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# Spiropyrans: structural features and photochemical properties

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ABSTRACT. The structure of photochromic systems based on different classes of spiropyrans, which are promising materials for the optical recording of information and control of luminous fluxes is examined. The structural factors which affect the photochemical activity of spiropyrans and the stability of the coloured forms derived from them have been established. It is shown that the photochemical properties of spiropyrans occurs to a considerable extent because even in the ground state the $C_{spiro}-O$ bond being cleaved on photoexcitation is weakened and elongated through specific $n-\sigma^*$ orbital interactions. The effect of the nature, electronic state, and relative orientation of the heteroatoms in the spiro centre on the efficiency of $n-\sigma^*$ interactions is analysed. The formation of different strong intermolecular associates and solvates has been found in the crystalline structure of the coloured forms of spiropyrans, which to a considerable degree determines the stabilisation of the complex resonance structure of these compounds.

The bibliography includes 92 references.

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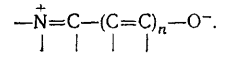
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## I. Introduction

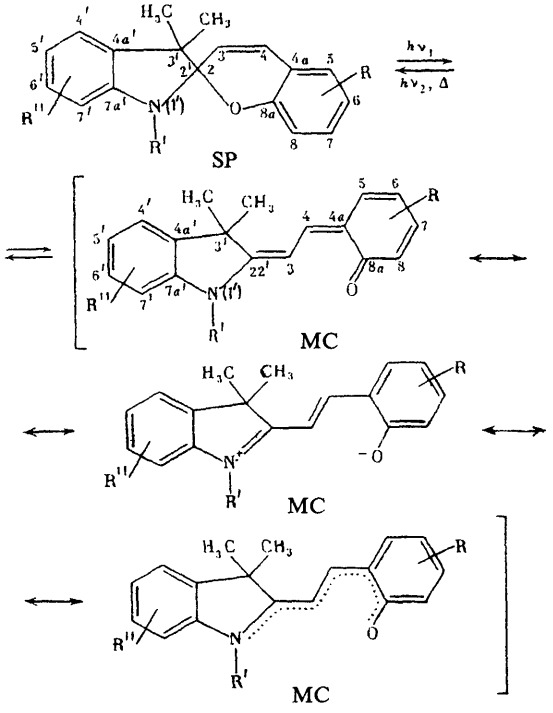
Photochromic materials based on different classes of spiropyrans (SPs) are widely used at the present time for the production of light filters that regulate luminous fluxes, photochromic organic media for recording and processing optical information, and in other areas of science and technology.[1] Among the different classes of photochromic materials, indoline spiropyrans are distinguished by their high sensitivity and resolving power, and they exhibit photochromic properties in solution, in polymer matrices, and even in the solid state, which is very convenient for their practical application.

Photolysis of virtually colourless spiropyrans leads to the formation of dyes, the electronic absorption spectra of which occur in the region of ~400 to 700 nm and have a complex pattern that depends on the structure of the SP, the nature and position of the substituents, the solvents, the temperature, and other factors. Many SPs also have thermochromic properties. Despite intensive research in this field, the mechanism of photochromic SP reactions and the relationship between their structure and photochemical properties are still not fully understood.

It was established[2,3] from spectroscopic and quantum-chemical data that photo- and thermal coloration of indoline SPs is due to a valence isomerisation related to cleavage of the $C_{spiro}-O$ bond and formation of a merocyanine type of coloured structure



The photochemical activity of an SP can depend to a considerable extent on the energy of the $C_{spiro}-O$ bond and its polarity,[4] the charge distribution on the atoms of the pyran ring,[5] and the degree of electronic interaction between the indoline and pyran sections of the molecule.[6–8] The stability of the resulting merocyanine (MC) and its spectroscopic properties are related to the degree of planarity of the chromophoric chain,[9] the presence of intramolecular H-bonds stabilising the structure,[10] and the degree of equivalence of the orders of π-bonds in the chromophore.[11] These factors, which affect the photochemical properties of SPs, primarily depend on the structure of the initial SPs and the resulting MC forms.



Therefore a systematic X-ray study of these compounds is important not only for an understanding of the structural mechanism of the photochromic reactions of SPs but also for establishing the relationship between their structure and photochemical properties.

At the present time the synthesis of SPs of practical importance is related to a varied structural modification of these systems which improves their performance characteristics, such as quantum yield of photolytic conversions, lifetime of the open form, and a high number of conversion cycles without substantial decomposition of the SP. Nevertheless, X-ray diffraction studies on SPs only started in the middle of the 1970's.[12,13]

## II. Structure of indoline spiropyrans

### 1. Effect of structure on photochemical properties

An X-ray diffraction study of the initial 1',3',3'-trimethyl-6-nitro-8-bromospiro(indoline-2,2'-[2*H*-1]benzopyran) [SP(I)] (R' = $CH_3$, $R^6$ = $NO_2$, $R^8$ = Br) and its photochemical conversion product—MC(I)—was first successfully carried out in 1980.[14] Spiropyran SP(I) has thermochromic properties and at room temperature in solution is in equilibrium with its open form. Spiropyran (I) was obtained as yellow crystals by crystallisation from toluene on irradiation with light from an incandescent lamp. The photoproduct MC(I) was isolated from ethanol as dark red crystals. The general shape of the SP(I) molecule is shown in Fig. 1. The nonplanar indoline and benzopyran residues are situated approximately at right angles to each other in the molecule. The indoline residue has a dihedral angle of 27° along the line of N(1')...C(3'), and the benzopyran residue has a dihedral angle of 16.1° along the ling of O(1)...C(3) and 6.6° along the line of O(1)...C(4). The dihedral angle between the O(1)C(22')C(3) plane of the benzopyran ring and N(1')C(22')C(3') plane of the indoline ring at the C(22') spiroatom is 87.2°. The bond lengths and bond angles in the SP(I) molecule are similar to the corresponding values in spiropyrans SP(II) and SP(III) which were studied previously (II: R' = Ph, $R^8$ = $NO_2$;[12] III: R' = Ph, $R^6$ = Cl, $R^8$ = $NO_2$ [13]). In spiropyrans SP(I)–SP(III) the $C_{spiro}$–O bond [1.492(3)–1.496(4) Å] is considerably longer than normal C–O bonds in six-membered oxygen-containing heterocycles [1.41(1)–1.43(1) Å].[15–17]

The general shape of the MC(I) molecule is shown in Fig. 2. In crystals of MC(I) isolated from a solution of non-absolute alcohol, the MC(I) molecules are solvated with water molecules. The change

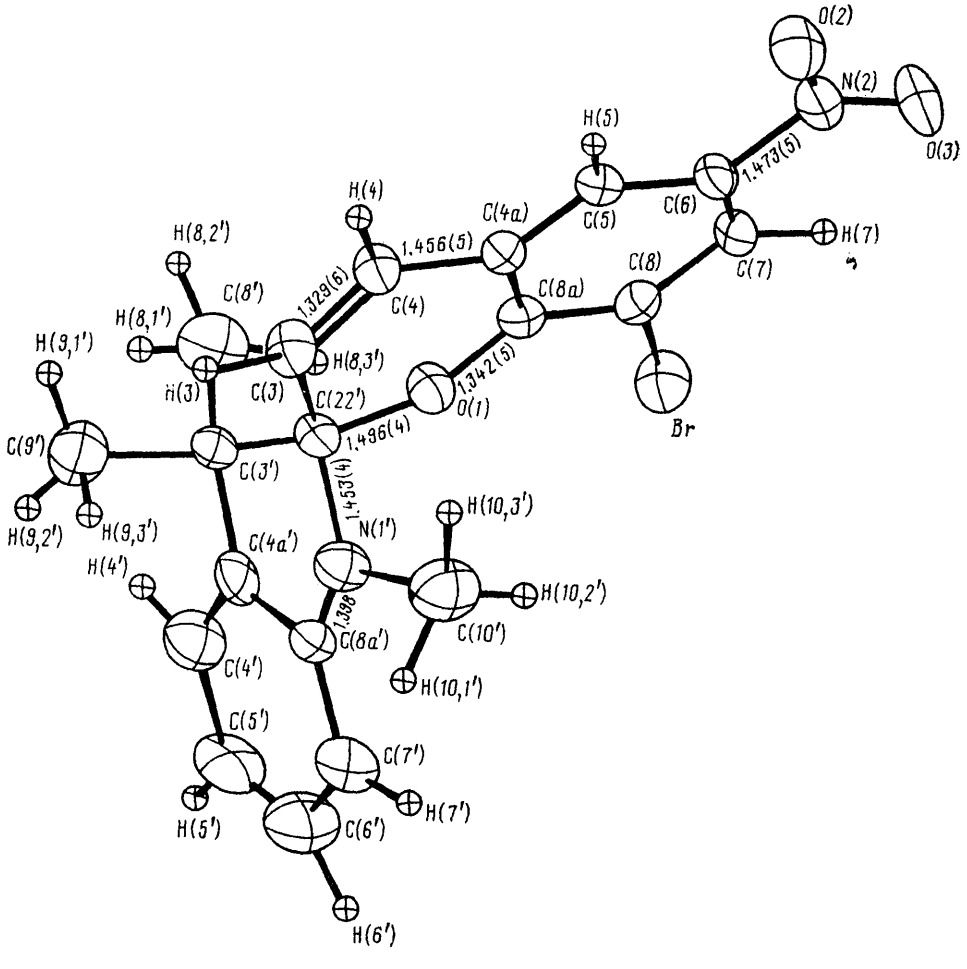



**Figure 1.** General shape of the SP(I) molecule.

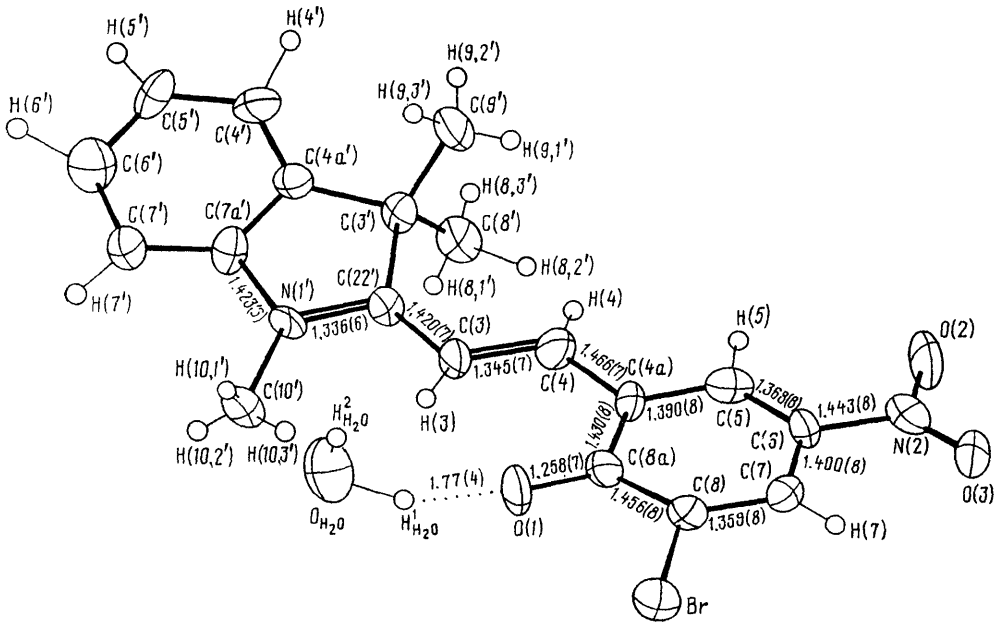



**Figure 2.** General shape of the MC(I) molecule.

to an open form is accompanied by a complete redistribution of bond lengths, typical for the merocyanine chromophore.[11] In this case the length of the single N(1')–C(22') bond, equal to 1.453 Å in SP(I), decreases to 1.336(6) Å in MC(I) and is of approximately the same magnitude as the length of a C=N double bond in five-membered heterocycles (1.29–1.33 Å).[15] The electrocyclic cleavage of the $C_{spiro}$–O(1) bond in SP(I) leads to a marked decrease in the length of the bond between the O(1) atom and the benzene ring in MC(I); the O(1)–C(8*a*) bond contracts to 1.258(7) Å. The length of this bond matches the length of the zwitterion bond in the *DL*-serine molecule, for example [1.26(1) Å].[15] The size of the C(4*a*)C(8*a*)C(8) bond angle in MC(I) [115.4(5)°] is considerably smaller than the usual value of 120°, which is an indication of the increase in σ-electron repulsion from the O(1) atom as a result of the localisation of a substantial negative charge on this atom. This type of distribution of bond lengths suggests that the MC(I) molecule has a bipolar structure [Fig. 3, form (A)]. On going from the closed form to the photoproduct the length of the C(6)–N(2) bond is reduced from 1.473(5) Å in SP(I) to 1.443(8) Å in MC(I) and at the same time the N(2)–O(2) and N(2)–O(3) bonds increase in length while the O(2)N(2)O(3) angle [122.3(6)°] decreases relative to the "equilibrium" value of 126.4° in aromatic nitro compounds[18] (see Figs. 1 and 2). This suggests that there is an increase in *s* character of the atomic orbitals of the N(2) atom participating in the formation of the C(6)–N(2) bond,[19] and is an indication of a strong resonance interaction between the $NO_2$ group and the benzene ring. The simultaneous elongation of the C(4*a*)–C(8*a*) and C(8*a*)–C(8) bonds and contraction of the C(7)–C(8) bond in the benzene ring (see Fig. 2) suggest that there is a significant contribution of the resonance quinoid form (B) to the structure of the *p*-nitrophenolate residue (Fig. 3).

It is also noticeable that the length of the C(5)–C(6) bond is reduced to 1.368(8) Å, which with the simultaneous contraction of the C(22')–C(3) bond [1.420(7) Å] compared to the length in SP(I) [1.483(5) Å] or even to the length of a single $C_{sp^3}$–$C_{sp^3}$ bond (1.46 Å)[20] and some elongation of the C(3)–C(4) bond [1.345(7) Å] compared to the length of this bond in SP(I) [1.329(6) Å] indicate that there is an appreciable contribution of the resonance quinoid form (C) to the structure of MC(I) (Fig. 3). The mixing of structures (B) and (C) leads to delocalisation of electron density between the C(4a)–C(5) and C(5)–C(6) bonds and they decrease in length at the same time, consequently these bonds are shortened to a lesser degree than the C(7)–C(8) bond.

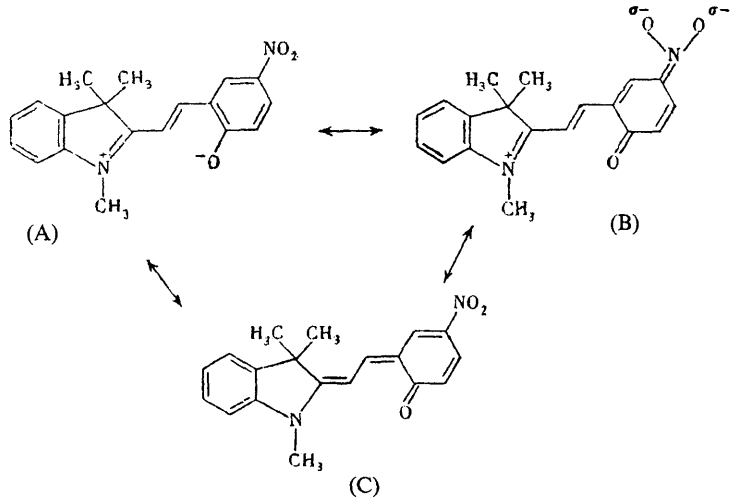



**Figure 3.** Resonance forms that mainly contribute to the structure of MC molecules.

**Table 1.** Main structural parameters of indoline spiropyrans SP(I)–SP(XI).

| Spiropyran | Substituents | | | Bond lengths*1, Å | | | | Angles, deg | | | | | Projection of the N(1′) atom from the plane of C(22′)–C(7a′)–C(R′) | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | R′ | R″ | R | C(22′)–O | C(22′)–N(1′) | O–C(8a) | N(1′)–C(7a′) | α | β*2 | γ*2 | τ | Δ | | |
| (I) | $CH_3$ | — | 6-$NO_2$, 8-Br | 1.496 | 1.453 | 1.342 | 1.398 | 27.0 | 16.1 | 6.6 | 169.5 | 160.2 | 0.26 | [14] |
| (II) | $C_6H_5$ | — | 8-$NO_2$ | 1.492 | 1.432 | 1.356 | 1.413 | 30.7 | −11.7 | −3.3 | 169.6 | 126.4 | 0.13 | [12] |
| (III) | $C_6H_5$ | — | 6-Cl, 8-$NO_2$ | 1.497 | 1.445 | 1.356 | 1.393 | 28.7 | −17.1 | −10.2 | 171.2 | 116.8 | 0.21 | [13] |
| (IVa)*3 | $CH_3$ | — | 6-$NO_2$ | 1.485 | 1.451 | 1.359 | 1.407 | 25.2 | 3.8 | 0 | 166.1 | 141.7 | 0.27 | [23] |
| (IVb)*3 | $CH_3$ | — | 6-$NO_2$ | 1.487 | 1.437 | 1.354 | 1.407 | 23.8 | −15.5 | −5.3 | 164.6 | 123.1 | 0.24 | |
| (V) | $CH_3$ | 5′-$NO_2$ | — | 1.452 | 1.453 | 1.361 | 1.380 | 27.2 | 1.4 | 1.9 | 168.8 | 145.2 | 0.26 | [24] |
| (VI) | $CH_3$ | — | 7-$OCH_3$ | 1.471 | 1.442 | 1.370 | 1.394 | 33.2 | −14.6 | −4.1 | 174.2 | 125.4 | 0.28 | [29] |
| (VII) | $C_6H_5$ | — | 5,6-$C_6H_3NO_2$ | 1.460 | 1.450 | 1.372 | 1.416 | 28.5 | −14.1 | −0.8 | 168.2 | 129.7 | 0.12 | |
| (VIII) | $CH_2C_6H_5$ | — | 6-$NO_2$ | 1.478 | 1.445 | 1.351 | 1.412 | | | | | | 0.34 | [25] |
| (IX)*3 | $CH_3$ | — | 6-$NO_2$, 8-Br | 1.486 | 1.434 | 1.333 | 1.386 | 29.9 | −3.1 | −1.6 | 169.5 | 139.6 | 0.29 | [27] |
| (X) | $CH_3$ | 4′,5′-$C_6H_4$ | 6-$NO_2$ | 1.478 | 1.438 | 1.336 | 1.383 | 33.1 | −3.2 | 0 | 171.5 | 141.8 | 0.30 | [26] |
| (XI) | $CH_3$ | — | 4-Cl, 6-$NO_2$ | 1.479 | 1.438 | 1.343 | 1.402 | 29.7 | 0 | 1.5 | 170.0 | 141.3 | 0.30 | [30] |

Note. For numbering of the atoms, see Fig. 4, for angle notation, see text.

*1 Errors in determining the bond lengths constitute 0.003–0.006 Å.
*2 The positive angles correspond to a deflection towards the R′ substituent on the N(1′) atom, negative angles correspond to a deflection towards the *gem*-methyl groups on the C(3′) atom.
*3 Two independent molecules in the cell with a different structure.

The question concerning the presence of hydrogen bonds between the O(1) and H(3) atoms remains problematic. Even though the distance of O(1)...H(3) [2.28(5) Å] is short and the H(3) hydrogen atom, as follows from quantum-chemical calculations of charges on MC(I) atoms, must be fairly acidic, the small twist about the C(4)–C(4*a*) bond and the increase of the C(3)C(4)C(4*a*) bond angle to 127.4(5)° and C(4*a*)C(8*a*)O(1) bond angle to 125.0(6)° may indicate repulsion between the O(1) and H(3) atoms. A similar repulsion evidently occurs between the H(4) and C(3′) atoms, leading to an increase in the C(3)C(22′)C(3′) bond angle to 129.5° and the C(22′)C(3)C(4) angle to 123.9(5)° and an 11.7° twist about the C(22′)–C(3) bond.

Thus, the open form MC(I) has the zwitterionic, sterically most favourable, *trans*-cisoid structure (A) with some contribution from the resonance forms (B) and (C) (Fig. 3).

The X-ray diffraction studies carried out confirmed that when an SP molecule absorbs a quantum of light the $C_{spiro}$–O bond is cleaved in the pyran section of the molecule. The resulting sterically most favourable *trans*-cisoid isomer of MC is further stabilised in the crystalline state through the formation of hydrogen bonds with a molecule of water of crystallisation. Solvation of the O(1) oxygen atom of the phenolate residue in solution evidently also plays a significant role, which is confirmed, for example, by the increase in proportion of the photoform on going to more polar solvents.[21] Therefore it may be assumed that in solution, as in the crystalline state, that the isomer with the structure of MC(I) is the most stable of the possible isomers. This is supported by a spectroscopic study,[22] in which it is concluded that the *trans*-cisoid form is the most stable in solution.

In the SP molecule the $C_{spiro}$–O bond is elongated and is evidently the weakest. Therefore cleavage of the $C_{spiro}$–O bond in the SP molecule may in many respects be determined by this structural factor. Particular attention will be given subsequently to the following questions: 1) the structural factors that cause the $C_{spiro}$–O bond to increase in length; 2) correlation between the length of this bond, its strength, and the photochemical activity of the SP; 3) a detailed study of the structural factors which stabilise the photolytic form.

## 2. Specific $n-\sigma^*$ orbital interactions in indoline spiropyran molecules

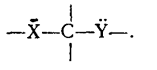
In this section the structural features of indoline SPs will be discussed in detail. The possible nature of the structural changes in the SP structure on photoexcitation and the effect of the structure on the quantum yield of photocoloration of these SPs are analysed, taking into account the orbital nature of the excited photochemically active states (PCAS).

### a) Structural features of SP molecules in the ground electronic state

The main structural parameters of the SPs investigated are given in Table 1. In spiropyrans SP(I)–SP(IV)[12–14,23–30] the indoline and benzopyran residues of the molecules are approximately at right angles to each other but are not planar (Fig. 4). The indoline residue has the conformation of a flattened envelope with an inflection (dihedral angle α) along the line of N(1′)...C(3′) (dihedral angle α is in the range 23–30°, see Table 1). This type of structure for an indoline heterocycle is due to an essentially pyramidal

configuration of the N(1′) nitrogen atom, which reduces the conjugation between the unshared electron pair (UEP) of the N(1′) atom and the π-system of the benzene ring. In fact, the N(1′)–C(7*a*′) bond length in spiropyrans SP(I)–SP(XI), equal to 1.380(5)–1.416(5) Å, is greater than in corresponding systems with a planar trigonal structure of the N atom (1.36–1.37 Å), but matches the length of the N–Ph bond (1.39–1.42 Å) in molecules with a pyramidal structure of the N atom.[31–36] The projection of the N(1′) atom from a plane passing through the C(7*a*′) and C(22′) atoms and the carbon atom of the R′ substituent joined to the N(1′) atom is 0.12–0.34 Å. This is an indication of the substantial $sp^3$ character of the UEP of the N atom situated approximately perpendicular to the plane of these three atoms. The unshared electron pairs of the O atom are not equivalent;[37] they have a π- and σ-character and have different configurations. Thus, the UEP σ-electron density is situated in the plane of the C(22′)OC(8*a*) atoms while the UEP π-electron density occurs perpendicular to this plane. With such a structure of the SP the $C_{spiro}$–O bond of the pyran heterocycle occupies a *trans*-position relative to the UEP of the N(1′) atom and the $C_{spiro}$–N(1′) bond of the indoline heterocycle is *trans* relative to the π-UEP of the O atom. This type of structure can cause specific orbital interactions between the electronegative heteroatoms and the UEP of the N and O atoms bonded to a tetrahedral carbon atom (the anomeric effect).[38,39] This interaction may be described in terms of an $n$–σ* interaction between the UEP ($n$) of the heteroatom and the antibonding σ*-orbital of the adjacent polar bond located mainly on the positive carbon atom of the spiro centre[40] (Fig. 5). Since the electronegativity of the oxygen atom is greater than that of the nitrogen atom, and the UEP energy of the O atom is lower than the UEP energy of the N atom, the antibonding σ*-orbital of the $C_{spiro}$–O bond will be lower in energy than the antibonding orbital of the $C_{spiro}$–N(1′) bond, while the nonbonding orbital of the N(1′) atom will be higher in energy than the nonbonding orbital of the O atom. Consequently interactions between the $n$-electrons of the N(1′) atom and the σ*-orbital of the $C_{spiro}$–O bond are decisive in the spiro centre.[30]

Ideas about hyperconjugation have in recent years been widely used[41] to account for the structural consequences of the anomeric effect in different residues of the type



As a result of population of the antibonding orbital of the $C_{spiro}$–O bond, this type of interaction should lead to a strengthening of the $C_{spiro}$–N(1′) bond and a weakening of the $C_{spiro}$–O bond, which appears respectively as a contraction and elongation of these bonds. In fact, the $C_{spiro}$–N(1′) bond lengths in the SPs studied are in the range 1.432(4)–1.453(4) Å and prove to be considerably shorter than the normal lengths of C($sp^3$)–N($sp^3$) bonds (1.47–1.48 Å) in five-membered heterocycles,[15] while the $C_{spiro}$–O bond lengths are in the range 1.452(4)–1.497(5) Å and prove to be considerably longer than normal C–O bonds (1.41–1.43 Å)[15–17] in six-membered heterocycles.

The effectiveness of this hyperconjugation must depend to a considerable extent on the geometric configuration of the UEP of the N(1′) and O atoms and the $C_{spiro}$–O and $C_{spiro}$–N(1′) bonds on the one hand and the electronic state of the N and O atoms on the other hand. In all of the SPs studied the spiro centre has a sterically strained structure. Because of the rigidity of the tetrahedral structure of the spiro centre and the same conformation of the indoline ring, the $C_{spiro}$–O bond makes an angle (τ) of 165–171° with the UEP of the N(1′) atom (see Table 1).

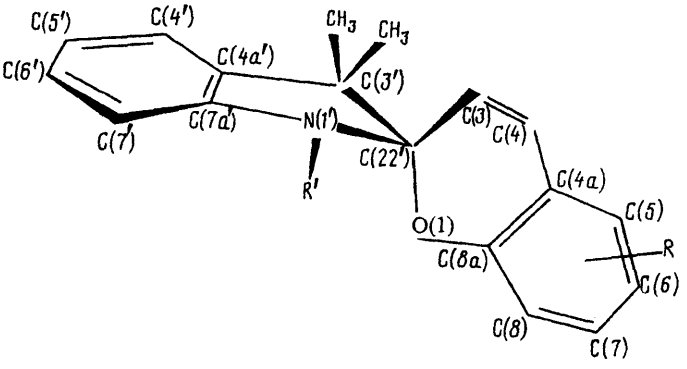



**Figure 4.** Schematic structure of SP molecules and the numbering of their atoms.

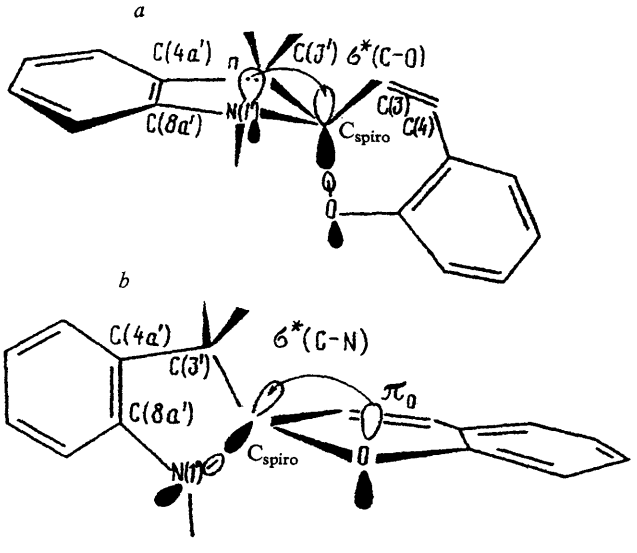



**Figure 5.** $n$[N(1)]–σ*($C_{spiro}$–O) (*a*) and $n$(O)–σ*[$C_{spiro}$–N(1′)] (*b*) orbital interactions in SP molecules.

The conformation of the benzopyran residue is more flexible in these molecules. The pyran ring in an SP is nonplanar and is considerably folded along the line of O...C(3) (angle β) by 0–17° and less significantly along the line of O...C(4) (angle γ) by 0–10°. The conformation of the six-membered heterocycle in an SP is evidently determined by steric factors in the molecule and by packing effects of the molecules in the crystal rather than by the electronic effect of substituents. Confirmation of this is provided by the structure of SP(IV), in which in one of the independent molecules [SP(IV*a*)] the benzopyran ring is virtually planar while in the other [SP(IV*b*)] there are inflections with angles of 15.5° and 5.3°

respectively along the lines of O...C(3) and O...C(4). In spiropyrans SP(I), SP(IV*a*), and SP(V) the benzopyran residue is bent towards the R′ substituent while in spiropyrans SP(II), Sp(III), SP(IV*b*), SP(VI)–SP(X) it is bent towards the geminal methyl groups on the C(3′) atom.

The structural features described lead to a variable orientation of the π-electron density of the UEP of the O atom and the $C_{spiro}-N(1')$ bond (angle Δ, see Table 1). Thus in SP(II), SP(III), SP(IV*b*), SP(VI), and SP(VII) the angle between them is only 116–130°, in SP(IV*a*), SP(IX)–SP(XI) it is about 140°, and in SP(V) and SP(I) it is 145.2 and 160.2°. Thus, the $\pi(O)-\sigma^*[C_{spiro}-N(1')]$ interaction, which has an opposite effect to the $n[N(1')]-\sigma^*(C_{spiro}-O)$ interaction, will strengthen with an increase in the angle Δ.

The electronic state of the N and O atoms depends on the nature and position of the substituents in the indoline and benzopyran residues. Introduction of an electron-acceptor (EA) molecule into the benzopyran residue at the *para*- and *ortho*-positions relative to the O atom should lead to an increase in conjugation of π-electron density of the UEP of the O atom with the benzene ring through further transfer of electron density from the O atom to the π-system of the phenyl group and the EA substituent. In fact, in spiropyrans SP(I) to SP(IV) and SP(VIII)–SP(XI) with EA substituents at these positions the O–C(Ph) bond lengths of 1.333(5)–1.357(5) Å and the C(Ph)–$N(NO_3)$ bond lengths of 1.459(5)–1.473(5) Å are shortened and similar to the lengths of the corresponding bonds in nitrophenols.[42,43] A decrease in electron density on the O atom causes a further polarisation of the $C_{spiro}-O$ bond, which leads to a decrease in energy of the σ*-orbital of the $C_{spiro}-O$ bond and its localisation on the C spiroatom to an even greater degree.[40] This helps to strengthen the $n[N(1')]-\sigma^*(C_{spiro}-O)$ interaction and to further weaken and lengthen the $C_{spiro}-O$ bond compared to that in an unsubstituted SP, in which this bond must be stronger and shorter. Thus, as a result of specific orbital interactions in the photochromic indoline SPs, the $C_{spiro}-O$ bond, which is cleaved on photoexcitation, is the weakest and most elongated even in the ground state.

### b) Nature of the structural changes in SP molecules during photoexcitation

The characteristics identified in the structure of SPs should have a substantial effect on the photochromic properties of these compounds. Since the photophysical and photochemical properties of organic molecules to a large extent depend on their structure in the excited state, we shall examine the nature of the structural changes in these molecules that take place on photoexcitation. The nature of such changes, in turn, depends on the type of electronic transition of the molecule in a photochemically active state (PCAS). The conversion of SP(I)–SP(IV) molecules to a PCAS on exposure to UV light with $\lambda > 300$ nm is caused by electronic transitions in the benzopyran part of the SP of the type $\pi l-\pi^*$ in molecules without EA substituents and of the type $\pi l-\pi^*\pi n^*$ in molecules with EA substituents in the benzopyran residue (see the review of Kholmanskii et al[44] and the references in it). It has been reliably established that these transitions constitute transitions with intramolecular charge transfer (ICT), mainly from the *l*-orbital of the oxygen atom and the π-orbital of the C(3)=C(4) bond to the phenyl group and the EA substitutent†.

† In this review[44] the π-orbital of the oxygen atom is identified as the *l*-orbital.

This ICT must lead to a decrease in electron density on the O(1) atom. Thus, for 2*H*-chromene it was found using the CNDO(S) method[45] that charge transfer from the O atom during the $S_0 \rightarrow S_3$ transition is 0.060 e. The decrease in charge on the O atom will be compensated by the σ-electrons of the $C_{spiro}-O$ bond, which should cause it to undergo further polarisation. As was shown above, this type of redistribution of electron density should lead to an increase in the $n[N(1')]-\sigma^*(C_{spiro}-O)$ interaction in SP molecules and a further contraction of the $C_{spiro}-N(1')$ bond and weakening and elongation of the $C_{spiro}-O$ bond in the excited state. These conclusions are in agreement with the results of calculations using the MINDO-3 method on cleavage of the C–O bond of chromenes in an unexcited state.[46] It follows from the calculations that the length of the $C_{spiro}-O$ bond in the transition state, where cleavage of this bond occurs, is the same in all of the calculated molecules and constitutes ~1.95 Å. In the opinion of Simkin et al.,[46] the greatest proportion of the energy of activation for opening of the chromene rings is consumed on stretching the $C_{spiro}-O$ bond, the length of which at the initial stage of the reaction very accurately represents the reaction coordinate.

In spiropyran SP(V) the lowest electronically excited PCAS is the $^{1,3}(\pi l,\pi^*\pi n^*)$ state with ICT from the N(1′) atom to the phenyl residue and $NO_2$ group.[47] Therefore, the energy of the $n[N(1')-\sigma^*(C_{spiro}-O)$ interaction in the excited PCAS of SP(V) must be lower than in SP(IV), and the elongation of the $C_{spiro}-O$ bond in SP(V) is less than in SP(IV) (Table 1).

It has been shown[48] that a significant change in length of any bond in the excited state of the molecule assists the nonequilibrium transfer of electronic excitation energy of the molecule to the vibrational energy of this bond. Therefore, in an SP the vibrations of the weakened and elongated $C_{spiro}-O$ bond may be excited the most intensely, assisting its final heterolytic cleavage.

### c) Effect of structure of SPs in the ground and excited states on their photochemical properties

Let us compare the features identified in the structure of SPs in the ground state and the nature of the structural changes in the excited state with their photochemical activity. Unfortunately, there is no information in the literature on the quantum yields of photocleavage of a bond ($\nu$) while the quantum yields of photocoloration $\varphi_{AB}$[44] represent the efficiency of photolytic conversion without taking into account the reverse formation of the closed form of an SP (from the *cis*-cisoid isomer) directly after bond cleavage. It is evident that in general the relationship $\varphi_{AB} \leqslant \nu$ is always true.

The photochemical properties of SP(I)–SP(IV) are described in detail in the literature.[44] The greatest length of the $C_{spiro}-O$ bond in the ground state, the length of which agrees within the limits of error in these SPs, has been established for these compounds. The nature of the subsequent change in length of this bond in the excited state of SP(I)–SP(IV) differs considerably. Charge transfer from the O atom to the $NO_2$ group will depend on the position of the $NO_2$ group in the benzene ring relative to the O(1) oxygen atom. The greatest transfer of charge will occur in an SP with these atoms at the *para*-position. Therefore in SP(I) and SP(IV) the $C_{spiro}-O$ bond in the excited state will be weaker and longer than in SP(II) and SP(III), which have the $NO_2$ group at the *ortho*-position. In accordance with this, the quantum yields of photocoloration for SP(IV) and SP(I) (0.60 and 0.45 respectively) are higher than for SP(II) and SP(III) (0.13 and 0.05).[29] Introduction of Br and Cl atoms into the benzopyran residue of the SP leads to additional ICT

from these atoms on to the π-system of the benzene ring as a result of mesomeric effects, which reduces ICT from the O atom. Moreover, Cl and Br, being heavy atoms increase the efficiency of intersystem crossing and radiationless deactivation of triplet states. Consequently, the quantum yields of the photolytic reaction of SP(I) and SP(III) are lower than for SP(IV) and SP(II) respectively.

As has already been mentioned, the $C_{spiro}-O$ bond in SP(V) in both the ground and excited states is elongated and weakened to a lesser degree than in SP(IV), and the quantum yield of photocoloration for SP(V)[47] is lower than for SP(IV). Nevertheless, this value for SP(V) is still fairly high (0.3). Kholmanskii et al.[47] believe that the high quantum yield of photocoloration of SP(IV) is due to an exchange interaction between an unpaired electron formed in the excited state on the N(1′) atom and the electrons of the σ-orbital of the $C_{spiro}-O$ bond. This type of interaction may assist cleavage of the $C_{spiro}-O$ bond.

The *cis*-cisoid isomer formed directly after cleavage of the $C_{spiro}-O$ bond in an SP is unstable and can readily revert to the initial form. In SP(I)–SP(V) the $NO_2$ group evidently plays a significant role in the stabilisation of the resulting intermediate. This group is known[49] to have amphi-electronic (π-acceptor and π-donor) properties depending on the electronic nature of the molecular residue of which it forms a part. In electron-rich systems the $NO_2$ group exhibits π-acceptor properties while in electron-deficient systems it has π-donating properties. Therefore, the $NO_2$ group will stabilise the open form of SP(I)–SP(IV) through delocalisation of the negative charge from the oxygen atom and formation of a quinoid structure (as was shown by Aldoshin et al.),[14] while the open form of SP(V) will be stabilised through donation of electron density to the cationic indoline part of the molecule.

Unfortunately, no information exists on the structure of unsubstituted SP. Using the arguments developed above, it may be assumed that the length of the $C_{spiro}-O$ bond in it should be intermediate between the length of this bond in SP(IV) and SP(V) and hence the quantum yield for cleavage of this bond should be high. However, the *cis*-cisoid intermediate formed by cleavage of this bond must be extremely unstable and there is a high probability that it would be converted to the initial closed form, which would significantly reduce the quantum yield of photolytic conversion of unsubstituted SP. In fact, quantum-chemical calculations on unsubstituted chromenes[46] showed that on the potential energy surface of the excited state there is no energy minimum that corresponds to a *cis*-cisoid structure.

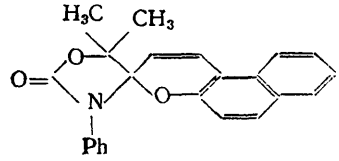
Thus, cleavage of the $C_{spiro}-O$ bond in the excited state may to a large extent be due to the further weakening and elongation of this bond during photoexcitation resulting from the same structural factors which caused the elongation and weakening of this bond in the ground state. Therefore, elongation of the $C_{spiro}-O$ bond in the ground state may serve as one of the criteria for photochemical activity in these compounds.

### d) Effect of the nature and position of the substituents in SP molecules on the length of the $C_{spiro}-O$ bond

The results of X-ray diffraction analysis showed that transferring the $NO_2$ group from the *para*- to the *ortho*-position and also the introduction of electronegative halogen atoms into these positions actually has no effect on the length of the $C_{spiro}-O$ bond (see Table 1). At the same time, introduction of EA substituents into the indoline residue of the SP should lead to an increase in delocalisation of the UEP of the N(1′) atom in the π-system of the indoline benzene ring and a decrease in efficiency of interaction of this UEP with the σ*-orbital of the $C_{spiro}-O$ bond.

Support for this is provided by the results of an X-ray diffraction study on 1,3′,3′-trimethyl-5′-nitrospiro(indoline-2,2′[2*H*-1]benzopyran) [SP(V)] with the $NO_2$ group at the 5′-position of the indoline residue[24] (Table 1). In SP(V) the indoline and benzopyran parts of the molecule are also at right angles to each other. The benzopyran residue is virtually planar, as in SP(I)–SP(IV), and has the conformation of an envelope with dihedral angle along the line of N(1′)...C(3′) of 27.2°. The unshared electron pair of the N(1′) atom and the $C_{spiro}-O$ bond are at an angle of 168.8° while the π-UEP of the O atom and the $C_{spiro}-N(1')$ bond are at an angle of 145.2°. Introduction of the $NO_2$ group into the indoline residue at the *para*-position relative to the N(1′) atom leads to a contraction of the N(1′)–C(Ph) bond to 1.380(2) Å compared to the length of this bond [1.393(4)–1.413(5) Å] in SP(I)–SP(IV), SP(VIII), and SP(XI). The length of the N(1′)–C(Ph) bond in SP(I)–SP(IV), SP(VIII), and SP(XI) is similar to the length of the corresponding bond [1.413(3) Å] with a considerable contribution of the UEP of the N atom to the π-system of a neighbouring carbonyl group.[50] The lengths of the N(1′)–C(Ph) and (Ph)C–N($NO_2$) bonds [1.380(2) and 1.461(2) Å] respectively] in SP(V) are similar to the corresponding bond lengths in *p*-nitroaniline [1.371(4)–1.380(5) Å and 1.450(5)–1.460(5) Å),[51,52] which is an indication of the increase in conjugation of the UEP of the N(1′) atom in SP(V) with the π-system of the benzene ring. As a result of this, the $n[N(1')]-\sigma^*(C_{spiro}-O)$ interaction decreases and the $C_{spiro}-N(1')$ bond only decreases in length to 1.453(2) Å and the $C_{spiro}-O$ bond is only extended to 1.452(2) Å.

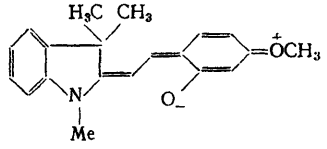
Confirmation of the effect of the electronic state of the N atom on the length of the $C_{spiro}-O$ bond is provided by the results of X-ray diffraction studies on SP(XXIII)[53] (SPs of this class are examined later in Section V). In SP(XXIII), as a result of the amide conjugation of the UEP of the N atom with the π-electron system of the carbonyl group, the activity of the UEP and efficiency of $n-\sigma^*$ interaction must be even lower than in SP(V). Therefore the $C_{spiro}-N$ bond (1.47 Å) becomes hardly any shorter while the $C_{spiro}-O$ bond (1.44 Å) is much less elongated than in SP(V).




SP(XXIII)

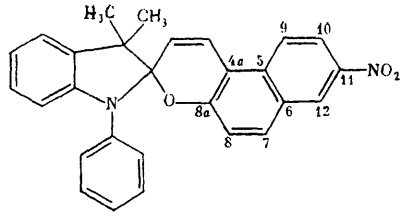
It is not possible to obtain crystals of unsubstituted SP that are suitable for X-ray diffraction analysis. The SP(VI) molecule appears to have a structure which is closest to that of unsubstituted SP.[29] The $CH_3O$ group is known[54] to have very weak EA properties regardless of its position in the benzene ring. This group exhibits strong electron-donating (ED) properties when it is at the *ortho*- and *para*-positions of a benzene group. Thus, a $CH_3O$ group at the 7-position of the benzopyran residue should have a weak effect on the electronic configuration of this residue and the molecular structure of 1,3′,3′-trimethyl-7-methoxyspiro(indoline-2,2′-[2*H*-1]benzopyran) (VI: $R' = CH_3$, $R^7 = OCH_3$) should be similar to the structure of unsubstituted SP.

The main structural parameters of SP(VI) are given in Table 1. The structure of the SP(VI) molecule is similar to the structure of SP(II), SP(III), and SP(IV*a*). The C(7)–O(2) bond of the methoxy group is bent by 15.6° from the plane of the phenyl residue. The length of the $C_{spiro}$–O bond [1.471(3) Å] is intermediate between the lengths of the same bonds in SP(I)–SP(IV) [1.485(4)–1.496(4) Å] and in SP(V) [1.452(2) Å]. Thus, even if the 7-$OCH_3$ group is able to exert a weak ED effect on the benzopyran fragment of the SP, the $C_{spiro}$–O bond in unsubstituted SP will be weakened and elongated not less than in SP(VI). However, in contrast to unsubstituted SP, the 7-$CH_3O$ group in SP(VI) stabilises the resulting MC form, being involved in conjugation as shown in the diagram



Therefore SP(VI) in solution and even in the solid state becomes coloured on irradiation with UV-light.[55]

An X-ray diffraction study was carried out[28] on 1′-phenyl-3′,3′-dimethyl-11-nitrospiro(indoline-2,2′-[2*H*-1]naphthopyran) [SP(VII)], which contains an additional benzene ring annelated at the 5- and 6-positions.



SP(VII)

The main structural parameters of SP(VII) are given in Table 1. SP(VII) has a structure which is similar to that of SP(II), but annelation of the additional benzene ring and transfer of the $NO_2$ substituent to the 11-position lead to a contraction of the $C_{spiro}$–O bond to 1.460(2) Å compared to the length of this bond [1.492(3) Å] in SP(II). Although the $C_{spiro}$–O bond is still longer than a normal C–O bond,[15–17] its shorter length in SP(VII) compared to SP(II) indicates that there is a weakening of the $n[N(1')]-\sigma^*(C_{spiro}-O)$ interaction in this molecule. As the geometric configuration of the UEP of the N(1′) and O atoms and $C_{spiro}$–O and $C_{spiro}$–N(1′) bonds in SP(II) and SP(VII) is the same (Table 1), the decrease in $n-\sigma^*$ interaction in SP(VII) may be due to a change in the electronic state of the O(1) atom in the spiro centre. In fact, the O(1)–C(8*a*) bond in SP(VII) is longer [1.372(3) Å] than that in SP(II) [1.356(3) Å]. This suggests that there is decrease in conjugation of the π-system of the naphthalene residue with the π-UEP of the O(1) atom, leading to a reduction in polarity of the $C_{spiro}$–O(1) bond and a weakening of the $n-\sigma^*$ interaction. This is also supported by the contraction of the C(22′)–N(1′) bond to only 1.450(3) Å, whereas in SP(II) this bond decreases to 1.432(3) Å.

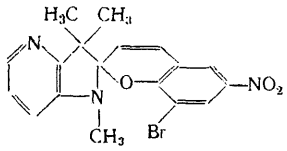
Thus, the presence of an additional benzene ring at the 5,6-position of the benzopyran residue and the transfer of the $NO_2$ group to the 11-position cause some contraction and strengthening of the $C_{spiro}$–O bond in SP(VII) compared to SP(I)–SP(VI), which in turn leads to a decrease in photochemical activity of naphthospiropyrans (NSPs).

Particular attention should be given to the fact that the quantum yield for photolytic conversion of an NSP, in contrast to SP(I), SP(III), and SP(IV), has proved very sensitive to the nature of the R′ substituent on the N(1′) atom. While replacement of R′ = $CH_3$ by R′ = Ph in spiropyrans has no effect on the quantum yield of photolytic conversion,[44,56] in NSPs the same change leads to a sharp fall in the value of φ—from 0.6 (R′ = Me) to 0.08 (R′ = Ph) in SP(VII).[57]

A structural analysis of the series SP(I), SP(IV)–SP(VI), SP(IX), and SP(XI) with R′ = $CH_3$ shows that the N(1′) atom in all of these compounds has the same pyramidal coordination and projects from the plane of the atoms bonded to it by 0.24–0.28 Å. Replacement of the $CH_3$ group on the N(1′) atom by the more bulky benzyl group, i.e. going from SP(IV) to SP(VIII), leads to an increase in the height of the pyramid to 0.34 Å but in other respects has no effect on the structure of the SP(VIII) molecule[25] (Table 1). Replacement of a $CH_3$ group by a $C_6H_5$ group makes it possible to conjugate the UEP of the N(1′) atom with the π-system of the benzene ring, the efficiency of which will be determined by the degree of coplanarity of the Ph-ring with the coordination plane of the N(1′) atom. In SP(II) and SP(VII), with values of the dihedral angle between these planes equal to 43.9 and 34.8° respectively, the N(1′) atom only projects from the plane of the three atoms bonded to it by 0.13 and 0.12 Å respectively, the UEP of the N(1′) atom conjugates with the π-system of the Ph substituent, and the activity of the UEP of N(1′) will therefore decrease. The fall in the quantum yield for photolytic conversion of SP(VII) may be related to weakening of the $n[N(1')]-\sigma^*(C_{spiro}-O)$ interaction. The dihedral angle between the plane of the Ph ring and the coordination plane of the N(1′) atom in SP(III) is 80° and N(1′) atom projects from the C(22′)C(7*a*)C(Ph) plane by 0.21 Å. Unfortunately, there are no data on the quantum yield for photolytic conversion of an SP(II) derivative with R′ = $CH_3$ and it was not possible to conduct an X-ray diffraction analysis of SP(III) and SP(VII) with R′ = $CH_3$ and SP(I) and SP(IV) with R′ = $C_6H_5$ because of the poor quality of the crystals, so the very interesting and important question concerning the effect of the degree of conjugation of the UEP of the N(1′) atom with a $C_6H_5$ residue on the quantum yield of photolytic conversion of SPs has no clear answer for the time being.

The synthesis of new photochromic SPs based on 4-azaindole has been reported.[58] The SPs obtained readily dissolve in polar and nonpolar solvents and some of them even in water. The small bathochromic shift of the long-wavelength absorption band of these compounds is due, in the opinion of Maisuradze et al.,[58] to the increase in EA properties of the pyridine ring in comparison to a benzene ring. The photosensitivity of azaindoline SPs towards UV radiation proved to be no lower and in some cases even higher than the photosensitivity of their indoline analogues.

The X-ray structural analysis of 1,3′,3′-trimethyl-6-nitro-8-bromospiro(4-azaindoline-2,2′-[2*H*-1]benzopyran) [SP(IX)] has been carried out.[27]



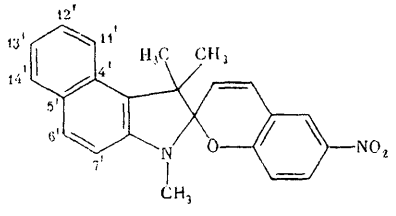
SP(IX)

The main structural parameters of SP(IX) are given in Table 1. Since the pyridine ring has stronger EA properties than the benzene ring, the length of the N(1′)–C(7*a*′) bond [1.386(6) Å] has a

tendency to decrease and although within the limits of experimental error it matches the length of this bond in SP(I) [1.398(5) Å] and in SP(V) [1.380(2) Å], it is shorter than in SP(II)–SP(IV) and SP(VI)–SP(VIII) [1.394(3)–1.416(4) Å]. These results indicate that there is some increase in conjugation of the UEP of the N(1′) atom with the π-system of the pyridine ring. However, the $C_{spiro}-O(1)$ bond [1.486(6) Å] in SP(IX), as in SP(I) [1.496(4) Å], is still elongated, which is an indication of strong $n[N(1')]-\sigma^*[(C_{spiro}-O(1)]$ interactions in the SP(IX) molecule. Moreover, in SP(IX), in contrast to the SP(I), the benzopyran ring is virtually planar and the π-UEP of the O(1) atom makes an angle of only 139.6° with the $C_{spiro}-N(1')$ bond rather than 160.2° as in SP(I). Therefore the $n[O(1)]-\sigma^*[C_{spiro}-N(1')]$ interaction in SP(IX) will be weaker than in SP(I). This is suggested by the greater contraction of the $C_{spiro}-N(1')$bond in SP(IX)—to 1.434(7) Å compared with 1.453(4) Å in SP(I).

Thus, in SPs based on 4-azaindole, just as in their indoline analogues, $n[N(1')]-\sigma^*(C_{spiro}-O)$ orbital interactions remain strong and the $C_{spiro}-O$ bond is elongated.

As has already been mentioned above, the quantum yield of photocleavage of the $C_{spiro}-$bond in SPs in many respects depends on the length of this bond in the ground state and the degree of ICT from the oxygen atom of the pyran ring to the benzene ring in the excited state, affecting a further weakening and stretching of the $C_{spiro}-O$ bond. In order to distinguish the influence of these factors, it is necessary to study SPs whose molecules would have the same structure in the ground state but a different pattern of electronic transitions in the excited state. The subject chosen for such a study was 1′,3′,3′-trimethyl-4′,5′-benzo-6-nitrospiro(indoline-2,2′-[2*H*-1]benzopyran [SP(X)].[26] It was assumed that annelation of an additional ring at the 4′- and 5′-positions of the indoline residue would have no substantial effect on the structure of the spiro centre



SP(X)

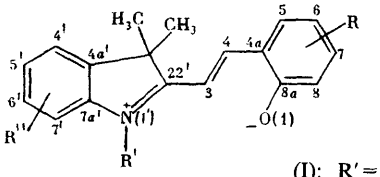
in SP(X) relative to SP(IV), but as had been shown in two studies[8,56] would lead to intramolecular energy transfer (IET) from the pyran heterocycle to the indoline system and would lower the efficiency of photocoloration of SP(X) compared to SP(IV).

The main structural parameters of SP(X) are given in Table 1. Spiropyrans (X) and (IV) have the same structure. The benzopyran residue in SP(X) is virtually planar, as in the SP(IV*a*) molecule. The $C_{spiro}-O(1)$ bond is extended to 1.478(7) Å and within the limits of experimental error it matches the average length of this bond in SP(IV) [1.486(4) Å]. Since annelation of the benzene ring at the 4′- and 5′-positions of the indoline residue does not affect the structure of the spiro centre in the SP(X) molecule, which has the same characteristics as in SP(IV), the decrease in the quantum yield for photolytic conversion of SP(X) to 0.026, compared to 0.60 for SP(IV),[56] is evidently due solely to radiationless deactivation processes in the excited state, in particular with ICT from the pyran to the indoline ring. With such a transfer of energy, ICT from the O(1) oxygen atom to the benzene ring and the nitro group of the benzopyran residue is substantially reduced. Therefore it may be assumed that in the excited state the interaction between the UEP of the N(1′) atom and the σ*-orbital of the $C_{spiro}-O(1)$ bond will be weaker in SP(X) than in SP(IV), and although the C(22′)–O(1) bond in SP(X) is elongated and weakened in the ground state it will undergo cleavage with greater difficulty.

Another factor which has a considerable effect on the efficiency of the photochemical conversion of SPs is a process which competes with the photoreaction, namely, the radiationless deactivation of excited states through internal conversion and intersystem crossing. It is known[59] that the presence of heavy atoms substantially increases the rate of all "singlet⟷triplet" processes, and therefore heavy atoms are effective quenchers of excited states. It has already been noted in Section II.2c that the introduction of heavy Cl and Br atoms into the 6- and 8-positions of the benzopyran residue does not have any substantial effect on the structure of the SP but reduces the quantum yield of photoconversion of these compounds. This type of influence from heavy atoms in the benzopyran residue may be due either to the effect of heavy atoms increasing the radiationless deactivation of excited states or to the mesomeric donor effect of these atoms decreasing ICT from the oxygen atom to the phenyl residue. In order to study the role of heavy atoms in SP molecules, X-ray diffraction analysis was conducted on 1,3′,3′-trimethyl-4-chloro-6-nitrospiro(indoline-2,2′-[2*H*-1]benzopyran [SP(XI)],[30] which contains a Cl atom at the 4-position of the benzopyran residue. The Cl atom at the 4-position of the pyran ring does not have any marked effect on the geometry of the molecule and the distribution of bond lengths in it. The SP(XI) molecule has a structure which is the same as that of SP(IV). As in SP(IVa), the benzopyran part of the molecule in SP(XI) is virtually planar. The C(22′)–N(1′) bond length of 1.438(2) Å and C(22′)–O(1) bond length of 1.479(2) Å within the limits of experimental error match the values of these bond lengths in SP(IV) (see Table 1). Nevertheless, the photochemical activity of SP(XI) proves to be considerably lower than the photochemical activity of SP(IV). In the excited state the Cl atom at the 4-position also should not affect ICT from the O atom to the benzene ring. Therefore, the reduction in photochemical activity of SP(XI) is apparently due solely to the effect of the Cl atom as a heavy atom.

## III. The structure of open merocyanine forms of indoline spiropyrans

Since one of the important characteristics of photochromic systems based on SPs is the lifetime of the open merocyanine forms of SPs, it is necessary to carry out a detailed study of the structure of MCs and to identify the structural factors which stabilise SPs in the open state. The structure of different MCs and the energy of their intermolecular interactions in crystals, and the thermodynamic and kinetic stability of the isomers identified will then be examined.



MC

(I): $R'=CH_3$, $R^6=NO_2$, $R^8=Br$;
(II): $R'=C_5H_{11}$, $R^6=NO_2$, $R^8=Br$;
(III), (IV): $R'=p\text{-}CH_3C_6H_4$, $R^6=NO_2$, $R^8=NO_2$, $R''=CH_3$;
(V): $R'=H$, $R^6=NO_2$, $R^8=NO_2$.

## 1. Molecular structure of merocyanines

In crystals of MC(I) the bipolar structure (A) appears to be stabilised to a considerable extent through solvation of the negatively charged O(1) oxygen atom by a water molecule (Fig. 2), which may substantially affect the electronic structure and stability of the MC molecule.

The crystalline structure of solvates of MC(I) provides a basis for the assumption that replacement of a methyl group on the N(1′) atom in the indoline ring by a more bulky group can inhibit solvation of the phenolate oxygen atom. In order to confirm this hypothesis, an X-ray diffraction study was carried out on the pentyl-substituted MC(II), in which the pentyl substituent on the N(1′) atom is similar to the methyl group in terms of its electronic properties.[60,61] The MC(II) molecule does not form solvates in the crystalline state. Just as in MC(I) crystals, MC(II) molecules (Fig. 6) have an almost planar *trans*-cisoid structure. The slight deviation from planarity manifests itself in twists about the C(22′)–C(3), C(3)–C(4), and C(4)–C(4*a*) bonds of 5.5, 6.7, and 8.6° respectively.

The distribution of bond lengths in the MC(II) molecule is in general terms similar to the distribution of bond lengths in the MC(I) molecule. However, the absence of solvate water molecules in MC(II) crystals leads to some redistribution of electron density in the MC(II) molecule. Thus, the length of the O(1)–C(8*a*) bond is reduced to 1.228(6) Å, which corresponds to the length of a C=O double bond.[15] Contraction of the O(1)–C(8*a*) bond in MC(II) is accompanied by a further decrease in bond angle of C(4*a*)C(8*a*)C(8) to 112.8(1)°, which is an indication of the increasing importance of σ-electron repulsion from the O(1) atom. The C(4*a*)–C(8*a*) and C(8a)–C(8) bonds are extended even more and the C(7)–C(8) bond is shorter in comparison with the lengths of these bonds in MC(I). As in the MC(I) molecule, the N(2)–C(6) bond [1.437(6) Å] is considerably shorter than this bond in the closed form,[14] the O(2)N(2)O(3) angle [121.5(5)°] being even smaller than the "equilibrium" value. This type of structure for the *p*-nitrophenolate residue suggests that there is a greater contribution of the resonance quinoid form (B) (see Fig. 3) to the zwitterion structure (A) of unsolvated MC(II) molecules compared to solvated MC(I) molecules. As in MC(I), the contribution of the canonical form (C) is appreciable in MC(II) molecules (see Fig. 3). The N(1′)–C(22′) bond in MC(II) [1.316(5) Å] is even shorter than in MC(I), which is an indication of its complete double bond character and that the positive charge is mainly located on the N(1′) atom.

Thus, the research carried out indicated that the structure of open forms of SPs can be represented by resonance forms (A) (the greatest contribution), (B), and (C), with the contribution of each of these forms varying in accordance with the nature of the substituents in the molecule. Stabilisation of open MC molecules must be related to the stabilisation of one of these resonance structures. The structure of MC(I) crystals suggests that solvation of the O(1) phenolate atom stabilises the zwitterion structure directly to a greater extent. Stabilisation of the canonical structure (C) can be achieved,

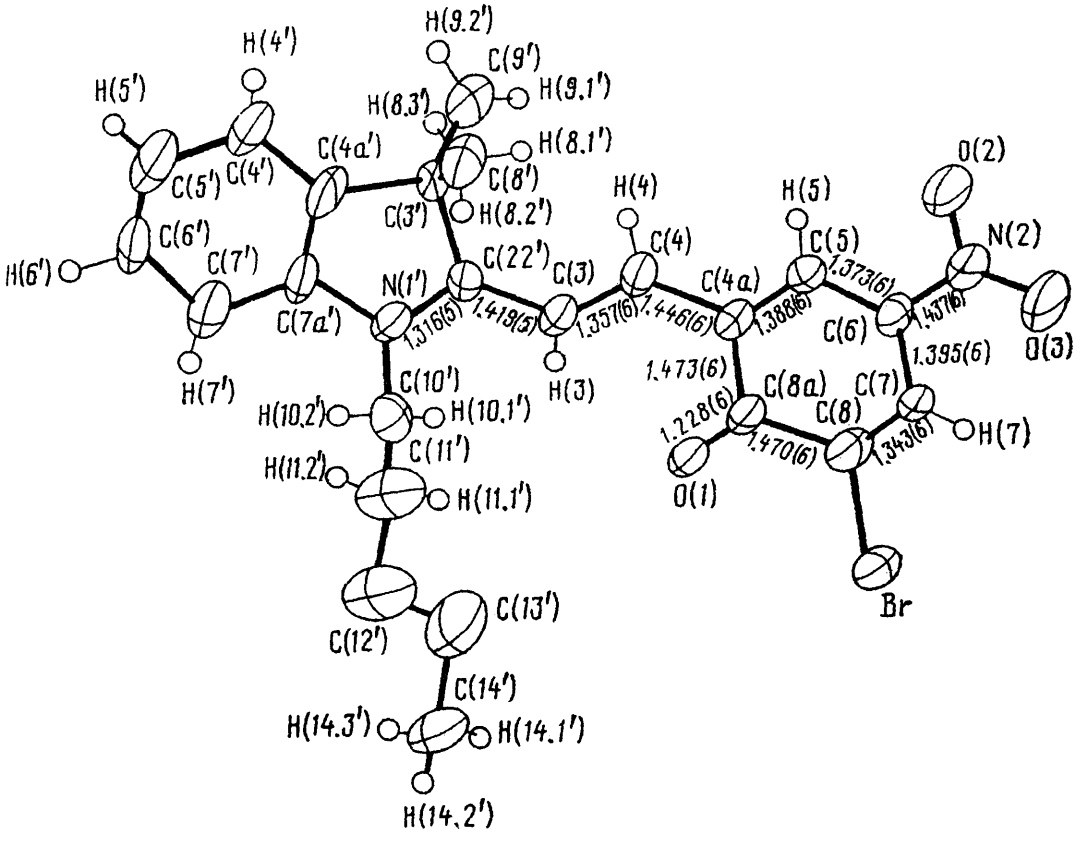
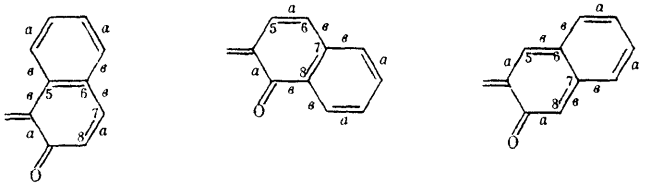



**Figure 6.** General shape of the MC(II) molecule.

for example, through annelation of additional benzene rings to the phenolate ring. At the same time annelation of additional benzene rings at the 5,6- and 7,8-positions will further stabilise form (C) because of the preservation of aromaticity and specificity of structure of a naphthalene residue with shortened "*a*" bonds and elongated "*b*" bonds, while annelation at the 6,7-position will lead to its destabilisation.



In MC(I) and MC(II) *p*-$NO_2$ substituents in the phenolate ring displace the equilibrium towards the quinoid form (B) and hence stabilise the unstable zwitterion form. It was suggested[61] that introduction of an additional $NO_2$ group into the *ortho*-position relative to the O(1) atom of this residue should increase the stability of the open MC form. X-Ray diffraction analysis of such a merocyanine, MC(III), showed that this compound crystallises in two polymorphic forms—monoclinic and rhombic.

In the monoclinic form MC(III) molecules have a nearly planar *trans*-structure (Fig. 7) with slight deflections about the C(22′)–C(3), C(3)–C(4), and C(4)–C(4*a*) bonds of 3.1, 4.7, and 2.7° respectively, which is similar to the structure of MC(I) and MC(II). However, in contrast to MC(I) and MC(II), the phenolate oxygen atom in MC(III) in almost equal probability occupies the *S-cis*- or *S-trans*-positions relative to the C(4)–C(4*a*) bond. Thus, the *trans*-cisoid isomer and *trans*-transoid isomer, which has been detected experimentally for the first time, occur in equal ratios in the crystalline state.

The *trans*-transoid isomer, which constitutes ~50% of a crystal, is solvated by a water molecule [O(1′)...O($H_2O$) distance is 2.44 Å], which also occupies ~50% of the independent positions. The hydrogen bond formed in the solvate is one of the shortest hydrogen bonds.[62] As a result of the phenolate residue being randomly oriented in two positions, the distribution of bond lengths in it is averaged out and it is not possible to make any conclusion about the nature of the redistribution of bond lengths on introducing a second $NO_2$ group into the *ortho*-position relative to the O(1) atom. However, the C(6)–N(3) and C(8)–N(2) bond lengths with both nitro groups are shortened (see Fig. 7) and the O(2)N(2)O(3) and O(4)N(3)O(5) angles [121.3(6) and 120.0(6)°] are smaller than the "equilibrium" values. This suggests that there is a strong resonance interaction between these groups and the π-system of the benzene ring. The C(4*a*)–C(5) and C(4*a*)–C(8*a*) bonds are elongated while the C(6)–C(7) and C(7)–C(8) bonds are shortened (see Fig. 7) in comparison with the normal value of a bond length in a benzene ring. The remaining bond lengths in the MC(III) molecule within the limits of experimental error match the bond lengths in the MC(I) and MC(II) molecules, although the N(1′)–C(22′), C(22′)–C(3), and C(3)–C(4) bonds are somewhat longer.

X-Ray structural analysis of the rhombic form [MC(IV)] showed[61] that the two isomers—*trans*-cisoid and *trans*-transoid—also occur in crystals of this polymorph in nearly equal proportions. The pattern of distribution of bond lengths in MC(IV) within the limits of experimental error is in line with the distribution of bond lengths in MC(III).

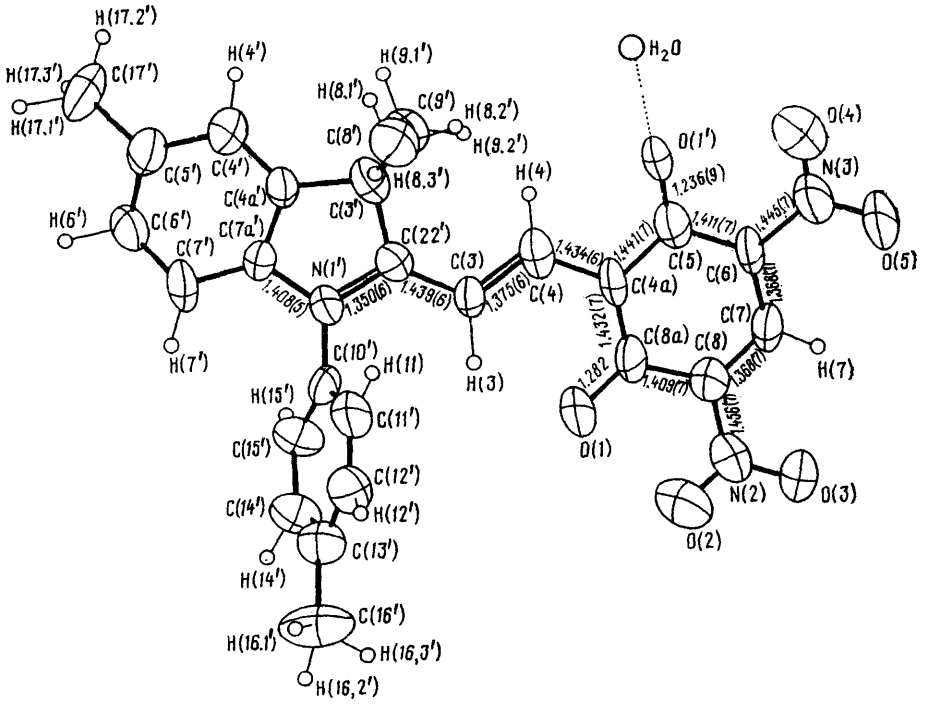



**Figure 7.** General shape of the MC(III) molecule.

Crystals of MC(IV), like crystals of MC(III), contain solvate water molecules which occupy ~50% of the independent positions. However, in contrast to MC(III), it is the sterically less accessible O(1) atom of the *trans*-cisoid isomer that is solvated [O(1)...$O_{H_2O}$ distance is 2.97(3) Å] rather than the O(1) atom of the *trans*-transoid isomer, which causes the phenyl substituent on the N(1′) atom to deviate from the plane of the molecule by 87.9°. In crystals of MC(IV) there are also other water molecules that do not solvate the MC molecules, and they occupy about 25% of the independent positions and are situated at an O...O distance of 2.30 Å from the solvating water molecules.

Thus, solvation of the phenolate O atom is evidently typical for MC molecules in polar solvents if steric factors do not prevent this.

The introduction of an additional $NO_2$ group into the phenolate residue stabilises a further isomer—the *trans*-transoid form—which evidently exists in solution in equilibrium with the *trans*-cisoid isomer, resulting in their co-crystallisation. This conclusion made it necessary to conduct a more detailed study of the structure of the *trans*-transoid isomer. An X-ray diffraction study was carried out on the *o,p*-dinitro-substituted MC(V), in which the hydrogen atom of the vinyl group is replaced by a $CH_3$ group, which must inhibit the formation of the *trans*-cisoid isomer. In fact, in crystals of MC(V) the molecules have a *trans*-transoid structure (Fig. 8) and are linked together in a chain via a strong O(1)...$H_{N(1')}$ hydrogen bond [1.70(4) Å]. The steric interactions which occur between the atoms of the methyl group of C(10) and the *syn* H(5) atoms "eject" the phenolate residue from the plane of the molecule by a turn of 20.3° about the C(4)–C(4*a*) bond. However, this turn is evidently not sufficient to reduce the steric strain in the molecule, and the tendency to retain a planar structure with delocalised electron density prevents a further loss of planarity by the molecule, resulting in the C(4)C(3)C(10) bond angle being distorted to 124.6(4)° and the C(3)C(4)C(4*a*) and C(4)C(4*a*)C(5) angles are even changed to 133.3(4) and 127.0(4)°. Twists of the groups about the C(22′)–C(3) and C(3)–C(4) bonds only amount to 6.1 and 8.3°. The O(1)–C(8*a*) bond length [1.269(5) Å] is similar to the length of this bond in the MC(I) molecule, where the O(1) atom, as in MC(V), particpates in the formation of a strong hydrogen bond. These bonds are longer than the O(1)–C(8*a*) bond in the MC(II) molecule, in which the O(1) atom does not participate in intermolecular hydrogen bonding. The size of the intramolecular bond angle of C(4*a*)C(8*a*)C(8) [115.4(5) Å] in MC(V) is also close to that for the same angle in MC(I), which suggests that there is the same σ-electron repulsion from the O(1) atoms in both molecules.

It was surprising to find that in MC(V) the C(6)–N(2) bond length [1.480(7) Å] within the limits of experimental error matches the lengths of the same bonds in closed SPs,[30] and is not shorter than them as in MC(I) and MC(II). The size of the O(2)N(2)O(3) bond angle [125.0(6)°] is close to the "equilibrium" value of this angle in aromatic nitro compounds.[18] All of this is an indication of the much weaker resonance interaction between the *p*-$NO_2$ group in MC(V) and the π-system of the phenolate residue than in MC(I) and MC(II). The length of the C(8)–N(3) bond [1.462(6) Å] is shorter than C(6)–N(2) although it is still longer than in MC(I) and MC(II). The O(4)N(3)O(5) bond angle [121.6(5)°] is also less than the "equilibrium" value. Since it was shown[18] that there is no correlation between the length of a $C_{Ac}$–$N_{NO_2}$ bond and the angle of rotation of the $NO_2$ group about this bond, the results obtained suggest that there is a greater resonance interaction between the *o*-$NO_2$ group and the π-system of the benzene ring than for the *p*-$NO_2$ group. In the benzene ring two bonds—C(4*a*)–C(8*a*) and C(8*a*)–C(8)—are elongated while only the C(7)–C(8) bond is appreciably shortened (see Fig. 8). Taking into account this structure of the *o*,p-dinitrophenolate residue, such a distribution of

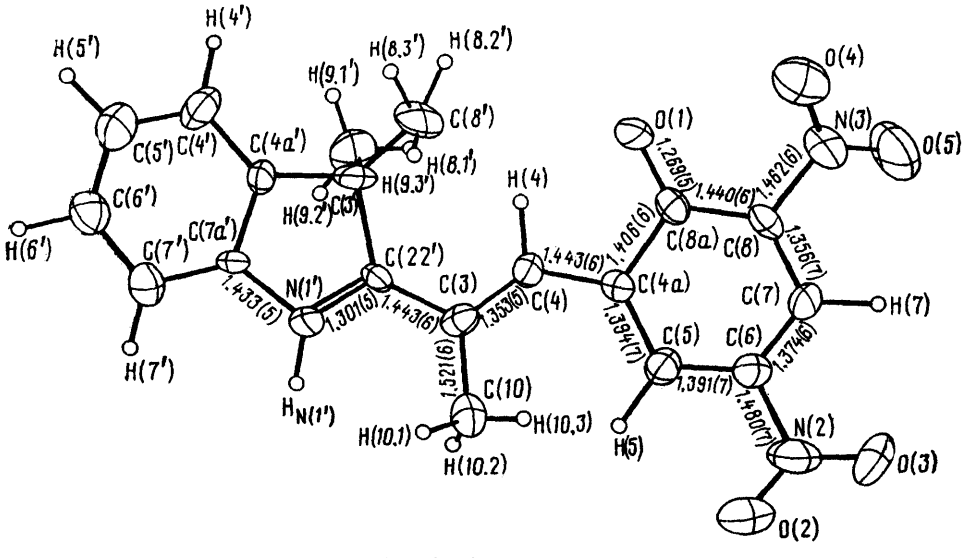
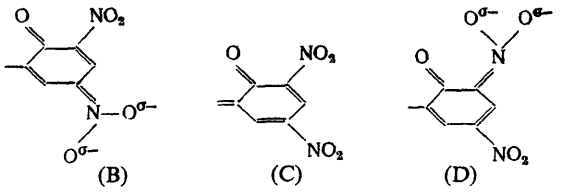



**Figure 8.** General shape of the MC(V) molecule.

the bond lengths in the phenolate ring is unlikely to result from the contribution of the resonance quinoid forms (B) and (D) but has more complex origins.

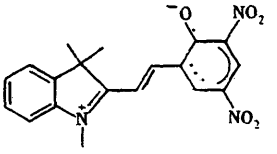


(B) (C) (D)

The contribution of the quinoid form (C) to the structure of the phenolate residue also appears to be small, and the increase in length of the C(22′)–C(3) bond to 1.443(6) Å and the further contraction of the N(1′)–C(22′) bond to 1.301(5) Å compared to the lengths of these bonds in MC(I) and MC(II) is an indication of the decrease in contribution of this form to the structure of the complete MC(V) molecule. The overall distribution of bond lengths in the phenolate residue may occur as a result of σ-electron repulsion from the negatively charged O(1) atom and the electron-acceptor effect of the $NO_2$ substituents. The latter conclusion is consistent with the statistical data of Holden and Dickinson,[18] according to which the bond lengths in the benzene ring adjoining a nitro group have a tendency to shorten.

It should be noted that despite the statistical disordering of the *o,p*-dinitro-substituted phenolate residue in MC(III) and MC(IV), the distribution of bond lengths in them is similar to that found in MC(V).

Thus, the MC(V) molecule with *o*- and *p*-$NO_2$ groups in the phenolate residue mainly has the bipolar structure (E) with appreciable disruption of aromaticity in the phenolate ring.



(E)

As was mentioned above, an important characteristic of an SP is the number of cycles for the photolytic conversion

$$SP \overset{h\nu}{\rightleftarrows} MC$$

without appreciable decomposition of the system. It is known[63] that SPs containing 8-$OCH_3$ and 6-$NO_2$ substituents in the benzopyran part of the molecule are more stable to decomposition. The structure of the merocyanine form of 1-hydroxyethyl-3,3′-dimethyl-6-nitro-8-methoxyspiro(indoline-2,2′-[2*H*-1]benzopyran [MC(VI)] (Fig. 9) has been studied.[64] In the crystalline state MC(VI) molecules are linked together through strong chains of hydrogen bonds of the type O(1)...$H_{O(4')}$ [1.78(3) Å] [O(1)...O(4′) = 2.64(1) Å], which results in elongation of the O(1)–C(8*a*) bond to 1.253(4) Å, which is typical for zwitterion molecules, in which the length of this bond is 1.26 Å. However, in other respects the distribution of bond lengths in MC(VI) differs substantially from

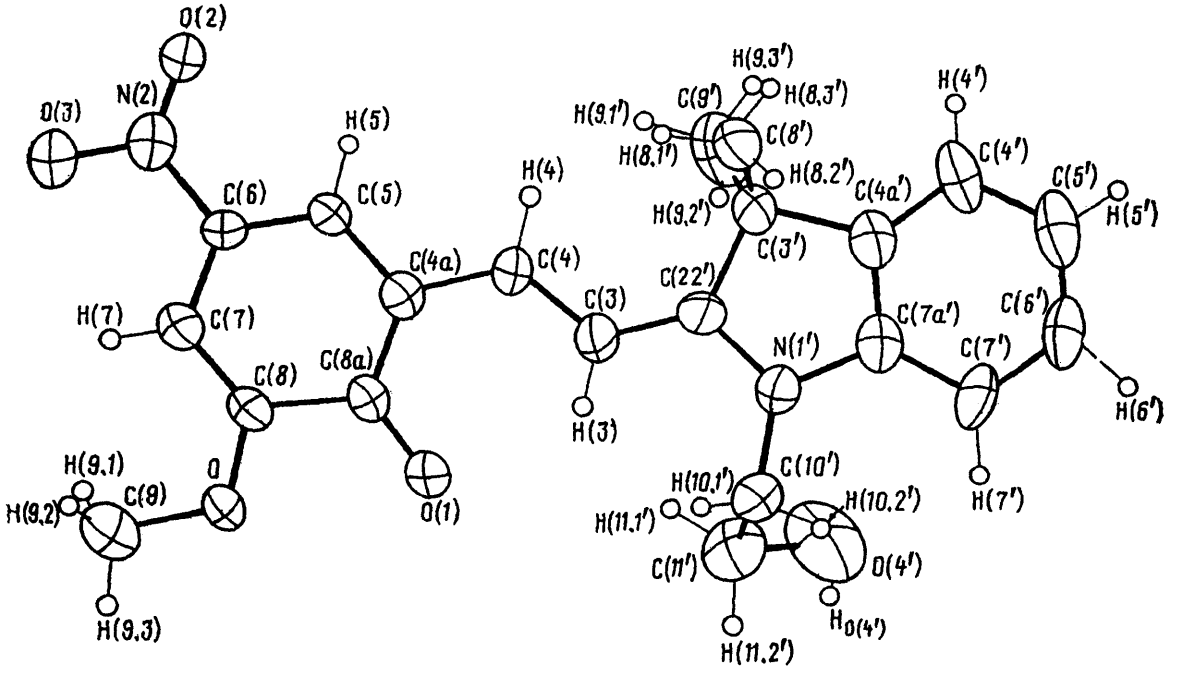


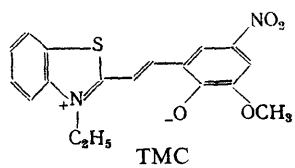

**Figure 9. General shape of the MC(VI) molecule.**

that in MC(I)–MC(V); the N(1′)–C(22) and C(3)–C(4) bonds [1.352(4) and 1.366(4) Å respectively] are elongated while the C(22′)–C(3) and C(4)–C(4*a*) bonds [1.403(4) and 1.444(4) Å] are shortened. This type of distribution of bond lengths in MC(VI) and at the same time the C(5)–C(6) and C(7)–C(8) bonds decreasing in length to 1.376(4) and 1.345(5) Å suggests that there is an increase in contribution of the quinoid form (C) (see Fig. 3) to the structure of MC(VI). The decrease in zwitterion character of the MC(VI) molecule and the greater contribution of the less reactive quinoid form to its structure may be responsible for the increase in stability of this system.

## 2. Geometric isomers of merocyanine forms

A study of the geometric isomerism and relative stability of the isomers of the open merocyanine forms is very important for an understanding of the mechanism of photochromism in SPs and to account for the spectroscopic behaviour of MCs, in particular the positions and occurrence of long-wavelength absorption, which together with the photoactivity of SPs and the stability of MCs constitute an important property which determines the practical application of SPs.[2,65] Many theoretical studies[46,66–68] have dealt with the question of the relative stability of the isomers of small model SPs and MCs and the effect of different substituents on their spectroscopic properties.

X-Ray diffraction analysis of MC(I)–MC(VI) showed that only the planar *trans*-cisoid and *trans*-transoid isomers exist in the crystalline state. The first of these occurs in crystals of MC(I)–MC(IV), MC(VI), and the open form of a benzothiazole SP–(TMC)—as studied by Miler-Strenger et al.,[69] while the second occurs together with the *trans*-cisoid isomer in crystals of MC(III) and MC(IV), whose molecules contain two nitro substituents in the phenolate residue.




TMC

It was concluded from the results of quantum-chemical calculations[61] that the *trans*-cisoid and *trans*-transoid isomers of MCs are similar in energy. In MCs with a single nitro group in the phenolate residue there is a substantial transition barrier between them, but introduction of two nitro substituents into the *ortho*- and *para*-positions of the phenolate residue lowers this barrier to such an extent that these isomers can readily undergo interconversion in solution. In fact, co-crystallisation of both isomers of the *o,p*-dinitro-substituted MC(III) and MC(IV) may also indicate that the packing energy of these isomers is virtually the same and in solution they occur in approximately equal concentrations.

The lowering of the rotation barrier about the C(4)–C(4*a*) bond when two electron-acceptor nitro groups are introduced into the phenolate residue is evidently related to the increased contribution of form (E) to the structure of this type of molecule, reducing the π–π interaction between this residue and the remaining part of the molecule.

The results obtained cast doubt on the theory that the complex nature of the absorption spectrum of open merocyanine forms of SPs is due to the presence of four different stereoisomers in the solid state and in solution.[70,71] Furthermore, calculations on the absorption spectra of model isomers of 2*H*-chromenes show that these isomers are indistinguishable in the region of long-wavelength absorption.[66] In several studies[72–76] the suggestion that coloured and colourless forms of SPs are associated has been made in order to account for the spectroscopic properties of MCs. The similarity of the absorption spectra of MCs in nonpolar solvents (at low temperatures), in an amorphous state, and in thin homogeneous crystalline films suggests that the coloured form of SPs in the liquid and solid states has the same structure. Hence there is definite interest in the packing of MC molecules and energy of intermolecular interaction in crystals.

## 3. Nature of the molecular packing and energy of intermolecular interactions in merocyanine crystals

Since this question has been discussed by us in detail in a review article,[61] we shall only report here the main results and conclusions of this study.

The crystalline structure of open merocyanine forms of SPs is an indication of the well-defined tendency of MC molecules to form different aggregates. This is due to the planar structure and high polarity of MC molecules, and consequently, in addition to van der Waals forces, electrostatic and dipole–dipole interactions also play a significant role in the formation of aggregates. Calculations of the energy of crystalline MC structures show that the electrostatic interaction in the aggregates can amount to ~50% of the van der Waals interaction. The strongest aggregates are formed in MC(II) crystals, in which the molecules are arranged in stacks on top of each other according to the principle "head over tail". The pairing energy of the van der Waals and electrostatic interactions, without even taking account of the dipole–dipole interaction, in these stacks is approximately –26 kcal $mol^{-1}$. Solvated MC molecules form different aggregates through strong hydrogen bonds according to the principle "head to head" and "head to head, tail to tail".

Bulky alkyl substituents on the N(1′) atom can inhibit solvation of the *trans*-cisoid isomer of MCs, although they do not prevent the formation of "head to tail" aggregates. A methyl substituent on the N(1′) atom does not inhibit the solvation of *trans*-cisoid isomers of MCs. Solvation of a phenyl-substituted MC results in the phenyl substituent turning about 90° from the plane of the molecule and disrupting the conjugation of the UEP of the N(1′) atom with the π-system of the Ph residue, which is evidently balanced by the gain in energy from solvation of the molecule. Solvated molecules of *trans*-cisoid MC isomers form aggregates through hydrogen bonds with solvate molecules.

In the *trans*-transoid isomers the substituents on the N(1′) atom do not inhibit solvation. A solvated *trans*-transoid MC isomer can form both "head to tail" aggregates and aggregates with solvate molecules. In MC(I) crystals the aggregates comprise solvated MC molecules joined by a hydrogen bond. In these associates the molecules are arranged "head to head" at an angle of ~110° to each other, so the electrostatic attraction energy between them is reduced but the total energy of the van der Waals and electrostatic interactions is approximately –22 kcal $mol^{-1}$. In crystals of MC(V) the strongest aggregates (~–17 kcal $mol^{-1}$) are formed through the molecules being linked via hydrogen bonds in chains and also through intermolecular interactions in parallel to the molecules arranged "head to head" in layers. In the crystalline structure of MC(VI) repeating chains in which the pairing energy of intermolecular interactions is –10 kcal $mol^{-1}$ can be distinguished.

The formation of quite strong aggregates in crystals of MC(I)–MC(VI) with different types of packing provides a basis for

the assumption that these aggregates can also be preserved in solution. In crystals only the energetically most stable forms of molecular association and those most favourable for packing usually occur, and so in MC solutions these aggregates can be even more diverse. At the same time in nonpolar aprotic solvents, for MC molecules not bound through a specific intermolecular interaction with solvent molecules formation of "head to tail" aggregates is the most probable. In protic polar solvents, formation of solvates combined into different associates through hydrogen bonds is the most probable. The formation of solvates and aggregates is a further factor stabilising the highly polar merocyanine forms and a more probable cause of the complex absorption spectrum of MCs than the proposed existence of various isomers.

## IV. Effect of the nature and relative orientation of the heteroatoms in the spiro centre on the structure and photochemical properties of spiropyrans

The considerable influence of specific $n-\sigma^*$ orbital interactions of the heteroatoms in the spiro centre of indoline SPs on the structure and photochemical properties of these compounds suggests that a change in the nature and relative orientation of the heteroatoms in the spiro centre can be an effective means of modifying the structure and obtaining new classes of photochromic SPs. Therefore in this section we shall examine the structure of SPs containing different heteroatoms in the spiro centre.

### 1. Structural features of indoline spirothiopyrans containing S and N heteroatoms in the spiro centre

Aldoshin et al.[77] carried out an X-ray diffraction study on 1′phenyl-3,3′-dimethyl-6-nitrospiro(indoline-2,2′-[2*H*-1]benzothiopyran) [SP(XII)] (Fig. 10).

Replacement of the oxygen atom in SP(IV) by a sulphur atom [SP(XII)] resulted in a reduction of photoconversion activity of the latter at 293 K ($\varphi \approx 0.1$) compared to that of SP(IV) ($\varphi = 0.76$)[44] in solutions of dimethylformamide and toluene. At 77 K in polystyrene and polymethyl methacrylate the photochemical activity of SP(XII) increases ($\varphi = 0.7$) whereas the photochemical activity of SP(IV) ($\varphi = 0.1$) decreases markedly under the same conditions.

This type of behavioural pattern of SP(XII) compared to SP(IV) becomes clear if its structure is analysed. In SP(XII), as in other photochemically active SPs, the C(22′)–S bond [1.866(2) Å] which is cleaved on photoexcitation is considerably longer than the corresponding bonds in six-membered heterocycles (1.80–1.83 Å).[16,17] The C(22′)–N(1′) bond [1.484(3) Å] in SP(XII), in contrast to that in SP(IV), is not shortened, and its length corresponds to the lengths of normal $C_{sp^3}-N$ bonds (1.47–1.48 Å) in five-membered heterocycles.[15] Therefore elongation of the $C_{spiro}-S$ bond in SP(XII) cannot be accounted for using the concept of $n-\sigma^*$ interactions in the spiro centre proposed for SPs.

Replacement of the oxygen atom at the spiro centre by a sulphur atom, which has an ionisation potential similar to that of the nitrogen atom,[78] evidently levels out the donating capacities of the UEP of the S and N atoms. Furthermore, the C(22′)SC(8*a*) bond

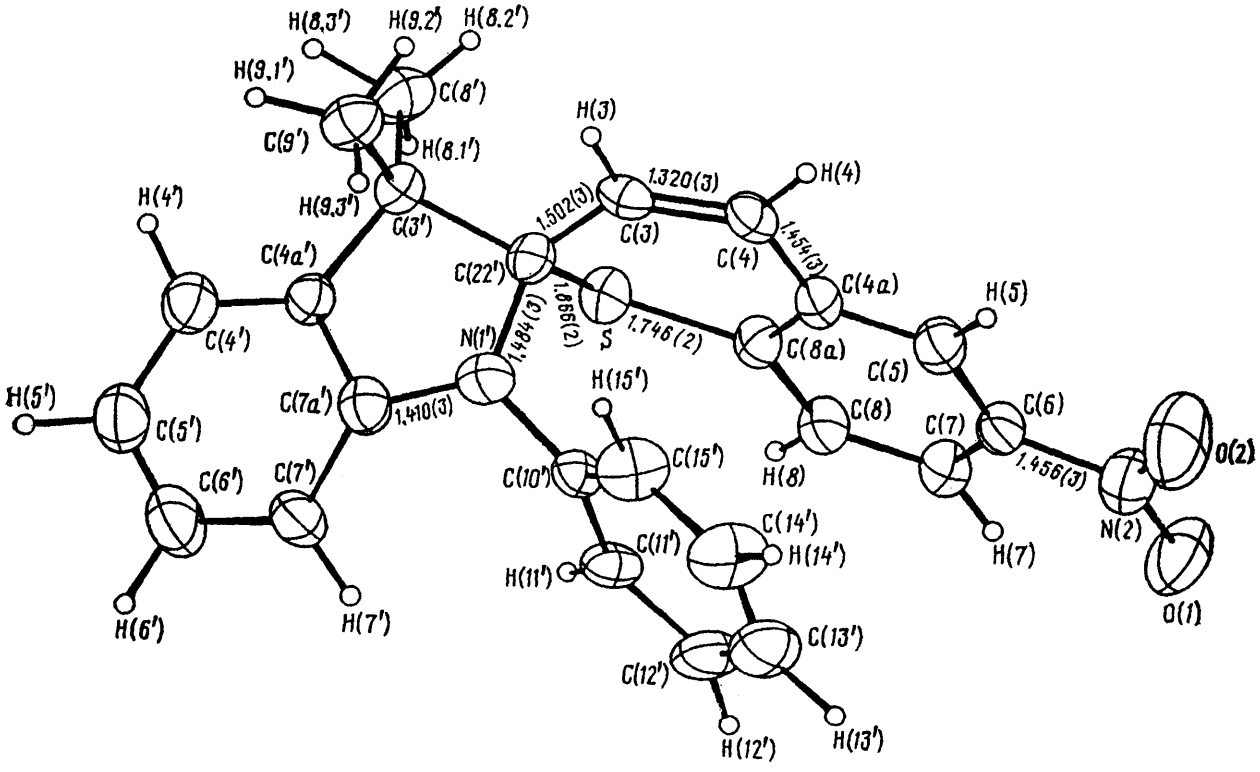



**Figure 10.** General shape of spirothiopyran SP(XII).

angle in SP(XII) proved to be 101.9°, whereas in SP(I)–SP(IX) the C(22′)O(1)C(8*a*) angles are in the range 120–124°. These findings could suggest that hybridisation of the S atom in SP(XII) is close to $sp^3$ while the O atom in SP(I)–SP(XI) is close to $sp^2$-hybridisation. With $sp^3$-hybridisation of the heteroatom there is a substantial decrease in conjugation of its UEP with the π-system of the benzene residue, hence the polarity of the C(22′)–S bond in SP(XII) will be much less than the polarity of the C(22′)–O bond in SP(I)–SP(XI) and the $n$[N(1′)]–σ*[C(22′)–S] interaction in SP(XII) will be weaker than the $n$[N(1′)]–σ*[C(22′)–O] interaction in SP(I)–SP(XI). Elongation of the C(22′)–S bond compared to the C(22′)–O bond in SP(I)–SP(XI) and the resulting withdrawal of the UEP of the S atom from the σ*-orbital of the C(22′)–N(1′) bond also reduces the $n$(S)–σ*[C(22′)–N(1′)] interaction, so in SP(XII) these $n$–σ* interactions are evidently small and balance each other.

The elongation of the C(22′)–S bond to 1.866(2) Å in SP(XII) has been attributed[77] to steric interactions between the *gem*-methyl groups and the heteroatom of the thiopyran ring. These interactions give rise to distortion of the indoline residue and its inflection along the line of C(3′)...N(1′) in the closed forms SP(I)–SP(XI), while in SP(XII), which contains the more bulky S atom compared to an O atom, the $C_{spiro}$–S bond is further elongated.

Because of the $sp^3$-hybridisation of the S atom and the weak overlap of its UEP with the π-system of the benzene ring, no significant positive charge develops on the S atom[18,56] during photoexcitation of the lowest electronic levels of the thiopyran residue in the SP(XII) molecule. Therefore, in contrast to SP(I)–SP(XI), in SP(XII) and in the excited state the $n$–σ* interactions will have no substantial effect on the length of the $C_{spiro}$–S bond and its cleavage. For this reason the mechanism of α-cleavage of this bond proves ineffective for SP(XII).[47] The observed photochemical properties of SP(XII) are evidently related to a vibrational mechanism for cleavage of the $C_{spiro}$–S bond, in which the electron excitation energy will be unequally converted into vibration energy of the weakest individual bonds.[48] In a spirothiopyran this is the $C_{spiro}$–S bond, whose vibrations should be excited more than the others. When there is steric hindrance between the S and C(8′) atoms, this results in cleavage of the $C_{spiro}$–S bond. Support for the decisive role of a vibrational mechanism of bond cleavage in spirothiopyrans is provided by the absence of any noticeable electronic effect from the 6-$NO_2$ group on their photochemical properties, in contrast to the SPs described by Betelson.[2]

Vibrational cleavage of the less polar $C_{spiro}$–S bond compared to $C_{spiro}$–O in spirothiopyrans can occur homolytically rather than heterolytically as in SP(I)–SP(IX). In contrast to SP(I)–SP(XI), the coloured form of SP(XII) is evidently not the most stable zwitterion structure but is only its thermodynamically unstable, intermediate isomer X.

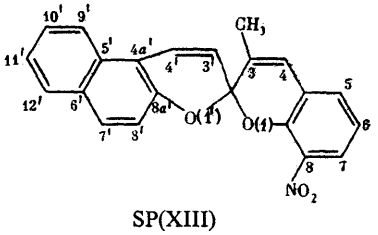
$$(A) \xrightarrow{h\nu} (A^*) \xrightarrow{\varphi_{breaking}} (X) \xrightarrow{\varphi_{colour}} (B)$$

When the temperature is lowered to 77 K this isomer (X) is stabilised and the quantum yield of the reaction increases. At 293 K in solution the reverse dark reaction (X)→(A) is efficient, and the quantum yield of reaction is low, although according to the results of flash photolysis the short-lived coloured form is formed in solution (in small quantities) even at 293 K.

## 2. Structure of "symmetrical" spiropyrans consisting of two benzopyran residues

It was demonstrated in IV.1 that the efficiency of orbital hyperconjugation in the spiro centre, which affects the photochemical properties of SPs to a considerable extent, depends both on the geometric configuration of the UEP of the heteroatom and the adjacent bonds and on the electronic properties of the heteroatoms. Since "symmetrical" spiropyrans contain the same heteroatoms in the spiro centre, their electronic properties and the efficiency of $n$–σ* interactions will mainly depend on the electronic state of the heteroatoms as determined by the nature and position of substituents in the benzopyran residue.

An X-ray study of SP(XIII) (Fig. 11) has been carried out.[79]



SP(XIII)

The orientation of the π-UEP of the O(1) and O(1′) atoms relative to the adjacent C(22′)–O(1′) and C(22′)–O(1) bonds in SP(XIII) is the same, with angles of 159.2 and 161.4° being formed respectively. Nevertheless, the bond lengths of C(22′)–O(1) [1.459(1) Å] and C(22′)–O(1′) [1.434(2) Å] in the spiro centre of SP(XIII) proved to be different. Introduction of the electron-withdrawing $NO_2$ group into the 8-position of SP(XIII) leads to a contraction of the O(1)–C(8*a*) bond to 1.358(2) Å, which, as in SP(II) and SP(III) where the lengths of these bonds are 1.356(3) Å, suggests that there is an increase in conjugation of the π-UEP of the O(1) atom with the π-system of the benzene ring.

Annelation of an additional benzene ring at the 5′, 6′-position of the benzopyran residue results in an elongation of the corresponding O(1′)–C(8*a*′) bond to 1.377 Å, which, as in SP(VII) where the length of this bond is 1.372(3) Å, suggests that the conjugation of the π-UEP of the O(1′) atom with the π-system of the naphthalene ring is weakened. With this type of structure of the spiro centre of SP(XIII), the C(22′)–O(1) bond will be more polar and the π-UEP of the O(1′) atom will be more active, so that in the spiro centre the $n$[O(1′)]–σ*[C(22′)–O(1)] interactions, which lead to an elongation of the C(22′)–O(1) bond, will predominate. In this case the C(22′)–O(1′) bond proves to be only slightly longer than the normal value of 1.41–1.43 Å.[15–17]

The C(22′)–O(1) bond is elongated in SP(XIII) less than in the correspondig indoline spiropyrans SP(I)–SP(IV) and its length matches the length of the $C_{spiro}$–O bond [1.452(2) Å] in SP(V), in which the activity of the UEP of the N(1′) atom is less than in SP(I)–SP(IV). These results suggest that the efficiency of the resulting $n$–σ* interactions in a spiro centre containing two heteroatoms that are both O, despite their different electronic state, is less than in a spiro centre containing O and N atoms. Nevertheless, it opens up the possibility for developing new classes of photochromic SPs containing the same heteroatoms in the spiro centre but in different electronic states. In this case the structure and hence the photochemical properties of such SPs can be regulated by changing the electronic environment of the heteroatoms.

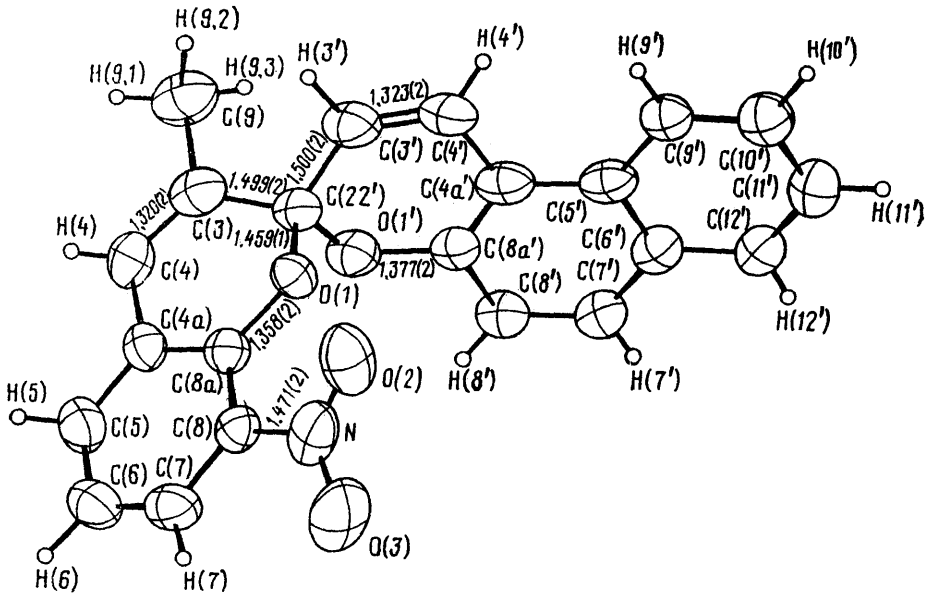
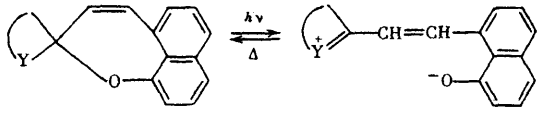



**Figure 11.** General shape of the "symmetrical" SP(XIII).

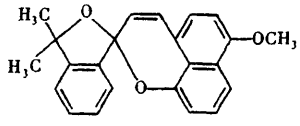
### 3. Structure of the first example of a spiro-2*H*-naphtho-[1,8-*bc*]oxepin

In accordance with ideas based on quantum-chemical calculations,[68] a long-wavelength band (1500–2000 nm) would be expected to occur in the electronic spectra of zwitterions X.




(Y) (X)

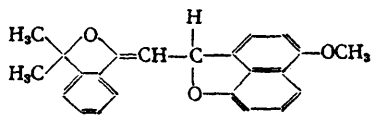
However, for a long time it was not possible to obtain spiropyrans (Y) containing seven-membered rings.[80] In 1986 a spiropyran of this type—SP(XIV)—was obtained for the first time and its structure studied.[81]




SP(XIV)

The general form of SP(XIV) is shown in Fig. 12. The dihedral angle between the O(1)C(22')C(3) and O(2)C(22')C(16) planes is equal to 89.9°. The oxaindan part of the molecule has an envelope configuration with a 25.0° angle of twist from the line of C(22')...C(13). Because of the rigid tetrahedral configuration of the C(22') spiroatom, the seven-membered oxepin ring is severely strained and has a distorted conformation. This type of conformation of the seven-membered ring leads to a change in the relative configuration of the π-UEP of the O(1) atom and the adjacent C(22')–O(2) bond in the spiro centre. While the π-UEP of the O(2) atom is oriented at an angle of 165.0° to the adjacent C(22')–O(1) bond and this proves to be favourable for $n^{\pi}$[O(2)]–σ*[C(22')–O(1)] orbital interaction, the π-UEP of the O(1) atom is oriented at an angle of 110.4° to the adjacent C(22')–O(2) bond, which actually suggests that there is no reverse $n^{\pi}$[O(1)]–σ*[C(22')–O(2)] interaction. Therefore, in SP(XIV) the efficiency of the interaction between the π-UEP of the O(2) atom and the σ*-orbital of the C(22')–O(1) bond increases, which results in a contraction of the C(22')–O(2) bond to 1.409 Å and an elongation of the C(22)–O(1) bond to 1.455(3) Å.

In the seven-membered ring, with an angle of deviation from the O(1)–C(8*a*) bond of 63.3°, the π-UEP of the O(1) atom is directed inside the heterocycle towards the C(4) atom, although it deviates from the line of O(1)...C(4) by approximately 38°. Taking into account the short interatomic distance of O(1)...C(4) (2.88 Å) and distortion of the C(3)C(4)C(4*a*) bond angle to 130.3°, it may be assumed that there is an attractive secondary interaction between the O(1) atom and C(4) atom destabilising the heterocycle.[79] It would appear that these structural features of SP(XIV) are responsible for its rapid conversion in solution on irradiation with a mercury lamp (313 nm filter) compound (P) rather than compound (Y).[81]




(P)

## V. Structure, photo- and thermo-chromic properties of 2-oxaindan spiropyrans with polycondensed chromene residues

### 1. Structure of 2-oxaindan spiropyrans

It has already been mentioned, that the significant improvement in performance of SPs, and primarily the increase in stability of their

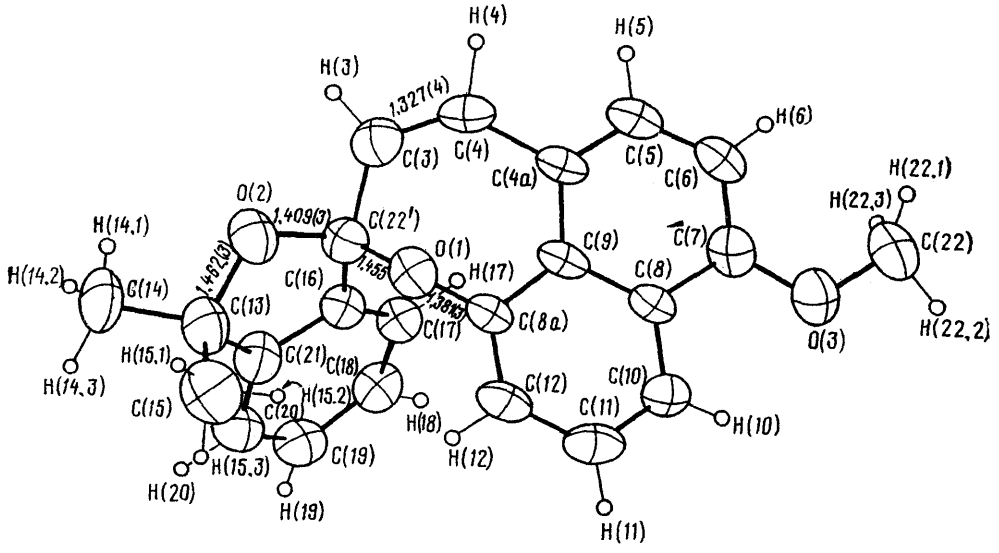
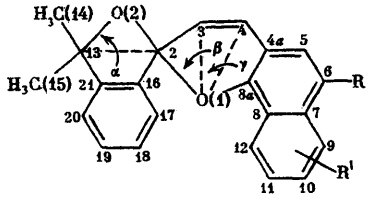



**Figure 12.** General shape of spiro-2*H*-naphtho[1,8-*bc*]oxepin.

photoinduced forms may be achieved by the introduction of strong electron-acceptor substituents into the benzopyran residue. However, such substituents considerably reduce the photostability of SPs,[63] thus severely limiting in scope the practical application of materials based on them.[83] Hence a study was made of the 2-oxaindan spiropyrans SP(XV)–SP(XVIII), whose photocoloured forms are stabilised through increasing the size of the π-system of the quinoid residue by means of annelation of additional arene rings to the 7,8-bond of the benzopyran part of the molecule.[84]




SP(XV)–(XVIII)

(XV): R = H, R' = H;
(XVI): R = H, R' = 10,11-benzo
(XVII): R = Br, R' = H;
(XVIII): R = $NO_2$, R' = H.

An X-ray study of SP(XV)–SP(XVIII) showed that these compounds have the same conformation. The naphtho(anthraceno)-pyran and oxaindan parts of the molecule are positioned approximately at right angles to each other. The dihedral angle between the O(1)C(2)C(3) and O(2)C(2)O(16) planes is 93–95°. In all of the SPs studied the pyran and oxaindan residues are nonplanar. The first has a folded conformation with dihedral angles along the lines of O(1)...C(3) and O(1)...C(4) of 21.4 to 28.6° and 10.2 to 13.3° respectively, while the second has the conformation of an envelope with an angle of inflection along the line of C(2)...C(13) equal to 15.5–17.3°. The structure of one of the spiropyrans studied is shown in Fig. 13 and their main structural parameters are given in Table 2.

In the same way as in the previously studied indoline SPs, the $C_{spiro}$–O(1) bond is elongated in SP(XV)–SP(XVIII). However, while in SP(I)–SP(XI) the lengths of these bonds are in the range 1.460(2)–1.496(4) Å, in SP(XV)–SP(XVIII) these bond lengths are in the range 1.444(1)–1.465(2) Å. At the same time in the unsubstituted SP(XV) this bond [1.444(1) Å] is the least elongated in comparison with the lengths of normal C–O bonds (1.41–1.43 Å) in six-membered heterocycles. Annelation of an additional benzene ring to SP(XVI) has virtually no effect on the length of the C(22')–O(1) bond [1.447(1) Å]. The introduction of electron-acceptor substituents into the 6-position of the naphthopyran residue—Br in SP(XVII) and particularly the $NO_2$ group in SP(XVIII)—results in this bond being extended to 1.455(3) Å and 1.465(2) Å respectively (Table 2). In the oxaindan residue of SP(XV)–SP(XVIII) the C(22')–O(2) bond was shortened to 1.417(1)–1.407(3) Å compared to the normal length of a C–O bond in five-membered heterocycles (1.426 Å).[85] As the C(22')–O(1) bond increases in length, the C(22')–O(2) bond has a tendency to contract, whereas the O(2)–C(13) bond in these SPs remains elongated (see Table 2).

In the spiro centre of SP(XV)–SP(XVIII) there are two heteroatoms which are both oxygen. In those systems in which two oxygen atoms are bound to an anomeric carbon atom, the efficiency of the $n-\sigma^*$ interaction will primarily depend on the geometric configuration of the UEP of the oxygen atoms and the electronic state of these atoms.

The compounds studied [SP(XV)–SP(XVIII)] have the same conformation with similar values of angles τ and Δ (see Table 2). However, the electronic states of the O(1) and O(2) atoms in them differ substantially. The O(1) atom is bound to the aromatic π-system of the naphthalene or anthracene residues, the bond lengths of O(1)–C(8*a*) [1.354(2)–1.377(1) Å] are similar to the lengths of the corresponding bonds in α-naphthol (1.37 Å)[86] and suggest that there is significant conjugation of the UEP of the O(1) atom with the neighbouring π-system. This conjugation will increase the polarity of the C(22')–O(1) bond relative to the polarity of the C(22')–O(2)

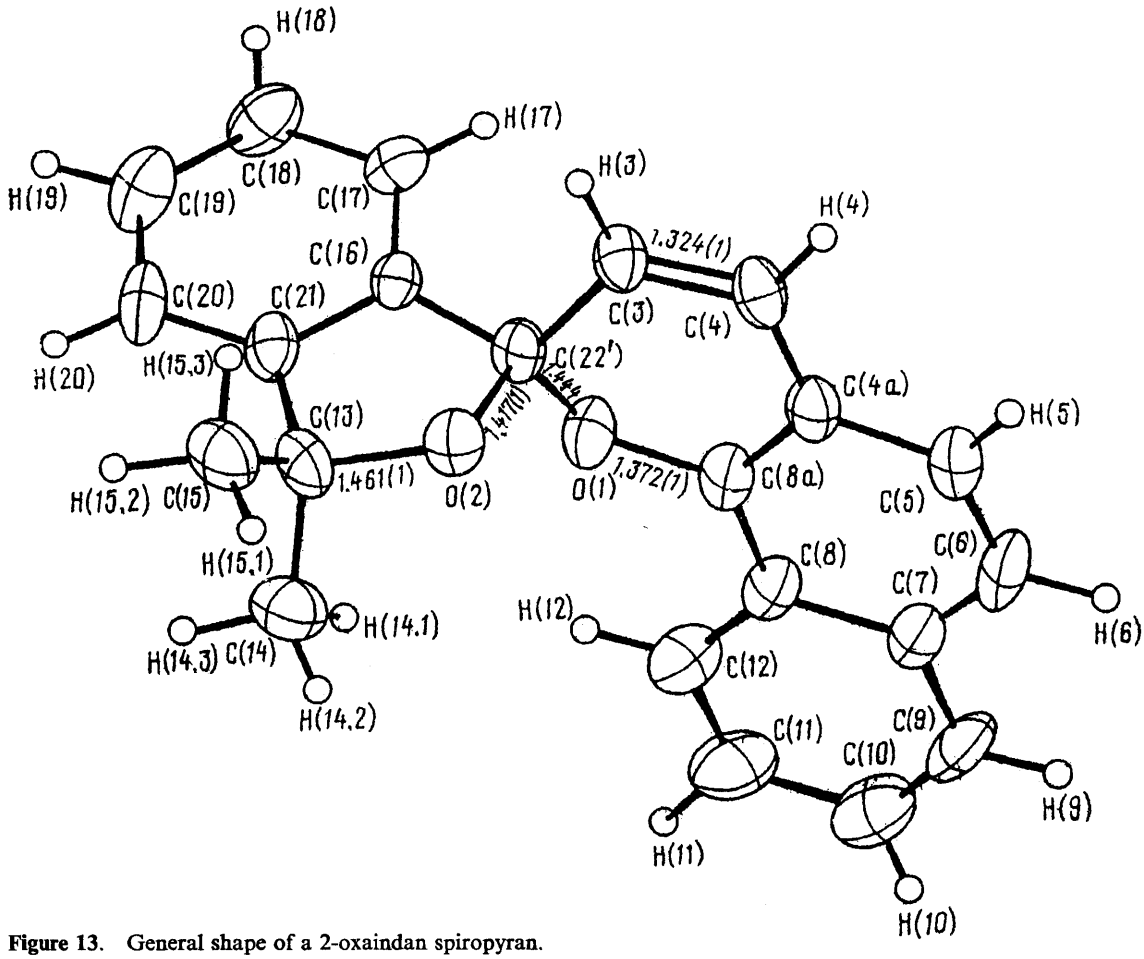
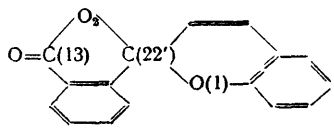


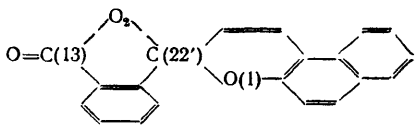

**Figure 13.** General shape of a 2-oxaindan spiropyran.

bond and decrease the activity of the UEP of the O(1) atom compared to the activity of the UEP of the O(2) atom. Therefore in these spiropyrans the $n[O(2)]-\sigma^*[C(22')-O(1)]$ interactions should be stronger than the $n[O(1)-\sigma^*[C(22')-O(2)]$ interactions and may be responsible for the elongation of the C(22')–O(1) bonds and contraction of the C(22')–O(2) bonds found in these SPs. In the same way as in SP(XIII), these interactions are weaker in SP(XV)–SP(XVIII) than in SP(I)–SP(XI), which contain different heteroatoms (O and N) in the spiro centre, and the lesser elongation of the $C_{spiro}-O(1)$ bond in SP(XV)–SP(XVIII) is related to this.

In SP(XIX) and SP(XX), which were studied previously,[87,88]




СП (XIX)

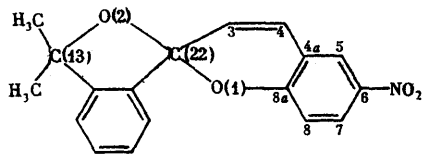



SP(XX)

the π-UEP of the O(2) atom are conjugated with the π-bond of the neighbouring carbonyl group, as is indicated by the length of the O(2)–C(13) bond (1.35–1.37 Å), therefore the $n-\sigma^*$ interactions of the O(1) and O(2) atoms in these molecules are small and the lengths of the C(22')–O(1) bonds (1.42 and 1.399 Å) are of normal magnitude.

Introduction of the electron-acceptor substituents Br and $NO_2$ into the 6-position of the naphthalene residue gives rise to an elongation of the C(22')–O(1) bond, which increases as the electron-acceptor properties of the substituents increase [1.455(3) Å in SP(XVII) and 1.465(2) Å in SP(XVIII)]. At the same time there is a contraction of the O(1)–C(8*a*) bond to 1.366(3) Å in SP(XVII) and 1.354(2) Å in SP(XVIII) compared to the length of this bond in SP(XV) and SP(XVI), in which it amounts to 1.372(1) and 1.377(1) Å respectively. This suggests that there is an increase in conjugation of the UEP of the O(1) atom with the π-system of the naphthalene residue on introduction of electron-acceptor substituents, so the elongation of the C(22')–O(1) bond in SP(XVII) and SP(XVIII) is related to the strengthening of the $n[O(2)]-\sigma^*[C(22')-O(1)]$ interaction in these compounds, which also results in a contraction of the C(22')–O(2) bond in SP(XVII) and SP(XVIII) to 1.413(3) and 1.407(3) Å respectively in comparison with the length of this bond in SP(XV) and SP(XVI), where it is equal to 1.417(1) Å.

It is interesting that in the analogous benzopyran SP(XXI)[89]



SP(XXI)

with an $NO_2$ group at the *para*-position relative to the O(1) atom, the C(22′)–O(1) bond is less elongated (1.452 Å) and the O(1)–C(8*a*) bond (average 1.366 Å) is less contracted than in SP(XVIII). These results suggest that the electron-acceptor effect of the $NO_2$ group on the O atom is more marked in a naphthalene residue than in a benzene residue.

In order to confirm the electronic rather than steric nature of the elongation of the C(22′)–O(1) and O(2)–C(13) bonds and contraction of the C(22′)–O(2) bond, conformational calculations on a model SP were carried out.[84] After minimisation of the energy of strain in the molecule the length of the C(22′)–O(1) bond in it proved to be of normal magnitude (1.422 Å) while the lengths of the C(22′)–O(2) (1.434 Å) and O(2)–C(13) (1.439 Å) bonds were the same and close to normal values.

## 2. Thermal valence isomerisation of SPs

Spiropyrans SP(XV)–SP(XVIII) have distinct thermochromic properties in solutions of polar and nonpolar solvents. From the values calculated from dynamic NMR data for the free energy of activation of thermally induced valence isomerisation of SP(XV)–SP(XVIII)[84] and certain other SPs that were studied[90] and comparing them with the lengths of the $C_{spiro}$–O(1) bonds in these compounds the following conclusions could be drawn:

1) a variation in structure of the heterene and pyran residues of the SP molecule has no substantial effect on the free energy of activation of the SP;

2) there is no correlation between the $C_{spiro}$–O(1) bond length in SP(XV)–SP(XVIII) and the free energy of activation.

The lack of this correlation, which was also predicted from quantum-chemical calculations,[91] evidently arises because the $C_{spiro}$–O(1) bond length in the ground transition state (the region of thermochromic cleavage), as was demonstrated by Simkin et al.,[46] is almost constant (~1.95 Å) and differs considerably from the length of this bond in the initial state. Therefore the small changes in length of this bond which occur as a result of structural factors do not have any substantial effect on the energy of activation for cleavage of this bond.

## 3. Photochromism of 2-oxaindan spiropyrans

The photochromic properties of SP(XV)–SP(XVIII) in liquid and solid solutions are exhibited over a wide temperature range (from 77 to 273 K). By using the technique of flash photolysis it is possible to observe reversible photocoloration even at 20 °C. In order to determine the relative photochemical activity of SP(XV)–SP(XVIII), Aldoshin et al.[84] studied the ease of photocoloration ("colorability") of these compounds. The results of a study of the "colorability" of SP(XV)–SP(XVIII) compared to the $C_{spiro}$–O(1) bond length are given in Table 3. It is clear from Table 3 that these values vary in a similar manner, the highest photochemical activity being exhibited by SP(XVIII) with the most elongated bond. This apparently occurs because the $C_{spiro}$–O(1) bond length in the excited transition state is much shorter than that in the ground transition state. Consequently, the reaction barriers of SPs in the excited states are markedly reduced. Therefore the photochemical activity for coloration of an SP proves to be sensitive to even small changes in the $C_{spiro}$–O(1) bond length in the ground state, which result from the influence of different structural factors in SP molecules.

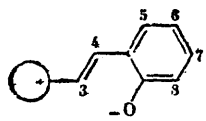
Unfortunately, it was not possible to carry out an X-ray diffraction study of the resulting open coloured form of 2-oxaindan SPs, and the structure of the coloured products can only be assessed

**Table 2.** Main structural parameters of 2-oxaindan spiropyrans studied.

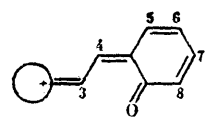
| SP | Substituents | | Bond lengths*1, Å | | | | Angles, deg | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | R | R′ | C(22′)–O(1) | C(22′)–O(2) | O(1)–C(8*a*) | O(2)–C(13) | α | β | γ | τ*2 | Δ*3 |
| (XV) | H | — | 1.444 | 1.417 | 1.372 | 1.461 | 17.3 | 21.4 | 10.2 | 159.6 | 159.8 |
| (XVI) | H | 10,11-benzo | 1.447 | 1.417 | 1.377 | 1.461 | 16.3 | 22.2 | 10.3 | 158.4 | 159.8 |
| (XVII) | Br | — | 1.455 | 1.413 | 1.366 | 1.457 | 16.1 | 26.8 | 13.3 | 158.9 | 155.7 |
| (XVIII) | $NO_2$ | — | 1.465 | 1.407 | 1.354 | 1.458 | 15.5 | 28.6 | 11.4 | 160.1 | 155.5 |

*1 Errors in determining the bond lengths constitute 0.001–0.003 Å.
*2 Angle between the π-UEP of the O(2) atom and the C(2)–O(1) bond.
*3 Angle between the π-UEP of the O(1) atom and the C(2)–O(2) bond.

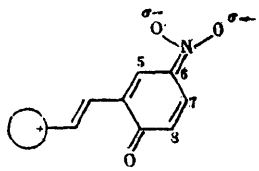
from indirect evidence. The X-ray diffraction study of the open forms of indoline SPs showed that they have the zwitterion structure (A) with an appreciable contribution from the canonical structure (C).



(A)



(B)



(C)

However, in contrast to indoline SPs, SP(XV)–SP(XVIII) and SP(XXII) reveal bathochromic shifts of the photoinduced absorption bands on increasing the polarity of the medium, regardless of the nature of the substituents.[92] These findings suggest that the quinoid structure makes a decisive contribution to the structure of the coloured form. It was suggested above (see Section III) that annelation of additional benzene rings to the phenolate residue at the 5,6- and 7,8-positions should stabilise the quinoid structure (C) while annelation at the 6,7-position would destabilise this structure. The increase in the lifetime of SPs on going from SP(XV) to SP(XVI) supports this view and is an indication of the important role of this method for stabilising an open SP form.

**Table 3.** "Colorability" of spiropyrans SP(XV)–SP(XVIII) and the $C_{spiro}$–O(1) bond length.

| SP | "Colorability"* | $C_{spiro}$–O(1) bond length, Å |
|---|---|---|
| (XV) | 0.22 | 1.444 (1) |
| (XVI) | 0.32 | 1.447 (1) |
| (XVII) | 0.36 | 1.455 (3) |
| (XVIII) | 0.46 | 1.465 (2) |

*The colorability is determined from the initial absorption $A_0$ of solutions of photochromic SPs under exactly the same irradiation conditions (temperature, SP concentration, length and volume of cell, irradiation intensity). Indoline SP(IV) is most frequently used as the reference compound, for which $A_0 = 1$.

The introduction of electron-acceptor substituents into the naphthopyran residue of these SPs also increases the lifetime of the open forms. The nitro group with its strong electron-acceptor properties has the greatest stabilising effect. As in indoline SPs, the stabilisation of the coloured products of SP(XVIII) with electron-acceptor substituents appears to be related to the increased contribution of the resonance form (C) to their structure.

An additional factor for stabilisation of the coloured forms of these SPs may also be the formation of different intermolecular associates, as takes place for the open merocyanine forms of indoline SPs. At the same time, the more extended the conjugated π-system of the SP, the more stable (through π–π interaction) may be the associates.

## VI. Conclusion

Thus, as a result of analysing the structure of different classes of spiropyrans, the structural factors which affect their photochemical properties have been established.

It has been shown that the photochemical properties of spiropyrans in many respects is due to the fact that even in the ground state the $C_{spiro}$–O bond, which undergoes cleavage on photoexcitation, is weakened and elongated through specific $n-\sigma^*$ orbital interactions, which on going to excited photochemically active states are even further strengthened, thus assisting the cleavage of this bond. It has been established that the photochemical activity of spiropyrans depends on the length of the $C_{spiro}$–O bond in the ground state and the nature of the change in length of this bond in the excited state. At the same time the photochemical activity of spiropyrans proves to be more sensitive to the length of the $C_{spiro}$–O bond being cleaved than does the thermochromic activity.

A study has been made of the effect of different substituents in the benzopyran and indoline residues, the nature, electronic state, and relative orientation of the heteroatoms in the spiro centre, and the size of the heterocycles on the efficiency of $n-\sigma^*$ interactions in spiropyran molecules and on the length of the $C_{spiro}$–O bond in the ground state.

The structure of the photoconversion products of spiropyrans and the stereochemical factors responsible for stabilising it have been examined. For the coloured photoforms of spiropyrans in the crystalline state the formation of different strong intermolecular associates and solvates has been detected, which to a considerable degree govern the stabilisation of the complex resonance structure of spiropyrans not only in the crystalline state but also in solution, which is a more probable cause of the complex absorption spectrum of these compounds than the proposed existence of various isomers.

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