Photochromism of 6′-Cyano-Substituted Spironaphthooxazines in the Solid Phase

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Abstract

For three 6′-cyano-substituted spironaphthooxazines (SNO), photochromic properties were revealed in the films obtained from melts. Quantum yields were determined for the forward and reverse photochemical reactions. Unlike phenanthroline-containing spirooxazines, SNO polycrystals do not exhibit photochromic properties.

Key words: photochemistry, photochromism, quantum yield, spirooxazines, polycrystalline films

INTRODUCTION

Organic photochromic compounds are promising for the creation of various photosensitive systems such as optical media with non-linear absorption, optical data storage systems, optical switches [1]. Of particular interest are compounds, whose photochromic properties are conserved in the crystalline state [1, 2]. The main advantage of crystalline photochromes consists in an increased resistance with respect to photodegradation caused usually by the reactions involving the molecules of a solvent (or polymeric matrix). Only few compounds retain photochromic properties in the monocrystalline or polycrystalline state. These classes of compounds include diarylethenes [3, 4] salicylaldehyde derivatives [1, 5] arylhydrazides [6], fulgides [7] and certain chromenes [8].

Spiropyrans and spirooxazines belong to one of the major classes of organic photochromes. Until recently it was believed that they are not photoactive in the crystalline state [9]. This was explained by the absence of free space required for the isomerization. Exceptions considered Salt

crystals those include pyridinium fragment [9–11], or compounds with a very large size of one of the functional groups with cavities in the crystal packing [12] were considered as exceptions. However, recently published results [13, 14] suggest that the photochromism of spirooxazines in the crystalline state represents a phenomenon not so rare as previously thought. To continue the studies initiated in [14], in the present work we investigated spiro compounds photoactive in the polycrystalline state.

EXPERIMENTAL

We studied the photochemistry of three 6′-cyano-substituted spironaphthooxazines (SNO1, SNO2 and SNO3) with different substituents at the 5 position of the indoline fragment of the molecule (Scheme 1). The synthesis and physicochemical properties of SNO were described in [15, 16]. The SNO photochromism in methanol and toluene solutions was described in [16]; no marked photodegradation was observed for the compounds during several tens of cycles.
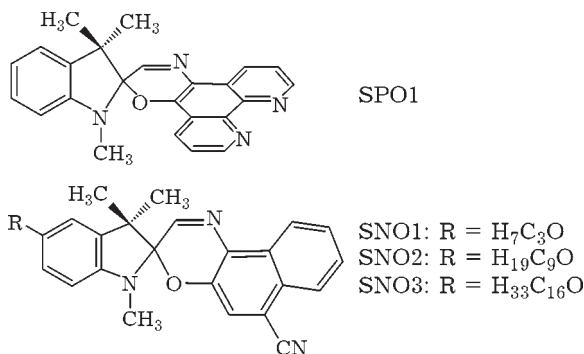
Scheme 1.

Spirooxazines SNO represent polycrystalline powders. The photochemistry of these compounds in the solid phase was compared with the photochemistry phenanthroline containing spirooxazine SPO1 (see Scheme 1), whose properties were investigated in [14].

In this work, we used three types of samples. The samples of the first type represented SNO powder placed between two polished quartz plates. The presence of microcrystals results in an increased light scattering and in increasing the background absorbance (optical density) of the sample, most pronounced in the UV region of the spectrum. The samples of the second type in the form of films were prepared from SNO solutions. As solvents, acetonitrile and isopropanol (Aldrich) were used. The films on quartz substrates were prepared by solvent evaporation in ambient air at a room temperature. The samples were then placed in a desiccator and kept at a pressure of about 0.1 Torr for 3−5 h to remove solvent and water residues. The samples of the third type were prepared from SNO melts; they represented transparent films. The phase composition of the second and third type film samples was not determined. Theoretically, they could represent either polycrystalline or amorphous films; it could be possible that both phases are present in these samples.

The relative inhomogeneity of optical absorption along the film with area about 3 cm^2 for the samples of the second and third types was not higher than 30 and 10 %, respectively. For the quantitative measurements we used the samples of the third type being the best in quality with respect to optical properties.

The samples under investigation were irradiated with light from a DRSh-500 high-pressure mercury lamp with a set of glass filters to isolate the radiation with a desired wavelength, or from laser diodes (Sensor Electronic Technology, Inc., the USA). The quantum yields of photolysis in solid state were evaluated as described in [14]. The UV absorption spectra were registered using an Agilent 8453 spectrophotometer (Agilent Technologies), the kinetic curves of thermal reactions were registered using a kinetic mode of the device.

RESULTS AND DISCUSSION

The photochromic transformations of spirooxazines and spiropyrans similar in structure are caused by the transitions (Scheme 2) between a closed spiro-form (A) and an open merocyanine form (B). In the closed form the indoline and the oxazine fragments of the molecule are almost perpendicular to each other, with no conjugated double bonds. The molecule in the open form has a substantially flat geometry and a unit p electron conjugated system. In accordance with the structure, the closed form exhibits optical absorption only in the ultraviolet region of the spectrum, whereas the open form has very intense absorption in the visible region of the spectrum (the extinction coefficient amounting to about 50 000 M^{-1}cm^{-1}). As a rule, the irradiation of spirooxazines in the UV region of the spectrum results in blue colouring the samples because of a photochemical reaction: A → B. The reverse reaction (B → A) can
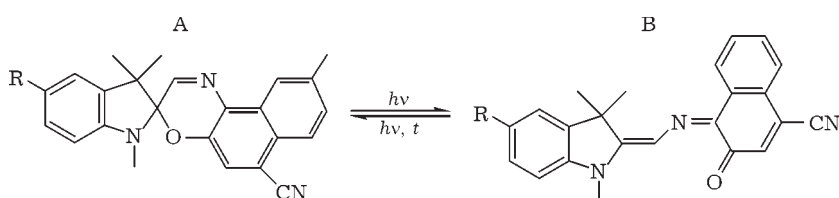
Scheme 2.

occur both in a thermal and a photochemical manner.

Typically, spirooxazines represent an equilibrium mixture of open and closed forms. For the SNO, the equilibrium at a room temperature is strongly shifted towards the closed form; the content of the open form isomer is lower than 0.5 % [16]. For the spirooxazine SPO1 studied in [14], the samples of all three types were photoactive. In this case, a fundamentally important role is played by the photochromism inherent in the first type samples (powders), since they are certainly polycrystalline, whereas the film samples could include the amorphous phase.

For 6′-cyano-substituted spironaphthooxazines, the situation appeared fundamentally different. The SNO samples of the first and second type do not exhibit photochromic properties at all. At the same time, the third type of the samples those were obtained *via* solidifying the melts exhibited photochromic properties.

Figure 1 demonstrates spectral changes those occur in the course of forward (A → B) and reverse (B → A) photochemical reactions. It could be seen that the irradiation of SPO1 films within the UV region at the initial stage of the process initiates mainly to the main A→ B transition (see Fig. 1, *a*). Under prolonged irradiation photochemical reaction B → A becomes important, which results in the achievement of photo steady state condition. The quantum yield of the forward reaction was determined from the initial part of photokinetic curves. The thermal reaction B → A is slow occurring, so one could determine the quantum yields of the reverse reaction upon excitation in the absorption band of the B form. In order to do this, using the
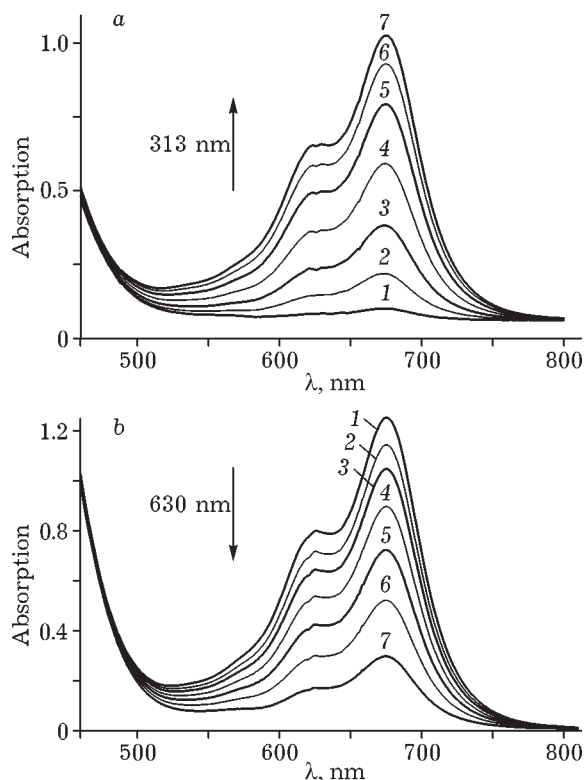

Fig. 1. Spectral changes in the photolysis of SNO1 sample according to reactions A → B (*a*) and B → A (*b*): *a* − irradiation at the wavelength of 313 nm, duration, s: 0 (*1*), 8 (*2*), 25 (*3*), 60 (*4*), 120 (*5*), 180 (*6*), 240 (*7*); *b* − irradiation of A form at the wavelength of 313 nm (*1*) and 630 nm (*2*−*7*); the duration of irradiation, s: 120 (*1*), 10 (*2*), 20 (*3*), 40 (*4*), 90 (*5*), 180 (*6*), 600 (*7*).

photolysis in the UV region we accumulated a sufficiently high concentration of B form, where after we determined the quantum yield of its photolysis under visible light irradiation. The quantum yields of the direct and reverse reactions for the samples of the third type are

TABLE 1

Quantum yields for the forward (313 nm) and reverse (630 nm), photochemical reactions, and the parameters of the thermal reaction B → A (approximation according to eq. (1)) for the SNO (sample type 3)

Samples	$T_{m. p.}$*, °C	T_{gl}, °C	$\varphi_{A \to B}$			D_1	τ_1, s	A_2	τ_2, s
			Toluene (313 nm)**	313 nm	630 nm				
SNO1	160	27	0.13	0.012	0.08	0.62	$4.1 \cdot 10^3$	0.27	$1.3 \cdot 10^5$
SNO2	135	0	0.13	0.082	0.033	0.68	230	ND	ND
SNO3	85	−33	0.135	0.076	0.027	0.61	130	ND	ND

Note. ND − no data.

*According to [15].

**According to [16].

presented in Table 1. For comparison, there are the values of the quantum yields for the forward photolytic reaction in solutions (toluene).

The behaviour of the films observed, to all appearance, could be caused by the difference in the phase composition of the samples of the first, second and third types. The samples of the second type (type 2), obtained by means of the evaporation of the solvent from the solution, represent polycrystalline films, and like the samples of the first type (type 1), they exhibit no photochemical activity. Photochemically active samples of the third type (type 3) obtained by means of cooling the melt represent a supercooled liquid or glass. The glass transition temperature $T_{gl} \approx 0.67$ m. p. [17].

Table 1 presents data concerning the melting point values and glass transition temperature for SNO we determined according to [15]. It can be seen that the films consisting of spirooxazine SNO1 having the greatest melting point are amorphous, whereas the films of SNO2 and SNO3 represent viscous supercooled liquids. This could be confirmed by the kinetic behaviour of the reverse thermal reaction B → A.

The kinetic curves for SNO1 are non-exponential, which is typical of the reactions in the solid phase. There are different approaches to the description of the kinetics of chemical reactions in the solid phase, and one of them is connected with using the polyexponential function

$$D(\lambda, t) = \sum D_i(\lambda) \exp(-t / \tau_1) + D_{fin} \qquad (1)$$

where $D(\lambda, t)$ is the value of absorbance (optical density) varying with time, at the absorption band of B form; $D_i(\lambda)$ and τ_i are the amplitude factor and the characteristic time for the *i*-th term of the expansion, respectively; D_{fin} is the final absorbance (optical density). The experimental kinetic curves for the SNO1 samples obtained from the melt (Fig. 2) could be adequately described by means of biexponential functions. The values for the parameters of corresponding exponents are presented in Table 1. For SNO2 and SNO3 those represent viscous liquids, the kinetic curves are exponential (see Table 1). It should be noted that the lifetime value of the B form are close to the values inherent in liquid solutions [15, 16].
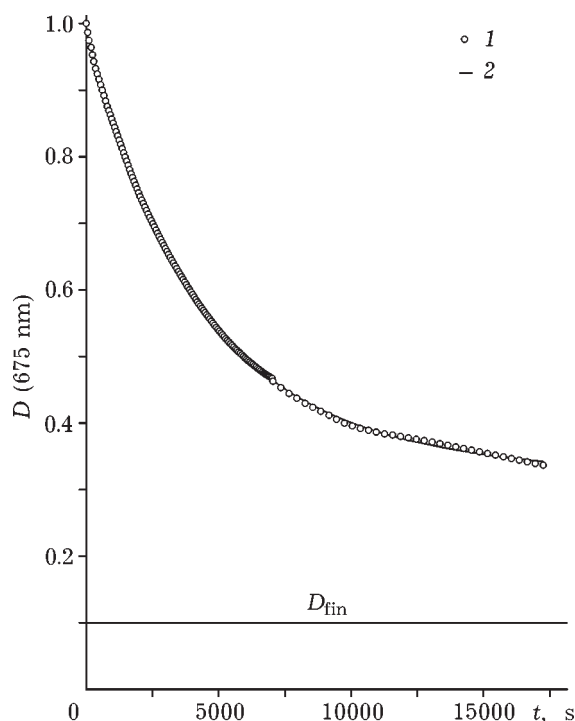
CONCLUSION

The results obtained indicate that the photochromism exhibited by spiro compounds in the solid phase could depend to a considerable extent on the method of sample preparation. In contrast to amorphous films, photochromism is seldom observed for polycrystalline samples. According to kinetic and photochemical parameters, amorphous films are similar to solutions.

Fig. 2. Kinetics of thermal reaction B → A A for SNO1 (sample type 3): *1* − experimental curve, *2* − approximation according to eq. (1) with parameters presented in Table 1. The horizontal line corresponds to the equilibrium value of the absorbance (optical density) D_{fin}.

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