Dichroism of absorption and polarization of phosphorescence of molecules of the closed form of nitrobenzospirothiopyran

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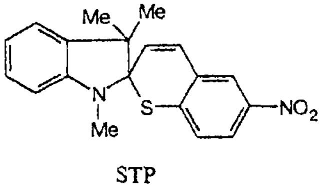
The spectral-polarization characteristics of absorption and phosphorescence of molecules of the initial form of nitro-substituted indolinospirobenzothiopyran were studied in oriented polyethylene films and in solutions with different polarity. An oscillator model of the electron transitions responsible for the formation of absorption and luminescence spectra was suggested. It was established that the principal differences in the spectral and photophysical properties of the compound studied and its oxygen-containing analog are associated with the fact that the electronegativity of the S atom is lower than that of the O atom.

Key words: spirobenzopyrans, phosphorescence, polarization, dichroism.

The 1,3,3-trimethyl-6′-nitrospiro(indoline-2,2′-[2*H*-1]benzothiopyran) (STP) molecule exhibits pronounced photochromic properties. When irradiated with UV light, for example, the STP molecule is transformed from the initial state **A** into the colored form **B**, which absorbs light intensely in the visible region of the spectrum. In studies of STP, the colored form **B** has recieved the most attention,[1—5] because this form is characterized by a substantially larger bathochromic shift of the maximum of the long-wavelength absorption than the oxygen-containing analog, namely, nitrospirobenzopyran (SBP). However, replacement of the O atom in the benzopyran fragment of the spiro compound should also affect the photophysical and photochemical properties of the initial form **A**, which, in turn, should be seen in a change in the characteristics of the luminescence spectrum compared to those of the SBP molecule. The absorption and luminescence spectra of nitro-substituted spiro compounds consist generally of structureless overlapping bands, which are difficult to analyze. Therefore, the results of studies of the anisotropy of light absorption and emission are of importance. Based on these results, one can infer the nature of electron transitions and the orientations of their moments relative to the atomic core of the molecule as well as the mechanism of the spin-orbital interaction. In this work, we studied for the first time the dichroism of absorption of STP and the polarization of phosphorescence of the closed form of STP molecules in oriented polyethylene films and in solutions with different polarity, and compared our results with the data on its oxygen-containing analog, namely, SBP.[6—8]



STP

Experimental

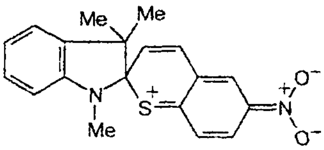
1,3,3-Trimethyl-6′-nitrospiro(indoline-2,2′-[2*H*-1]benzothiopyran) was synthesized and purified according to the known procedure.[4] Polyethylene was purified by extraction in boiling chloroform. The purities of the samples were confirmed by the absence of impurity luminescence. STP molecules were introduced into polyethylene according to a procedure reported previously.[9] Stretching of polyethylene films, determination of the degree of dichroism, and calculations of the directions of the moments of electron transitions were carried out analogously to the procedure reported in Ref. 8 in which the dichroism of absorption of the initial form of the SBP molecule in polyethylene was studied. The corrected phosphorescence spectra, the phosphorescence polarization and excitation spectra, and the lifetime of the triplet state were measured in rectangular quartz cells on an instrument according to procedures reported previously.[7,8,10] Light petroleum and 1-propanol were used as solvents vitrified at 77 K. The concentration of STP in solutions was ~10^{-5} mol L^{-1}. Dichroism of absorption was studied at 300 K. Luminescence and its polarization were studied at 77 K. The degree of polarization of phosphorescence (*P*) in oriented polyethylene films was measured by exciting luminescence with light polarized along the axis of stretching of the polymer. The angles between oscillators of electron transitions were calculated from the data on polarized luminescence according to a procedure reported previously.[11]

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1143—1146, June, 1997.

Results and Discussion

The absorption spectrum of the initial form of STP in polyethylene (Fig. 1) has three overlapping bands with maxima at 340, 280, and 245 nm. This figure also shows the spectrum of SBP in polyethylene for comparison (spectrum *2*),[8] which is characterized by four bands at 335, 265, 300, and 245 nm. According to the interpretation reported in Ref. 6, two of these bands (at 335 and 265 nm) belong to electron transitions localized in the benzopyran fragment, whereas the bands at 300 and 245 nm belong to transitions localized in the indoline fragment of the molecule. Because the indoline fragment remains unchanged in going from SBP to STP, it can be suggested that in the spectrum of STP, the band at 300 nm, which is related to this fragment, is masked by the more intense band of the benzothiopyran fragment, which is bathochromically shifted from 265 nm (in SBP) to 280 nm (in STP). Therefore, the bathochromic shifts of the bands belonging to the benzothiopyran fragment and the more extended long-wavelength edge of the absorption spectrum of STP are two principal differences in the absorption spectra of STP and SBP that result from replacement of the O atom by an S atom. It can be suggested that in the spectrum of STP, the absorption band of the $n\pi^*$ electron transition $S_0 \rightarrow S_1$ appears in the 360—400 nm region. An analogous band could occur also in the spectrum of SBP. However, in the case of STP this band would have a larger extinction coefficient, and it would be shifted to the low-energy region, apparently, due to the fact that the electronegativity of the S atom is lower than that of the O atom.

It can be seen from the spectrum of the dichroism of absorption of the initial form of STP in oriented polyethylene films that the degree of dichroism (*d*) in the region of the second electron $S_0 \rightarrow S_2$ transition (340 nm) is +25%, but it sharply decreases to +10% at 300 nm, which confirms the suggestion that the band of the $S_0 \rightarrow S_3$ transition localized in the indoline fragment occurs in this region. Therefore, the published data on SBP[6—8] and the data on the polarization spectra obtained in this work suggest that the absorption spectrum of the initial form of STP molecules is formed by the following electron transitions: one $n\pi^*$ transition with the participation of electrons of the lone pair of the S atom (λ_{max} = 380—400 nm) and four $\pi\pi^*$ transitions. The second and the fourth transitions (λ_{max} = 340 and 280 nm, and d = 25 and 15%, respectively) are localized in the benzothiopyran ring, whereas the third and fifth transitions (λ_{max} = 300 and 245 nm, and d = 10 and 20%, respectively) are localized in the indoline fragment. We determined the directions of the oscillators of the electron transitions in the corresponding fragments of the molecule from the values of the degree of dichroism *d* in the individual bands of the absorption spectrum.[9] We found that the direction of the moment of the $S_0 \rightarrow S_2$ transition is close to the direction of the line between the S atom and the N atom of the nitro group (Fig. 2), *i.e.*, this transition, as in the case of SBP, is made possible by the intramolecular transfer of charge from the heteroatom of the pyran ring to the nitro group. Thus, the excited state S_2 of the STP molecule can be represented by the following structure:



The fact that the electronegativity of the S atom is lower than that of the O atom leads[12] to an increase in the effective charge that oscillates under the action of light. This causes the bathochromic shift of the band of the transition of the intramolecular charge transfer in the STP molecule. The direction of the oscillator of the $S_0 \rightarrow S_4$ transition in the STP molecule also coincides with that of the corresponding transition in the SBP molecule,[9] and this oscillator is, apparently, made possible by promotion of one electron of the double bond to the π-electron system of the benzothiopyran fragment. This system, unlike the π-system of the benzopyran fragment, is characterized by higher contribution (compared to the O atom) from electrons of one of the two lone electron pairs of the S atom (based on the data of X-ray structural analysis,[13] this pair has a π character), which also results in the bathochromic shift of the corresponding absorption band. The directions of the oscillators of the transitions localized in the indoline fragment and the corresponding maxima of the bands completely coincide with those for SBP.[8]

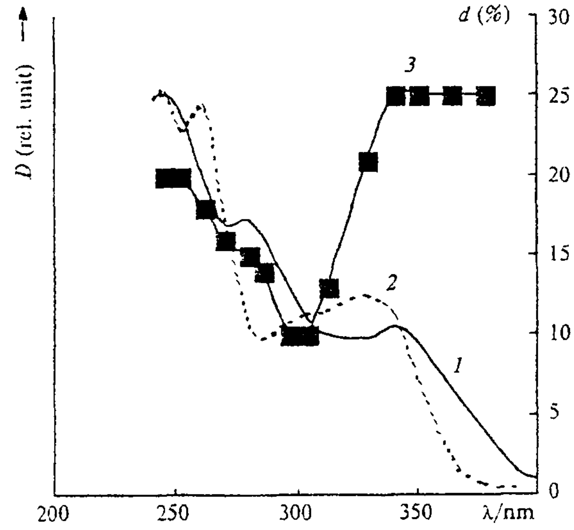


Fig. 1. Absorption spectra of molecules of the initial form of STP (*1*) and SBP (*2*) (according to the published data[9]) and dichroism of absorption of STP in nonoriented (*1* and *2*) and oriented polyethylene (*3*) at 300 K.

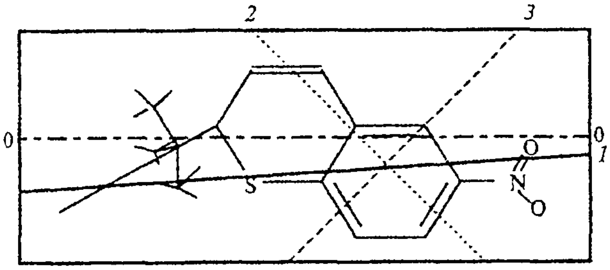


Fig. 2. Structural and oscillator models of the benzothiopyran fragment of the STP molecule; 0—0 is the axis of orientation of the molecule after stretching of the polymeric film. The directions of oscillators of the electron transitions: *1*, $S_0 \to S_2$; *2*, $S_0 \to S_4$; and *3*, $T_1 \to S_0$.

Form A of the STP molecule exhibits phosphorescence. Its spectra in solutions with different polarity are given in Figs. 3 and 4. The excitation spectra recorded in the region of individual bands of the structured emission spectra coincide with each other, whereas the long-wavelength region of the excitation spectrum corresponds to the absorption spectrum. The shape of the phosphorescence spectrum in light petroleum and its position virtually coincide with those of form A of SBP.[6—8] However, the lifetime of the phosphorescent state of STP is approximately 3 times smaller than that of SBP and is equal to 0.013 s. In the phosphorescence spectra in light petroleum and polyethylene, the short-wavelength band at 475 nm belongs purely to the electron transition $T_1 \to S_0$, and two other bands, which are separated from the first band by a distance of 1520 and 2700 cm^{-1}, have a vibronic nature. The value of the degree of polarization of phosphorescence *P* is +12% in the region of the $S_0 \to S_2$ transition (for SBP,[7] this value is +5%) and decreases to −12% in the band of the $S_0 \to S_4$ transition. The existence of the rather intense $n\pi^*$ type absorption band suggests that the phosphorescent state of the STP molecule occurs as a result of mixing of the singlet $n\pi^*$ state S_1 with the unperturbed triplet level T_1^0 *via* spin-orbital interaction. To test this suggestion, we measured the polarization characteristics of phosphorescence of STP in stretched polyethylene films after excitation of luminescence with linearly polarized light whose polarization plane was parallel to the axis of stretching of the polymer (see Fig. 3). The degree of polarization of phosphorescence of this sample increased to +35%, indicating that the oscillator of the $T_1 \to S_0$ transition lies in the plane of the benzopyran fragment, *i.e.*, no admixture of $n\pi^*$ states is present because the oscillator of the $n\pi^*$ transition is perpendicular to the plane of the heterocycle, and when this oscillator is mixed with the triplet state, the orientation of the molecules that occurs with stretching of the polymer should not change the value of *P*.

Therefore, replacement of the O atom in the benzopyran ring of the indoline nitro-substituted photochromic spiro compound by a S atom results in a decrease in the decay time and an increase in the degree of polarization of phosphorescence of the initial form of STP molecules. Because the S atom can be considered as an inner heavy atom, its effect on the lifetime of the triplet state is known.[14] The presence of the S atom results in the fact that spin-forbidden transitions, such as the intercombination conversions $S_1 \to T_1$ and $T_1 \to S_0$ and phosphorescence emission $T_1 \to S_0$, become more allowed, which leads to a decrease in the lifetime of phosphorescence in STP. The increase (compared to SBP) in the degree of polarization of phosphorescence upon excitation of the 0—0 band of the $S_0 \to S_2$ transition is indicative of a decrease in the angle α between the oscillators of this transition and the $T_1 \to S_0$ transition (50° and 45° for SBP[7] and STP, respectively).

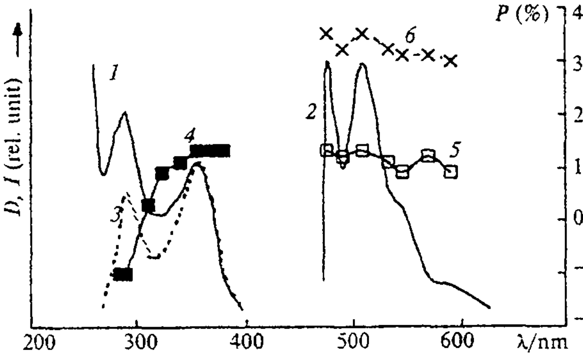


Fig. 3. Absorption spectrum (*1*), phosphorescence spectrum (*2*), phosphorescence excitation spectrum (*3*), phosphorescence polarization spectrum (*4*) and the dependence of *P* on the emission wavelength λ (*5* and *6*) of the molecule of form A of STP in light petroleum (*1*—*5*) and in oriented polyethylene films (*6*) at 77 K.

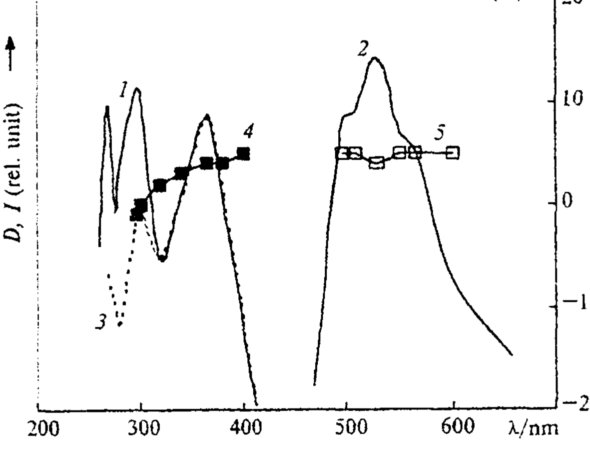


Fig. 4. Absorption spectrum (*1*), phosphorescence spectrum (*2*), phosphorescence excitation spectrum (*3*), phosphorescence polarization spectrum (*4*), and the dependence of *P* on the emission wavelength (*5*) of the molecule of the initial form of STP in 1-propanol at 77 K.

Taking into account that the directions of the moments of the $S_0 \rightarrow S_i$ transitions (i = 2—5) remained unchanged when the heteroatom was replaced, it can be concluded that the direction of the oscillator of the phosphorescence transition $T_1 \rightarrow S_0$ changed. As was demonstrated previously,[8] the triplet state T_1 of form A of SBP was formed by mixing the wave functions of two singlet states S_2 and S_4 with the wave function of the purely triplet state T_1^0. Then, taking into account the first-order approximation,[14] the following equation is true for the wave functions of the corresponding states:

$$T_1 = T_1^0 + \frac{\langle S_2 | H_p | T_1^0 \rangle}{E(T_1) - E(S_2)} \cdot S_2 + \frac{\langle S_4 | H_p | T_1^0 \rangle}{E(T_1) - E(S_4)} \cdot S_4 , \qquad (1)$$

where H_p is the Hamiltonian of the spin-orbital interaction. As can be seen from Eq. (1), the larger the contribution of a particular singlet state S_i to the wave function of the triplet state, the closer the directions of the moments of the $T_1 \rightarrow S_0$ and $S_i \rightarrow S_0$ transitions. The contribution of admixing singlet states also substantially depends on the energy interval ΔE_{ST} between the triplet and the corresponding singlet levels (Table 1). Note that in going from 300 to 77 K, the absorption bands were shifted bathochromically, which is, apparently, associated with an increase in the degree of conjugation of the nitro group with the aromatic ring.[15] Because the relative change in ΔE_{ST} in going from SBP to STP is larger for the S_2 state ($[\Delta E_{ST}(S_2)_{SBP} - \Delta E_{ST}(S_2)_{STP}]/\Delta E_{ST}(S_2)_{SBP} = 0.17$) than for S_4 ($[\Delta E_{ST}(S_4)_{SBP} - \Delta E_{ST}(S_4)_{STP}]/\Delta E_{ST}(S_4)_{SBP} = 0.12$), the contribution of the singlet state S_2 to the wave function of the triplet state is higher for STP than for SBP, which leads to a decrease in the angle α and an increase in the degree of polarization of phosphorescence.

In a polar solvent (1-propanol), bathochromic shifts of the phosphorescence spectra and phosphorescence excitation spectra of form A of STP were observed (950 and 690 cm^{-1}, respectively; see Fig. 4). The degree of polarization P in the 0—0 phosphorescence band decreases to 5%, and the polarization spectrum is similar to the analogous spectrum of the SBP molecule. Note that the characteristics of the polarization spectrum of the SBP molecule are virtually insensitive to the polarity of the medium.[7] This difference in the effect of the polarity of the medium on the luminescence properties of STP and SBP can be explained as follows. It can be suggested that in 1-propanol, hydrogen bonds are formed between the molecules of the solvent and the photochrome. This leads to shifts of the bands, broadening of the vibronic components, and often to inversion of the nπ* and ππ* excited electron levels in the electronic absorption and luminescence spectra.[16] This inversion is due to the fact that the formation of an H bond in the molecule usually causes a bathochromic shift of the band of the ππ* transition, whereas the band of the nπ* transition is hypsochromically shifted. Therefore, the ππ* level may be the lowest excited level. Because the nπ* transition in the STP molecule is substantially more intense than that in SBP, in which transitions of this type were not observed,[7,8] this inversion, apparently, occurs in 1-propanol. As a result, the shape of the phosphorescence polarization spectrum differs from that obtained in light petroleum and becomes similar to that of SBP. Also, shifts of the absorption bands that occcur as a result of H-bonding apparently change the contribution of the corresponding singlet states to the wave function of the triplet state (see Eq. (1)), which, as was demonstrated previously, changes the polarization characteristics of phosphorescence.

Therefore, replacement of the O atom by an S atom in the pyran ring substantially changes the photophysical and spectral characteristics of the molecule, which is caused by the fact that the electronegativity of the S atom is lower than that of the O atom and by the effect of the inner heavy atom.

Table 1. Values of the energies of transitions (E/cm^{-1}), singlet-triplet intervals, and their changes for molecules of the closed form of SBP and STP in light petroleum at 77 K

Compound	$E(T_1)$	$E(S_2)$	$E(S_4)$	$\Delta E_{ST}(S_2)$	$\Delta E_{ST}(S_4)$
SBP	21052[a]	29412[b]	37037[b]	8360	15985
STP	21052	28011	35087	6959	14035

[a] Published data.[8] [b] Published data.[6]

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Received September 30, 1996