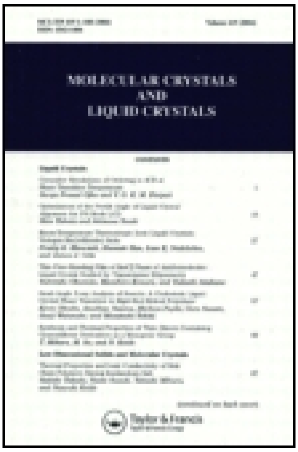

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Relative Investigation of the Properties for Monomer and Dimer Photochromic Spirocompounds

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RELATIVE INVESTIGATION OF THE PROPERTIES FOR MONOMER AND DIMER PHOTOCHROMIC SPIROCOMPOUNDS

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Abstract Compounds containing two photochromic fragments have been investigated. The structure and solvent effects on the absorption spectra and kinetic of the thermal relaxation of the colored form produced under UV irradiation were studied. The hypsochromic displacement of the absorption bands and the increase of the life - time of the open form for the dimer spirobenzopyran as compared with the monomer analog was found. This data indicate that the closed and opened forms are interacted with each other. For the dimer spironaphthoxazines similar interaction is not found. The photodegradation for these compounds under UV light are also studied.

INTRODUCTION

The photochromic spirocompounds have attracted a large attention because of the various possibilities of their practical applications [1,2]. The photochromism of these compounds is due to reversible cleavage of the C-O bond of the pyran heterocycle under UV irradiation and following cis - trans isomerization with formation of the open relatively thermostable colored merocyanine structure. By the ring-closure reaction this colored form returned to the initial state. These processes are strongly depend on the molecular structure and the nature of surrounding.

The intramolecular interactions can show a large influence on the properties of bridged spirocompounds. The investigation of the these compounds can give information about the influence of the interaction between the individual molecular fragments on the photophysics and photochemistry of these compounds. We have synthesized and investigated spectral and kinetic characteristics for the dimers of photochromic spirocompounds in comparison with the monomer compounds in the organic solvents. Before the dimer of spiropyran has been studied in various polymer matrixes [3] but without the comparison with the corresponding monomer molecular structure.

EXPERIMENTAL

The studied compounds are monomers and dimers of spirobenzopyrane (MSPP, DSPP) and spironaphthoxazines (NSNO, DSNO 1 and DSNO 2) (Fig. 1).

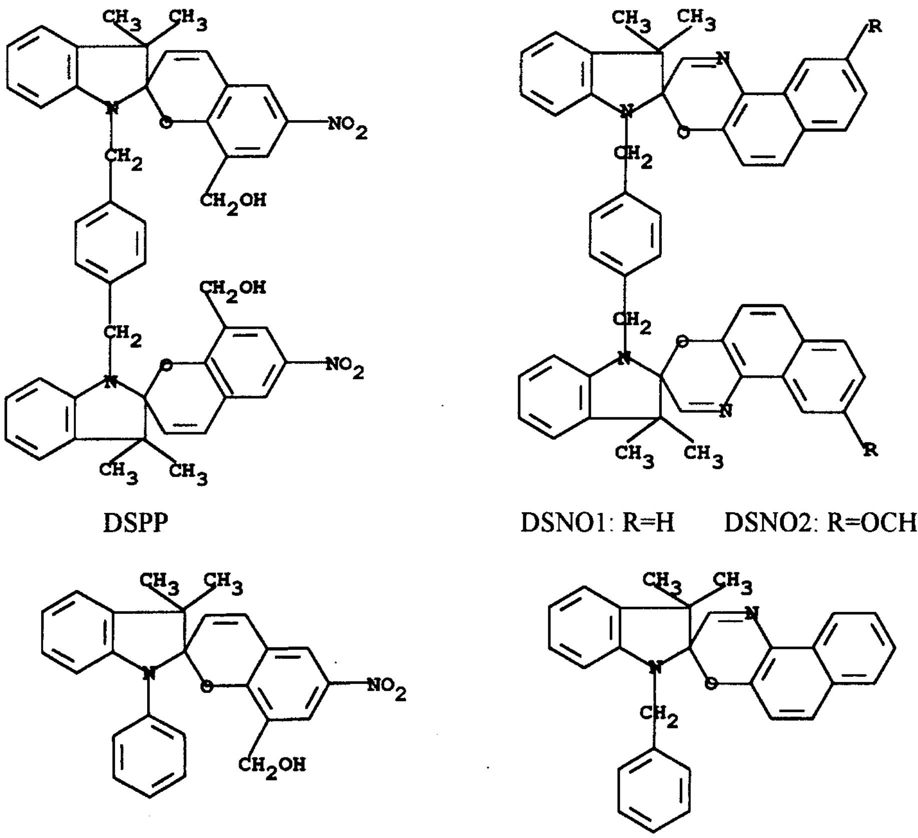
The absorption spectra of closed forms were recorded using the Shimadsu UV-3100 spectrophotometer. The absorption spectra of the open form and kinetic thermal relaxation for the colored forms were recorded by the flash photolysis method [4]. The rate constants of thermal bleaching were measured at the temperature 298 K. The concentration of photochromic compounds was equal 2×10^{-4} mol/ dm^3. The photodecomposition is realized by the use of the filtered UV irradiation (320-380 nm) from 250 W Hg-lamp (100 mJ/cm^2). The kinetics of photodegradation reaction were studied following the disappearance of the colored form under steady-state UV irradiation at the wavelength coinciding with the maximum absorption band for the photoinduced form. The fatigue resistance was defined as the half time of absorption degradation for the solutions of studied compounds.

RESULTS AND DISCUSSION

Interaction of two chromophoric groups in covalently linked compounds results as a rule in shifts of absorption bands in electronic absorption spectra as compared to the spectra of the isolated chromophores. The magnitude of the shift is determined by the charge interaction of these two interacting groups.

A large likeness of the absorption spectra of the initial forms of these compounds and their analogs (Fig.2, 3) can be due to a poorly interaction between of two fragments of the dimer compounds in the initial state because of the low dipolemoment of their closed forms.

The absorption spectra of the DSPP photoinduced form are shifted to the short wavelength region in comparison with the compound MSPP ($\Delta\lambda$ = 18 nm in toluene) (Fig.2). This effect can result from the intramolecular interaction between



DSPP

DSNO1: R=H DSNO2: R=OCH$_3$

MSPP

MSNO

FIGURE 1 The structures of the monomer and dimer spirocompounds the photoinduced merocyanine fragment and the closed form of the another fragment of a dimer molecular.

The absorption spectra of the DSNO 1 photoinduced form are weak changes their positions as compared with the monomer compound MSNO (Fig.3). It is only observed the some increasing of the intensity of short-wave absorption bands. This fact is result from the weakness interaction between the two fragments of a dimer molecule both in initial and photoinduced states.

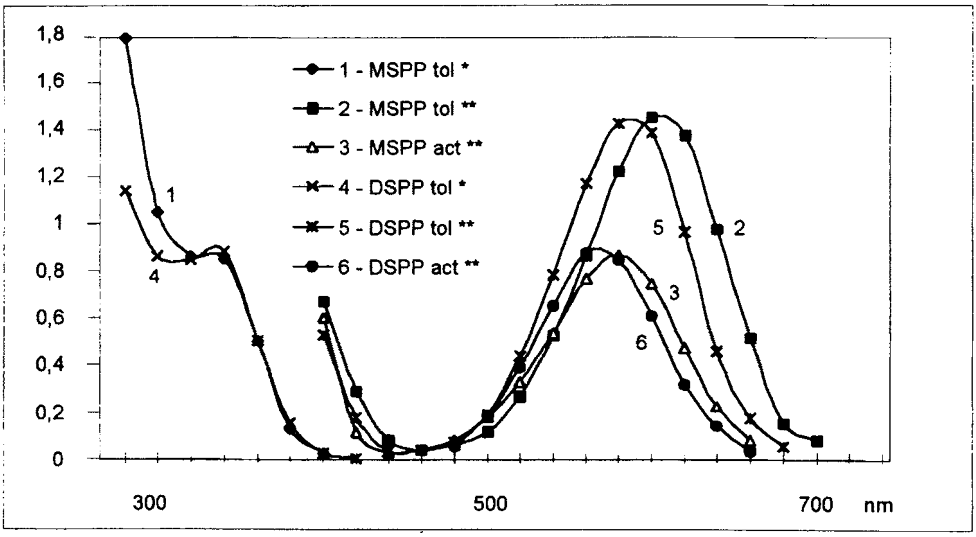


FIGURE 2 Absorption spectra of the closed (*) and open (**) forms of the photochromic spirocompounds MSPP and DSPP.

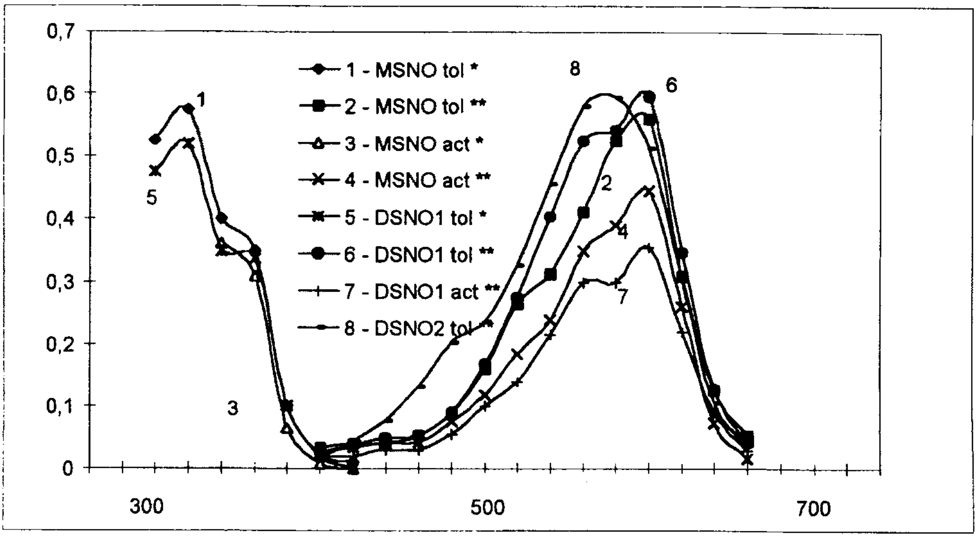


FIGURE 3 Absorption spectra of the closed (*) and open (**) forms of the photochromic spirocompounds MSNO, DSNO 1 and DSNO 2.

TABLE 1 Parameters of the photochromic spirocompounds.

Comp.	Solv.	λ^B_{max} nm	T_{deg}, min	K_{BA}, s^{-1}	Comp.	Solv.	λ^B_{max} nm	T_{deg}, min	K_{BA}, s^{-1}
MSPP	tol	605	3,7	0,14	DSPP	tol	587	2,7	0,047
MSPP	thf	595	0,75	0,08	DSPP	thf	582	0,7	0,043
MSPP	act	580		0,06	DSPP	act	570		0,038
MSPP	acnit	565		0,052	DSPP	acnit	550		0,028
MSNO	tol	595	48	0,36	DSNO1	tol	596	32	0,32
MSNO	thf	596	18,5	0,95	DSNO1	thf	596	18	1,10
MSNO	act	596		1,00	DSNO1	act	598		1,50
MSNO	acnit	598		3,60	DSNO1	acnit	598		3,80
DSNO2	tol	574		0,22	DSNO2	thf	580		0,59

tol=toluene, thf=tetrahydrofuran, act=acetone,acnit=acetonitrile.

The introduction of the methoxy group into the oxazine fragment (DSNO 2) leads to the some hypsochromic shift of the dimer absorption band as compared with unsubstituted dimer spiroxazine.

The different influence of the connection of two fragments on the absorption spectra of the photoinduced forms is due to the different nature of the photoinduced open forms of these compounds. The spirobenzopyran dimer DSPP and its monomer analog MSPP have an electron acceptor group (nitro group) and theirs photoinduced open forms have the high dipole moment. This feature may lead to an intramolecular electrostatic interaction between open and closed forms in these dimer molecules.

Unlike compounds MSPP and DSPP the photoinduced open forms of spironaphthoxazines MSNO and DSNO 1 have quinoid structure which possesses a lower dipole moment and, consequently, poorly interaction with another fragment of the dimer molecular. Besides, the quinoid part of the compound DSNO1 may be located away from the its closed fragment. The absorption bands of the open forms of MSPP and DSPP exhibits a hypsochromic shift with increasing solvent polarity (Table 1). The ground-state of the open forms of these molecules have the bipolar configuration.

The shift of the absorption bands for the colored form of the dimer compound DSPP relatively to the corresponding monomer compound MSPP decreased with the increasing of the dielectric constant of the medium (from 18 nm in toluene to 10 nm in acetone). It indicates on the decreasing efficiency of electrostatic interaction between open and closed fragments of the spirobenzopyran dimer in circumstances where the solvate environment is formed.

In contrast , the weakness positive solvatochromism was found for compounds MSNO, MSNO1 and MSNO2 (Table 1). The red shift is due to a higher dipole moment for the excited state of spiroxazines as regards to one in the ground state. The bathochromic shift indicates that the ground-state of these compounds have the configuration of the quinoid form.

The constant of thermal relaxation for the colored form of studied photochromic compounds depends on the structure of these compounds as well as the polarity of used solvents (Table 1). So, the dimer spirobenzopyran DSPP have more lower constant of thermal relaxation of the colored form than corresponding monomer spirobenzopyran MSPP, while for the monomer MSNO and dimer DSNO 1 from spironaphthoxazines have similar constants. The different influence of the molecular structure on the constant of thermal relaxation for these compounds is caused the above mentioned difference between the electron structure of the open form of nitro-substituted spirobenzopyrans and spironaphthoxazines.

The increase of solvent polarity leads to some decrease of the rate constant of thermal discoloration for the solution of the monomer MSPP and the dimer DSPP . The bipolar structure of the colored forms for these compounds possesses ability to the formation of the solvent environment around each of two charge center of the open form, that leads to the stabilization of the colored form and the increase of its life - time with increasing the solvent polarity.

For the solutions of the monomer MSNO and the dimer DSNO 1 for spironaphthoxazines it was found the noticeable acceleration of the ring-closure reaction (Table 1). This fact is attributable to the quinoid nonpolar structure of the colored form of these compounds, which may be solvated as a whole. The molecule have the more hard solvate environment in the more high polar solvents. It is caused by increasing the rate constant of ring-closure reaction.

Besides, the reversible coloration reaction, the photochromic compounds undergo also photochemical induced degradation under UV irradiation. The photochemical decomposition of these compounds leads to the formation products of the radical type. The dimers of photochromic compounds have slightly lower resistance to the photodegradation as compared with the their monomer analogs, especially in toluene. The decrease of the fatigue properties towards UV light for dimer compounds is attributable to the negative influence of the radical products of the one pyran fragment on the another one.

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CONCLUSIONS

It is shown that unlike spironaphthazines the dimer of nitro - substituted spiropyran manifests the hypsochromic spectral shift and the increase of the life - time of the photoinduced form as compared with the monomer compound. These experimental data are assosiated with the difference of the molecular electronic structure of these compounds.

These conclusions are supported by the difference of solvatochromism for nitro - substituted spiropyrans and spiroxazines.

The observed lower fatigue resistance of dimers as compared with monomer compounds is assosiated with the structure of dimers.

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