH and CHO groups in the [2H]-chromene portion of the spiropyran **4c** molecule was established by analogy with spiropyran **6** in [6].



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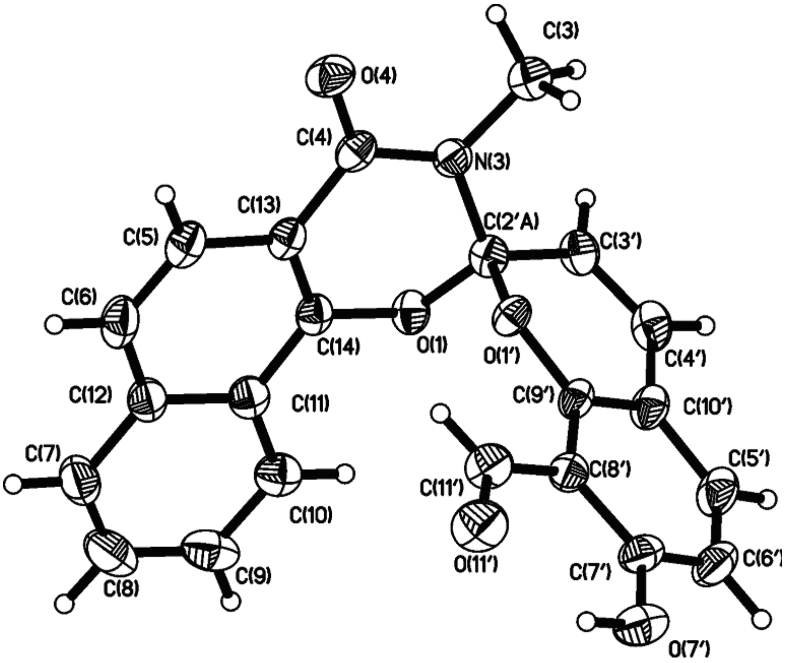
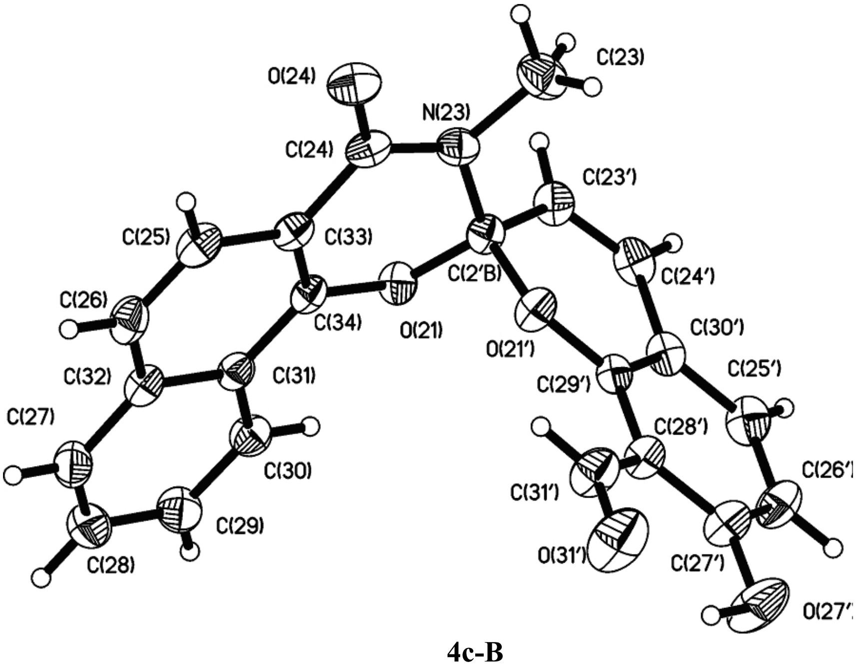
Compound **4c** crystallized as two independent molecules, the general shape of which is shown in Fig. 1 (notice that the numbering of atoms of the second molecule is increased by 20 relative to the numbering of the first molecule). The two independent molecules differed insignificantly from one another in the character of bond length distribution (Table 3) and size of valence angles (Table 4). In both independent molecules of the investigated compound the benzopyran with an additional annelated benzene ring and the benzoxazinone fragments, as in the previously investigated indoline and benzoxazinone derivatives of spiropyrans, are located completely orthogonal to one another and are individually nonplanar.



4c-A



4c-B

Fig. 1. General form of the independent molecules **4c-A** and **4c-B.**

The nonplanarity of the additionally annelated benzoxazinone fragment in the independent molecule **4c-A** is caused by a twist along the line N(3)···O(1) at an angle of 37.3°, and the nonplanarity of the benzopyran fragment is caused by twists along the lines C(3')–O(1') and C(4')–O(1') at angles of 20.30° and 8.10° respectively. The nonplanarity of the analogous fragments in the independent **4c-B** molecule is caused by twists along the lines N(23)···O(21) at an angle of 30.3° and C(23')–O(21') and C(24')–O(21') at angles of 15.9° and 5.4° respectively. The previously studied compound **6** without the additionally annelated benzene ring has a similar structure [6]. The nonplanarity of the benzoxazinone fragment in this compound is caused by a twist along the line of N(3)···O(1) of 33.9°, but the nonplanarity of the benzopyran fragment is caused by the twists along the lines C(3')–O(1') and C(4')–O(1') at angles of 22.6° and 7.5° respectively. The atoms O(1), C(4), N(3), O(4), and O(21), C(24), N(23), O(24) are disposed in the planes of the corresponding naphthalene fragments. The geometric structure of the C_{spiro}–node and the benzopyran fragment in the independent molecules of compound **4c** are analogous to the structure of the previously investigated indoline and benzoxazine spiropyrans. As in compound **6,** the inclusion in the additionally annelated benzoxazinone fragment of compound **4c** of a carbonyl group C(4)=O(2) leads to a significant change in the electronic and geometric picture of the structure of the N–node. The emergence of atoms N(3) and N(23) from the corresponding planes of the coordinating C(2'A), C(4), and C(3) of compound **4c-A** and C(2'B), C(24), C(23) of compound **4c-B** was 0.171 and 0.162 Å respectively (0.152 Å in compound **6**). The sum of the valence angles at the N(3) atom was 355.6° and at the N(23) atom was 356.1° (356.1° in compound **6**). The length of the amide bond in the independent molecules **4c-A** and **4c-B** was equal respectively, N(3)–C(4) = 1.375(4) and N(23)–C(24) 1.375(4) Å (1.361(3) Å in compound **6**), which indicates the appreciable conjugation of the unshared electron pair of the N atom with the π-bond of the carbonyl group. The amide conjugation significantly weakens the interaction of the unshared electron pair of the N atom with the σ^*-orbital of the C_{spiro}–O(1') bond. In addition, the geometric disposition of the C_{spiro}–O(1') bond relative to the coordinated plane of the nitrogen atom, C_{spiro}C(4)C(3) becomes less favorable for orbital n-σ^* interactions. On the other hand, presence of a formyl group at the C(8') atom increases the electron-withdrawing influence at the O(1') atom. This is indicated by some

TABLE 3. Bond Lengths (*l*) in the Two Independent Molecules of Compound **4c**

Bond	*l*, Å	Bond	*l*, Å	Bond	*l*, Å
O(1)–C(14)	1.370(3)	C(2'A)–C(3')	1.491(4)	C(28)–C(29)	1.405(5)
O(1)–C(2'A)	1.419(4)	C(3')–C(4')	1.325(4)	C(29)–C(30)	1.348(4)
O(4)–C(4)	1.219(3)	C(4')–C(10')	1.440(5)	C(30)–C(31)	1.417(4)
N(3)–C(4)	1.375(4)	C(5')–C(6')	1.355(5)	C(31)–C(34)	1.412(4)
N(3)–C(2'A)	1.425(4)	C(5')–C(10')	1.398(5)	C(31)–C(32)	1.418(4)
N(3)–C(3)	1.463(4)	C(6')–C(7')	1.391(5)	C(33)–C(34)	1.362(4)
C(4)–C(13)	1.460(4)	C(7')–C(8')	1.405(4)	C(2'B)–O(21')	1.447(3)
C(5)–C(6)	1.349(5)	C(8')–C(9')	1.390(4)	C(2'B)–C(23')	1.485(4)
C(5)–C(13)	1.431(4)	C(8')–C(11')	1.423(4)	O(21')–C(29')	1.366(3)
C(6)–C(12)	1.424(5)	C(9')–C(10')	1.382(4)	O(27')–C(27')	1.337(4)
C(7)–C(8)	1.376(6)	O(21)–C(34)	1.372(3)	O(31')–C(31')	1.211(4)
C(7)–C(12)	1.411(5)	O(21)–C(2'B)	1.406(3)	C(23')–C(24')	1.311(4)
C(8)–C(9)	1.381(6)	O(24)–C(24)	1.223(3)	C(24')–C(30')	1.444(4)
C(9)–C(10)	1.361(5)	N(23)–C(24)	1.378(4)	C(25')–C(26')	1.362(5)
C(10)–C(11)	1.410(5)	N(23)–C(2'B)	1.433(4)	C(25')–C(30')	1.391(4)
C(11)–C(14)	1.413(4)	N(23)–C(23)	1.454(4)	C(26')–C(27')	1.377(5)
C(11)–C(12)	1.426(4)	C(24)–C(33)	1.459(4)	C(27')–C(28')	1.409(4)
C(13)–C(14)	1.356(4)	C(25)–C(26)	1.350(5)	C(28')–C(29')	1.392(4)
O(1')–C(9')	1.357(3)	C(25)–C(33)	1.423(4)	C(28')–C(31')	1.437(4)
O(1')–C(2'A)	1.446(3)	C(26)–C(32)	1.410(4)	C(29')–C(30')	1.381(4)
O(7')–C(7')	1.339(4)	C(27)–C(28)	1.360(5)		
O(11')–C(11')	1.224(4)	C(27)–C(32)	1.400(5)		

shortening of the O(1')–C(9') bond in comparison with analogous compounds to 1.357(3) Å in the independent **4c-A** molecule and 1.366(3) in the independent **4c-B** molecule. The increase in the electron-withdrawing effect of the 8' substituent increases the polarity of the C_{spiro}–O(1') bond and additionally strengthens the n–σ^* interaction in

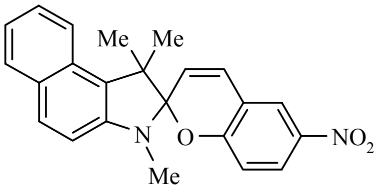
TABLE 4. Values of Angles (ω) in the Two Independent Molecules of Compound **4c** according to X-ray Structural Analysis

Angle	ω, deg	Angle	ω, deg
C(14)–O(1)–C(2'A)	116.0(2)	C(34)–O(21)–C(2'B)	118.3(2)
C(4)–N(3)–C(2'A)	119.3(2)	C(24)–N(23)–C(2'B)	121.5(2)
C(4)–N(3)–C(3)	118.7(3)	C(24)–N(23)–C(23)	117.9(3)
C(2'A)–N(3)–C(3)	117.6(2)	C(2'B)–N(23)–C(23)	116.7(3)
O(4)–C(4)–N(3)	121.9(3)	O(24)–C(24)–N(23)	121.5(3)
O(4)–C(4)–C(13)	123.3(3)	O(24)–C(24)–C(33)	123.5(3)
N(3)–C(4)–C(13)	114.7(3)	N(23)–C(24)–C(33)	115.0(3)
C(6)–C(5)–C(13)	120.5(3)	C(26)–C(25)–C(33)	120.7(3)
C(5)–C(6)–C(12)	121.9(3)	C(25)–C(26)–C(32)	121.7(3)
C(8)–C(7)–C(12)	121.2(4)	C(28)–C(27)–C(32)	121.5(3)
C(7)–C(8)–C(9)	120.6(4)	C(27)–C(28)–C(29)	119.7(3)
C(10)–C(9)–C(8)	120.5(4)	C(30)–C(29)–C(28)	121.0(3)
C(9)–C(10)–C(11)	120.7(4)	C(29)–C(30)–C(31)	120.4(3)
C(10)–C(11)–C(14)	123.6(3)	C(34)–C(31)–C(30)	123.2(3)
C(10)–C(11)–C(12)	119.5(3)	C(34)–C(31)–C(32)	117.8(3)
C(14)–C(11)–C(12)	116.9(3)	C(30)–C(31)–C(32)	119.0(3)
C(7)–C(12)–C(6)	123.9(3)	C(27)–C(32)–C(26)	122.8(3)
C(7)–C(12)–C(11)	117.5(3)	C(27)–C(32)–C(31)	118.5(3)
C(6)–C(12)–C(11)	118.5(3)	C(26)–C(32)–C(31)	118.7(3)
C(14)–C(13)–C(5)	117.7(3)	C(34)–C(33)–C(25)	118.1(3)
C(14)–C(13)–C(4)	121.2(3)	C(34)–C(33)–C(24)	120.6(3)
C(5)–C(13)–C(4)	121.0(3)	C(25)–C(33)–C(24)	121.3(3)
C(13)–C(14)–O(1)	119.9(3)	C(33)–C(34)–O(21)	120.5(3)
C(13)–C(14)–C(11)	124.3(3)	C(33)–C(34)–C(31)	123.0(3)
O(1)–C(14)–C(11)	115.7(3)	O(21)–C(34)–C(31)	116.5(2)
C(9')-O(1')–C(2'A)	119.8(2)	O(21)–C(2'B)–N(23)	112.5(2)
O(1)–C(2'A)–N(3)	112.0(2)	O(21)–C(2'B)–O(21')	107.8(2)
O(1)–C(2'A)–O(1')	106.3(2)	N(23)–C(2'B)–O(21')	105.1(2)
N(3)–C(2'A)–O(1')	105.6(2)	O(21)–C(2'B)–C(23')	105.6(2)
O(1)–C(2'A)–C(3')	105.3(2)	N(23)–C(2'B)–C(23')	113.2(3)
N(3)–C(2'A)–C(3')	115.4(3)	O(21')–C(2'B)–C(23')	112.6(2)
O(1')–C(2'A)–C(3')	111.9(3)	C(29')–O(21')–C(2'B)	121.4(2)
C(4')–C(3')–C(2'A)	119.9(3)	C(24')–C(23')–C(2'B)	121.2(3)
C(3')–C(4')–C(10')	122.1(3)	C(23')–C(24')–C(30')	122.1(3)
C(6')–C(5')–C(10')	123.4(3)	C(26')–C(25')–C(30')	123.2(3)
C(5')–C(6')–C(7')	119.0(3)	C(25')–C(26')–C(27')	119.2(3)
O(7')–C(7')–C(6')	118.2(3)	O(27')–C(27')–C(26')	118.7(3)
O(7')–C(7')–C(8')	121.8(3)	O(27')–C(27')–C(28')	121.5(3)
C(6')–C(7')–C(8')	120.0(3)	C(26')–C(27')–C(28')	119.9(3)
C(9')–C(8')–C(7')	118.8(3)	C(29')–C(28')–C(27')	119.0(3)
C(9')–C(8')–C(11')	121.4(3)	C(29')–C(28')–C(31')	120.5(3)
C(7')–C(8')–C(11')	119.8(3)	C(27')–C(28')–C(31')	120.4(3)
O(11')–C(11')–C(8')	125.1(3)	O(31')–C(31')–C(28')	125.3(4)
O(1')–C(9')–C(10')	121.0(3)	O(21')–C(29')–C(30')	121.0(3)
O(1')–C(9')–C(8')	117.0(2)	O(21')–C(29')–C(28')	117.6(3)
C(10')–C(9')–C(8')	122.0(3)	C(30')–C(29')–C(28')	121.4(3)
C(9')–C(10')–C(5')	116.9(3)	C(29')–C(30')–C(25')	117.3(3)
C(9')–C(10')–C(4')	117.4(3)	C(29')–C(30')–C(24')	117.7(3)
C(5')–C(10')–C(4')	125.7(3)	C(25')–C(30')–C(24')	124.9(3)

comparison with previously studied spiropyrans. As a result of this the bond lengths of C(2'A)–O(1') = 1.446(3) and C(2'A)–O(1) = 1.419(4) Å in the independent **4c-A** molecule and C(2'B)–O(21') = 1.447(3) and C(2'B)–O(21) = 1.406(3) Å in the independent **4c-B** molecule, analogous to the values in compound **6** of C(2'2)–O(1') = 1.454(2) and C(2'2)–O(1) = 1.414(2) Å.

The molecular structure of both independent molecules **4c-A** and **4c-B**, like the molecular structure of the previously studied compound **6**, is characterized by the presence of strong intramolecular hydrogen bonds between the hydroxyl hydrogen atom and the formyl oxygen atom. The parameters of the intramolecular hydrogen bonds were O(11')···H(7') = 1.86(3), O(11')···O(7') = 2.598(4) Å, O(11')H(7')O(7') = 130.8° in the **4c-A** molecule and O(31')···H(27') = 1,62(3). O(31')···O(27') = 2.629(4) Å, O(31')H(27')O(27') = 124.9° in the **4c-B** molecule (O(3')···H(2') = 1.63(3), O(2')···O(3') = 2.586(3) Å, O(2')H(2')O(3') = 145.6° for compound **6**).

Spiropyrans **4a,b** did not display photochromic properties on irradiation of their alcoholic solutions in the stationary mode at low (-70°C) temperatures regardless of the wavelength of the activating irradiation (λ_{max} 313, λ_{max} 365 nm, or unfiltered light).



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However on carrying out the experiment in toluene at room temperature solutions of spiropyrans **4** containing π-withdrawing groups at position 6' displayed photochromic properties (Fig. 2, Table 5). In general an additionally annelated benzene ring led to a reduction in the lifespan of the photoinduced form, which is in good agreement with the results of the investigation of 1,3,3-trimethyl-4,5-benzo-6-nitrospiro(indoline-

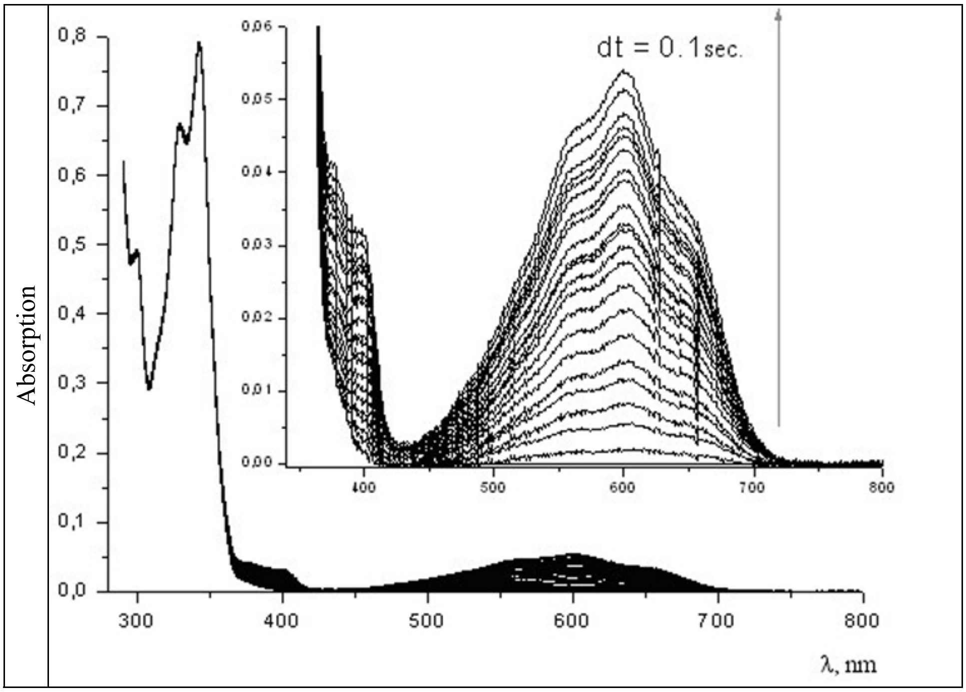

Fig. 2. UV absorption spectrum of spiropyran **4b** in toluene before and after irradiation in the stationary mode with light of λ_{max} 365 nm at 20°C.

TABLE 5. Characteristics of the Absorption Spectra of Spiropyrans **4** in Toluene at 20°C

Compound	R	λ^{A}_{max}, nm	ε (λ^{A}_{max}), $M^{-1}cm^{-1}$	Photoinduced form	
				(λ^{B}_{max}), nm	τ, sec
4a	6'-Me	300	6190	Not observed under the experimental conditions	
4b	6'-Me 8'-CHO	329 342	6710 7940	600	0.89
4c	7'-OH 8'-CHO	343	6690	Not observed under the experimental conditions	
4e	8'-NO_2	298 327	8000 7740	576 sh 615	3.1
4f	6'-OMe	327	6780	Not observed under the experimental conditions	
4g	6'-Cl	300	6540	Not observed under the experimental conditions	

2,2'-[2H-I]-benzopyran (**7**), and shows that the strong reduction of the quantum yield of photoconversion on annelation of an additional nucleus in the hetarene fragment of an indoline spiropyran may possibly be explained by the unradiating deactivation of the activated state (for example, by the intramolecular transfer of energy from the pyran ring to the indoline) [5].

EXPERIMENTAL

The IR spectra were recorded in nujol on a Specord IR-75 prism double-beam spectrometer (calibration of sample with polystyrene). Electronic absorption spectra were obtained on a Agilent 8453 spectrophotometer. The ^{1}H NMR spectra were recorded on Bruker 250 (250 MHz) and Varian Unity 300 (300 MHz) instruments in impulse Fourier mode in $CDCl_3$. Standard was the residual proton signal in $CDCl_3$.

3-Methylspiro(2,3-dihydronaphtho[2,1-*e*][1,3]-oxazin-4-oxo-2,2'-[2H]-chromenes) 4a-g. A mixture of 2,3-dimethyl-4-oxodihydronaphtho[2,1-*e*][1,3]oxazinium perchlorate (**1**) [7] (3.25 g, 0.01 mol) and the appropriate aldehyde (0.01 mol) in acetic acid (15 ml) was boiled for 3 min. The reaction mixture was cooled, the precipitated salt **3** was filtered off, and washed with absolute ether. Triethylamine (1.5 ml, 0.01 mol) was added to a solution of the residue in absolute ether (50 ml). After 6 h the ether was decanted and evaporated, The residue of spiropyran was crystallized from alcohol (Tables 1 and 2).

The parameters of the unit cell of a crystal of spiropyran **4c** and the three-dimensional set of intensities were obtained on a KUMA 4 four-circle diffractometer with $\omega/2\theta$ scanning (MoKα-radiation, graphite monochromator) at 293(2) K. Absorption was not calculated, $\mu_{MoK\alpha}$ = 0.102 mm^{-1}. Light-yellow crystals of **4c** (alcohol) were triclinic: $C_{22}H_{15}NO_5$, M = 373.35; a = 7.7400(15), b = 13.256(3), c = 17.370(4) Å, α = 97.03(3), β = 93.84(3), γ = 97.15(3)°. V = 1748.9(6) Å^3, Z = 4, ρ_{calc} = 1.418 g/cm^3, space group P-1. The intensities of 6830 reflections were measured at $2\theta \leq 50.1°$ from a monocrystal of size 0.4×0.4×0.35 mm. Averaging of measured equivalent reflections F^2(hkl) and $\sigma(F^2)$ resulted in 6051 independent reflections. Those 2779 reflections having $F^2 > 4\sigma(F^2)$ were used in subsequent calculations. The structure was solved by the direct method with the SHELXS-97 [8] program and refined by the full matrix least squares method on F^2 with the SHELXL-97 program [8] in an anisotropic approximation for the non-hydrogen atoms. In the crystal structure of **4c** all the H atoms were located in an electron density Fourier difference synthesis. Subsequently the coordinates and isotropic thermal parameters of all the H atoms were calculated in the least squares procedure according to the "rider" model [8]. In the final cycle of the full matrix refinement the absolute displacements of all 100 varied parameters of the structure were less than 0.001 σ. The closing interatomic distances and valence angles are given in Tables 3 and 4. Final refinement parameters were $R_1 = 0.051$, $wR_2 = 0.132$ for reflections observed with $I \geq 2\sigma(I)$; $R_2 = 0.069$, $wR_2 = 0.155$ for all measured reflections, quality of fit S was 0.862 and 0.862 respectively, maximum and minimum electron density 0.222 and –0.358 eÅ^{-3}.

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