Aggregation of nitrosubstituted spiropyranes in polymeric films

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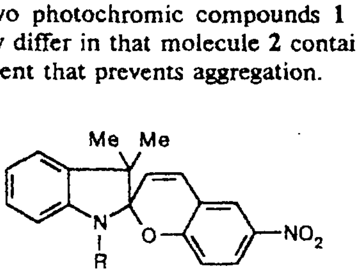
Absorption, luminescence, and luminescence polarization spectra of associates of photochromic molecules of nitrosubstituted indolinospiropyranes in the closed form in polymeric films at high temperatures were studied. The efficiency of the formation of the associates depends on the structure of the photochrome molecules and the nature of the polymeric matrix. A scheme of phototransformations of the associates taking into account the exciting light wavelength was suggested.

Key words: photochromism; luminescence; nitrosubstituted indolinospiropyranes, association.

The practical use of photochromic compounds is mainly related to the possibility of introducing them into polymeric films, whose thickness should be sufficiently small to provide a high resolution ability[1] of the film. Highly concentrated solutions of a photochrome should be used to achieve a sufficient optical density, which results, according to the photochromic behavior of the molecules in solutions,[2–6] in the formation of their associates. Aggregation of molecules may affect photophysical and photochemical processes occurring in the system after absorption of a photon and, hence, the mechanism of the photochromic transformation.

In this connection, it is of interest to study the spectral luminescence properties of associates of nitrosubstituted indolinospiropyranes (ISP), the most studied representatives of photochromic spiro compounds,[1,7] in polymeric films with diverse polarity. In this work, two photochromic compounds **1** and **2** are studied. They differ in that molecule **2** contains a bulky alkyl substituent that prevents aggregation.



1, 2

R = H (**1**), $C_{16}H_{33}$ (**2**)

Experimental

Luminescence, luminescence excitation and polarization spectra as well as curves of phosphorescence decay were obtained at 77 K using a special setup[3] according to previously described procedures.[3] Absorption spectra were measured at 293 K. A DRSh-1000 mercury lamp was used as the source of the photoactivating radiation.

Compounds **1** and **2** were synthesized and purified by previously described methods.[2] Indolinospiropyranes were introduced into polystyrene (PS) and polymethyl methacrylate (PMMA) polymeric films prepared as follows: a solution of a mixture of the polymer and ISP in chloroform (chemical purity grade) was poured on glass supports, and the solvent was slowly evaporated. The thickness of the films was 20—30 μ. The concentration of molecules of the photochrome in the film was varied from 10^{-2} to $5 \cdot 10^{-1}$ mol L^{-1}.

Results and Discussion

Our previous studies have shown[2–6] that an increase in the concentration of nitrosubstituted ISP in solution results in their aggregation to give different associates, among which the formation of dimers of the A_2, AB, and B_2 types are the most probable, where A and B are the molecules of the initial and colored forms of ISP, respectively. The colored form of nitrosubstituted ISP with the bipolar structure is more prone to aggregation than the initial form A. Therefore, in nonpolar solvents, the formation of higher-molecular associates of the $(A^+B^-)A_n$ type is possible.[2,4] After bleaching of the colored form, these associates give the $(A^+A^-)A_n$ associates characterized by the absorption in the region of 430—450 nm. Studying the concentration dependence of the luminescence properties of compounds **1** and **2**, we have established[6] that the formation of dimers A_2 somewhat decreases the energies of the $S_0 \rightarrow S_1$ and $T_1 \rightarrow S_0$ transitions for each molecule of the closed form in the dimer. This results in a bathochromic shift of the absorption and phosphorescence bands compared

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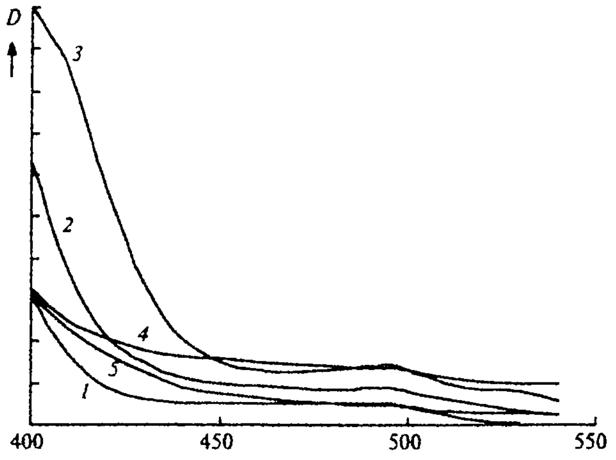


Fig. 1. Absorption spectra of spiro compounds **1** in PS (*1—3*) and PMMA (*4*) and **2** in PS (*5*): C/mol L^{-1} = $9.5 \cdot 10^{-2}$ (*1*), $2.1 \cdot 10^{-1}$ (*2*), $3.8 \cdot 10^{-1}$ (*3, 4*), and $2.1 \cdot 10^{-1}$ (*5*).

to the spectra of monomer A, *i.e.*, the excited state of the dimer A_2^* can be considered as a combination of two molecules (AA^*), one of which is excited. Neither absorption nor luminescence bands related to the dimer as the whole electronic system were observed.

Beginning from the concentration of $9 \cdot 10^{-2}$ mol L^{-1}, the absorption spectrum of compound **1** in the PS matrix contains a distinct shoulder with a maximum at 495 nm, whose intensity increases as the content of the photochrome increases (Fig. 1). The rate of the increase in the absorption intensity with λ_{max} = 495 nm differs from the rate of the increase in the absorption of the whole compound **1**, which proves that the shoulder in the region of 495 nm belongs to associates **1**, but not to any admixtures. The excitation in this region results in the appearance of fluorescence (λ_{max} = 505 nm) and phosphosrescence (λ_{max} = 640 nm), whose excitation spectra contain a band with λ_{max} = 495 nm (Fig. 2). The intensity of this luminescence decreases when the samples are photocolored and increases when they are thermally bleached, which also confirms the assignment of the luminescence observed to molecules of photochrome **1**. Similar behavior is also observed in the PMMA matrix (see Fig. 1); however, in this case, a higher concentration of the molecules is needed for the detection of the absorption band in the region of 495 nm. For compound **2** in the PS matrix, the band with λ_{max} = 495 nm does not appear in the spectrum up to the concentrations of 10^{-1} mol L^{-1}. Thus, these results suggest that the absorption band at 495 nm and the corresponding luminescence belong to the associates of the photochrome molecules.

Two experimental data preclude these associates being assigned to dimers A_2. First, based on the equation $[A_2]/[A]^2 = K_{eq}$ for the equilbrium constant of formation of the dimers according to reaction (1)

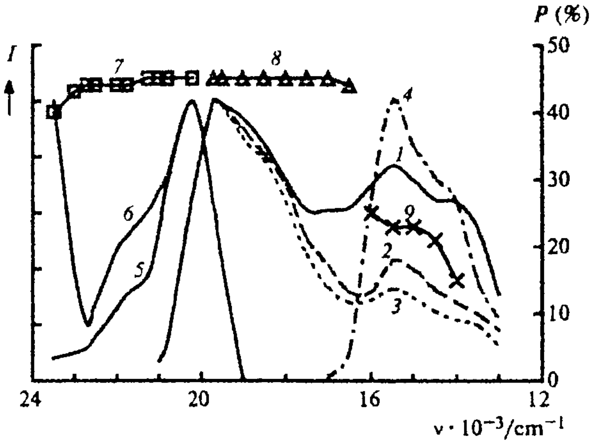


Fig. 2. Fluorescence and phosphorescence (at different durations of drying of the polymeric film) (*1—3*), phosphorescence (*4*), fluorescence (*5*) and phosphorescence (*6*) excitation, and fluorescence polarization (*7*) spectra and dependences of the degree of polarization (*P*) on the wavelength of fluorescence (*8*) and phosphorescence (*9*) emission for associates of the initial form of **1** in PS at 77 K (spectrum *5*, at 300 K).

$$A + A \rightleftharpoons A_2, \qquad (1)$$

the fulfillment of Eq. (2) should be expected at any initial concentration of photochrome:

$$\ln D_d = 2 \ln D_m + \text{const}, \qquad (2)$$

where D_d and D_m are the optical densities of the absorption bands of the dimers and monomers, respectively. However, the treatment of the data by Eq. (2) for the D values of the absorption bands at λ = 350 nm (monomers) and 495 nm (associates) does not result in a linear dependence, which is likely related to the formation of dimers and associates with higher orders in the system. Second, since the configuration of the dimer at which planar benzopyrane fragments of individual ISP molecules are arranged one above another (which is normal for dyes[8,9]) seems to be the most probable, the existence of the long alkyl substituent in the indoline part should not have a substantial effect on the efficiency of the formation of the dimers, as has been observed previously.[6]

Therefore, it can be considered that the absorption in the region of 495 nm belongs to the aggregates of the photochrome molecules with the degree of association ≥2. These associates will be designated as A_n. Perhaps aggregates with different degrees of association, in which some portion of associated molecules play the role of the solvate shell, absorb in this region. In any case, it can be assumed that the absorption band with λ_{max} = 495 nm is assigned to the whole associate as a single molecule and it is the band of its electronic transition $S_0 \rightarrow S_1$. Then the excited state of this associate after the absorption of the light with the wavelength of 495 nm $(A_n)^*$ cannot be considered as a combination of mol-

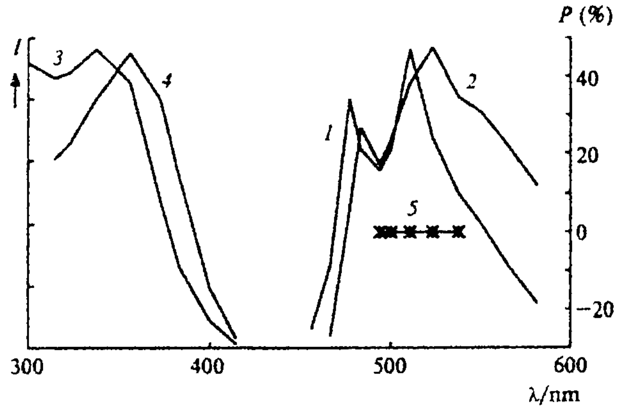


Fig. 3. Phosphorescence spectra of the initial form of **1** in the monomeric state (*1*, λ_{exc} = 350 nm) and in the associate (*2*, λ_{exc} = 420 nm), absorption (*3*) and phosphorescence excitation spectra of molecule **1** in the associate (*4*) (Ref. 6) and the dependence of the degree of polarization (*P*) on the wavelength of phosphorescence emission at excitation with λ_{exc} = 420 nm in PS at 77 K (*5*).

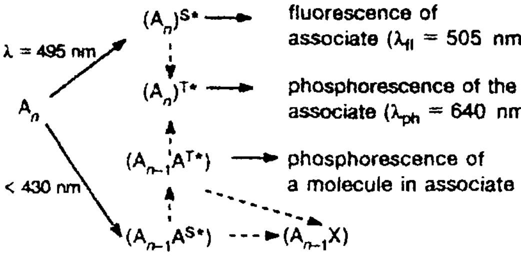
ecules, one of which is in the excited state. This conclusion is confirmed by the existence of the fluorescence of the associate, since the monomers of the initial form of nitrosubstituted ISP do not fluoresce.[7] More evidence of this are the high degrees of fluorescence and phosphorescence polarization of associate A_n (see Fig. 2), because we observed that the phosphorescence of form A is almost completely depolarized (Fig. 3) upon the excitation in the long-wave edge of the absorption band of the initial form (λ_{exc} = 380—410 nm) when only one molecule[6] is excited in the associate ($A_{n-1}A^*$). The latter is probably related to the fact that after the light with this wavelength was absorbed, the energy is transferred from one molecule to another, which results in the depolarization of the phosphorescence for the chaotically organized associate.

Let us consider the data on the luminescence in more detail. The fluorescence spectrum of associate A_n has a maximum at 19 700 cm^{-1} and a shoulder at 18 200 cm^{-1} (remote from the maximum by 1500 cm^{-1}). The fluorescence excitation spectrum also contains a maximum at 20 200 cm^{-1} and a shoulder at the same distance from the maximum (at 21 700 cm^{-1}). Evidently, the main maxima in the fluorescence and absorption spectra can be assigned to the 0—0-bands of the electronic transitions $S_1 \rightarrow S_0$ and $S_0 \rightarrow S_1$, respectively, and the shoulders in these spectra have a vibration-induced nature. Over the whole spectral region, the degree of phosphorescence polarization retains its high positive value (+45%), which makes it possible to simulate the first electronic transition for the absorption and emission of the associate by the harmonic oscillators coincident in direction.[10] The shape of the phosphorescence spectrum of the associate is almost similar to that of the phosphorescence spectrum (see Fig. 2). The degree of the phosphorescence polarization is equal to +25% in the 0—0-band of the transition $T_1 \rightarrow S_0$ and somewhat decreases (+15%) in the band of the vibrational nature. The coincidence of the shapes of the phosphorescence and fluorescence spectra testifies to the first electron-excited singlet level S_1 being admixed to the lower triplet state T_1 due to the spin-orbital coupling. Based on the values of the singlet-triplet interval (4000 cm^{-1}), the time of the phosphorescence decay ($5 \cdot 10^{-3}$ s for the excitation in the band with 495 nm), and the degree of phosphorescence polarization (+25%), it can be assumed[9] that the triplet level of the associate T_1 has the $\pi\pi^*$-nature. The relative intensities of the fluorescence and phosphorescence depend on the time of drying of the polymeric film. This is likely related to the traces of the solvent (chloroform) in the film. Due to the external heavy atom (Cl) effect,[9] chloroform forms a complex with the associate and thus enhances, on the one hand, the phosphorescence transition and, on the other hand, results in a relatively low value of the degree of phosphorescence polarization in the 0—0-band of the transition $T_1 \rightarrow S_0$ (+25%).

In the phosphorescence spectra of associates A_n, a sharp increase is observed in the region of wavelengths less than 430 nm, while in the fluorescence excitation spectrum measured at 300 K (to avoid the effect of the phosphorescence of an individual molecule of form A, which exists in the same region, see Fig. 3), a gradual decrease in the intensity is observed.

One of the possible reasons for this difference can be the following: the excitation in the absorption band of form A induces the emission of the delayed fluorescence of the *cis*-cisoid isomer[3] in the region of the emission of phosphorescence of the associate. However, in this case, this explanation is invalid, because a high concentration of the colored form of ISP is necessary for the emission of the delayed fluorescence, while the phosphorescence of the associates appears without preliminary UV irradiation of the sample as well. In addition, even if it is assumed that the sample contains a sufficiently great thermodynamically equilibrium amount of the colored form, the photocolorization of the sample, as has been established previously,[3] should result in an increase in the intensity of the delayed fluorescence. However, as indicated above, the photocolorization of the polymeric film results in a decrease in the intensity of the phosphorescence of the associate.

Since the dimers and associates, whose excited state can be presented as the combination ($A_{n-1}A^*$), absorb in the region of 380—410 nm,[6] for an explanation of the difference in the fluorescence and phosphorescence spectra, it can be assumed that the triplet excitation of one of the molecules of form A comprising associate A_n results in the transition of the whole associate to the triplet state followed by the emission of phosphorescence. For a singlet-excited molecule in the associate, the similar transition of the whole associate to the singlet-excited state does not occur, probably due to the short lifetime of this molecule. A similar difference in behavior of the triplet- and singlet-excited anthracene molecules during the formation of the dimers has been observed previously.[9,11] Then the scheme of the photophysical processes occurring in the associate at different wavelengths of the exciting light at 77 K (when nonradiative deactivation processes of excited states can be reasonably neglected[12]) can be presented as follows:



Here X is the photoinduced colored product, which is the so-called *cis*-cisoid isomer at 77 K.[3,7] It is noteworthy that no colorization of the samples is observed when they are irradiated with light with λ_{max} = 495 nm. This means that for photocolorizaion by light with a wavelength less than 430 nm, the triplet-excited molecule in the associate ($A_{n-1}A^{T*}$) has an additional way of the energy relaxation without the transition to the colored form, namely the transition to the triplet-excited state of the associate $(A_n)^T$. This way competes with the formation of the colored form. In order to confirm the scheme suggested, additional spectral luminescence and kinetic experiments should be carried out, which also include the measurement of the lifetime of the phosphorescent state of the associate at different excitation wavelengths. This will be performed elsewhere.

Thus, this work shows that an increase in the concentration of molecules of nitrosubstituted ISP in the polymeric matrix results in the formation of aggregates with a degree of association greater than or equal to two. Depending on the excitation wavelength, spectral luminescence and photophysical properties of the associate are determined either by the individual ISP molecule (component of the associate) or the whole associate.

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