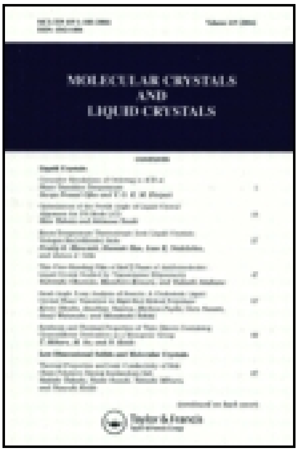

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochromic Properties of Novel Spirooxazines of the Naphthalene and Phenanthrene Series in Polymeric Films

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Version of record first published: 24 Sep 2006

To cite this article: N. E. Shelepin, A. V. Metelitsa, A. V. Vdovenko, V. A. Palchkov, M. I. Knyazhansky, S. I. Adamova, A. P. Panina & V. I. Minkin (1997): Photochromic Properties of Novel Spirooxazines of the Naphthalene and Phenanthrene Series in Polymeric Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 298:1, 175-180

To link to this article: http://dx.doi.org/10.1080/10587259708036158

Mol. Cryst. Liq. Cryst., 1997, Vol. 298, pp. 175-180
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PHOTOCHROMIC PROPERTIES OF NOVEL SPIROOXAZINES OF THE NAPHTHALENE AND PHENANTHRENE SERIES IN POLYMERIC FILMS

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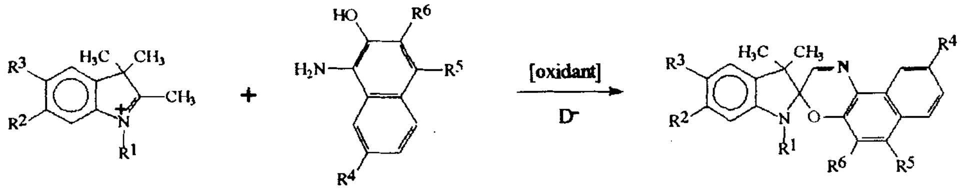
Abstract Novel spirooxazines of the naphthalene and phenanthrene series have been synthesized and studied in PMMA. All of them were found to be photochromic, with high fatigue resistance depending strongly on the structure of the oxazine moiety and substituents in the fragments of the spirocyclic molecule. The efficiency of the photocoloration depends mainly on the steric factors.

INTRODUCTION

Spirooxazines (SPOs) are well-known fatigue resistant photochromic spirocyclic compounds. [1] We have previously reported on the synthesis and spectral properties of some of the compounds of this type. [2] In the present work we describe the results of our further investigation into preparation and photochromic behavior of novel SPOs.

EXPERIMENTAL

The synthesis of spirooxazines was carried out with use of a new preparative procedure [3], in which aromatics or heterocyclics with vicinal amino and hydroxy groups are used, instead of derivatives of o-nitrosonaphtols. The advantage of this method is a possibility to easily introduce various substituents into the naphthooxazine ring.



Absorption spectra were detected on a "Specord M 40" spectrophotometer (Germany). Photochemical reactions were initiated by irradiation with the light of 250 W high-pressure mercury discharge lamp (DRSh-250). Glass filters were employed. A "Hitachi Perkin-Elmer 139" spectrophotometer (Japan) was used to measure time-dependent changes in optical density on irradiation of solutions of the samples and kinetics of dark bleaching. Polymethylmethacrylate (PMMA) films prepared were of about 10^{-4} m thickness. These contained $3 \cdot 10^{-3}$ - $8 \cdot 10^{-3}$ M l^{-1} of SPOs.

For the estimate of photocoloration efficiency parameter η was used: $\eta = \Phi / \Phi_{st}$, where Φ is quantum yield of the photocoloration of SPOs I - XI, Φ_{st} is quantum yield of the photocoloration of 6-NO_2-BIPS, as the standard. The sum $k^{ph}_B + k^{\Delta}$ (where k^{ph}_B is the rate constant of the formation of product of photoreaction and k^{Δ} is the rate constant of the thermal bleaching) was determined as the tangent of the slope of the photocoloration curve $D(\lambda^B_{max}) / D_{eq}(\lambda^B_{max}) = f(t_{irrad})$ extrapolated to the initial stage of the photoreactions (D and $D_{eq}(\lambda^B_{max})$ are optical densites in the maxima of the photoproduct absorption bands at a given time and in the photostationary state respectively). From a curve of the thermal bleaching, the values k^{Δ} were determined, and, thus, k^{ph} were calculated from the sum of k^{ph} and k^{Δ}.

$$- d[A] / dt = \Phi I_{abs}$$

where [A] is the concentration of the cyclic form of SPO; $I_{abs} = I_0(1 - 10^{-\varepsilon[A]l})S$ is an intensity of the absorbed light. When absorption at the wavelength of irradiation (365 nm) is less then 0.1, $I_{abs} = 2{,}303\ I_0\varepsilon[A]lS$.

For a unit of volume

$$- d[A] / dt = 2{,}303\ I_0\Phi\varepsilon[A] = k^{ph}_A[A]$$

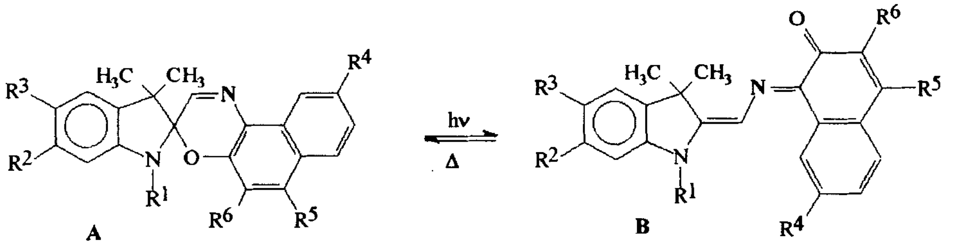
where $k^{ph}_A = 2{,}303 I_0\Phi\varepsilon^A_{365}$ is the rate constant for the process of depletion of the initial compound. Obviously, for the reaction $A \rightarrow B$, k^{ph}_A is equal to k^{ph}_B and

$$\eta = \frac{\Phi}{\Phi_{st}} = \frac{k^{ph}{}_B\,(\varepsilon^A{}_{365})_{st}}{(k^{ph}{}_B)_{st}\,\varepsilon^A{}_{365}}$$

Fatigue-resistance of SPOs has been determined under the continuous irradiation (irradiation wavelength was 365 nm, light intensity was $4.2 \cdot 10^{15}$ photon s^{-1}) of PMMA films of SPOs as the time ($\tau_{1/2}$) necessary for the lowering to half a value of optical density in the maximum of the long wavelength absorption band of the colored form of a SPO.

RESULTS AND DISCUSSION

Under UV-irradiation the spirooxazines I - XI in PMMA films undergo at room temperature thermally reversible photochromic transformation $A \rightleftarrows B$ (fig. 1).



I: R^1=CH_3, R^2=R^3=R^4=R^5=R^6=H; II: R^1=C_6H_{13}, R^2=R^3=R^4=R^5=R^6=H; III: R^1=CH_3, R^2=R^3=R^5=R^6=H, R^4=OCH_3; IV: R^1= R^3=CH_3, R^2= R^5=R^6=H, R^4=OCH_3; V: R^1= CH_3, R^2= R^5=R^6=H, R^3=NO_2, R^4=OCH_3; VI: R^1 = CH_3, R^2=R^3= R^4=H, R^5+R^6 = Benzo; VII: R^1=CH_3, R^2=R^3=H, R^4=NO_2, R^5+R^6=Benzo; VIII: R^1=C_2H_5Ph, R^2=R^3=H, R^4=NO_2, R^5+R^6 = Benzo; IX: R^1 = R^3 = CH_3, R^2 = H, R^4 = NO_2, R^5+R^6 = Benzo; X: R^1 = CH_3, R^2 = OCH_3, R^4 = NO_2, R^5+R^6 = Benzo; XI: R^1= CH_3, R^2 = H, R^3 = COOH, R^4 = NO_2, R^5+R^6 = Benzo

The longwave absorption of the SPOs I - V (λ_{max} =340 - 360 nm) is shifted hypsochromically ($\Delta\lambda$ = 8 nm) and bathochromically ($\Delta\lambda$ = 19 nm) on inclusion of electron donor (OCH_3) (III,V) and electron acceptor (NO_2) substituents respectively. The change of a naphthalene moiety by a phenanthrene one when going on from I to VI, does not significantly affect the spectral parameters (Table 1,Figure 1). An inclusion of a nitro group into the phenanthrooxazine fragment (VII) leads to a substantial modification of absorption spectra (Table 1, Figure 1). Spectra of SPOs VII - XI posssess longwave absorption bands with maxima at 282-288 nm and shoulders about 405 nm. No significant changes in the longwave absorption were observed when the substituents in the indoline moiety varied (X,XI).

TABLE I Photochromic characteristics of the SPOs I -XI (PMMA, 295 K)

Compounds	λ^{A}_{max}, nm	λ^{B}_{max}, nm	τ^{B}, s	η	$\tau_{1/2}$, s
I	345	594	10	1.23	21400
II	348	602	8	0.48	26400
III	337	585	11	0.42	39089
IV	336	593	11	0.13	29262
V	364	590	18	0.11	4122
VI	345	583	16	0.68	43620
VII	283	599	34	0.57	45100
VIII	282	597	21	0.28	42720
IX	282	607	31	0.27	42962
X	282	603	22	0.09	28478
XI	288	595	36	0.16	107479

The longwave absorption bands of the photoinduced colored products B lie in the range of 560-607 nm. The bands are apparently the superposition of those related to various configurational isomers of B and their conformers.

In PMMA films the dark bleaching reaction proceeds rather slowly (Table1) and, therefore, the coloration efficiency (η) may be assumed to be proportional to quantum efficiencies for the formation of B. This process consists of two consecutive steps, i.e. the C-O-bond cleavage and subsequent isomerizations. The compound I with the least bulky substituents has the highest value of η. It stems from the data of Table 1, that in rigid media, an increase in steric volumes of molecules of SPOs leads to decrease in their η–values.

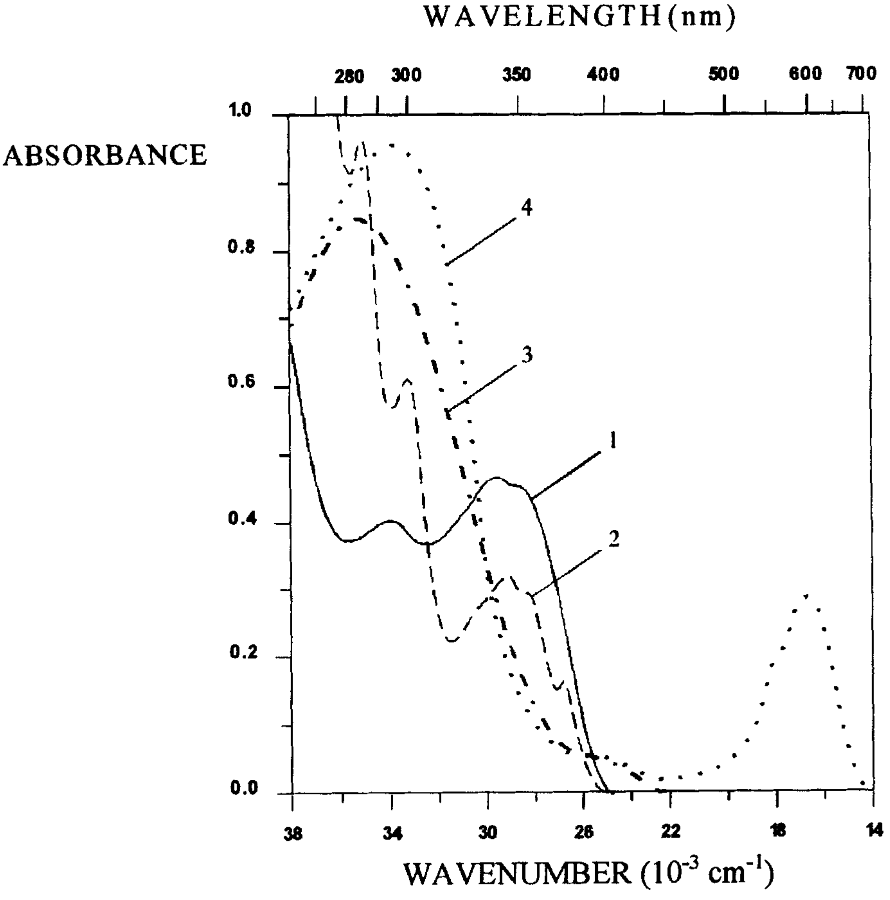


FIGURE 1. Absorption spectra of spirooxazines in PMMA films: 1 - SPO III; 2 - SPO VI; 3 - SPO XI befor irradiation; 4 - SPO XI after irradiation at 365 nm for 300 s.

Lifetimes (τ) of the colored forms B which characterize their kinetic stability depend on both electronic and steric factors. The role of the former is displayed by an increase in the values of τ with inclusion of electron withdrawing substituents into the indoline fragment (the data on compounds IV and V, X and XI are to be compared).

Insertion of a bulky substituent R^1 (compare I and II, VII and VIII) leads to lowering τ–values. On passing from naphthalene (I-V) to phenanthrene (VI-XI) derivatives, increase in τ–values was observed.

The compounds I-XI possess sufficiently high level of fatigue-resistance, higher than that of majority of other spirocyclic photochromes at the same conditions (Table 1). The $\tau_{1/2}$ – values achieve their maxima for the phenanthrene derivatives (VI-IX, XI). When the substituents with opposite electronic properties, i.e. electron releasing and electron withdrawing, are placed into different spiroconjugated moieties of the SPOs, this results in a noticeable decrease in their fatigue-resistance properties. On the contrary, the inclusion of the substituents of the same type into the different fragments leads to an increase in the fatigue-resistance (SPO XI).

CONCLUSIONS

The spirooxazines of the naphthaline and fenanthrene series I - XI are efficient photochromic compounds whose fatigue-resistance depends on the electronic nature of substituents in the spiroconjugated moieties. The coloration efficiency depends mostly on steric factors.

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