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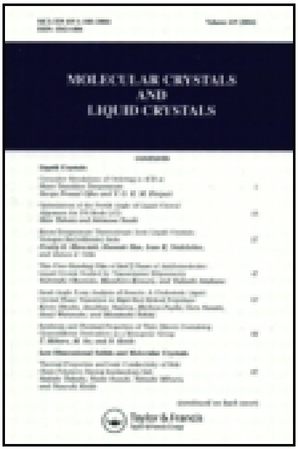

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Spiropyrans: Structural Features and Photochemical Properties

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SPIROPYRANS: STRUCTURAL FEATURES AND PHOTOCHEMICAL PROPERTIES

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Abstract It has been shown, that in the ground state the C_{spiro}-O bond, which is broken upon photoexcitation, is weakened and elongated because of specific orbital $n\text{-}s^*$ interactions. They become stronger in excited photochemically active state,thus facilitating the rupture of this bond.

The nature of products of spiropyran photoconversion and stereochemical factors of its stabilization have been investigated.

INTRODUCTION

Photochromic materials, based on various classes of spiropyrans (SP), are now widely used in different fields of science and technology. One of the main applications of these materials is in the field of light filters that regulate light fluxes, of photochromic organic media for recording and processing optical information. Systematical X-ray investigation of these compounds is important for understanding structural mechanism of spiropyran photochromic transformations and for determining the relation between their structure and photochemical properties.

At present, practically useful SP are obtained via structural modifying these systems. This improves the working characteristics, i.e., the quantum yield of photoconversion, the life time of the open form, and a high number of conversion cycles without visible decomposition of SP.

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STRUCTURE OF SP OF INDOLINE CLASS. INFLUENCE OF STRUCTURE ON PHOTOCHEMICAL PROPERTIES

Indoline and benzopyran fragments in all investigated SP of indoline class (SP I)[1] are located approximately perpendicular to each other and are nonplanar. The C_{spiro}-O bond 1.460(3)-1.496(4) Å is essentially elongated in comparison

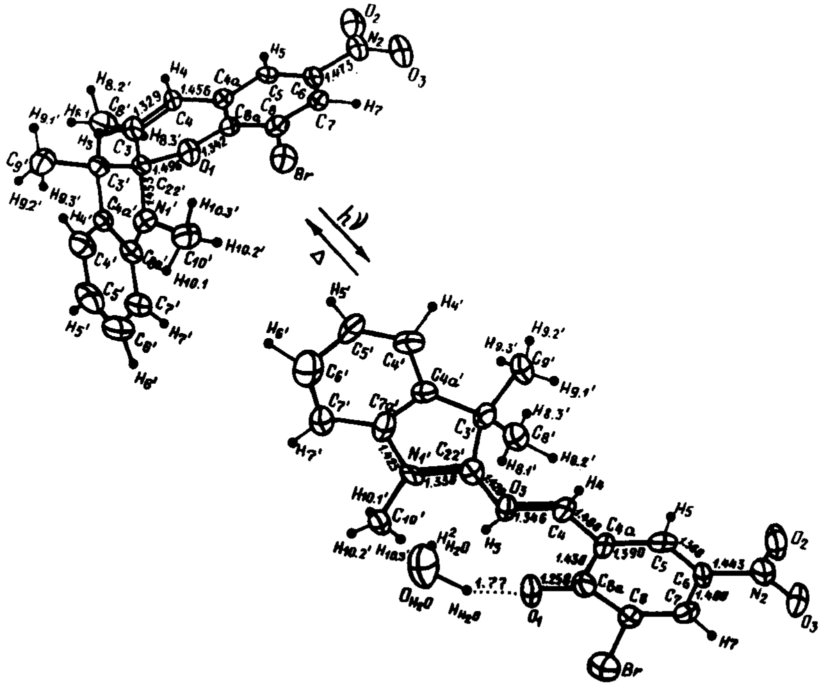

FIGURE 1 Structure of closed and open forms of the one of SP I

with the usual C-O bonds in the six-membered oxygen-containing heterocycles. The latter are equal to 1.41-1.43 (1) Å. That is, the C_{spiro}-O bond is the most weakened one, and the rupture of this bond may be determined, to some extent, by this structural factor.

Transition to an open form is accompanied by entire redistribution of the bond lengths, that is typical for the merocyanine (MC) chromofore. The MC open forms have the zwitter-ionic A structure with some contribution of the B and C resonance structures[2]. Some MC isomers are additionally stabilized in the crystals by hydrogen bonds with crystallization water molecules.

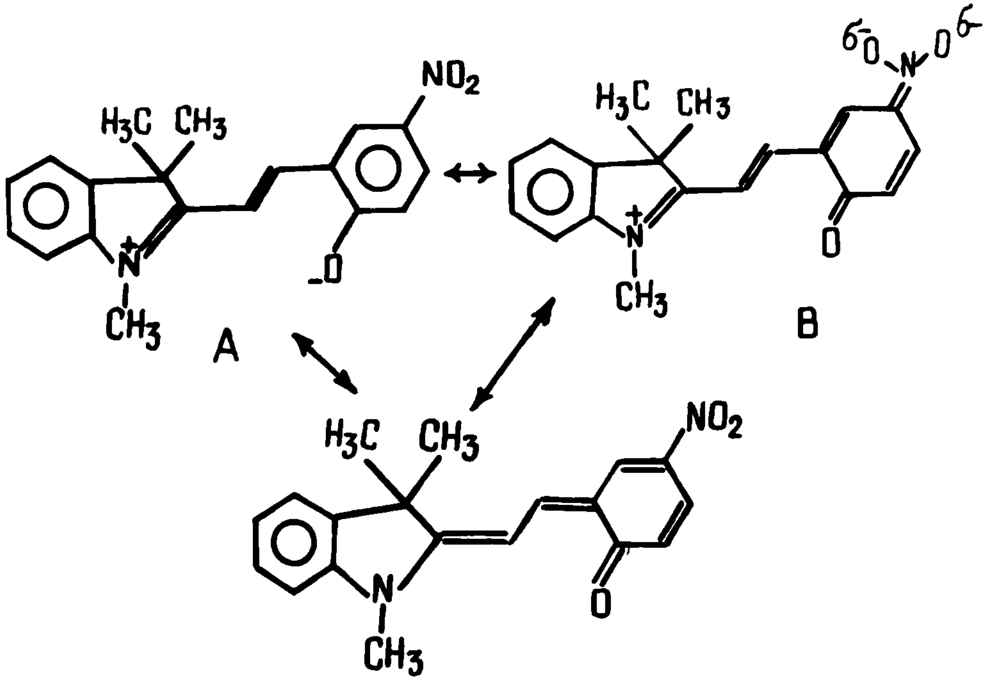

FIGURE 2 Structure of MC open form

In this connection, much attention is paid to the following points: (1) what structural factors cause elongation of the C_{spiro}-O bond; (2) is there a correlation between the length of this bond, its stability and the SP photochemical activity; (3) detailed investigation of the structural factors stabilizing the photoform.

Specific orbital n-σ^* Interactions in the Indoline SP I Molecules

1. Specific features of the SP molecule structure in the ground electron state.

The SP structure leads to the specific orbital n-σ^* interactions of the lone electron pairs (n) of heteroatoms

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O and N_1' with σ^*-unoccupied orbitals of the neighbour polar bonds that are localized mainly on the positive carbon atom of the C_{spiro}-junction. The oxygen atom is more electronegative than the nitrogen atom, and energy of its lone

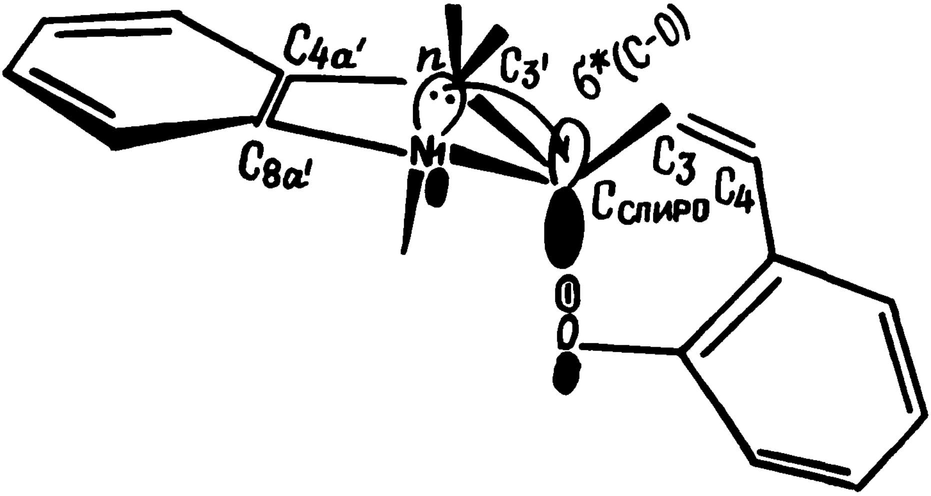

Figure 3 Specific electron interactions in SP

electron pair is lower than that for the nitrogen atom. Therefore, energy of the unoccupied orbital of the C_{spiro}-O bond must be lower than analogous value for the C_{spiro}-N bond, and energy of the nonbonded nitrogen atom orbital will be higher than energy of the nonbonded oxygen atom orbital. Hence, interactions of the n- electrons of the N_1' atom with the σ^*-orbital of the C_{spiro}-O bond must be the most important ones in spiro-junction. In conclusion, the specific orbital interactions in photochromic indoline SP result in the weakening and elongation of the C_{spiro} - O bond in ground state, which is broken upon photoexcitation.

Character of the Structural Changes in the SP Molecule upon Photoexcitation.

Excitation of the SP I molecule into photochemically active

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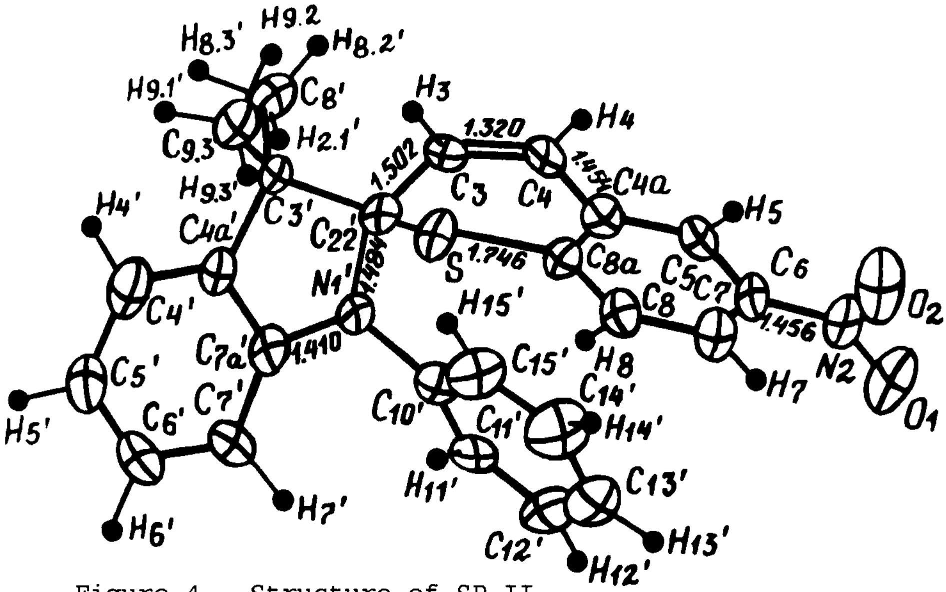

Figure 4 Structure of SP II

The Structure of "Symmetrical" SP, Containing (O,O)-Heteroatoms in the Spiro-centre.

There are two similar oxygen heteroatoms in the spiro-centre of these compounds. In such systems, effectivity of the n-σ^* interaction, in the first place, depends on the geometrical dislocation of oxygen atoms lone electron pair and the electron state of these atoms.

The investigated symmetrical SP III have similar conformation.

However, the electron state of O_1 and $O_{1'}$ differs considerably. Introduction of an electron-seeking nitrogroup into 8-position leads to the shortening of the O_1-C_{8a} bond to 1.358(2)Å. This testifies for the increase of conjugation of the O_1 π-lone electron pair with the π-system of the benzene ring.

Annelation of additional benzene nuclei into the 5'-6'-position of the benzopyran fragment leads to the elongation of the $O_{1'}$-$C_{8a'}$ bond up to 1.377(2)Å. This testifies for the weakening of conjugation of the $O_{1'}$ π-lone electron pair with the π-system of the naphthalene cycle. In this molecule, the $C_{22'}$-O_1 bond is more polar, and the $O_{1'}$ π-lone

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state by ultra-violet radiation (more than 300 nm) is due to the electron transitions of the πl-π^* type in the benzopyran part of SP without an electron-seeking substituent, and of the πl-$\pi^*\pi n^*$ type when such a substituent is present in the benzopyran fragment. These transitions are characterized by intramolecular charge transfer from the l-orbital of the oxygen atom O and the π-orbital of the C_3-C_4 bond onto the phenyl fragment and electron-seeking substituent. Such a transfer has to lead to the reduction of electron density on the oxygen atom O_1. The reduction will be compensated at the account of σ-electrons of the C_{spiro}-O bond causing its further polarization. Such redistribution of electron density leads to an increase of the n_{N_1} - σ^* (C_{spiro} - O) interaction in SP I molecules, a further shortening of the C_{spiro}-N_1' bond and a weakening and elongation of the C_{spiro} - O bond in the exccited state. Thus, the C_{spiro}-O bond rupture in the excited state can be due, to some extent, to the further weakening and elongation of this bond upon photo-excitation. It is connected with the influence of the same structural factors that cause elongation and weakening of this bond in the ground state. Therefore, elongation of the C_{spiro}-O bond in the ground state can be one of the criteria of photochemical activity of these compounds.

INFLUENCE OF THE HETEROATOM NATURE IN THE SPIRO-CENTRE OF SPIROPYRANS ON THEIR STRUCTURE AND PHOTOCHROMIC PROPERTIES

Specific Structural Features of Indoline Spiropyrans Containing (S,N)-heteroatoms in the Spiro-centre.

In SP II, $C_{22'}$-S bond (1.866(2)Å), which is broken upon photoexcitation, is considerably elongated because of steric interactions (not n-σ^* interactions). The length of the $C_{22'}$-$N_{1'}$ bond, 1.484(3) Å, is not shortened and coincides with the values of the C_{sp^3} - N bond lengths (1.47-1.48 Å) in five-membered heterocycles.

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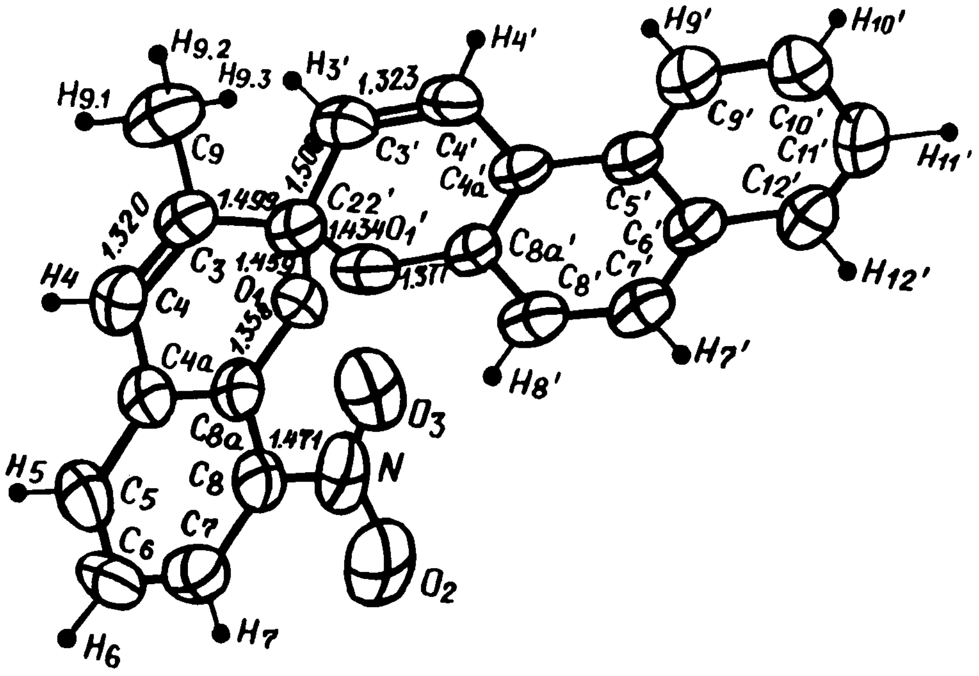

Figure 5 Structure of SP III

electron pair is more active. Therefore, $n_{O_{1'}}-\sigma^*$ $(C_{22'}-O_1)$ interactions lead to the elongation of the $C_{22'}-O_1$ bond. In these compounds, $C_{22'}-O_1$ (1.459(1)Å) and $C_{22'}-O_{1'}$ (1.434(2)Å) bond lengths in the spiro-centre appeared to be different.

In SP IV with five- and seven-membered heterocycles interaction of the O_2 atom π-lone electron pair with the σ^*-orbital of the $C_{22'}-O_1$ bond is effective. It leads to the shortening of the $C_{22'}-O_2$ bond and elongation of the $C_{22'}-O_1$ bond, which is broken upon photoexcitation.

In SP V, containing (2O,2C) spiro-centre, the electron state of the oxygen atoms is different, because the O_1 atom is connected with the aromatic π-system of naphthalene or anthracene fragments. The O_1-C_{Ph} bond lengths are equal to 1.354(2) - 1.377(1)Å. This testifies for considerable conjugation of the O_1 atom lone electron pair with the

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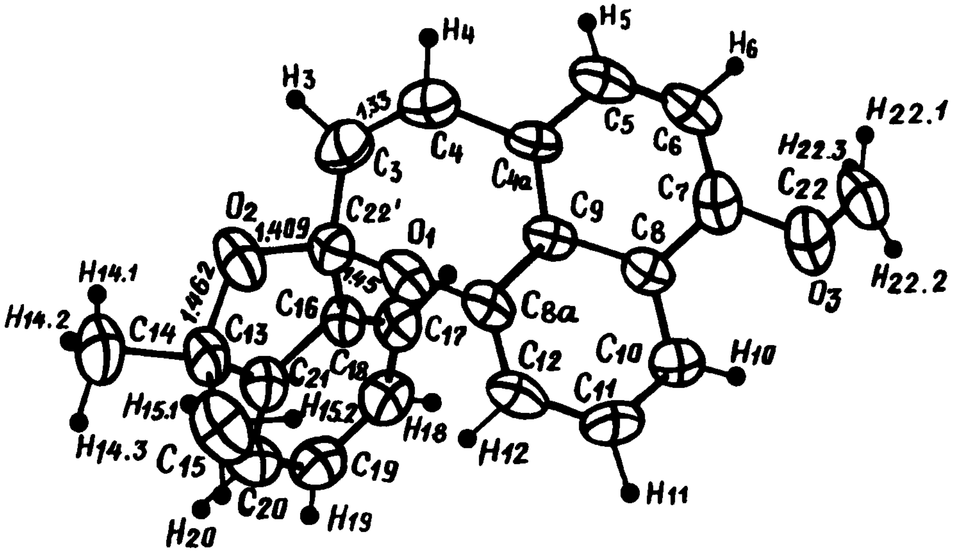

Figure 6 Structure of SP IV

neighbouring π-system. Such conjugation increases polarity of the $C_{22'}-O_1$ bond, as compared to $C_{22'}-O_2$, and decreases activity of the O_1 atom lone electron pair in comparison with the O_2 atom. In this SP, the $n_{O_2}-\sigma^*$ $(C_{22'}-O_1)$ interactions must be stronger than the $n_{O_1}-\sigma^*$ $(C_{22'}-O_2)$ ones, thus causing the elongation of the $C_{22'}-O_1$ bonds and the shortening of the $C_{22'}-O_2$ bonds.

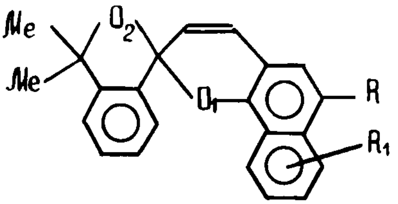

Figure 7 Structure of SP V

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