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Photochromism of nitrospironaphthoxazines and spiroanthroxazine

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Abstract

The photocolouration of spiroanthroxazine (**3**) and two nitrosubstituted spironaphthoxazines (**1** and **2**) and the subsequent thermal relaxation back to the ring-closed (spiro: Sp) form were studied by time-resolved techniques in solvents of low and high polarity. The photochemical ring opening of **1** or **2** occurs via singlet states, whereas the photomerocyanine of **3** is populated from a triplet state. The relaxation times at 25 °C range from 3 s for **1**–**3** in methylcyclohexane (MCH) to 200 s for **2** in ethanol. They are due to differences in the activation energy (77–90 kJ mol^{-1}) and the pre-exponential factor (0.3–6) × 10^{13} s^{-1}. The phosphorescence properties of **1**–**3** in MCH, methyltetrahydrofuran (MTHF) or ethanol at −196 °C are described. Deactivation of the excited merocyanine of **1** or **2**, upon excitation at 530 nm, into the Sp form occurs mainly in the excited singlet state, as indicated by bleaching at lower temperatures. For **3**, an additional bleaching due to the population of the triplet state takes place. The merocyanines of **1**–**3** exhibit fluorescence in glassy media at −196 °C, competing with the radiationless deactivation pathways of the excited singlet state. The effects of structure and medium properties on the photoprocesses and the mechanisms of photochromism and thermal decolouration are discussed.

Keywords: Spirooxazine; Photochromism; Isomerization; Triplet state; Quantum yield

1. Introduction

The photochromism and the thermal relaxation properties of spirooxazines (SOs) have been intensively studied [1–18]. There is a close relationship to 6-nitro-spiro[2*H*-1-benzopyran-2,2′-indolines] (6-NO_2BIPSs) which are subjects of fundamental photochemical investigations [16–28].

The ring-closed form (abbreviated as Sp) and the most stable merocyanine form (abbreviated as *trans*) are in equilibrium. UV excitation of the Sp form causes a ring-opening. For SOs and 6-NO_2BIPSs, this photocolouration occurs in the sub-nanosecond range [2,3,15,19,20]. Most BIPSs, not carrying a nitro group, have no permanent colour, since the thermal relaxation time ($\tau_{t\text{-}Sp}$) is generally too short in solution at room temperature. It is therefore difficult to measure the quantum yield of colouration (Φ_{col}) by steady-state methods. For several SOs at various temperatures, a major longer-lived and a minor shorter-lived relaxation time have been reported [6,14]. They are due to two distinctly different photomerocyanines and separate pathways for the thermal reaction back to the closed form. Generally, the photochemical properties and relaxation kinetics of several groups of spiro compounds are rather different [23].

In this paper, two nitro derivatives (**1** and **2**) of spironaphthoxazine and spiroanthroxazine (**3**) were studied for the first time by time-resolved techniques. The photochemical ring opening of **3** occurs via the triplet state. In contrast, introduction of a nitro group in SOs leads to a singlet pathway. A comparison of the results with those of spironaphthoxazine (**4**) and spirophenanthroxazine (**5**, phenanthrospiroindolineoxazine) provides the possibility of examining the specific role of structure and substituents on the photoprocesses and relaxation steps. Owing to the lack of colour of BIPSs and most SOs at room temperature, one could assume that the photochromism is quite different, but the present results show that this is not the case.

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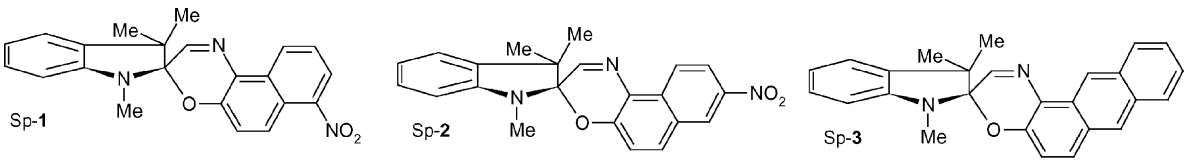


2. Experimental details

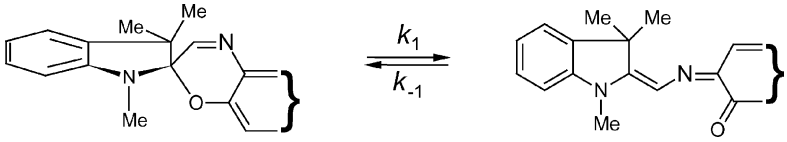
Compounds **1** and **2** [13], spironaphthoxazine (**4**) and spirophenanthroxazine (**5**) [14] were the same as used previously. The synthesis of anthracenospiroindolineoxazine (**3**) followed the method which has been described elsewhere [24]. The solvents (Merck) were of the purest spectroscopic quality available, e.g. toluene and acetonitrile: Uvasol; MCH and MTHF were purified by distillation. For excitation of the Sp form and the merocyanine, $\lambda_{exc} = 354$ and 530 nm (third and second harmonic from a Nd-laser, pulse width of 15 ns and energy <50 mJ) were used, respectively. In one case, an excimer laser (Lambda Physik) with $\lambda_{exc} = 308$ nm was used. The absorption spectra were recorded on a diode array (HP 8453). The experimental errors in $\tau_{t\text{-}Sp}$, $E_{t\text{-}Sp}$ and $\log A$ are typically ±7%.

Phosphorescence of molecular singlet oxygen at 1269 nm was detected after the pulse using a cooled Ge detector (North Coast, EO 817 FP), silicon and interference filters and an amplifier (Comlinear, CLC-103). The observed lifetime is $\tau_\Delta = 30$ μs in MCH and toluene and 70 μs in acetonitrile, as typical for these solvents. The quantum yield of formation of $O_2(^1\Delta_g)$ was obtained from the slope of the linear plot at the end of the pulse signal versus the laser intensity using optically matched solutions ($A_{354} = 0.4$) and acridine as reference with $\Phi_\Delta = 0.7$ [28]. The absorbance increase at the absorption maximum of the *trans*-merocyanine, λ_t, e.g. 10 μs after the pulse (ΔA_{col}) for optically matched conditions (e.g. $A_{354} = 0.8$), shows a linear dependence on the laser intensity and the slope, $P^{rel}_{col} = (\varepsilon_t \Phi_{col})$, was taken as a measure of colouration. The quantum yield was determined using the molar absorption coefficient of $\varepsilon_t = 8 \times 10^4\ M^{-1}\ cm^{-1}$ for **1** and **2**, $\varepsilon_t = 5 \times 10^4\ M^{-1}\ cm^{-1}$ for **3** and $\Phi_{col} = 0.29$ for **5** in ethanol as reference [10,14]. The emission spectra at −196 °C were recorded on a spectrofluorimeter (Spex-Fluorolog). For the quantum yield of phosphorescence optically matched solutions ($\lambda_{exc} = 350$ nm, $A_{350} = 0.6$) and 9,10-diphenylanthracene in ethanol as reference ($\Phi_f = 0.9$) were used. The fluorescence decay kinetics ($\Phi_{exc} = 580$–600 nm) were determined with an Edinburgh Instruments fluorimeter (F900). For this purpose, the samples were UV irradiated at 0 to −40 °C and then further cooled. The other methods are as described elsewhere [21–23].

3. Results and discussion

3.1. Photocolouration

For SOs, the ground state equilibrium (1) between the ring-closed Sp form and the most stable merocyanine is established.



(1)

At low temperatures equilibrium (1) is shifted toward the Sp form [6–11]. The absorption spectrum of nitrospironaphthoxazine **1** or **2** in polar solvents has two major bands with maxima in the UV (λ_{Sp}) and visible range (λ_t). In contrast, virtually no visible absorption could be observed on a time scale of a few seconds and longer upon UV irradiation of spiroanthroxazine **3** even in polar solvents at ambient temperature. However, upon pulsed excitation ($\lambda_{exc} = 354$ nm) of the Sp form, an absorption increase with maximum at $\lambda_t = 580$–620 nm was observed in all cases examined. The photochemical ring opening of nitrospironaphthoxazines is illustrated in Fig. 1a and examples for **3** are shown in Figs. 2a and 3a.

The quantum yields of colouration of **1**–**3** are compiled in Table 1. For NO_2BIPS, Φ_{col} is substantial in solvents of

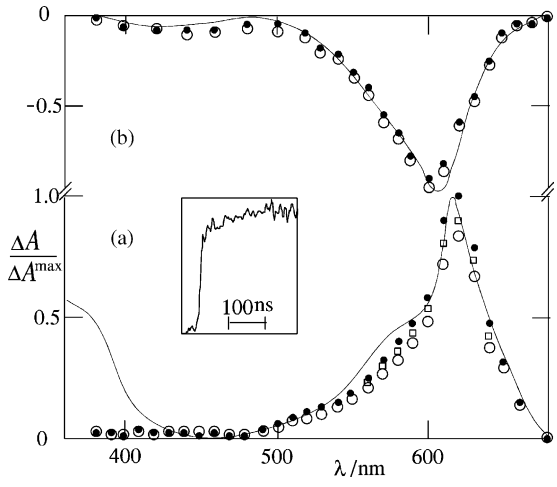


Fig. 1. Transient difference/absorption spectra of **1** (a) in acetonitrile at 25 °C, 20 ns (○), 0.1 μs (□) and 10 ms (●) after the 354 nm pulse, $\Delta A_T^{max} \leq 0.2$ (line: ground state); inset: signal at 570 nm, and (b) in argon-saturated MTHF at −50 °C after UV pre-irradiation at 0.1 μs (○) and 100 μs (●) after the 530 nm pulse.

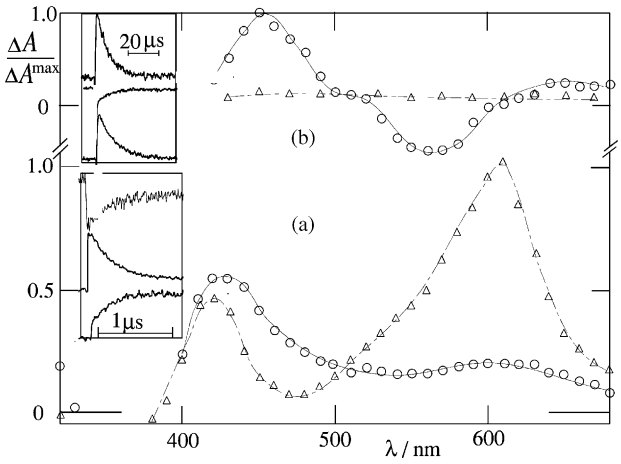


Fig. 2. Transient difference/absorption spectra of **3** in (a) air-saturated ethanol at 25 °C at 20 ns (○) and 1 μs (△) after the 354 nm pulse and (b) in argon-saturated ethanol at −100 °C after pre-irradiation with white light, <1 μs (○) and 10 μs (△) after the 530 nm pulse; insets: signals at (a) 370, 430 and 610 nm (upper to lower) and (b) 450, 560 and 650 nm.

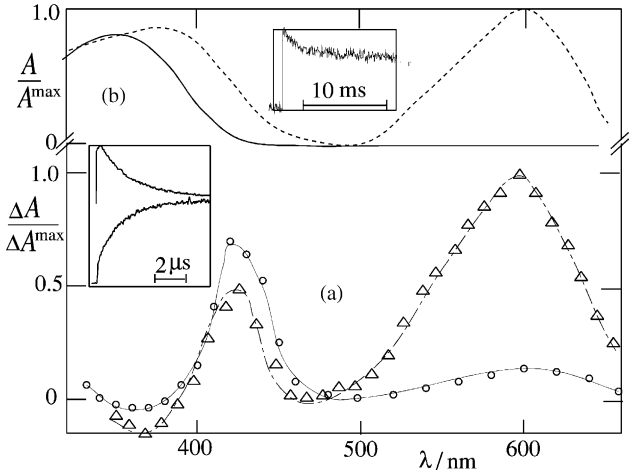


Fig. 3. Spectra of **3** in argon-saturated MCH at 25 °C (a) transients at 20 ns (○) and 10 μs (△) after the 354 nm pulse and (b) ground state absorption prior to and after 366 nm irradiation, full and dashed line, respectively; inset: signals at (a) 415 and 600 nm (upper to lower) and (b) at 600 nm and 80 °C.

low polarity and decreases strongly with increasing polarity [22], but this trend was not or only gradually found for **1**–**3** (Table 1). The same spectra as at 25 °C were recorded at higher temperatures and, apart from the most stable merocyanine, no photoisomer, in particular no *cis*-isomer, could

Table 1
Quantum yield Φ_{col} of colouration[a]

Compound	MCH	Toluene	MTHF	Acetonitrile	Ethanol
1	0.3	0.5	0.4	0.2	0.3
2	0.5	0.6	0.6	0.4	0.4
3	0.5	0.6	0.3	0.3	0.2

[a] In air-saturated solution at 25 °C, $A_{354} = 0.8$.

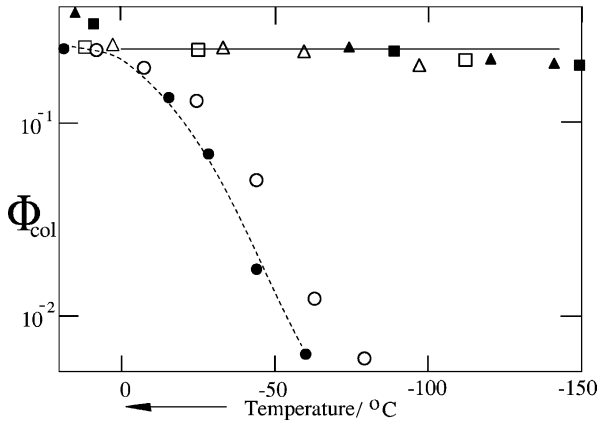


Fig. 4. Temperature dependence of Φ_{col} for **1** (squares), **2** (triangles) and **3** (circles) in MTHF (open symbols) and ethanol (full symbols).

be detected. Moreover, no significant change in Φ_{col} with temperature (typically 25–100 °C for MCH or toluene) was registered throughout. On the other hand, Φ_{col} of **3** in MTHF or ethanol decreases with decreasing temperature, but for **1** or **2** the lowering of the yield is much smaller (Fig. 4) and even at −196 °C colouration is noticeable. The values for **1** and **2** in petroleum ether at −196 °C are $\Phi_{col} = 0.002$ and $\Phi_{col} = 0.003$, respectively [13]. From the temperature dependence of Φ_{col} it follows that the colouration process of **3** requires an activation energy of 25–30 kJ mol^{-1}.

3.2. Singlet and triplet states

Phosphorescence with maxima at 490–540 nm was observed for **1**–**3** in MCH, MTHF or ethanol at −196 °C (Fig. 5b). The level of the triplet state is estimated from the onset of the spectrum of **1**, **2** and **3** in MTHF to be $E_T = 250$ and 245 kJ mol^{-1}, respectively. In contrast, no fluorescence of the Sp form was observed between 25 and −196 °C. The phosphorescence lifetime of **1** and **2** in ethanol is $\tau_p = 0.25$ s, that of **3** is 0.2 s. The quantum yield of phosphorescence is moderate or low, e.g. $\Phi_p = 0.02$ for **1** in MTHF and

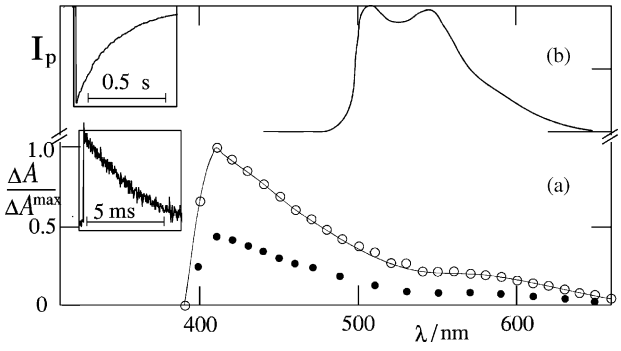
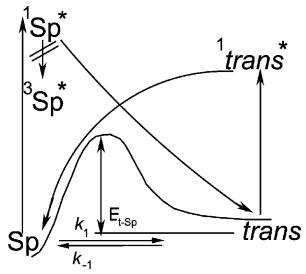


Fig. 5. (a) Transient absorption spectrum of **3** in argon-saturated ethanol at −150 °C, 1 μs (○) and 3 ms (●) after the 354 nm pulse, inset: signal at 420 nm, and (b) phosphorescence spectrum at −196 °C, inset: signal at 540 nm.



Scheme 1. Accounting for photochromism of **1** and **2** in solution at room temperature.

the highest value is $\Phi_p = 0.1$ for **3** in MCH. The results at −196 °C are in agreement with literature data in petroleum ether of $\Phi_p = 0.007$ and $\tau_p = 0.01$ s for **1** and $\Phi_p = 0.002$, and $\tau_p = 0.01$ s for **2** [13]. The phosphorescence intensity at 520 nm is maximum in rigid glasses and decreases with increasing temperature, as usual for this process [27], by several orders of magnitude in MCH, MTHF or ethanol, due to viscosity-induced changes in the triplet lifetime.

The photochemical ring opening of **1** or **2** occurs from the excited singlet state (^{1}Sp*) into the most stable merocyanine (Scheme 1) and practically no T–T absorption spectrum was detected at ambient temperature. Nevertheless, for **1** and **2** in all solvents at room temperature a minor component in the 100 ns range was observed in the grow-up kinetics (Fig. 1a). The origin of the colour appearance could be population of a shorter-lived triplet state with lower molar absorption coefficient than ε_t. Among the triplet states of 6-NO_2BIPS, that derivative with the 8-CO_2Me substituent can be regarded as a precedence for such a case with a triplet lifetime of $\tau_T = 0.1$ μs in acetonitrile [23]. In addition, a weak absorption around 430 nm (<10% of ΔA_{col}) following the pulse profile (≤15 ns) was observed in several cases, the largest effect was found for **1** in toluene. This signal is ascribed to a $S_1 \rightarrow S_n$ transition.

A T–T absorption of **1** and **2** under benzophenone-sensitised conditions in argon-saturated acetonitrile could not be detected, albeit energy transfer takes place, as concluded from the quenching of the triplet state of the donor and the corresponding delayed formation of the merocyanine form. Thus, sensitised population of the (not-resolved) triplet state occurs, as in other cases [14,23] and the triplet lifetime of **1** and **2** is estimated to be below 1 μs. A lower limit of $\tau_T \leq 0.4$ μs was obtained for **2** under acetone-sensitised conditions ($\lambda_{exc} = 308$ nm).

For spiroanthroxazine **3**, a strongly absorbing transient with maximum at $\lambda_T = 430$–440 nm concomitant with the pulse was detected prior to permanent colour formation. Examples of typical cases are shown in Figs. 2a and 3a. The transient, which is quenched by oxygen with the rate constant $k_{ox} = (1.5–2.5) \times 10^9$ M^{-1} s^{-1} (Table 2), is attributed to the lowest triplet state. The triplet lifetime (first-order decay) is $\tau_T = 2$–3 μs at 25 °C under argon. The observed triplet state is suggested to originate from the ring-closed Sp

Table 2
T–T absorption maximum, triplet lifetime, relative transient absorbances[a], quantum yield of formation of singlet oxygen and rate constant for quenching by oxygen for **3**

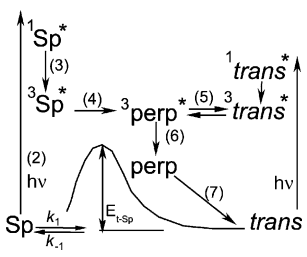
Solvent	λ_{TT} (nm)	τ_T (μs)	k_{ox} ($\times 10^9$ M^{-1} s^{-1})	$\Delta A_T/\Delta A_T^{max}$ [b]	Φ_Δ [c]
MCH	430	3	2	0.8	0.4
Toluene	440	2	2.5	1.0	0.5
Acetonitrile	430	3	2	0.6	0.3
Ethanol	440	2.5	1.5	0.4	

[a] In argon-saturated solution at 25 °C, $A_{354} = 2$.
[b] At $\lambda_{col} = 600$ nm.
[c] For optically matched oxygen-saturated solution.

form (^{3}Sp*) and/or a *trans*-merocyanine isomer (^{3}*trans**). For the latter case, an equilibrium with the perpendicular triplet state (^{3}perp*) is proposed (Scheme 2). This equilibrium accounts for the result that both the amounts of colour, i.e. *trans*-merocyanine, and the yield of the triplet state are virtually independent of the oxygen concentration. It is interesting to note that a ^{3}perp* → ^{3}*trans** equilibrium is well established for 6-NO_2BIPSs [21,22,27,28].

Since a certain part of the triplet state of **3** decays into the Sp form, oxygen is suggested to quench the ^{3}perp* rather than the ^{3}*trans** state. As limiting measure of the quantum yield of intersystem crossing (Φ_{isc}), Φ_Δ of formation of molecular singlet oxygen was used. The Φ_Δ values of **3** in oxygen-saturated solution are 0.3–0.5; note that under these conditions 98% of the triplet state is quenched. It should be emphasised that Φ_{isc} is largest in toluene, as concluded from Φ_Δ and the relative ΔA_T values in Table 2.

In viscous media at low temperatures, the triplet lifetime of **3** becomes much longer, e.g. 3 ms in ethanol at −150 °C, whereas the T–T absorption spectrum with maximum at 420 nm (Fig. 5a) resembles that at ambient temperature (Figs. 2a and 3a). Since Φ_{col} is much smaller (below the detection limit) under these conditions (Fig. 4), a route from the ^{3}Sp* state to the ^{3}*trans** state is excluded. On the other hand, the photochemical ring opening occurs at elevated temperatures from the ^{1}Sp* via the ^{3}Sp* state into the most stable merocyanine (Scheme 2). The excitation energy is probably located in the anthracene moiety and therefore the $T_1 \rightarrow T_n$ transitions are similar for the Sp and merocyanine forms. It should be emphasised that a possible contribution



Scheme 2. Accounting for photochromism of **3** in solution at room temperature.

Table 3
Inverse relaxation time $1/\tau_{t\text{-}Sp}$ (s^{-1}) obtained from the *trans*-photoisomer[a]

Compound	MCH	Toluene	Acetonitrile	Ethanol
1	0.3	0.2	0.1	0.016
2	0.3	0.06	0.02	0.005
3	0.3	0.2	0.2	0.1
4[b]	0.7 (18)[c]	0.7 (20)	1.5	0.7
5[b]	0.08 (160)	0.17 (120)	2.4 (60)	4 (40)

[a] Obtained at 25 °C in air- or argon-saturated solution; $A_{354} = 1$–3.
[b] Values for **4** and **5** are taken from [14].
[c] Values in parentheses refer to the minor component, see text.

of the singlet pathway for colouration of **3** has to be rejected, as judged from the coincidence of the kinetics of triplet decay and merocyanine formation (Figs. 2a and 3a).

3.3. Thermal ring closure

The relaxation time in several solvents at room temperature varies from ca. 3 s for **1**–**3** in MCH to 200 s for **2** in ethanol (Table 3). As usual for spiro compounds, $\tau_{t\text{-}Sp}$ depends strongly on the temperature. Plots of $\log 1/\tau_{t\text{-}Sp}$ versus $1/T$ are shown in Fig. 6 for **2** and **3** in several solvents in the range of 20 up to 100 °C. Pre-exponential factors of close to $10^{13}\ s^{-1}$ and the activation energies (Table 4) are derived from the linear dependences in all cases. For **3**, $E_{t\text{-}Sp} = 77$–$82\ kJ\ mol^{-1}$ with no significant effect of the medium, whereas for **2** a tendency to increase in polar solvents, up to $90\ kJ\ mol^{-1}$, was found. For NO_2BIPSs, the differences in $\tau_{t\text{-}Sp}$ at room temperature are mainly due to variations in the activation energy [22]. On the other hand, for spiro compounds not carrying a nitro group the pre-exponential factor rather than the activation energy changes significantly [23].

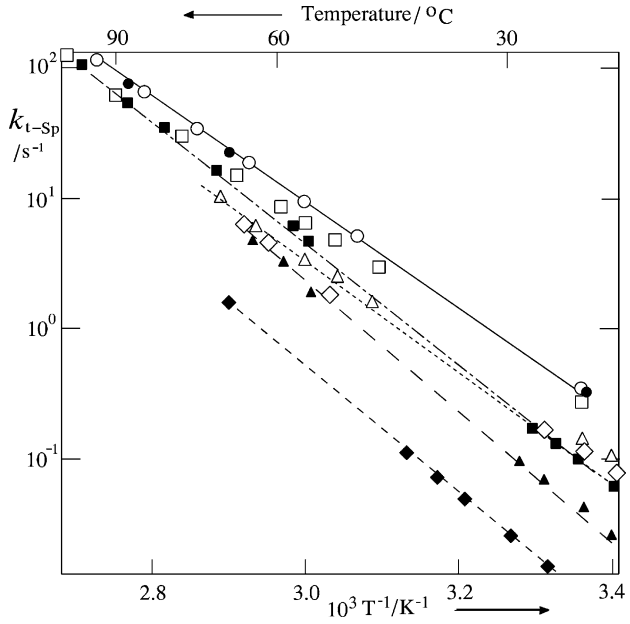


Fig. 6. Semilogarithmic plots of $1/\tau_{t\text{-}Sp}$ vs. $1/T$ for **2** (full symbols) and **3** (open symbols) in MCH (circles), toluene (squares), acetonitrile (triangles) and ethanol (diamonds).

Table 4
Activation parameters of thermal relaxation[a]

	$E_{t\text{-}Sp}$ ($kJ\ mol^{-1}$) (**2**)	$\log A$	$E_{t\text{-}Sp}$ ($kJ\ mol^{-1}$) (**3**)	$\log A$
MCH	77	12.5	77	12.7
Toluene	85	12.7	80	12.9
Acetonitrile	88	13.0	78	13.0
Ethanol	90	13.3	82	13.2

[a] In air- or argon-saturated solution; $A_{354} = 1$–3.

The relaxation of nitrospironaphthoxazines **1** and **2** in several solvents follows monoexponential decay throughout. However, for spiroanthroxazine **3** in MCH (inset in Fig. 3b) or toluene at 80 °C two decay components were observed. Other SOs also show a second minor relaxation component [5,6,14]. These values of 5–50 ms at 25 °C may be compared with $\tau_{t\text{-}Sp} = 0.5$–5 s for slow relaxation. The corresponding activation energy is comparable with the $E_{t\text{-}Sp}$ value of the major component. A bi-exponential thermal decolouration of SOs [6] is consistent with a fully established equilibrium between two photoisomers. Therefore, two separate steps leading to the ring-closure have been considered in addition to a third more twisted stereoisomer. The latter has spectroscopically and kinetically been observed on irradiation of the most stable photomerocyanine in several (but not all) solvents [14]. Replacing the naphthyl by the anthracene chromophore has no influence on the overall pattern and only minor effects on the thermal and photochemical parameters.

The major reason for the low efficiency of the overall photoinduced colour formation for **1**, **2** and **3** is not a too small Φ_{col} value (Table 1), but a relatively short relaxation time, at least in solvents of low polarity (Table 3). The short relaxation times of a few seconds are the consequence of rather large values of both activation energy and pre-exponential factor and the larger times in polar solvents are mainly due to larger $E_{t\text{-}Sp}$ values (Table 4). The thermodynamic activation parameters for relaxation of **4** and **5** in ethanol are entropies of $\Delta S^{\neq} = 6.7$ and $-23\ J\ mol^{-1}\ K^{-1}$, respectively, enthalpies of $\Delta H^{\neq} = 63$–$79\ kJ\ mol^{-1}$ and free energies of $\Delta G^{\neq} = 70$–$77\ kJ\ mol^{-1}$ [10]. The kinetics of ring opening are very fast and the efficiency of photocolouration is rather high [1–12]. Internal conversion to Sp in competition to ring opening via the singlet mechanism is less important for SOs than for NO_2BIPSs in polar solvents and BIPSs in solvents of low and large polarity [21–23].

3.4. Deactivation processes of the excited merocyanine form

Excitation at 530 nm of the merocyanine form of **1**–**3** (after pre-irradiation by UV or white light) leads to a bleaching at room temperature. Similar measurements were carried out at lower temperatures, where the $\tau_{t\text{-}Sp}$ values are sufficiently

long. Examples of the transient difference spectra are shown for **1** in MTHF (Fig. 1b) and **3** in ethanol (Fig. 2b). For **2** and **3** at −50 °C neither a triplet state nor a *cis*-isomer could be detected, in contrast to **4** or **5** where both appear [14]. The bleaching of **1** and **2** is due to a pathway of the singlet state (^{1}*trans**) into Sp (Scheme 1). For **3**, the bleaching is mainly due to the triplet state and the deactivation pathway leads from the ^{1}*trans** state into the quasi-stable merocyanine (Scheme 2).

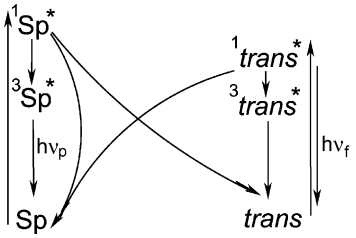
Nitrospironaphthoxazines **1** and **2** in MCH, MTHF or ethanol at −196 °C, after pre-irradiation at higher temperatures, exhibit fluorescence with maximum at λ_f = 690–710 nm, while λ_f of spiroanthroxazine **3** is blue shifted (Table 5). The level of the ^{1}*trans** state, estimated from the onset of the spectrum, is 184 kJ mol^{-1} for **1** or **2** and 190 kJ mol^{-1} for **3**. The fluorescence excitation spectrum is in agreement with the absorption spectrum. The fluorescence decay in glassy media could typically be fitted by two components and a longer lived one in less than 5% in all cases. The lifetimes (τ_f^1 and τ_f^2) are in the 0.2–3 ns range (Table 5) and the respective amplitudes are typically around 40–50%. The suggested origin of the two fluorescence lifetimes of **1**–**3** are the above-mentioned photoisomers. The contribution of both may slightly be influenced by the irradiation conditions prior the freezing. It should be mentioned that a red fluorescence from the merocyanine form of 6-NO_2BIPSs has been reported, e.g. τ_f = 0.2 ns in ethanol and 1.8–3.6 ns in polycarbonate films at room temperature and −196 °C [25,26].

The fluorescence signals of **1**–**3** (Scheme 3) strongly decrease with increasing temperature, as already reported for NO_2BIPSs [27]. This is consistent with τ_f < 0.2 ns at −60 °C for **1** or **3** in MCH, MTHF or for **1** in ethanol. Intersystem crossing is the main competing processes to the fluorescence emission from the ^{1}*trans** state of **3**, while for **1** or **2** the main competing processes is photochemical ring closure (Schemes 1 and 2).

Table 5
Fluorescence maximum and lifetimes[a]

	λ_f (nm)	τ_f^1 (ns)	τ_f^2 (ns)
MCH			
1	710	0.13	2.0
2	705	1.5	3.0
3	650	0.27	1.6
MTHF			
1	705	1.5	2.9
2	700	1.9	3.2
3	650	1.3	2.5
Ethanol			
1	695	0.2	2.2
2	695	1.4	3.0
3	640	1.3	3.0

[a] In air-saturated solution at −196 °C after pre-irradiation at −10 °C, λ_{exc} = 600 nm, A_{600} = 0.1–0.6.



Scheme 3. Accounting for photoprocesses of **1**–**3** in glassy media.

4. Conclusion

The photochromism of the nitrosubstituted spironaphthoxazines **1** and **2**, like spirooxazines **4** and **5**, where no triplet state could be detected at room temperature, is dominated by the ring opening via the singlet state. In contrast, triplet states become spectroscopically and kinetically observable for spiroanthroxazine **3**, where the ring opening occurs exclusively via the triplet state. This is a surprise insofar as ring opening of BIPSs and naphthalene or phenanthrene derivatives of SOs occurs via singlet states on the one hand, and for NO_2BIPSs via triplet states on the other. The quantum yield Φ_{col} of **1**–**3** at ambient temperature does not exhibit a substantial dependence neither on the type of spiro compound nor on the solvent polarity. The relaxation times and thus the activation parameters vary gradually for **1**–**3**, depending on the structural characteristics rather than solvent polarity.

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