STRUCTURES AND PHOTO- AND THERMOCHROMIC PROPERTIES OF SPIROPYRANS OF THE 2-OXAINDAN SERIES WITH POLYCONDENSED CHROMENE FRAGMENTS*

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Spiropyrans of the 2-oxaindan series with 2H-chromene fragments benzo- and 2,3-naphthoannelated at the 7–8 bond were synthesized. The molecular structures of four of the spiropyrans obtained were determined by x-ray diffraction studies, and their photo- and thermochromic properties were studied. Annelation of arene rings significantly increases the relative stabilities fo the photocolored forms of the spiropyrans. A correlation between the length of the C_{spiro}–O bond and the capacity of spiropyrans for photocoloration was discovered. In addition, the free energies of activation of the thermochromic transformations of spiropyrans determined by dynamic NMR spectroscopy are insensitive to variations in the length of the indicated bond.

Spiropyrans continue to be among the most promising types of photochromic compounds. It is known [2] that significant improvement in the operating characteristics of spiropyrans and, primarily, an increase in the stabilities of their photoinduced forms can be achieved by the introduction of strong electron-acceptor substituents, chiefly nitro groups, into the 2H-chromene fragment of the molecule. However, it has been shown [3, 4] that the indicated substituents simultaneously significantly decrease the photostabilities of spiropyrans, thereby sharply limiting the sphere of practical utilization of materials based on them [5]. In this connection, in the present research we chose to study spiropyrans of the 2-oxaindan series (I, II), stabilization of the photocolored forms of which is achieved through an increase in the volume of the π system of the quinoid fragment by means of annelation of additional arene rings at the 7–8 bond of the 2H-chromene part of the molecule. Data regarding the synthesis and data from photochemical and x-ray diffraction studies of the indicated compounds, as well as the results of a study of their thermochromic properties by ^{1}H dynamic nuclear magnetic resonance (DNMR), are set forth below.

1. Synthesis of Spiropyrans I and II

Spiropyrans of the 2-oxaindan series benzoannelated (Ia-c) and 2,3-naphthoannelated (II) at the 7–8 bond of the chromene fragment were obtained in 68-82% yields in accordance with the general method [6] by condensation in glacial acetic acid of 1,3,3-trimethyl-3H-isobenzofurylium perchlorate (III) with 1-hydroxy-2-naphthaldehydes IVa-c and 1-hydroxy-2-antraldehyde (IVd), respectively, with subsequent deprotonation of the resulting o-hydroxystyryl derivatives Va-d with dry ammonia in benzene.

The constants and the results of elementary analysis of spiropyrans Ia-c and II are presented in Table 1. Absorption bands of stretching vibrations at 1640-1655 cm^{-1}, which are characteristic for the C=C bond of chromenes, bands at 1615 cm^{-1}, which correspond to an aromatic system with a conjugated unsaturated group, and bands at 930-990 cm^{-1} (C_{spiro}–O) are present in their IR spectra. The PMR spectra contain two three-proton singlet signals of diastereotopic methyl groups of an oxaindan ring at 1.40-1.47 and 1.60-1.65 ppm and a quartet of an AB system of protons attached to the $C_{(3)}$–$C_{(4)}$ double bond with a spin-spin coupling constant (SSCC) of 10 Hz at 5.55-5.80 and 6.75-6.85 ppm. The spirocyclic structure of Ia-c

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TABLE 1. Spiro(2H-naphtho[1,2-b]pyran-2,1'-[2]oxaindans) (I) and Spiro(2H-anthra[1,2-b]pyran-2,1'-[2]oxaindan) (II)

Compound	mp, °C	Found, %		Empirical formula*	Calculated, %	
		C	H		C	H
Ia	99–100 [6]	84,1	5,8	$C_{22}H_{18}O_2$	84,1	5,7
Ib	141–143	67,1	4,4	$C_{22}H_{17}BrO_2$	67,2	4,3
Ic	152–153	73,7	4,8	$C_{22}H_{17}NO_4$	73,5	4,7
II	175–176	85,6	5,4	$C_{26}H_{20}O_2$	85,7	5,5

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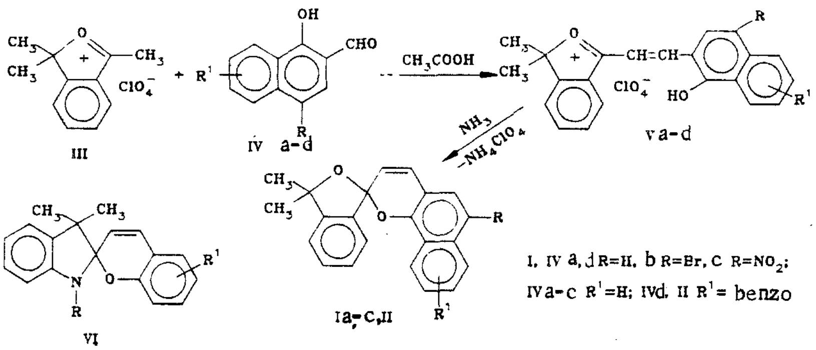
*The empirical formulas of Ib and Ic were also confirmed by determination of the percentages of bromine and nitrogen, respectively.

and II that follows from the spectral data presented was confirmed by direct x-ray diffraction studies.



I, IV a, d R=H, b R=Br, c R=NO_2;
IV a-c R^1=H; IVd, II R^1= benzo

2. Molecular Structures of Spiropyrans I and II

At present a sufficiently large amount of data on the crystal and molecular structures of compounds of the spiropyran series has already been accumulated [7-9]. However, data for compounds with benzannelated chromene fragments have not been previously obtained. The molecular structures of the synthesized spiropyrans Ia-c and II are presented in Figs. 1-4. The x-ray diffraction study showed that the naphtho(anthraceno)pyran and oxaindan parts of the molecules in all of the compounds are situated approximately orthogonal to one another. The dihedral angle between the $O_{(1)}C_{(2)}C_{(3)}$ and $O_{(2)}C_{(2)}O_{(16)}$ planes is 93-95°. The pyran and oxaindan fragments in all of the investigated compounds are nonplanar. The former has a puckered conformation with bending angles along the $O_{(1)}\ldots C_{(3)}$ and $O_{(1)}\ldots C_{(4)}$ lines of 21.4-28.6° and 10.2-13.3°, respectively, and the latter has an envelope conformation with a bending angle along the $C_{(2)}\ldots C_{(13)}$ line of 15.5-17.3°. As demonstrated for indoline spiropyrans VI [8, 9] the puckered conformation of the naphtho(anthraceno)pyran fragment is labile; it is determined by intramolecular steric conditions and the effects of packing of the molecules in the crystal and may change in solution.

Just as in previously investigated indoline spiropyrans VI [8, 9], the $C_{spiro}-O_{(1)}$ bond in I and II is elongated. However, whereas the length of this bond is 1.478(7)-1.496(4) Å in spiropyran VI, the length of the $C_{spiro}-O_{(1)}$ bond in Ia-c and II is 1.444(1)-1.465(2) Å; in unsubstituted Ia this bond [1.444(1) Å] is least elongated as compared with the lengths of normal C–O bonds (1.41-1.43 Å) in six-membered heterocycles [10]. Annelation of an additional benzene ring in spiropyran II has virtually no effect on the length of the $C_{(2)}-O_{(1)}$ bond [1.447(1) Å]. However, the introduction of electron-acceptor substituents – Br in Ib and particularly an NO_2 group in Ic – into the 6 position of the naphthopyran fragment leads to lengthening of this bond to 1.455(3) Å and 1.465(2) Å, respectively. In the oxaindan fragment of spiropyrans I and II the $C_{(2)}-O_{(2)}$ bond was found to be shortened to 1.417(1)-1.407(3) Å as compared with the normal values of the length of the C–O bond (1.462 Å) in five-membered heterocycles [11]. As the $C_{(2)}-O_{(1)}$ bond becomes longer, the $C_{(2)}-O_{(2)}$ bond displays a tendency to become shorter: 1.417(1), 1.417(1), 1.413(3), and 1.407(3) Å in Ia, II, Ib, and Ic,

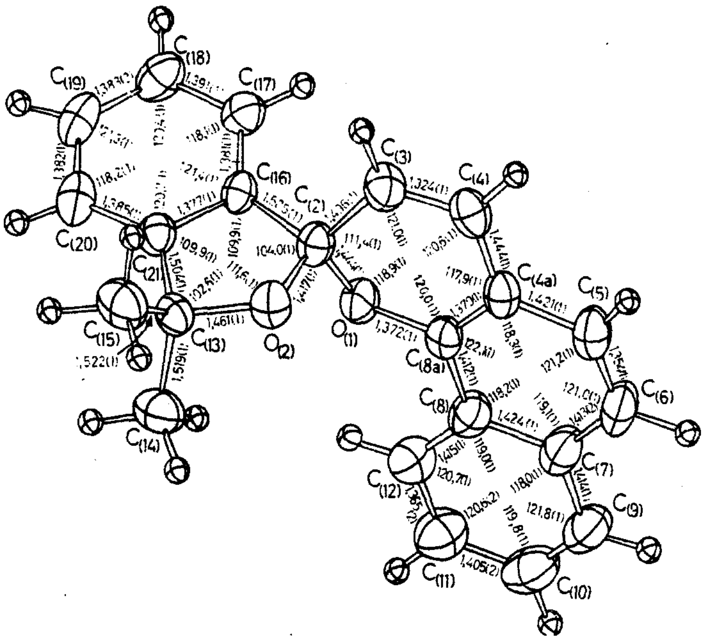


Fig. 1. Molecular structure of 3',3'-dimethylspiro(2H-naphtho[1,2-b]pyran-2,1'-[2]oxaindan) (Ia).

respectively. The $O_{(2)}-C_{(13)}$ bond in all of the investigated spiropyrans I and II remains anomalously elongated – 1.457(4)-1.461(2) Å.

Lengthening of the $C_{spiro}-O$ bond in indoline spiropyrans VI was explained within the framework of specific n–σ* orbital interactions of the unshared electron pair (UEP) of the essentially pyramidal nitrogen atom with the antibonding σ* orbital of the polar C–O bond at the spiro node (the anomeric effect), which give rise to shortening of the $C_{spiro}-N$ bond and lengthening of the $C_{spiro}-O$ bond [8, 9]. In I and II two identical oxygen heteroatoms are found at the spiro node. In [12] it was shown that the same n–σ* interaction is also realized when two oxygen atoms are bonded to an anomeric carbon atom. In such systems the effectiveness of the n–σ* interaction will depend primarily on the mutual geometrical orientation of the orbital of the UEP of the oxygen atoms and the electron state of these atoms. In particular, the preferableness of the α configuration as compared with the β configuration in pyranose sugars is due to the gain in energy of this interaction in the α conformation. The experimentally observed difference in the lengths of the C–O bonds in β-pyranoses is also explained by orbital n–σ* interactions [12]. It has been shown for the Me–O–C–O–Me fragment in dimethoxymethane that these interactions are most effective for the +sc and +ap conformations [θ = 60°, φ = 180°, where θ and φ are the $C_{(13)}O_{(2)}-C_{(2)}O_{(1)}$ and $O_{(2)}C_{(2)}-O_{(1)}C_{(8a)}$ dihedral angles, respectively].

The $C_{(13)}-O_{(2)}-C_{(2)}-O_{(1)}-C_{(8a)}$ fragment in Ia-c and II has the same conformation with close values of angles θ (96-101°) and (95-106°). However, the electron states of the $O_{(1)}$ and $O_{(2)}$ atoms differ substantially. The $O_{(1)}$ atom is bonded with the aromatic π system of the naphthalene or anthracene fragment, and the lengths of the $O_{(1)}-C$ bonds [1.354(2)-1.377(1) Å] are close to the values of the analogous lengths of the bonds in α-naphthol (1.37 Å) [13] and constitute evidence for significant conjugation of the UEP of the $O_{(1)}$ atom with the adjacent π system. This conjugation will decrease the activity of the UEP of the $O_{(1)}$ atom as compared with the $O_{(2)}$ atom, and the $n_{O(2)}-\sigma^*(C_{(2)}-O_{(1)})$ interactions in the investigated spiropyrans should therefore be stronger than the $n_{O(1)}-\sigma^*(C_{(2)}-O_{(2)})$ interactions and may cause the lengthening of the $C_{(2)}-O_{(1)}$ bonds and shortening of the $C_{(2)}-O_{(2)}$ bonds observed in I and II. These interactions in Ia-c and II are apparently weaker than in spiropyrans VI with different O and N heteroatoms at the spiro node, with which the smaller degree of lengthening of the $C_{spiro}-O_{(1)}$ bond in spiropyrans Ia-c and II is also associated.

In the previously investigated spiropyrans VIIa,b the UEP of the $O_{(2)}$ atom are conjugated with the π bond of the adjacent carbonyl group, as evidenced by the $O_{(2)}-C_{(13)}$ bond lengths (1.35-1.37 Å); the n–σ* interactions of the $O_{(1)}$ and $O_{(2)}$ atoms in these molecules are therefore insignificant, and the $C_{(2)}-O_{(1)}$ bond lengths (1.42 and 1.399 Å) remain normal [14].

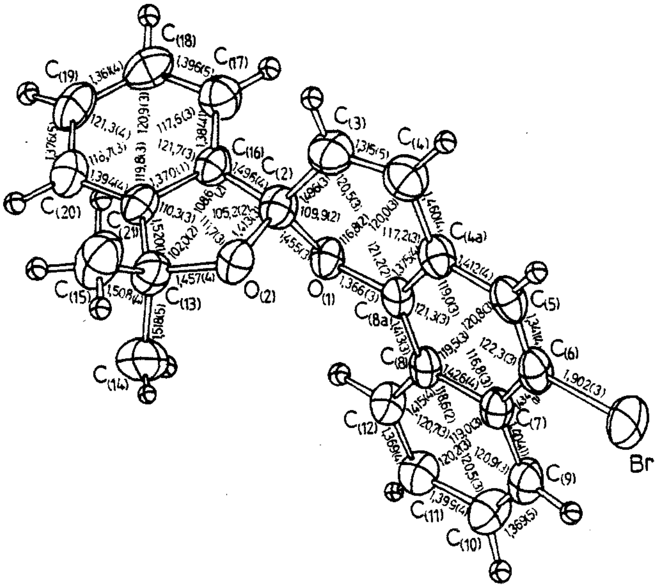
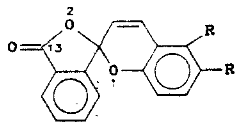
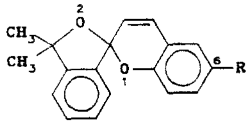


Fig. 2. Molecular structure of 6-bromo-3',3'-dimethylspiro-(2H-naphtho[1,2-b]pyran-2,1'-[2]oxaindan) (Ib).



VIIa,b



VIII, IX

VIIa, IX R=H; VIIb R+R=benzo; VIII R=NO$_2$

The introduction of electron-acceptor Br and NO$_2$ substituents into the 6 position of the naphthalene fragment gives rise to lengthening of the $C_{(2)}$—$O_{(1)}$ bond as compared with Ia and II, and this lengthening increases with intensification of the electron acceptor properties of the substituents: 1.455(3) Å in Ib and 1.465(2) Å in Ic. Shortening of the $O_{(1)}$—$C_{(8)}$ bond to 1.366(3) Å in Ib and to 1.354(2) Å in Ic as compared with the length of this bond in Ia and II [1.372(1) and 1.377(1) Å, respectively] occurs simultaneously. This constitutes evidence for an increase in conjugation of the UEP of the $O_{(1)}$ atom with the π system of the naphthalene fragment when electron-acceptor substituents are introduced, and the simultaneous lengthening of the $C_{(2)}$—$O_{(1)}$ bond in spiropyrans Ib,c is therefore associated with intensification of the $n_{O(2)}$—$\sigma^*(C_{(2)}$—$O_{(1)})$ interaction in these compounds. The tendency for shortening of the $C_{(2)}$—$O_{(2)}$ bond in Ib,c to 1.413(3) and 1.407(3) Å, respectively, as compared with the lengths of this bond in spiropyrans Ia and II [1.417(1) Å] may also be a confirmation of this.

It is interesting that in the analogous benzopyran compound VIII [15] with an NO$_2$ group in the para position relative to the $O_{(1)}$ atom the $C_{(2)}$—$O_{(1)}$ bond (1.452 Å) is lengthened to a smaller extent and the $O_{(1)}$—$C_{(8)}$ bond [1.366 Å (average)] is shortened to a smaller extent than in spiropyran Ic. These data indicate that the electron-acceptor effect of the NO$_2$ group on the O atom in the para position is manifested more strongly in the naphthalene fragment than in the benzene fragment. It is possible that the increase in the electron-acceptor properties of the NO$_2$ group in spiropyran Ic is associated either with the specific electron structure of the naphthalene fragment or with participation of the $O_{(3)}$ atom in hydrogen bonding with the 7-H atom in the peri position [at $C_{(9)}$ in Fig. 3]. The short $O_{(3)}$...7-H distance [2.09(3) Å] and the slight deviation (11.7°) of the NO$_2$ group from the plane of the naphthalene fragment may constitute evidence in favor of the latter. In the absence of hydrogen bonding between these atoms steric repulsion between them should have led to greater rotation of this group along the $C_{(6)}$...N bond. It is known [16] that the barrier to such rotation is low.

The $O_{(2)}$—$C_{(13)}$ bond in all of the investigated spiropyrans I and II is the same [1.457(4) 1.461(2) Å] and is elongated anomalously. From our point of view, the lengthening of this

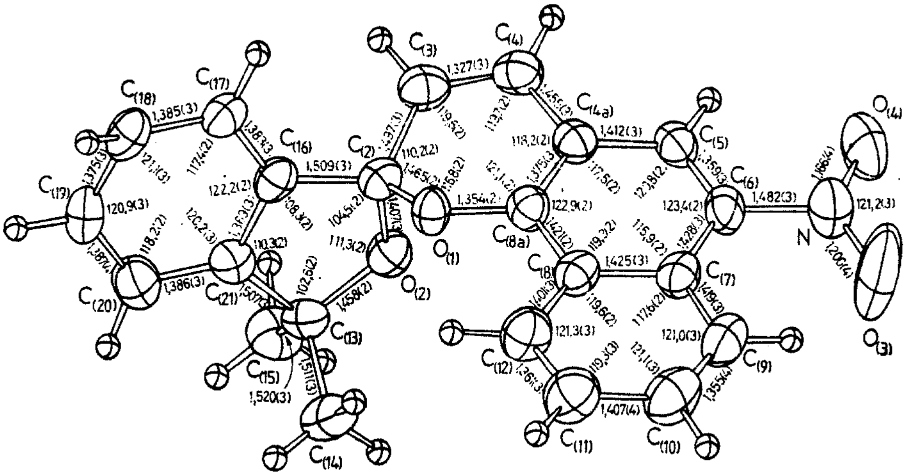


Fig. 3. Molecular structure of 3',3'-dimethyl-6-nitrospiro-(2H-naphtho[1,2-b]pyran-2,1'-[2]oxaindan) (Ic).

bond may be a consequence of shortening of the adjacent $O_{(2)}-C_{(2)}$ bond and was observed experimentally in a study of glycoside sugars and was confirmed theoretically in the case of dimeth oxymethane [12]. Conformational calculations of spiropyran IX were made to confirm the electronic rather than steric nature of the lengthening of the $C_{(2)}-O_{(1)}$ and $O_{(2)}-C_{(13)}$ bonds and the shortening of the $O_{(2)}-C_{(2)}$ bond. The geometry of Ia obtained by x-ray diffraction study was used as its starting geometry, and minimization of the conformational energy of the molecule was carried out with allowance for the energy of deformation of the bond angles, stretching of the bonds, deviations of the atoms from the plane of the conjugated bonds, torsion rotations about the bonds, and nonvalence interatomic interactions. After minimization, the strain energy of the model molecule of spiropyran IX was 31.4 kJ/mole and the length of the $O_{(1)}-C_{(2)}$ bond in it (1.422 Å) was not increased, while the lengths of the $O_{(2)}-C_{(2)}$ (1.434 Å) and $O_{(2)}-C_{(13)}$ (1.439 Å) bonds were identical and were also close to the normal values.

Thus the x-ray diffraction investigation of Ia-c and II showed that in these compounds, just as in indoline spiropyrans VI, the $C_{spiro}-O_{(1)}$ bond is elongated in the ground state as a result of specific orbital interactions at the spiro node. Since the length of this bond in the initial step of transformation of spiropyrans extremely accurately describes the total reaction coordinate [17], their thermo- and photochromic properties may depend to a considerable extent on the length of the $C_{spiro}-O_{(1)}$ bond in the starting ground state.

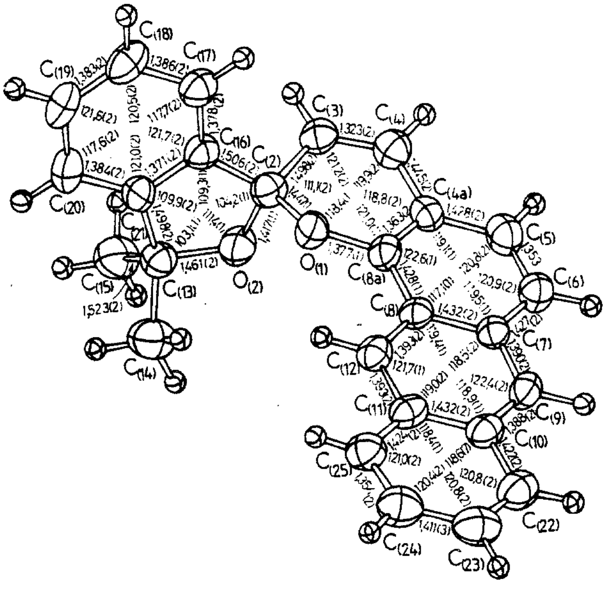


Fig. 4. Molecular structure of 3',3'-dimethyl-spiro(2H-anthra-[1,2-b]pyran-2,1'-[2]oxaindan) (II).

TABLE 2. Diastereotopic Splittings ($\Delta\nu$) and Coalescence Temperatures (T_c) of the Signals of the gem-Dimethyl Groups, Kinetic and Activation Parameters of the Thermal Opening of the Spiro Ring in Hexachlorobutadiene Determined by Dynamic NMR (DNMR) Spectroscopy, and $C_{spiro}-O_{(1)}$ Bond Lengths (ℓ_{C-O}) for Some Spiropyrans

Compound	$\Delta\nu$, Hz	T_c, °K	k_{298}, sec^{-1}	$\Delta G^{\neq}_{298}$, kJ/mole	l_{C-O}, Å
Ia	17,6	398	$9{,}66 \cdot 10^{-3}$	84,6	1,444(1)
	16,4**	393	$1{,}36 \cdot 10^{-3}$	89,2	
Ib	14,25	405	$1{,}9 \cdot 10^{-4}$	94,3	1,455(3)
Ic	13,5	398	$1{,}39 \cdot 10^{-3}$	89,2	1,465(2)
II	18,75	384	$5{,}5 \cdot 10^{-3}$	85,9	1,447(1)
X	14,0	413	$2{,}16 \cdot 10^{-2}$	82,5	—
	15,0**	403	$3{,}12 \cdot 10^{-2}$	81,7	
XI	17,25***	363	$1{,}05 \cdot 10^{-1}$	78,8	—
	10,25	359	$2{,}79 \cdot 10^{-2}$	82,1	
XII	11,75	378	$2{,}0 \cdot 10^{-3}$	84,2	—
XIII	13,6	380	$4{,}4 \cdot 10^{-3}$	85,0	—
	13,6***	400	$1{,}6 \cdot 10^{-4}$	94,7	
XIV	11,5^{4*}	369	$3{,}35 \cdot 10^{-3}$	87,2	—

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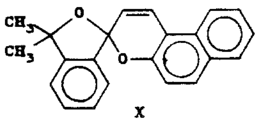
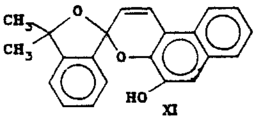

X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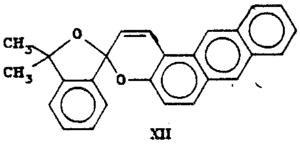
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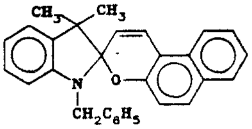
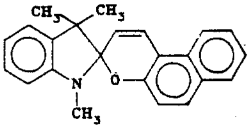

XIV


XIII

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*Spiropyran X was described in [6], spiropyrans XIII and XIV were described in [2], and XI and XII are described in the present paper (see the experimental section).

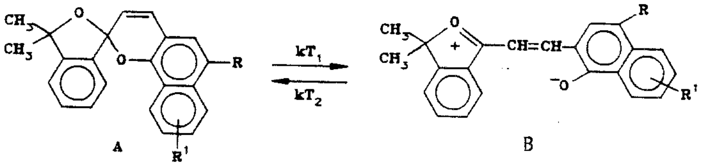
**In nitrobenzene.

***In benzonitrile.

^{4*}In o-dichlorobenzene.

3. Thermal Valence Isomerization of Spiropyrans I and II

Compounds Ia-c and II have pronounced thermochromic properties in solutions of polar and nonpolar solvents and contain, in the oxaindan fragment, indicator gem-dimethyl groups, which make it possible to study the thermally indiced valence isomerization A ⇄ B by dynamic NMR (DNMR) spectroscopy. The method has been previously used to study the thermochromic properties of spiropyrans [18, 19].



Determination of the dependence of the form of the lines of the signals of the indicator groups on the temperature (Fig. 5) makes it possible to calculate the rate constants of the exchange process at various temperatures, which, in turn, makes is possible to calculate the activation parameters from the Eyring equation. The calculated free energies of activation $\Delta G^{\neq}_{298}$ of the thermally induced valence isomerization of spiropyrans I and II as compared with the lengths of the $C_{spiro}-O_{(1)}$ bonds in these compounds, as well as the $\Delta^{\neq}_{298}$ values for a

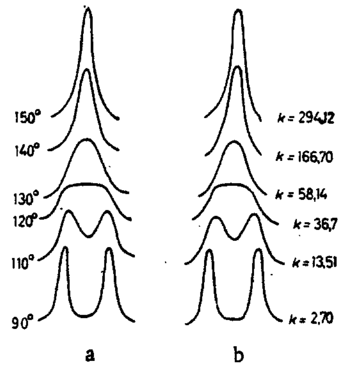


Fig. 5

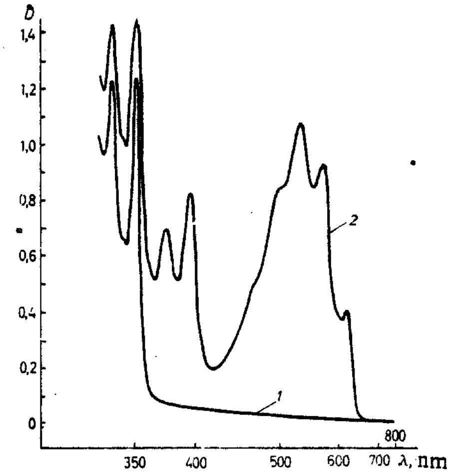


Fig. 6

Fig. 5. Experimental (in hexachlorobutadiene) (a) and theoretically calculated (b) forms of the lines of the signals of the methyl groups of spiropyran Ia at various temperatures.

Fig. 6. Electronic absorption spectrum of spiropyran Ia in isopentane–2-propanol (4:1) (c 10^{-5} mole/liter, –50°C): 1) cyclic form; 2) photocolored form.

number of spiropyrans that we previously investigated [18], are presented in Table 2. An analysis of the data obtained makes it possible to draw the following conclusions.

1. Varying the structure of the heterene and pyran fragments of the spiropyran molecules does not have a substantial effect on the free energy of activation, which ranges from 78.8 to 94.7 kJ/mole for a large number of compounds.

2. No correlation exists between the length of the C_{spiro}–$O_{(1)}$ bond in spiropyrans I and II and the free energy of activation; moreover, higher activation barriers of the thermochromic transformations are characteristic for Ib,c with the most elongated C_{spiro}–$O_{(1)}$ bonds.

The absence of the indicated correlation, which was also predicted on the basis of quantum-chemical calculations in [7, 20], is evidently associated with the fact that the length of the C_{spiro}–$O_{(1)}$ bond in the transition ground state (the region of thermochromic cleavage), as demonstrated by the MINDO/3 method for various compounds of this series [17], is virtually constant (~1.95 Å) and differs substantially from the length of this bond in the starting state. The small changes in the length of the indicated bond that arise under the influence of structural factors therefore do not have a substantial effect on the energy of activation of cleavage of the C–O bond.

4. Photochromism of Spiropyrans I and II

The photochromic properties of spiropyrans Ia-c and II in liquid and solid solutions are manifested over a broad range of temperatures from 77°K to 273°K. The use of the techniqu of pulse photolysis makes it possible to observe reversible photocoloration also at 20°C. The electronic spectra of the starting and photoinduced forms of Ia are presented in Fig. 6. The corresponding spectra of spiropyrans Ib,c and II differ only slightly. The λ_{max} values of the photoinduced forms are presented in Table 3.

To evaluate the relative photochemical activities of Ia-c and II we studied the ease of photocoloration ("colorability") of these compounds. This parameter was proposed in [21] for comparison of the capacities of various spiropyrans for photocoloration. The "colorability" is evaluated from the initial absorption A_0 of solutions of photochromic spiropyrans under strictly identical irradiation conditions: temperature, concentration of the compound, length and volume of the cuvette, and irradiation intensity. Indoline spiropyran VIa (R = CH_3, R^1 = 6-NO_2) is most often used as the standard compound with the assumption that A_0 = 1 for it [21] The results of the investigation of the "colorability" of Ia-c and II are presented in Table 3 It follows from them that this parameter and the length of the C_{spiro}–$O_{(1)}$ bond vary symbatically; Ic, with the most elongated bond, displays the greatest photochemical activity. Thus

TABLE 3. "Colorability" Parameters of Spiropyrans I and II in Toluene

Compound	"Colorability"*	λ_{max} of form B, nm**	Compound	"Colorability"*	λ_{max} of form B, nm**
Ia	0,22	530, 650	Ic	0,46	560, 675
Ib	0,36	530, 660	II	0,32	520, 640

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*Relative to spiropyran VIa.

**The positions of the absorption maximum and the long-wave edge, where ε = 0.05, are indicated.

TABLE 4. Effective Rate Constants for the Decolorization of the Photoinduced Forms of Spiropyrans of the 2-Oxaindan Series

Compound	k*, sec^{-1}	Compound	k*, sec^{-1}	Compound	k*, sec^{-1}
Ia I	0,04	II	0,015	IX	30
Ib I	0,03	VIII	0,45	6-Br-IX	27
Ic I	0,009				

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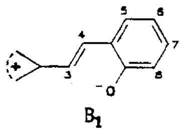
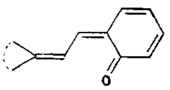
*At 20°C in toluene (Ia-c, II) or benzene (VIII, IX) [22] at a concentration of $5 \cdot 10^{-4}$ mole/liter.

the data obtained constitute evidence that the photochemical activities of spiropyrans I and II, in contrast to their thermochromic activities, depend on the length of the $C_{spiro}-O_{(1)}$ bond that is cleaved during photoexcitation. This is evidently due to the fact that in the excited states, as demonstrated on the basis of quantum-chemical calculations [17], the length of this bond in the transition structure is substantially smaller than in the transition structure of the ground state. The reaction barriers in the excited states also decrease appreciably as a consequence of this. The magnitudes of these barriers and the photochemical activity of coloration of spiropyrans therefore prove to be sensitive to small changes in the length of the $C_{spiro}-O_{(1)}$ bond in the ground state that develop under the influence of various structural factors in the molecule.

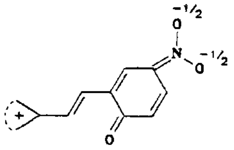
We investigated the kinetics of decolorization of the colored forms of spiropyrans I and II (Table 4) and discovered a complex dependence of their lifetimes on their structures. Unfortunately, we were unable to isolate photoisomers of I and II in a form acceptable for x-ray diffraction studies. Their structures can therefore be judged only from indirect data. An x-ray diffraction investigation of the open forms of spiropyran VI [23, 24] showed that they have zwitter-ionic structure B_1 with an appreciable contribution of canonical structure B_2.



B_1



B_2



B_3

However, I and II, as well as nonannelated spiropyrans of the 2-oxaindan series [22], regardless of the nature of the substituent, display, in contrast to spiropyran VI, bathochromic shifts of the photoinduced absorption bands with an increase in the polarity of the medium. These data constitute evidence for a definite contribution of a quinoid structure to the structure of the colored form. It has been assumed [23, 24] that annelation to the phenoxide fragment of additional benzene rings in the 5–6 and 7–8 positions should stabilize quinoid structure B_2, whereas annelation in the 6–7 positions should destabilize this structure. The increase in the lifetimes of the photoinduced forms of the spiropyrans in the order IX < Ia < II

TABLE 5. Crystallographic Characteristics of the Spiropyrans

Compound	a, Å	b, Å	c, Å	γ°	Space group	z	d_{calc}, g/cm³	M	V, Å³
Ia	8,582(4)	8,846(2)	22,379(5)	83,23(3)	$P2_1/n$	4	1,243(3)	314,38	1687(3)
Ib	12,522(2)	8,963(4)	8,605(2)	109,04(3)*	$P\bar{1}$	2	1,458(3)	393,28	901(3)
Ic	13,627(4)	11,037(4)	12,612(5)	73,03(3)	$P2_1/b$	4	1,323(4)	359,38	1814(3)
II	9,044(3)	8,758(2)	24,570(6)	82,23(3)	$P2_1/n$	4	1,323(4)	364,44	1928(3)

*α = 81.13(3)°, β= 95.57(3)°.

(Table 4) confirms this point of view and provides evidence for the substantial role of this mode of stabilization of the open form of spiropyrans of the 2-oxaindan series.

It is apparent from Table 4 that the introduction of electron-acceptor substituents into the naphthopyran fragment of spiropyrans also increases the lifetimes of the open forms; the nitro group, which is characterized by pronounced electron-acceptor properties, has the greatest stabilizing effect. Just as in the case of spiropyran VI, stabilization of the colored products of spiropyrans of the 2-oxaindan series with strong electron-acceptor substituents (Ic, VIII) is evidently associated with an increase in the contribution of resonance form B_3 to their structures. An additional factor responsible for stabilization of the colored forms of I and II may also be the formation of various intermolecular associates, as in the case of the open merocyanine forms of spiropyran VI [24]; the more extended the conjugated π system of I and II, the more stable the associates may be due to π—π interaction. The tendency for the formation of such associates is manifested even in the crystal structures of closed spiropyrans I and II with an orthogonal orientation of the oxaindan fragments. In particular, the formation of such associates may hinder trans-cis isomerization of quinoid form B_2 about the $C_{(3)}$—$C_{(4)}$ single bond, which is the first step of the dark decolorization of the colored forms of spiropyrans [25].

EXPERIMENTAL

The dynamic NMR (DNMR) spectra of 10-15% solutions of spiropyrans I, II, XI, and XII in hexachlorobutadiene were recorded with a Tesla BS-487 spectrometer (80 MHz). The conditions used to record the spectra and the methods used to calculate the rate constants and activation parameters of the thermally induced valence isomerization of the spiropyrans were presented in [18].

The absorption spectra of solutions of spiropyrans I and II and their photoinduced forms were recorded with a Specord UV-vis spectrophotometer with a low-temperature thermostatted cuvette chamber. A DRSh-250 mercury lamp with a light filter that isolates light with λ_{max} 313 and 365 nm was used as the exciting source. The kinetics of the decolorization of the photoinduced forms of spiropyrans I and II were investigated with a standard pulse-photolysis apparatus [27] with a time resolution of 10^{-5} sec. The relative capacities — "colorabilities" — of I and II for photocoloration were evaluated with the same apparatus under the following standard conditions: the solvent was toluene, the spiropyran concentration was $8 \cdot 10^{-7}$ mole/liter, the temperature was 18°C, the cuvette length was 21 cm, and the excitation energy was 470 J.

The experimental set of reflections (with $I \geq 2\sigma I$) from crystals of Ia-c and II of the type hk0—hk16 (2834), hk0—hk9 (2909), hk0—hk16 (1884), hk0—hk25 (2202) with $5.4° \leq \theta \leq 73.9°$, $2.4° \leq \theta \leq 26.1°$, $3.7° \leq \theta \leq 70.4°$, and $2.4° \leq \theta \leq 26.1°$, respectively, was obtained with a DAR-UM diffractometer in CuK_α and MoK_α (Ic, II) emissions. The structures were resolved by the direct method and the heavy-atom method with the complex of Rentgen-75 programs [28] and were refined successively by the block-diagonal and total-matrix method of least squares (MLS) in the anisotropic (nonhydrogen atoms) approximation. Only the positional parameters were refined for the hydrogen atoms, and isotropic heat parameters $B_{iso} = B_{tot} + 1$ were assigned to them. The final R values were 0.049, 0.066, 0.052, and 0.043 for Ia-c and II, respectively. The principal bond lengths and bond angles are presented in Figs. 1-4. The coordinates of the atoms can be obtained from the authors.

The principal crystallographic data for spiropyrans Ia-c and II are presented in Table 5.

3',3'-Dimethylspiro(2H-naphtho[1,2-b]pyran-2,1'-[2]oxaindans) I and II (Table 1 [6]). A 0.01-mole sample of the polycyclic o-hydroxy aldehyde (IVa-d) was added to a solution of

0.01 mole of 1,3,3-trimethyl-3H-isobenzofurylium perchlorate (III) in 10 ml of glacial acetic acid, and the mixture was heated at 100°C until the hydroxystyryl derivative (Va-d) began to crystallize. The intensely colored crystalline precipitate was removed by filtration and washed with glacial acetic acid and ether. The perchlorate (Va-d) was suspended in 20 ml of benzene, and a stream of dry ammonia was passed into the suspension until the precipitate became colorless and dissolved. The resulting solution of the spiropyran (Ia-c, II) was separated from the precipitated ammonium perchlorate by filtration and chromatographed with a column packed with aluminum oxide (elution with benzene) with collection of the fraction with R_f 0.9. The benzene was removed by distillation at reduced pressure. The spiropyrans obtaine were recrystallized from heptane (Ia-c) or ethanol (II).

3',3'-Dimethylspiro(3H-anthra[2,1-b]pyran-3,1'-[2]oxaindan) (XII). This compound was synthesized from perchlorate III and 2-hydroxy-1-anthraldehyde by a procedure similar to that used to obtain I and II. The product was obtained in 58% yield and had mp 173-174°C (from octane). PMR spectrum (deuterochloroform): 1.45 and 1.6 [3H each, s, 3',3'-$(CH_3)_2$], 5.75 (1H, d, J = 10 Hz, 3-H), and 6.9-8.4 ppm (13H, m, Ar-H and 4-H). Found, %: C 85.6, H 5.5. $C_{26}H_{20}O_2$. Calculated, %: C 85.7, H 5.5.

5-Hydroxy-3',3'-dimethylspiro(3H-naphtho[2,1-b]pyran-3,1'-[2]oxaindan) (XI). This compound was synthesized from perchlorate III and 2,3-dihydroxy-1-naphthaldehyde by a procedure similar to that used to obtain I and II. The product was obtained in 74% yield and had mp 132-133°C (from heptane). PMR spectrum (deuterochloroform): 1.44 and 1.57 [3H each, s, 3',3' $CH_3)_2$], 5.41 (1H, s, OH), 5.85 (1H, d, J = 10 Hz, 3-H), and 7.1-7.9 ppm (10H, m, Ar-H, and 4-H), Found, %: C 79.8, H 5.4. $C_{22}H_{18}O_3$. Calculated, %: C 80.0, H 5.5.

The starting polycyclic o-hydroxy aldehydes, viz., 1-hydroxy-2-naphthaldehyde (IVa), 1-hydroxy-2-anthraldehyde (IVd), 2-hydroxy-1-anthraldehyde, and 2,3-dihydroxy-1-naphthaldehyde in the synthesis of Ia, II, XI, and XII, respectively, were obtained by indirect formylation of the corresponding phenols by the method in [26]. 4-Bromo-2-hydroxy-1-naphthaldehyde (IVb) was obtained by bromination of aldehyde IVa with bromine in acetic acid, while 4-nitro-2-hydroxy-1-naphthaldehyde (IVc) was obtained by nitration of aldehyde IVa with concentrated nitri acid (d = 1.42).

LITERATURE CITED

1. A. V. Metelitsa, O. T. Lyashik, N. V. Volbushko, M. I. Knyazhanskii, E. A. Medyantseva, and V. I. Minkin, Zh. Org. Khim. (in press).
2. R. C. Bertelson, in: Photochromism, G. H. Brown (ed.), Wiley-Interscience, New York (1971), Chap. 3, p. 45.
3. G. D. Platonova, I. A. Belaits, and V. A. Barachevskii, Zh. Fiz. Khim., 54, 799 (1980).
4. D. Gaude, M. Le Baccon, R. Guglielmetti, and R. Gautron, Bull. Soc. Chim. Fr., No. 10, 489 (1979).
5. V. A. Barachevskii, V. M. Kozenkov, and E. D. Kvasnikov, Usp. Nauchn. Fotogr., 19, 108 (1978).
6. N. A. Voloshin, N. E. Shelepin, and V. I. Minkin, USSR Inventor's Certificate No. 518491; Byull. Izobret., No. 23, 75 (1976).
7. B. Ya. Simkin, S. P. Makrov, N. G. Furmanova, K. Sh. Karaev, and V. I. Minkin, Khim. Geterotsikl. Soedin., No. 6, 747 (1984).
8. S. M. Aldoshin and L. O. Atovmyan, Problems in Crystal Chemistry [in Russian], Nauka, Moscow (1984).
9. S. M. Aldoshin and L. O. Atovmyan, Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 2009 (1985).
10. B. P. Biryukov and B. V. Unkovskii, in: Crystal Chemistry. Advances in Science [in Russian], Vol. 9, All-Union Institute of Scientific and Technical Information (1974), p. 110; Vol. 11 (1976), p. 132.
11. Tables of Interatomic Distances and Configurations in Molecules and Ions, Vol. 1, The Chem. Soc., Burlington House, London (1965).
12. G. A. Jeffrey, J. A. Pople, J. S. Binkley, and S. Vishveshwara, J. Am. Chem. Soc., 100, 373 (1978).
13. B. Robinson and A. Hargreaves, Acta Crystallogr., 17, 944 (1964).
14. K. Sh. Karaev, N. G. Furmanova, and N. V. Belov, Kristallografiya, 26, 199 (1981); Dokl. Acad. Nauk SSSR, 262, 609 (1982).
15. K. Sh. Karaev, N. G. Furmanova, and N. V. Belov, Dokl. Akad. Nauk SSSR, 260, 1121 (1981).
16. J. R. Holden and S. Dickinson, J. Phys. Chem., 81, 1505 (1977).
17. B. Ya. Simkin, S. P. Makarov, and V. I. Minkin, Khim. Geterotsikl. Soedin., No. 8, 1028 (1982).

18. V. A. Lokshin, N. A. Voloshin, N. S. Trofimov, N. E. Shelepin, and V. I. Minkin, Izv. Severokavkaz. Nauchn. Tsentr Vyssh. Shkol. Estestv. Nauki, No. 1, 68 (1983).
19. S. Toppet, W. Quintens, and G. Smets, Tetrahedron, 31, 1957 (1975).
20. B. Ya. Simkin, S. P. Makarov, and V. I. Minkin, Khim. Geterotsikl. Soedin. (in press).
21. A. Samat, J. Kister, F. Garnier, J. Metzger, and R. Guglielmetti, Bull. Soc. Chim. Fr., Nos. 11-12, 2627 (1975).
22. V. A. Murin, V. A. Barachevskii, N. A. Voloshin, N. E. Shelepin, and V. I. Minkin, Opt. Spektrosk., 46, 1027 (1979).
23. S. M. Aldoshin and L. O. Atovmyan, Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 2016 (1985).
24. S. M. Aldoshin and L. O. Atovmyan, Mol. Cryst. Liq. Cryst. (in press).
25. O. Chaudé, Cah. Phys. (France), 50, 17 (1954); 51, 6.
26. V. A. Lokshin, N. S. Trofimova, N. E. Shelepin, and V. I. Minkin, USSR Inventor's Certificate No. 941346; Byull. Izobret., No. 25, 108 (1982).
27. I. M. Andreeva, E. A. Bondarenko, N. V. Volbushko, M. I. Knyazhanskii, E. A. Medyantseva, A. V. Metelitsa, V. I. Minkin, and B. Ya. Simkin, Khim. Geterotsikl. Soedin., No. 8, 1035 (1980).
28. V. I. Andrianov, Z. Sh. Safina, and B. L. Tarnopol'skii, Rentgen-75. Automated System of Programs for Decoding Crystals [in Russian], Chernogolovka (1975).

SYNTHESIS OF 2-CARBETHOXYBENZOFURAN DERIVATIVES

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A mixture of 3-formyl and 3-acetoxymethyl derivatives is formed in the oxidation of 2-carbethoxy-3-methyl-7-ethylbenzofuran with selenium dioxide. Reduction with lithium aluminum hydride gives 2,3-dihydroxymethyl derivatives, which are converted to 2,3-diformyl derivatives by successive oxidation. A number of derivatives of 3-methyl-7-ethylbenzofurancarboxylic acid were obtained.

Continuing our investigation of benzofuran derivatives [1-3], we studied the synthesis of previously undescribed 2-carbethoxybenzofuran derivatives. The starting 2-carbethoxy-3-methyl-7-ethylbenzofuran was obtained from o-ethylphenol by the Boheme method [4]. Its oxidation with selenium dioxide in glacial acetic acid led to 2-carbethoxy-3-formyl- and 2-carbethoxy-3-acetoxymethyl-7-ethylbenzofuran (II, III). 2,3-Dihydroxymethyl-7-ethylbenzofuran (IV) was obtained by the action of lithium aluminum hydride on II and III. Compound IV was oxidize by means of Ag_2CO_3 [5] to 2-hydroxymethyl-3-formyl-7-ethylbenzofuran (V), oxidation of which with pyridine chlorochromate led to 2,3-diformyl-7-ethylbenzofuran (VI). The reaction of dialdehyde VI with hydrazine hydrate leads to 6-ethylbenzofuro[2,3-d]pyridazine (VII). Similarly obtained from II was 3,4-dihydro-6-ethyl-4-oxobenzofuro[2,3-d]pyridazine (VIII), the reaction of which with benzyl chloride gives the corresponding N-benzyl derivative IX, while the addition to it of formaldehyde leads to 3,4-dihydro-3-hydroxymethyl-6-ethyl-4-oxabenzofuro[2,3-d]pyridazine (X). The hydrolysis of III gave 2-carbethoxy-3-hydroxymethyl-7-ethylbenzofuran (XI), which was converted to 2-carbethoxy-3-chloromethyl-7-ethylbenzofuran (XII) (see Scheme I below).

In addition, hydrolysis of starting ester I by the usual method [6] gave 3-methyl-7-ethyl benzofuran-2-carboxylic acid (XIII), which was converted to acid chloride XIV. The reaction of XIV with morpholine and phenothiazine leads to derivatives XVa,b. 2-(2-Benzothiazolyl)-7-ethylbenzofuran XVI was obtained in the reaction of acid chloride XIV with o-aminothiophenol, while N-(2-nitrophenyl)-3-methyl-7-ethylbenzofuran-2-carboxamide (XVII) was obtained in the reaction with o-nitroaniline. Reduction of the nitro group of XVII by means of $SnCl_2$ led to N-(2-aminophenyl)-3-methyl-7-ethyl-benzofuran-2-carboxamide (XVIII), cyclization of which under the influence of 4 H HCl gave 2-(2-benzimidazolyl)-7-ethylbenzofuran XIX (see Scheme II)

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