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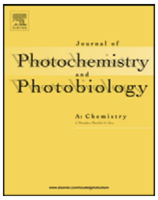
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Novel photochromic spirocyclic compounds of thienopyrroline series: 2. Spirooxazines

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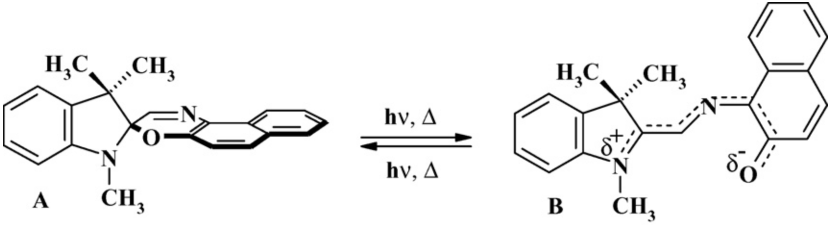
ABSTRACT

Photochromic properties of novel spirooxazines of the thienopyrroline series have been studied in comparison with those of an indoline analogue. Solvatochromism of the merocyanine photoisomers has been investigated using the Kamlet–Taft model. It has been found that inversion of the trends in the solvatochromic behavior of the spirooxazines takes place when passing from non-protogenic to protic solvents. Thienopyrroline spirooxazines possess relatively poor fatigue resistance. The origin of the processes causing their photodegradation has been studied.

1. Introduction

Due to their high fatigue resistance spirooxazines (SPOs) stand out against a background of other organic photochromic spirocyclic compounds [1,2]. The mechanism for the photochromic transformation of SPOs is determined by the stage of the reversible photochemical cleavage of the C_{spiro}–O bond in the oxazine ring resulting in the formation of the merocyanine isomers **B**.



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The starting point for the currently extensive study of SPOs was the discovery by Chu [3–5] in the beginning of the 1980s of the extraordinarily high photostability of spiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazine] **1** and its derivatives under continuous irradiation, which opened up a promising perspective for the use of these compounds in the design of materials with varying optical density. In recent years, photochromic organic compounds and SPOs in particular have been extensively studied because of their application in optical systems for recording and retrieval of information, as molecular switches, photodynamical chemosensors and biosensors, systems for accumulation of solar energy, transport systems, catalysis, in optoelectronics and optobioelectronics [6–8]. Due to the wide diversity of the technical applications of photochromic compounds, requirements with respect to their spectral, thermodynamic and kinetic characteristics are manifold and synthesis of the compounds with desirable properties must

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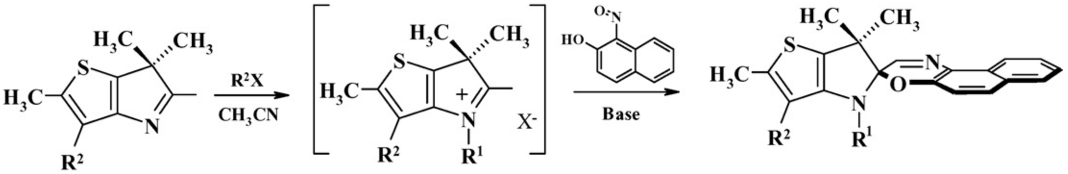
be based on the results of investigations into general relationships between their molecular structure and spectral and kinetic properties.

Because of the preparative accessibility and good photochromic properties the majority of the known spirooxazines are represented by the compounds containing an indoline ring as the heterocyclic fragment, whereas the replacement of this fragment of a SPO by other heterocyclic units is generally met with more complicated synthetic problems [9]. Only in recent years extended series of new spirooxazines in which indoline fragments are substituted by sterically hindered [10–13] or saturated [14,15] azaheterocycles have been synthesized. Other SPOs with heterocyclic moieties different from indoline include compounds with an azaindoline fragment [16] and a series of compounds with dibenzoxazepine moieties [17].

Recently we developed a convenient method for the synthesis of 3*H*-thieno[3,2-*b*]pyrroline derivatives under the Fischer reaction conditions and prepared the first spirooxazines based on these heterocycles [18]. Spirooxazines of the thienopyrroline series **4a**–**c** were prepared via the classical route from the appropriate thienopyrrolenines **2a**,**b** whose synthesis has been reported in detail elsewhere [19]. The first stage includes refluxing of an acetonitrile solution of compounds **2a**,**b** and alkylating agents to give thienopyrroline analogues of the Fischer's salts **3a**–**c**. The subsequent condensation of the thienopyrrolines (obtained *in situ* by a treatment of these salts with bases) with 1-nitroso-2-naphthol results in the targeted spirooxazines.



2a: R^2=H
2b: R^2=COOCH$_3$

3a: R^1=CH$_3$, R^2=H, X=TsO
3b: R^1=C$_2$H$_5$, R^2=H, X=I
3c: R^1=CH$_3$, R^2= COOCH$_3$, X=TfO

4a: R^1=CH$_3$, R^2=H
4b: R^1=C$_2$H$_5$, R^2=H
4c: R^1=CH$_3$, R^2= COOCH$_3$

Here we report on the study of photochromic properties of the thienopyrroline spirooxazines **4a**–**c** in comparison with their indoline analogue, indolinospironaphthooxazine **1**. Special attention has been focused upon solvatochromism of the merocyanines **B** (Scheme 1) which was studied on the basis of a linear solvation energy relationship (LSER) model. In addition, an attempt has been undertaken to clarify the origin of the photoinduced destructive processes occurring in solution of thienopyrroline SPO under UV irradiation.

2. Experimental

2.1. Materials

Indolinospironaphthooxazine **1** and 1,4-diazabicyclo[2.2.2] octane (DABCO) were purchased from Sigma–Aldrich. Spirooxazines of the thienopyrroline series **4a–c** were prepared according to the previously described procedure [18]. Solvents (hydrogen bond donating (HBD): methanol, ethanol, n-propanol, n-butanol, n-pentanol, n-hexanol, n-octanol, n-decanol; and non-HBD: n-hexane, triethylamine, diethyl ether, ethyl acetate, butyl acetate, tetrahydrofuran, 2-butanone, acetone, acetonitrile, cyclohexanone, DMF, DMSO, p-xylene, toluene, benzene, anisole, pyridine) were of spectrophotometric/UV–vis spectroscopy grade from Fluka, Sigma–Aldrich and Merck and were used as received without additional purification.

2.2. Instruments, absorption spectra and luminescence measurements

Absorption spectra were recorded with Agilent 8453 diode-array spectrophotometer supplied with a thermostated cell holder. The temperature of solutions was kept at 293 ± 0.2 K. Concentration of the photochromic compounds was of 3.0–5.5 × 10^{-5} mol dm^{-3}. Solutions (2 ml) were stirred in the four-windowed 10 cm × 10 cm quartz cell with a magnetic bar driven by a speed controlled motor. Setup consisting of the 200 W Hg Research Arc Source, liquid IR filter, set of optical bandpass filters and UV-VIS Liquid Light Guide (300–650 nm) from Newport Corp. was used as a light source. The light was brought with Liquid Light Guide to the cell compartment at the right angle to the probe beam of the spectrometer. The monochromatic light intensity was determined directly in the cell using either azobenzene ($I_0^{365} = 3.5 \times 10^{-5}$ mol dm^{-3} s^{-1}) or Aberchrome 540 ($I_0^{546} = 5.0 \times 10^{-5}$ mol dm^{-3} s^{-1}) actinometry [20–22]. To estimate the activation parameters for thermal bleaching reactions the pre-irradiated (365 nm) solutions were used and the rate constants were determined within 279–298 K temperature range.

For room temperature fluorescence/excitation spectra measurements, Varian Cary Eclipse spectrometer was used. The study of low temperature (77 K) luminescence spectra of both the spirocyclic and photoinduced merocyanine isomers was performed in ethanol using Elumin fluorescence spectrometer with a home-made quartz cryostat. Slightly cooled solutions of photochromes were pre-irradiated (365 nm) and then frozen to check the luminescence properties of the formed merocyanine isomers **B** (Scheme 1).

2.3. Solvatochromism of the merocyanine isomers and data processing

A principal advantage of the use of a diode-array spectrometer for a study of fast photoinitiated chemical reactions is the possibility to get with its help an instantaneous image of the spectrum and to appraise accurately proper position of an absorption band maximum. However, the 1 nm spectral resolution of Agilent 8453 is not sufficient for data processing with the powerful Kamlet–Taft model due to relatively small variation of the absorption band maxima within the range of the solvents used in the present work ($\Delta\lambda_{\max}$(non-HBD) ~ 30 nm; $\Delta\lambda_{\max}$(HBD) ~ 3–6 nm). In order to properly account for this obstacle absorption band maxima were determined based on the first derivative of a spectrum smoothed by a Savitzky-Golay 5-point filter. The values ($\nu_{\max}$) obtained with 1 cm^{-1} resolution (not accuracy) were further subjected to the multiple regression analysis.

2.4. Fatigue resistance of the photochromic system

The fatigue resistance of the photochromic system of thienopyrroline SPOs with respect to continuous UV irradiation was studied by exposing their solutions in toluene to the filtered