Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photochromism of the Spiropyran Thin Solid Films

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Version of record first published: 31 Aug 2006

To cite this article: B. S. Lukyanov, A. V. Metelitsa, M. B. Lukyanova, E. L. Mukhanov, N. I. Borisenko, Y. S. Alekseenko & S. O. Bezugliy (2005): Photochromism of the Spiropyran Thin Solid Films, Molecular Crystals and Liquid Crystals, 431:1, 351-356

To link to this article: http://dx.doi.org/10.1080/15421400590946730

Mol. Cryst. Liq. Cryst., Vol. 431, pp. 51/[351]–56/[356], 2005

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590946730

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New spiropyrans of indoline and benzoxazinone series were synthesized. Photochromic properties of this compounds in thin solid films have been investigated.

Keywords: absorption spectra; photochromism; spiropyran; thin solid film

INTRODUCTION

Spiropyrans are among the most important classes of photochromic compounds due to high quantum efficiency of their photoinduced rearrangements by the reversible photochemical broken of the C_{spiro}–O bond in the 2H-chromene ring (Scheme 1).

It must be pointed out that spiropyrans may show their photochromic properties in solution and in polymeric films [1]. For practical applications (recording and storage of optical information, 3-D memory etc.) is very important to use spiropyrans possessing photochromic

This work was financial supported by RUSSIAN FOUNDATION FOR BASIC RESEARCH (grant 04-03-32485), MINISTRY OF SCIENCE OF RUSSIAN FEDERATION (grant NSh-945.2003.3), CRDF–MINISTRY OF EDUCATION OF RUSSIAN FEDERATION (grant REC-004).

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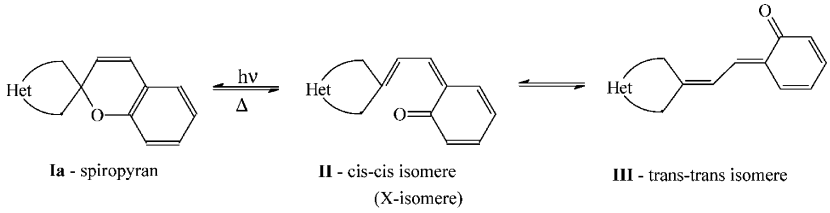


Ia - spiropyran **II** - cis-cis isomere (X-isomere) **III** - trans-trans isomere

SCHEME 1

properties in the solid phase. Some spiropyrans of indoline series were known as solid state photochromic compounds. For example, 1,3,3-trimethyl-5′-bromo-6′-Nitro-8′-methoxy-spiro-indoline-2,2′-[2H] chromene) and 1,3,3-trimethyl-7-phenyl-5′-bromo-6′-Nitro-8′-methoxy-spiro-indoline-2,2′-[2H] chromene show photochromic properties in the amorphous layer obtained after evaporation of solvent . Photochromic properties were lost after crystallization of this layers [2]. A film obtained after cooling of the 1,3,3-trimetyl-spiro-indoline-2,2′-[2H] chromene melt is light sensitive at 0°C. 1-Allyl-3,3,-trimetyl-6′-nitro-spiro-indoline-2,2′-[2H] chromene shows photochromic activity in the crystal state, however possesses very small light sensitivity [3].

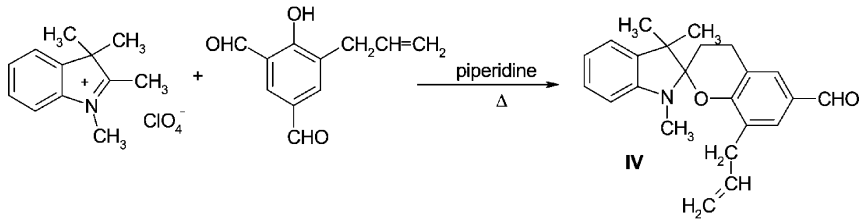
New spiropyrans both of indoline and benzoxazine series containing formyl group in [2H]-chromene fragment have been synthesized. Photochromic properties of this compounds thin solid films have been investigated.

EXPERIMENTAL

Thin solid films of spiropyrans were obtained during vacuum thermal deposition of target compounds onto quartz or glass plates. The VUP-4 apparatus was used for vacuum deposition (remaining pressure $\sim 1{,}5 \cdot 10^{-5}$ Torr, temperature of evaporation $\sim$250–400°C). Control of the film homogeneity had been realized with the polarity interference microscope MPI–5 (PZO Warzawa, Poland) by scanning two coordinate axis and observing interference signals. Electronic absorption spectra of the spiropyran thin solid films were taken using "Specord UV VIS" spectrophotometer supplied special rotating mirror. Documator DDB-2 (Germany) unit was used for irradiation.

RESULTS AND DISCUSSION

1,3,3-trimethyl-6′-formyl-8′-allyl-indoline-2,2′-[2H]-chromene **IV** containing free formyl group in 8′-position was synthesized (Scheme 2).



SCHEME 2

This spiropyran shows photochromic properties in thin solid films obtained during vacuum thermal deposition onto cooling glass or quartz plates. After irradiation by UV light $\lambda_{max} = 365$ nm photoinduced form of spiropyran **IV** ($\lambda_{max} = 567$ nm) was generated (Fig. 1).

The back reaction of the spiropyran **VI** photoinduced form of can run thermally or by visible light irradiation (Fig. 2).

Among three spiropyrans of benzoxazinone series containing formyl group in 6′ (**V**) or 8′ (**VI**, **VII**) position only compound **VI** shows photochromic properties in thin solid films obtained by vacuum thermal deposition (λ_{max} of photoinduced form 595 nm). However, their light sensitivity is very low.

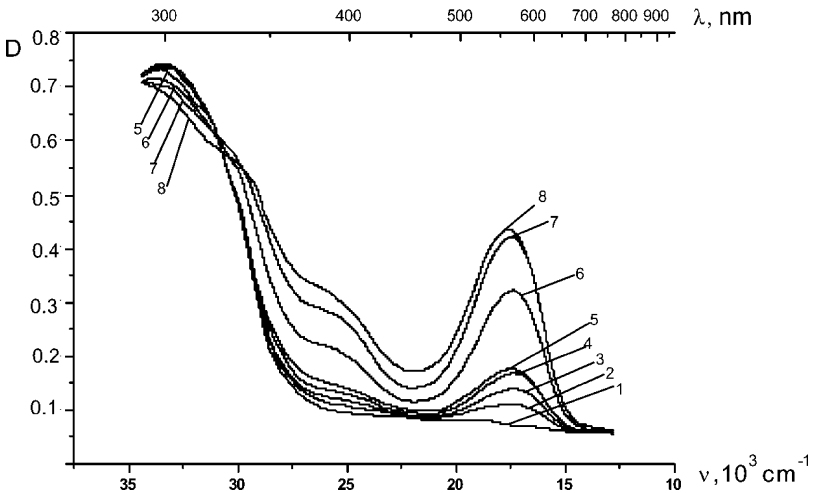


FIGURE 1 Changing of absorption spectra of thin solid film of spiropyran **IV** depended UV irradiation time: 1, 2, 3, 4, 5 – 0, 60, 120, 300, 600 sec irradiation ($\lambda_{max} = 365$ nm) correspondingly; 6, 7, 8 – following 60, 300, 600 sec irradiation ($\lambda_{max} = 313$ nm) correspondingly.

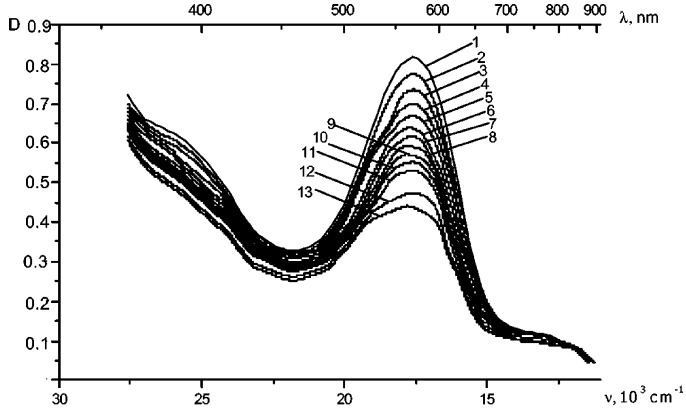
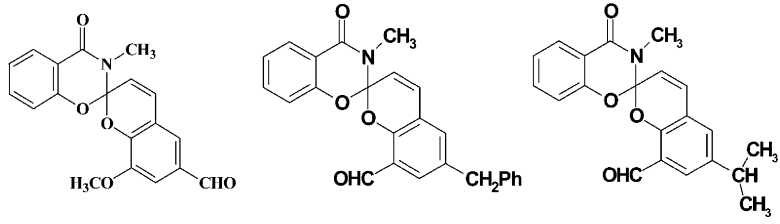
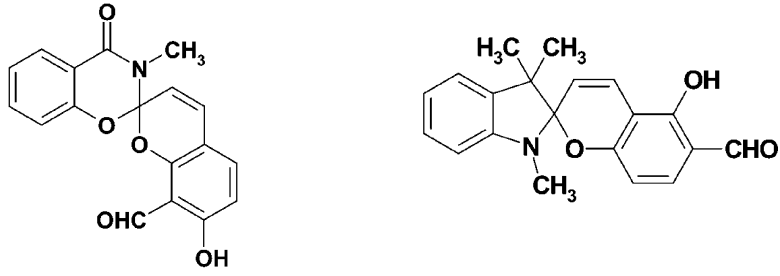


FIGURE 2 Changing of absorption spectra of thin solid film of the spiropyran **IV** photoinduced form: 1–11 – 0, 180, 360, 540, 720, 900, 1080, 1260, 1440, 1620, 1800 sec after irradiation by UV light ($\lambda_{max} = 365$ nm); 11, 12–following 60, 180 sec irradiation by visible light ($\lambda_{max} = 578$ nm); 13–following 180 sec irradiation by visible light ($\lambda_{max} = 546$ nm).



V **VI** **VII**

We have recently studied photochromic properties in solid state of 2 new spiropyrans **VIII** and **IX** containing ortho-located formyl and hydroxy groups.



VIII **IX**

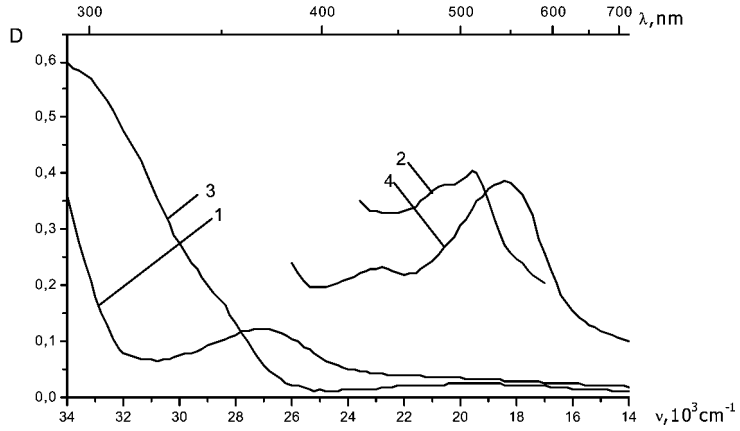


FIGURE 3 Absorption spectra of thin solid films of spiropyran **VIII** and **IX** before (curves 1, 3) and after (curves 2 and 4) irradiation by UV light ($\lambda_{max} = 365$ nm).

Absorption spectra of these compounds are represented at Figure 3. Long-wave maximums of photoinduced forms are at $\lambda_{max} = 520$ nm for **VIII** and 550 nm for compound **IX** correspondently.

Also photochromic properties of new spirocompound **X** were studied. Changing in absorption spectra of the thin solid film of

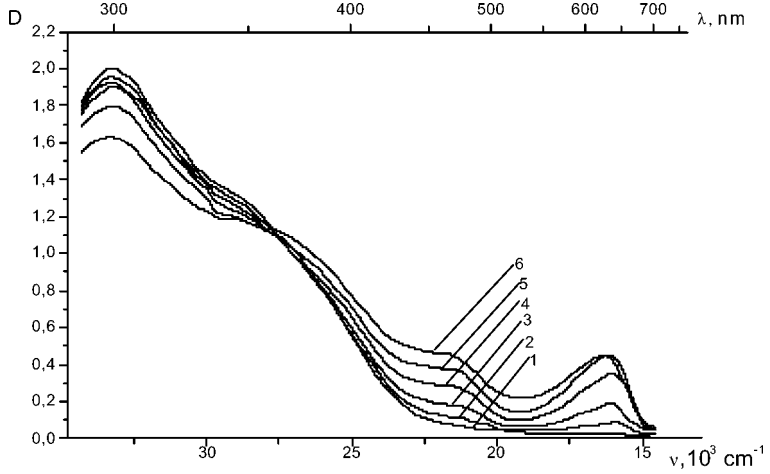
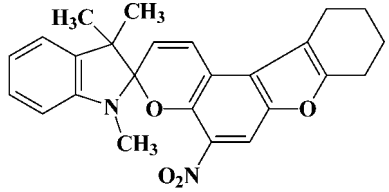


FIGURE 4 Changing of absorption spectra of thin solid film of spiropyran **X** depended on UV irradiation time: 1, 2, 3, 4, 5 – 0, 30, 120, 240, 360 sec irradiation correspondingly.

TABLE 1 Spectral Characteristics of Compounds **IV–X**

Number of compound	λ_{max} of photoinduced form, nm
IV	567
V	–
VI	595
VII	–
VIII	520
IX	550
X	630

spiropyran **X** as a result of UV light irradiation was examined and represent at Figure 4.



X

All obtained spectral characteristics are summarised at Table 1.

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