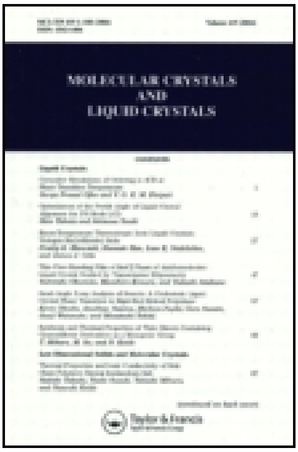

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochromic and Spectrokinetic Properties of Vacuum-Deposited Films of Spirobenzopyrans

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To cite this article: N. A. Voloshin, A. V. Metelitsa, N. S. Trofimova, A. V. Vdovenko, M. I. Knyazhansky, N. E. Shelepin & V. I. Minkin (1997): Photochromic and Spectrokinetic Properties of Vacuum-Deposited Films of Spirobenzopyrans, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 298:1, 169-173

To link to this article: http://dx.doi.org/10.1080/10587259708036157

Mol. Cryst. Liq. Cryst., 1997, Vol. 298, pp. 169–173
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PHOTOCHROMIC AND SPECTROKINETIC PROPERTIES OF VACUUM-DEPOSITED FILMS OF SPIROBENZOPYRANS

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Abstract Novel formylsubstituted spiropyrans of the indoline series have been synthesized. Reversible photochromism was observed in vacuum-deposited thin thin solid films of the spirans obtained by evaporation under a pressure of $2 \cdot 10^{-5}$ Torr and a boat temperature of 130-180 °C. Kinetic characteristics of the photochromic transformations depend mostly on the bulkiness on the substituents in both indoline and 2H-chromene fragments of the spiropyrans. An irreversible photoreaction leading to photodegradation of the photochromic system occurs on prolonged UV-irradiation of thin solid films of the spiropyrans.

INTRODUCTION

Spiropyrans are among the most efficient organic photochromes[1] capable of manifestation of photochromism in solid amorphous forms [2-4]. The photochromic properties of spiropyrans are known to be enhanced by the presence of strong electron acceptor substituents in 6 and/or 8 positions of their 2H-chromene fragment[1,4,5]. This papers describes photochromic properties of vacuum-deposited films of a series of recently synthesized 1',3',3'-trimethyl[2H-1-benzopyran-2,2'-indolines] containing electron acceptor formyl group in one of these positions [6].

EXPERIMENTAL

Synthesis of spiropyrans I-VII was carried out as described in [6], where also data on melting points and spectral characterization of these compounds were listed.

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 timedependent changes in optical density on irradiation of solutions of the samples and to study the kinetics of dark bleaching. Thin solid films of SPP I-VII were prepared by thermal vacuum deposition of spiropyrans on quartz plates. Evaporation of the compounds I-VII was carried out under the pressure of $5\cdot10^{-5}$ Torr and a boat temperature of 130 - 180°C.

For the estimate of photocoloration efficiency parameter η was used: $\eta = \Phi / \Phi_{st}$, where Φ is quantum yield of the photocoloration of spiropyrans I - VII in a film, Φ_{st} is quantum yield of the photocoloration of I, as the standard. The sum $k^{ph}{}_{B} + k^{\Delta}$ (where $k^{ph}{}_{B}$ is the rate constant of the formation of q_a product of the 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 photoreaction. (D and $D_{eq}(\lambda^{B}{}_{max})$ are optical densities 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 a spiropyran; $I_{abs} = I_0(1 - 10^{-\varepsilon[A]l})S$ 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

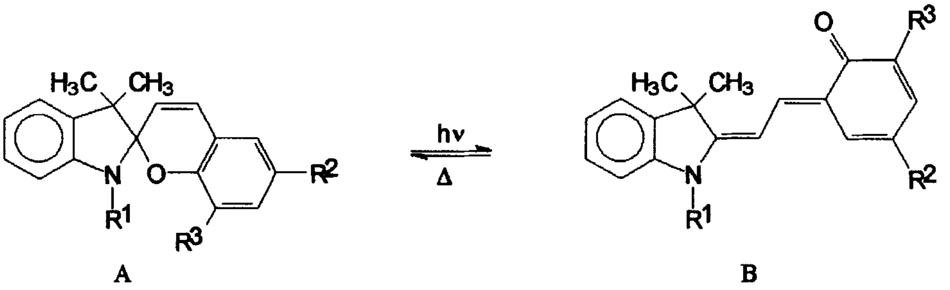
$$- d[A] / dt = 2{,}303\, I_0\Phi\varepsilon[A] = k^{ph}{}_{A}[A]$$

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 → B, $k^{ph}{}_{A}$ is equal to $k^{ph}{}_{B}$ and

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

RESULTS AND DISCUSSION

In Table 1 the data obtained on the spectral characteristics of the initial (A) and photocolored (B) forms of spiropyrans I-VII in vacuum-deposited films, kinetic parameters of the photocoloration and dark bleaching reaction are collected.



I: $R^1 = R^2 = CH_3$, $R^3 = H$; II: $R^1 = R^3 = CH_3$, $R^2 = CHO$; III: $R^1 = R^2 = CH_3$, $R^3 = CHO$; IV: $R^1 = CH_2Ph$, $R^2 = CH_3$, $R^3 = CHO$; V: $R^1 = CH_2Ph$, $R^2 = OCH_3$, $R^3 = CHO$; VI: $R^1 = CH_3$, $R^2 = OCH_2Ph$, $R^3 = CHO$; VII: $R^1 = CH_2Ph$, $R^2 = OCH_2Ph$, $R^3 = CHO$

TABLE I Photochromic characteristics of spiropyrans I -VII in vacuum-deposited thin solid films.

Compounds	λ^A_{max}, nm	λ^B_{max}, nm	λ^C_{max}, nm	η	τ^B, s
I	320	610	-	1	3.6
II	335	584	458	0.33	640
III	366	635	488	0.94	82
IV	364	648	485	0.53	132
V	385	672	490	0.29	158
VI	381	651	485	0.55	108
VII	378	657	488	0.24	220

Position of longwave absorption of the spirocyclic forms A, λ_{max} =320 - 385 nm (Figure 1), originated from an eletronic transition localized in the 2H-chromene fragment.[7] does not depend on the nature of the substituents in the indoline fragment (spiropyrans III and IV, V, VII), but is significantly affected by the electron acceptor (II-IV) or electron donor (V-VII) substituents in the 2H-chromene moiety .

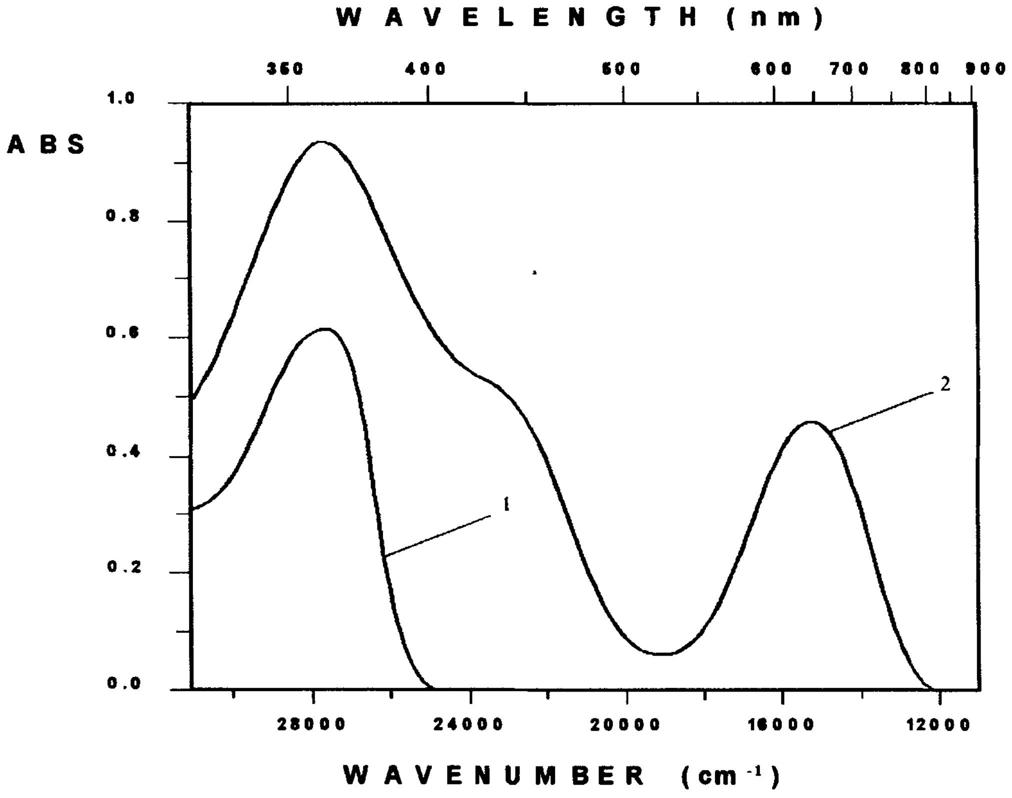


FIGURE 1. Absortion spectra of a vacuum-deposited film of spiropyran III before (1) and after irradiation (365 nm) for 300 s

On the contrary position of the longwave absorption band of the colored merocyanine form B, λ_{max} =584 - 672 nm (Figure 1) having is affected by introduction of substituents to any of these fragments. With inclusion of an electron acceptor substituent in the 8-position (III) or an electron donor substituent in the 6-position (V,VI) the longwave absorption band of the isomer B is shifted bathochromically, whereas an electron acceptor group in the position 6 (II) exerts an opposite action at the position of this band.

Whereas, the presence of electron acceptor and, in particular, formyl group in positions 6 and /or 8 of a chromene fragment of spirobenzopyranindolines enhances the colorabilities of their vacuum-deposited films as compared with those of the spiropyrans not containing such the substituents[4,6], the relative efficiencies of the photocoloration (η) of the spiropyrans are somewhat lower than those of the standard spiropyran I.

Kinetics of decoloration of the photoinduced forms of all the studied spiropyrans in vacuum-deposited films has an exponential character. lifetimes of the colored forms B which characterize their stability vary in the range of several seconds to dozen of minutes. The bulkier are substituents in the indoline and 2H-chromene moieties of the spiropyrans I-VII, the longer are the lifetimes of their ring-opened colored forms. This correlation should, certainly, be explained by steric hindrances set up by such the substituents to occurrence of the configurational isomerizations in B preceding the ring-closing reaction.

Prolonged irradiation (> 10^4 s) of thin solid films of spiropyrans results in an irreversible photoreaction with formation of an unindentified photoproduct absorbing in the spectral region 485-488 nm. Similar spectral changes were also observed in the course of photodecomposition of 1',3',3'-trimethyl-6-hydroxyspiro[2H-1-benzo-pyran-2,2'-indoline] in a vacuum-deposited film [8]. These were assigned to a photooxidation process accompanied by cleavage of the C_{spiro}-O bond.

ACKNOLEGEMENT

The work is supported by the program "The Scientific and Applied photochemistry" (of the State Committee of the Highest Education).

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