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Novel photochromic spirocyclic compounds of thienopyrroline series: 2. Spirooxazines

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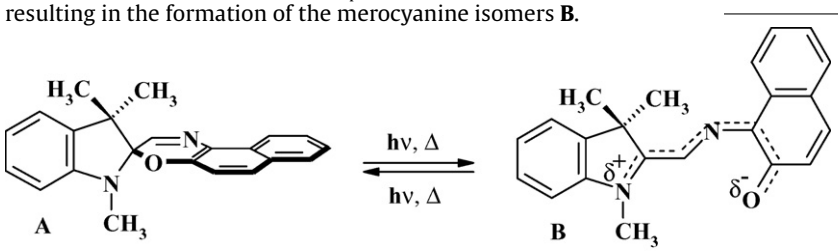
ABSTRACT

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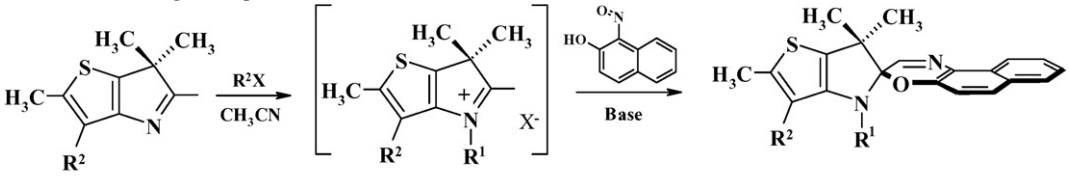
be based on the results of investigations into general relationships between their molecular structure and spectral and kinetic properties.

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.

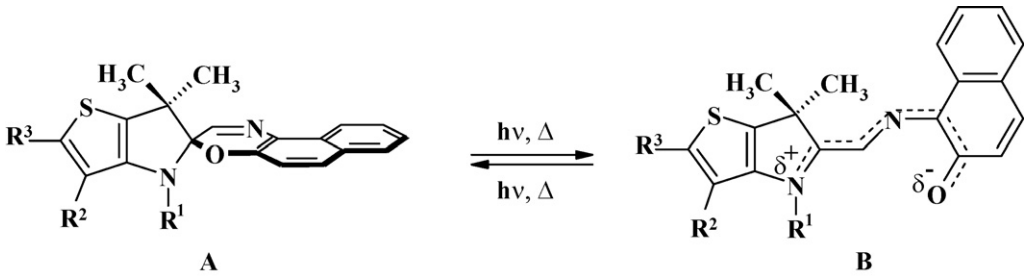
For room temperature fluorescence/excitation spectra measurements, Varian Cary Eclipse spectrometer was used. The study of low temperature (77 K) luminescence spectra of both the spirocyclic and photoinduced merocyanine isomers was performed in ethanol using Elumin fluorescence spectrometer with a home-made 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 (ν_{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



Scheme 1. General scheme for the reversible rearrangement of photochromic thienopyrroline SPO.

365 nm light at 293 K. During the first 40 s the absorbance at the maximum of the longest wavelength band of the formed merocyanine isomer increases to its maximum and the system reaches the "photostationary state". On extinguishing the irradiation the photochromic system was allowed to thermally equilibrate. The durability values $V_{1/2}$ were estimated as the number of the photocoloration–thermobleaching cycles for which "photostationary" absorbance at a merocyanine band maximum was half reduced. In order to provide for the comparable starting experimental conditions, concentration of the compounds **1**, **4b** and **4c** was adjusted to the equal initial absorbance at 365 nm. The DABCO containing solutions were non-degassed ones with 1,4-diazabicyclo[2.2.2]octane taken in 15-fold excess relative to a photochrome.

3. Results and discussion

3.1. Absorption and luminescent properties of the spirooxazine photochromic system

Spectral data obtained for the spirooxazine photochromic system (**1**, **4a–c**) are listed in Table 1. In solution, the longest wavelength absorption band of the spirocyclic form **A** of spirooxazines **4a–c** has a maximum in the 342–351 nm region (molar absorption coefficients ε_{max} = 5160–7010 $dm^3\ mol^{-1}\ cm^{-1}$). As expected, the absorption spectra of the spirocyclic form **A** for both the thienopyrroline spirooxazines **4a–c** and the indoline SPO **1** are similar (Fig. S1, index "S" stands for supplementary) because the spectra of spiropyrans and spirooxazines are well approximated by the superposition of the spectra of nearly orthogonal and, thus, weakly interacting moieties of the composite spirocyclic molecule [23]. For the ring-closed isomers **A**, the longest wavelength absorption band and the next shorter wavelength one may be assigned to the photochemically active 2H-4-azapyran moiety and to the heterocyclic moiety, respectively [5,24,25].

As seen from the data given in Table 1 the spectral properties of the spirocyclic isomers **A** of thienopyrroline spirooxazines **4a–c** and the indoline SPO **1** are slightly affected by the polarity and nature of the solvent. No luminescence of the spirocyclic isomer **A** was observed for spirooxazines **1** and **4a–c** in the temperature range of 77–293 K, except for the reported earlier [26,27] very weak fluorescence of a SPO **1** at 416 nm (in acetonitrile).

UV irradiation of solutions of spirooxazines **1**, **4a–c** results in the coloration caused by the photoinitiated ring-opening reaction leading to the formation of the merocyanine (colored) isomer **B** (Scheme 1). The pattern of spectral changes for the photochromic rearrangements of SPO **4a–c** (Fig. 1) closely resembles those for both SPO **1** and other spirooxazines [28–32]. The longest wavelength absorption bands of the merocyanine isomers **B** of the thienopyrroline SPO **4a–c** with maxima at 610–633 nm are red shifted with respect to that of the indoline derivative **1** and their position is notably sensitive to substitution in the heterocyclic moiety of the molecule as distinct from the longest wavelength absorption of spirocyclic isomers **A**.

The **A** ⇌ **B** rearrangement of SPO **4a–c** in solution exhibits reversibility through both the thermal and photochemical back reactions. Due to the relatively fast thermal bleaching at room temperature the fluorescence study of the colored isomer **B** was performed in ethanol solution at T = 77 K. The merocyanine isomers **B** of spirooxazines **4a–c** display fluorescence with maxima of the emission bands at 667–670 nm. The excitation spectra well match the absorption ones. In comparison with SPO **1** the fluorescence maxima of the merocyanine forms of SPO **4a–c** are shifted

Table 1
Spectral properties of the photochromic spirooxazines (SPO): absorption band maxima ($^A\lambda^{abs}_{max}$) and molar absorption coefficient (ε_{max}) of the spirocyclic form **A**; absorption ($^B\lambda^{abs}_{max}$), fluorescence ($^B\lambda^{flu}_{max}$) and its excitation ($^B\lambda^{ex}_{max}$) band maxima of the merocyanine **B**.

SPO	Toluene		Acetonitrile		Ethanol			
	$^A\lambda^{abs}_{max}(\varepsilon_{max})$	$^B\lambda^{abs}_{max}$	$^A\lambda^{abs}_{max}(\varepsilon_{max})$	$^B\lambda^{abs}_{max}$	$^A\lambda^{abs}_{max}(\varepsilon_{max})$	$^B\lambda^{abs}_{max}$	$^B\lambda^{ex}_{max}$ [a]	$^B\lambda^{flu}_{max}$ [a]
	nm ($M^{-1}\ cm^{-1}$)	nm	nm ($M^{-1}\ cm^{-1}$)	nm	nm ($M^{-1}\ cm^{-1}$)	nm	nm	nm
1	303 (7340) 320 (7650) 349 (5390)	594	–	600	304 (6970) 318 (7450) 348 (5270)	611	605	680
4a	305 (7390) 319 (7120) 350 (5520)	618	302 (7030) 316 (6850) 347 (5260)	621	304 (6980) 318 (7010) 349 (5470)	632	623	667
4b	305 (6960) 319 (6660) 351 (5160)	620	304 317 349	624	305 (6920) 318 (6810) 350 (5260)	633	627	670
4c	308 (6550)[b] 321 (8520) 346 (7010)	610	305[b] 319 342	616	306 (6100)[b] 320 (7960) 342 (6360)	626	627	670

[a] Measurements at 77 K.
[b] Soulder.

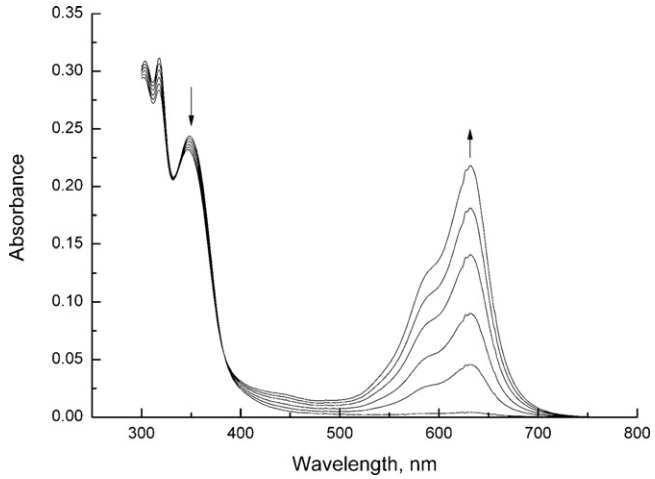


Fig. 1. Absorption spectra of SPO **4a** in ethanol (T = 293 K, [c] = 4.42 × 10^{-5} M) under irradiation (365 nm, dt = 1 s).

to the blue spectral region. The lesser Stokes shifts observed in the case of the thienopyrroline SPO may indicate a stabilizing effect of the thienopyrroline fragment on the excited state geometry of the merocyanine isomer **B**.

3.2. Solvatochromism of the merocyanine isomers

In order to study solvatochromic properties of the colored isomers **B** of SPO **1**, **4b** and **4c**, positions of their absorption band maxima (ν_{max}) were determined in a number of non-protogenic and protic solvents (Table 2). Assuming that the change of the absorption band maxima is collinear to the variation of the $S_0 \rightarrow S_1$ transition energy, several solvatochromic models (Brooker [33], Dimroth–Reichardt [34,35] and Kamlet–Taft [36]) were tested to correlate spectral characteristics of the solute **B** on the properties of solvents (Fig. S2–S11). The most statistically significant and informative correlations were found within the Kamlet–Taft LSER model:

$$\nu = \nu_0 + s \cdot \pi^* + a \cdot \alpha + b \cdot \beta + \ldots$$

where ν_0, s, a and b are solvent-independent coefficients characteristic of the process ($S_0 \rightarrow S_1$ transition) and indicative of its sensitivity to the surrounding medium properties: π^* is a polarity/polarizability parameter of a solvent, α is its hydrogen bond donation (HBD) ability, and β is its hydrogen bond acceptance (HBA) or electron pair donation ability to form a coordinative bond. Advantage of the Kamlet–Taft approach is that the contributions of different types of solute–solvent interaction can be resolved and compared. Moreover, different solvatochromic trends which could be formed by different groups of solvents can be recognized.

Results of the regression analysis collected in Table 3 illustrate the solvatochromic behavior displayed by the colored isomers **B** of SPO **1**, **4b** and **4c**. As one may expect, for all the compounds under study the transition energy is independent on β parameters of the solvents since the merocyanines **B** possess no structural preconditions to serve as hydrogen bond donors.

The colored isomers **B** display quite different solvatochromic behavior in solutions of non-HBD and HBD solvents (Figs. 2 and 3). In non-HBD solvents, bathochromic shifts of the merocyanine absorption band (SPO **1**, **4b** and **4c**) are observed with increase in a polarity/polarizability (π^*) parameter of the solvent. This positive solvatochromism evidences that due to the non-specific solute–solvent interactions the solvation of a molecule in its excited state (with the dipole moment μ_e) is stronger than that in the ground state (the dipole moment is μ_g), i.e. $\mu_g < \mu_e$. The sensitivity coefficient s is proportional to the transition energy change per unit of π^* scale and indicative of dipole moment change ($\Delta\mu$) under the electronic transition. Therefore, the $\Delta\mu$ value is increased in the sequence **4b** → **4c** → **1**. Spectral data for n-hexane and triethylamine solutions of SPO **1** were considered as outliers since the absorption band shapes substantially differ from the shapes typical of other solutions (Fig. S12).

Table 2
Absorption band maxima (ν_{max}, × 10^3 cm^{-1}) of the merocyanine isomer **B** and solvatochromic parameters of the Kamlet–Taft (π^*, α and β)[a], Dimroth–Reichardt ($E_T(30)^N$)[b] and Brooker (χ_R, χ_B)[c] LSER models.

No.	Solvent	ν_{max}(**1**)	ν_{max}(**4b**)	ν_{max}(**4c**)	π^*	α	β	$E_T(30)^N$	χ_R	χ_B
1	n-Hexane	17.186	16.561	16.869	−0.04	0	0	0.009	50.9	–
2	Triethylamine	17.376	16.403	16.722	0.14	0	0.71	0.043	49.3	–
3	Diethyl ether	17.123	16.367	16.685	0.24	0	0.47	0.117	–	–
4	Ethyl acetate	16.880	16.188	16.488	0.45	0	0.45	0.228	47.2	–
5	Butyl acetate	16.888	16.185	16.466	0.46	0	0.45	0.241	–	–
6	Tetrahydrofuran	16.803	16.105	16.375	0.55	0	0.55	0.207	46.6	–
7	2-Butanone	16.734	16.053	16.329	0.60	0	0.48	0.327	–	–
8	Acetone	16.721	16.066	16.293	0.62	0.08	0.43	0.355	45.7	50.1
9	Acetonitrile	16.675	16.035	16.221	0.66	0.19	0.40	0.460	45.7	53.7
10	c-Hexanone	16.602	15.940	16.202	0.76	0	0.53	0.281	–	–
11	DMF	16.502	15.909	16.124	0.88	0	0.69	0.404	43.7	51.5
12	DMSO	16.397	15.811	16.008	1.00	0	0.76	0.444	42.0	–
13	p-Xylene	16.908	16.176	16.442	0.45	0	0.12	0.074	–	–
14	Toluene	16.845	16.124	16.391	0.54	0	0.11	0.099	47.2	41.7
15	Benzene	16.772	16.071	16.316	0.59	0	0.10	0.111	46.9	–
16	Anisole	16.595	15.929	16.176	0.73	0	0.32	0.198	–	–
17	Pyridine	16.457	15.801	16.023	0.87	0	0.64	0.302	43.9	50.0
18	Methanol	16.421	15.857	15.994	0.60	0.93	0.66	0.762	43.1	63.0
19	Ethanol	16.373	15.796	15.967	0.54	0.83	0.75	0.654	43.9	60.4
20	n-Propanol	16.347	15.761	15.954	0.52	0.78	0.90	0.617	44.1	-
21	n-Butanol	16.331	15.744	15.941	0.47	0.79	0.84	0.602	44.5	56.8
22	n-Pentanol	16.314	15.731	15.930	0.40	0.84	0.86	0.586	–	–
23	n-Hexanol	16.308	15.723	15.930	0.40	0.80	0.84	0.559	–	–
24	n-Octanol	16.308	15.711	15.918	0.40	0.77	0.81	0.537	–	–
25	n-Decanol	16.312	15.711	15.946	0.45	0.70	0.82	0.525	–	–

[a] From Refs. [36–38].
[b] Normalized values from Ref. [35].
[c] From Ref. [33].

Table 3
Results of multiple regression analysis obtained within solvatochromic Kamlet–Taft model: the offset (ν_0), and the respective sensitivity coefficients (s, a and b).

SPO	ν_0 ($\times 10^3$ cm^{-1})	s ($\times 10^3$ cm^{-1})	a ($\times 10^3$ cm^{-1})	b ($\times 10^3$ cm^{-1})	n[a]	$\lvert r\rvert$[b]	SD[c]	p-Value[d]
Non-HBD solvents								
1	17.339 ± 0.020	−0.977 ± 0.030	–	0	15	0.9937	0.022	<0.0001
4b	16.524 ± 0.016	−0.756 ± 0.027	–	0	17	0.9908	0.028	<0.0001
4c	16.853 ± 0.019	−0.881 ± 0.031	–	0	17	0.9911	0.033	<0.0001
HBD solvents								
1	15.978 ± 0.023	+0.407 ± 0.030	+0.210 ± 0.034	–	8	0.9916	0.005	<0.0001
4b	15.263 ± 0.019	+ 0.449 ± 0.026	+0.348 ± 0.029	–	8	0.9975	0.004	<0.0001
4c	15.801 ± 0.016	+ 0.310 ± 0.033	0	–	8	0.9668	0.006	<0.0001

[a] Number of points analyzed.
[b] Absolute value of correlation coefficient.
[c] Standard deviation.
[d] Statistical parameter used to estimate if there is a correlation; the less value within 0–1 range the more significant correlation.

In the case of HBD solvents, the overall variation of the $S_0 \rightarrow S_1$ transition energies is determined by the following two key factors: (i) van der Waals type interactions (π^* parameter) and (ii) ability of solvent to donate a proton in a solvent-to-solute hydrogen bond (α parameter).

Positive sensitivity coefficient s means an increase in the $S_0 \rightarrow S_1$ transition energy with increase in the polarity/polarizability parameters (π^*) of the alcohols. The observed hypsochromic shift implies the higher dipole moment of the merocyanines **B** in their ground state in comparison with that in its excited state, i.e. $\mu_g > \mu_e$. Therefore, due to the specific HBD interaction between a protic solvent and the phenolate oxygen of a merocyanine the formed solvate possesses higher ground state dipole moment compared to that of the merocyanine in solutions of non-HBD solvents.

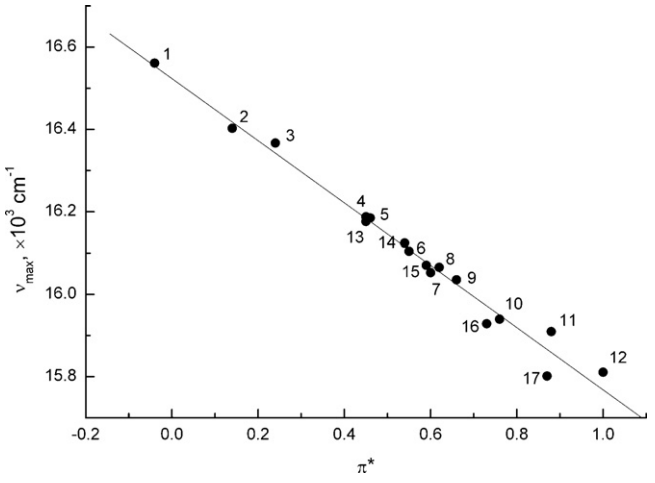


Fig. 2. Correlation diagram for SPO **4b**: the absorption band maxima of the merocyanine isomer vs. π^* parameter of the non-HBD solvents.

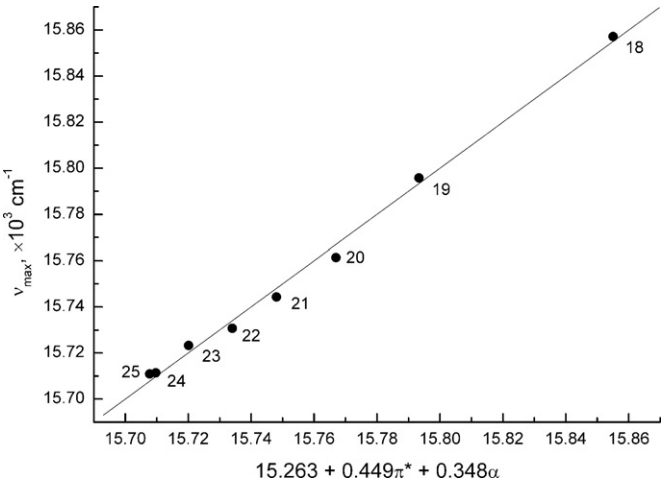


Fig. 3. Correlation diagram for SPO **4b**: the absorption band maxima of the merocyanine isomer vs. function of π^* and α parameters of the HBD solvents.

For the compounds **1** and **4b**, statistically significant coefficients a clearly indicate the formation of hydrogen bonds in solutions of alcohols. The positive values of a imply that the hydrogen bonds are formed in the ground state of the merocyanines, while being dissociated/weakened under excitation. Close values obtained for the s and a coefficients indicate that both type of the interactions related to these have comparable contributions to the overall solvatochromic behavior of the merocyanines **1** and **4b**. An addition of the methoxycarbonyl group in the 6-position of the thienopyrroline moiety of **4c** leads to a unique spectral properties of its solutions in HBD solvents. While no dependence on the α parameter ($a = 0$) was found in this case, the coefficient s remains to have a positive value, as typical for the compounds **1** and **4b**. Zero value of a may signify either the interactions of solvent-to-solute hydrogen bond type are virtually absent or that the effects exerted by hydrogen bonding on the S_0 and S_1 electronic states of the merocyanine isomer of **4c** are approximately equal. We suppose that in the case of compound **4c** the hydrogen bonding takes place as the inversion of the solvatochromic dependence on π^* parameter when passing from non-HBD solvents to alcohols is found to be a common feature for all spirooxazines studied.

The offset values ν_0 correspond to the $S_0 \rightarrow S_1$ transition energy for the medium with zero values for the parameters π^*, α and β, i.e. it is inherent and solvent-independent property of a merocyanine. The higher ν_0 values obtained for thienopyrroline merocyanines **4b** and **4c** are in agreement with the observation on that their spectra are red shifted with respect to that of indolinospironaphthooxazine **1**. Addition of a methoxycarbonyl group in 6-position of the thienopyrroline moiety leads to the increase in the $S_0 \rightarrow S_1$ transition energy. At the same time for all studied spirooxazines, relatively large bathochromic shifts are observed when passing from non-HBD solvents to alcohols.

3.3. Kinetics of the thermal fading reaction of the thienopyrroline spirooxazines

Kinetic characteristics of the back thermal reaction converting the thienopyrroline merocyanines **B** (**4a**–**c**) to their ground state ring-closed form **A** were determined in toluene, acetonitrile and ethanol solutions. All the reactions have been found to strictly follow the first order kinetics (Fig. 4). No significant changes in the shape of the merocyanine long wavelength absorption band were detected in the course of the thermal bleaching, the observation of which is in line with the assumption that the rearrangement occur-

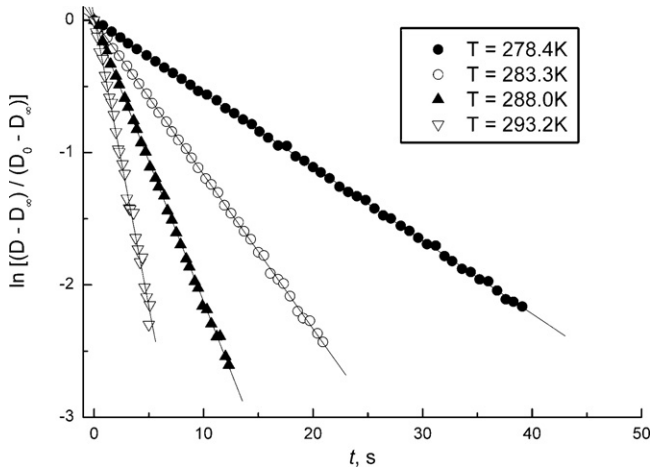


Fig. 4. First order kinetics of the thermal bleaching for SPO **4a** in acetonitrile at different temperatures (D_0, D and D_∞ are the initial, current and equilibrium absorbance at 621 nm, respectively).

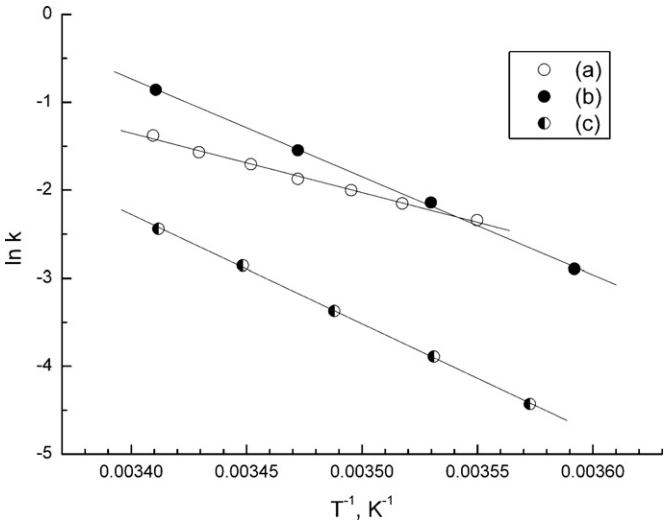


Fig. 5. Arrhenius plot for the thermal bleaching of SPO **4a** in (a) toluene, (b) acetonitrile and (c) ethanol solutions.

ring under the stationary-state conditions involves mainly one of several possible merocyanine isomers [39–41].

No absorbance of the colored merocyanine isomer is observed in the spectrum at equilibrium state, which means that the thermal reaction results in the complete **B** → **A** conversion and the obtained kinetic data conform to the true first order rate constants for the thermal back reaction. These are listed in Table 4 along with the corresponding activation parameters and the kinetic data SPO **1**, for comparison. The lifetimes of the merocyanine isomers **B** measured at different temperatures are given in Table S1.

Whereas at room temperature thermal bleaching of the merocyanines **4a–c** is accelerated with increase in the non-HBD solvent polarity, for the lower temperatures this trend does not hold, as it is pointed by the Arrhenius plots (Fig. 5 and Fig. S13). Faster fading is observed in a solution of polar acetonitrile at 293 K, even though the calculated energy barrier (E_a or $\Delta H^{\neq}$) is higher than those in toluene. An obvious explanation is the contribution of the positive activation entropy (Table 4). On the basis of the activation parameters obtained one can come to the following relationships:

$$\Delta S^{\neq}(\text{toluene}) < 0 < \Delta S^{\neq}(\text{acetonitrile}) < \Delta S^{\neq}(\text{ethanol})$$

$$\Delta H^{\neq}(\text{toluene}) < \Delta H^{\neq}(\text{acetonitrile}) < \Delta H^{\neq}(\text{ethanol})$$

Generally, the kinetic behavior of SPO **4a–c** is similar to that reported earlier for SPO **1** [24,42–45]. The most significant common feature of this process is a notable increase in the activation barrier (E_a or $\Delta H^{\neq}$) to the thermal back reaction when passing from non-polar to polar solvents. It should, however, be noted that the results obtained in the present work cannot be explained within a prevalent opinion that the transition state structures for the conversion of merocyanines (whose structures are better described by the quinonoid resonance forms) to their ring-closed isomers are much more polar than those of the rearranging species [24,42].

Assuming that the transition state structures appeared along the ring-closure **B** → **A** reaction path in different solvents are not notably affected by the solvation, it may be supposed that for the thienopyrroline SPO **4a–c** both spirocyclic (**A**) and merocyanine (**B**) isomers are more stabilized in a polar medium compared with the relatively less polar transition states. The negative $\Delta S^{\neq}$ value for the **B** → **A** reaction in a toluene solution reasonably reflects the activation entropy mostly free of the solvation effects. Positive $\Delta S^{\neq}$ values for the rearrangements occurring in polar solvents include a significant contribution resulted from changes in a solvation shell. This conclusion is corroborated by the literature data [24,45,46] (Fig. S15). The entropic term due to solvation/desolvation is expected to become larger in ethanol which is a HBD solvent.

Table 4
Kinetic parameters for thermal bleaching reaction **B** → **A**: the rate constant (k) at T = 293 K, the Arrhenius pre-exponential factor (k_0) and the activation energy (E_a), entropy ($\Delta S^{\neq}$) and enthalpy ($\Delta H^{\neq}$) of activation.

SPO	Solvent	Arrhenius equation			Eyring equation	
		k (s^{-1})	k_0 (s^{-1})	E_a (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})
1[a]	Toluene	0.202	2.1×10^{10}	61.5	−55.3	59.0
	Acetonitrile	0.962	1.4×10^{15}	84.3	36.5	81.8
	Ethanol	0.258	1.3×10^{15}	87.2	36.4	84.7
4a	Toluene	0.252	2.5×10^{9}	56.3 ± 1.8	−73 ± 6	53.9 ± 1.8
	Acetonitrile	0.424	1.3×10^{16}	92.6 ± 1.9	56 ± 7	90.2 ± 2.0
	Ethanol	0.087	2.1×10^{17}	103.1 ± 1.2	79 ± 4	100.7 ± 1.2
4b	Toluene	0.275	1.3×10^{11}	65.5 ± 2.1	−40 ± 7	63.1 ± 2.1
	Acetonitrile	0.403	8.6×10^{13}	80.4 ± 1.4	14 ± 5	78.0 ± 1.4
	Ethanol	0.070	4.0×10^{16}	99.5 ± 3.3	65 ± 11	97.1 ± 3.3
4c	Toluene	0.322	9.1×10^{12}	75.4 ± 1.4	−5 ± 5	73.1 ± 1.4
	Acetonitrile	2.703	6.2×10^{15}	85.8 ± 5.0	50 ± 18	83.5 ± 5.0
	Ethanol	0.952	1.3×10^{17}	96.1 ± 2.2	74 ± 8	93.7 ± 2.2

[a] The activation parameters are taken from Ref. [45].

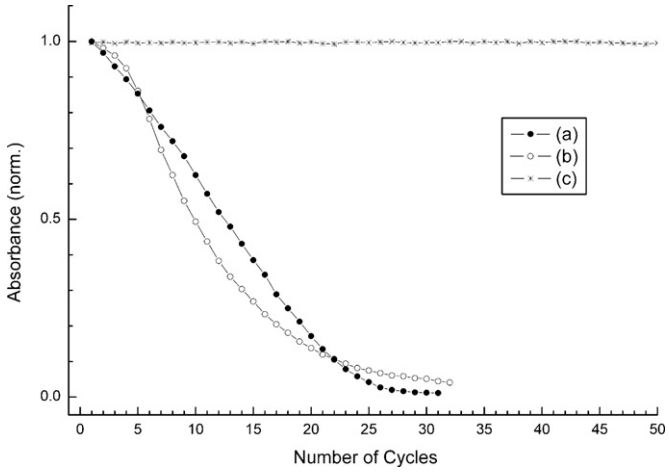


Fig. 6. Degradation curves: normalized "photostationary" state absorbance at merocyanine band maximum of SPO (a) **4b**, (b) **4c** and (c) **1** in toluene solutions under air vs. number of photocoloration–thermobleaching cycles.

3.4. Fatigue resistance properties of the thienopyrroline spirooxazines

UV irradiation of solutions and polymeric films of SPO that initiates their photochromic rearrangements is inevitably accompanied by the side irreversible reactions resulted in photodestruction of the photochromic species and contamination of a photochromic material. The intensity of the destructive processes depends on a variety of factors (structure, medium and irradiation conditions). It is well documented in the literature [47] that the destructive processes involve both bond breaking processes within photochromic molecule and interactions with molecules of solvent, impurities, oxygen and various products of the photodegraded system. According to the Malatesta's classification [47] photodegradation and photooxidation constitute two principal channels of light-induced destruction of spiropyrans and spirooxazines. In their turn, oxidizing processes may be treated as the interactions of photochromes with singlet or ground state triplet oxygen differing in the reaction mechanisms [48].

The studied thienopyrroline SPO have been found to be a subject to substantial photodegradation. Under continuous UV irradiation (365 nm) of its solutions the "photostationary" level of absorbance of the longest wavelength absorption band of the merocyanine isomer gradually reduces. At the same time, a new absorption band ($\lambda_{max} \sim 516$–518 nm) arises to be assigned to one of the products of irreversible reactions (Fig. S16). This product undergoes further thermal and photochemical conversions that can be followed by the observed depletion of the absorption band in the 516–518 nm region.

In order to evaluate the fatigue resistance of SPO **4b** and **4c** the dependence of the "photostationary" absorbance at the maximum of the merocyanine longest wavelength band on the number of the photocoloration–thermobleaching cycles was studied and compared with that of the indoline analogue **1** (Fig. 6). The durability values ($V_{1/2}$) for SPO **4b** and **4c** were found to be 10 and 13, respectively (Table 5), which are at least one order of value lower than $V_{1/2}$ for SPO **1**. Therefore, it must be concluded that spirooxazine of thienopyrroline series are much more degradable compared with the reference SPO **1**.

The role of oxidizing processes in the overall photodestruction was estimated by measuring durabilities ($V_{1/2}$) of SPO **4b** and **4c** in both O_2-saturated and degassed (under argon) solutions (Fig. 7 and S17). As seen from the data given in Table 5, SPO **4b** and **4c** show similar fatigue behavior under variation of

Table 5
Durability ($V_{1/2}$) as a measure of fatigue resistance property for toluene solutions at 293 K.

SPO	Solution under oxygen	Solution under air	Solution under argon	DABCO containing solution
1	–	≫100	–	–
4b	8	13	14	20
4c	8	10	13	62

oxygen concentration in solutions. The durability value is diminished ($V_{1/2} \sim 8$) under O_2-saturation and increased ($V_{1/2} \sim 13$–14) in the degassed solutions (under Ar-saturation). In the O_2-saturated solutions, the yield of the product of the irreversible reaction increases (Fig. 7b and S17b). To estimate a contribution of the reaction of the photochromes with singlet oxygen $V_{1/2}$ values were determined for the solutions containing an efficient singlet oxygen quencher 1,4-diazabicyclo[2.2.2]octane [49]. This led to the substantial improvement of the fatigue resistance of SPO **4b** and **4c**. The $V_{1/2}$ values were raised to 20–60 cycles (Fig. 7 and S17).

Therefore, degassing of the solutions increases the $V_{1/2}$ value by 1–3 cycles, while the addition of DABCO provides for the further enhancement of the durability by 7–50 cycles. In agreement with the previous study [50] this finding points to that the DABCO effect is caused by either its action as a quencher of the destructive triplet state of the photochrome [51,52] or through neutralizing highly reactive products of its photodegradation [53] rather than through quenching singlet oxygen. Although a thiophene moiety is known [54,55] to favor a triplet state population, the former path is unlikely to occur since no phosphorescence was observed for the compounds **4b** and **4c**.

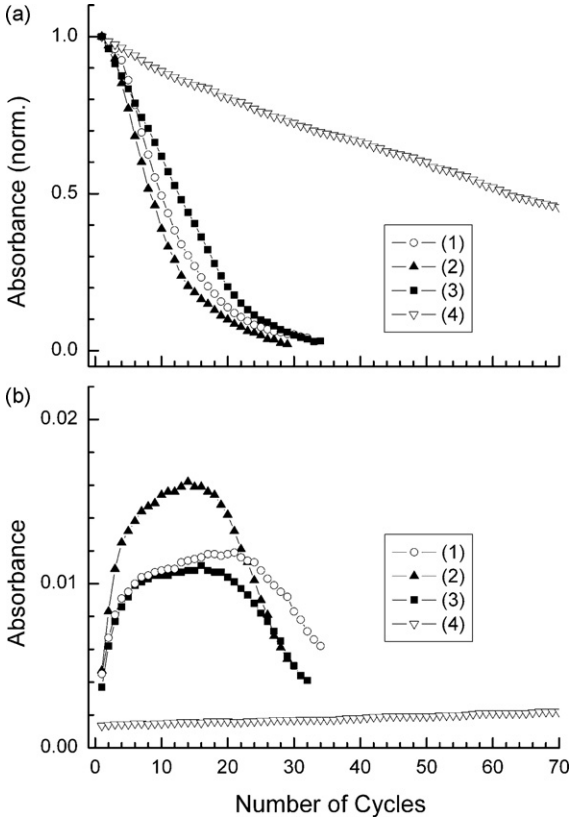


Fig. 7. Degradation curves for SPO **4c** in toluene: (a) normalized "photostationary" state absorbance at 610 nm and (b) absorbance ($\lambda_{obs} = 518$ nm) at the end of cycle in (1) solution under air, (2) solution under oxygen, (3) solution under argon and (4) DABCO containing solution vs. number of photocoloration–thermobleaching cycles.

4. Conclusions

Spirooxazines of the thienopyrroline series (**4a**–**c**) possess photochromic properties typical of other photochromic spirooxazines, e.g. of indoline analogue **1**. Replacement of the indoline moiety by the thienopyrroline one in spirooxazine molecule has no drastic effect on both the spectral and kinetic characteristics, but results in relatively poor fatigue resistance due to readily occurring under UV irradiation oxidizing processes. Side reactions of the SPO with the products of photodegradation represent the dominant channel of the destruction processes.

Solvatochromism of the merocyanine isomers of both the thienopyrroline and indoline SPOs has been analyzed on the basis of the Kamlet–Taft LSER model. Inversion of the solvatochromic behavior has been revealed on passing from non-protogenic to protic solvents. This phenomenon was discussed in terms of the varied polarities of the merocyanine isomers.

On the basis of the activation parameters obtained for the thermal bleaching of SPO **4a**–**c** a conclusion has been made on the lower polarity of the transition state as compared with the ground state merocyanines **B**.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.05.025.

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