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Photoprocesses in Spirooxazines and Their Merocyanines

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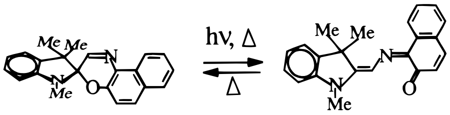
The photocoloration of four spirooxazines upon excitation of the closed form and the subsequent relaxation were studied in various solvents at different temperatures. The relaxation kinetics contain a minor shorter-lived component and a major longer-lived one. Both are activated processes leading back to the ring-closed form; the activation energy is typically 70 kJ mol^{-1}. The activation parameters are used as a basis to examine the photomerocyanine form(s), where weak fluorescence appears in glassy media at −196 °C. Excitation (at 530 nm) of the photomerocyanine in solvents of different polarity at room and lower temperatures leads to reversible bleaching in the visible range and weak absorption in the UV. The lifetime at 25 °C is in the 0.5−5 μs range and the activation energy is 21−29 kJ mol^{-1}. These oxygen-insensitive changes are attributed to cis−trans photoisomerization. The mechanism of photochromism and relaxation and the photoprocesses in spirooxazine-derived merocyanines are discussed.

Introduction

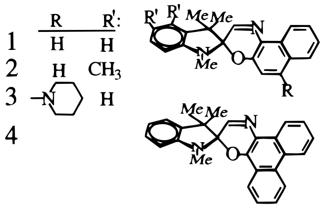
Indoline spirobenzopyrans (BIPSs[1]) and especially their 6-nitro-substituted derivatives (NO$_2$-BIPSs) have been investigated intensively[2−13] because of the wide application potential, e.g., in information processing. The photochromism of the spiropyran/photomerocyanine couple has been reviewed previously.[1−3] The photocoloration is fast[7] and the quantum yield (Φ_{col}) is in the 0.2−0.9 range for NO$_2$-BIPSs and lower (<0.1) for BIPSs.[1−13] A deeper insight into the mechanism has been obtained for NO$_2$-BIPSs, where the cleavage of the spiro C−O bond the subsequent ring opening occurs in the triplet manifold.[9−13] The colored merocyanine isomers have a zwitterionic character.[1−7] The photophysics, trans → cis photoisomerization, and the thermal back-reaction of NO$_2$-BIPS-derived merocyanines were characterized at various temperatures.[9,10]

A related system is given by spirooxazines (SOs). The spectroscopic, photophysical and photochemical properties of SOs have been studied by Chu[14,15] and several groups over the years.[16−42] This class of photochromic compounds has also attracted much attention due to its versatile applications, e.g., for ophthalmic lenses.[33] The spiroindoline part is nearly orthogonal with respect to the naphth- or phenanthroxazine part. Cleavage of the spiro C−O bond is efficient, $\Phi_{col} = 0.2-0.7$,[18,25,27,28] and the kinetics of the overall photocoloration takes place in the picosecond range.[16,17,21,26] The ground state equilibrium is on the side of the closed (colorless) form and after irradiation the open (colored) form reverts almost completely back.[14,18,20,27,28,39]



Also for the 6-nitro-substituted derivatives (NO$_2$-SOs) the kinetics of the overall photocoloration of SOs are in the picosecond range and a triplet precursor has a lifetime of 6 ns.[37] The ground state equilibrium and the relaxation kinetics of SOs, in contrast to several NO$_2$-BIPSs,[4−6] are rather independent of the solvent polarity.[1,2] The photostability and the degradation processes of SOs is the subject of various studies.[34] The properties of the merocyanine isomers are not fully understood, albeit information has been obtained by the two-pulse two-color technique.[22,23]

CHART 1



In this paper, the photophysical and photochemical properties of three naphthospiroindolineoxazines (**1**−**3**) and a phenanthrospiroindolineoxazine (**4**) were studied by nanosecond laser photolysis in solution at various temperatures. Irradiation into the most stable photomerocyanine in several solvents at lower temperatures leads to reversible bleaching. The activation parameters of these changes, which are attributed to photoisomerization, are determined and mechanistic implications are discussed (Chart 1).

Experimental Section

Compounds **1** (also denoted as naphthoxazine-spiroindoline or spiroindoline-naphthoxazine) and **4** were from Aldrich and purified by recrystallization, whereas **2** and **3** were synthesized according to methods described elsewhere.[14,15] The solvents (Merck) were of the purest spectroscopic quality available, e.g., acetonitrile (Uvasol); methylcyclohexane (MCH), 2-methyltetrahydrofuran (MTHF), butyronitrile (Fluka), and ethanol were purified by distillation. The absorption spectra were recorded on a Perkin-Elmer 540 spectrophotometer and the emission spectra on Spex-Fluorolog and Perkin-Elmer LS-5 spectrofluo-

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TABLE 1: Absorption Maxima of the Sp and *trans*-Merocyanine Forms, Ratio of Absorbances, and Relaxation Time of the Trans Isomer(s)[a]

compd	solvent	λ_{Sp} (nm)	$\lambda_t{}^b$ (nm)	A_t/A_{Sp}	$\tau_{t-Sp}{}^c$ (s)
1	cyclohexane	315	580	<0.001	1.4
	toluene	316	585	<0.001	1.3
	acetone	<320	590	<0.002	0.7
	acetonitrile	315	595	<0.002	0.7
	ethanol	319	610	<0.002	1.4
2	toluene	300	575	<0.001	2.8
	acetonitrile	300	580	<0.005	2.1
3	toluene	362	565	0.002	19
	acetonitrile	360	585	0.008	1.7
4	cyclohexane	340	575	0.008	13
	toluene	340	585	0.03	6
	acetone	350	595	0.05	0.9
	acetonitrile	335	590	0.13	0.4
	ethanol	340	600	0.15	0.25

[a] At 25 °C. [b] Obtained at the pulse end using $\lambda_{exc} = 354$ nm. [c] Compare Table 3.

rimeters. Time-resolved experiments were performed by excitation with the second or third harmonic from a Nd laser (JK Lasers), $\lambda_{exc} = 530$ or 354 nm, respectively; in some cases the 308 nm line of an excimer laser (Lambda Physics, EMG 200) was used. The laser setup was essentially the same as used previously.[9−13] Absorbances of 0.5−2 (in 1 cm cuvettes) were typically used for $\lambda_{exc} = 354$ nm, corresponding to SO concentrations of 0.1−0.4 mM, and for $\lambda_{exc} = 530$ nm, the concentrations were <0.1 mM. The kinetics of decoloration were measured after a 308 or 354 nm pulse using appropriate interference filters, e.g., 593 nm. The increase in absorbance at λ_t (e.g., 1 μs after the pulse) for optically matched conditions (e.g., $A_{354} = 1.0 \pm 0.03$) is linear with the laser intensity. The slope was taken as the relative quantum yield for coloration ($\Delta A_{col}{}^{rel}$).

Results and Discussion

Ground State Properties. The absorption spectrum of each SO in several solvents at ambient temperature has a major maximum (λ_{Sp}) at 300−360 nm which is due to the closed form (denoted as Sp). In several cases the absorption spectrum contains a second weak band with maximum (λ_t) at 560−600 nm (Table 1). This band is attributed to the respective *trans*-merocyanine isomer (denoted as trans) which is in equilibrium with the Sp form.

$$\mathrm{Sp} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{trans} \tag{1}$$

An example for **4** in acetonitrile is shown in Figure 1a. The molar absorption coefficient at λ_{Sp} is $\epsilon_{Sp} = (0.5-1.0) \times 10^4$ $M^{-1}cm^{-1}$,[27] and the values of the *trans*-merocyanine at λ_t (ϵ_t) are relatively large and show some variation with structure and solvent (Table 2).

Based on $\epsilon_t/\epsilon_{Sp} = 3.8$ and using the ratio of absorbances A_t/A_{sp} at 20 °C, the equilibrium constant k_1/k_{-1} was obtained as 0.8×10^{-3}, 4×10^{-3}, and 20×10^{-3} for **3** in toluene, acetonitrile, and formamide, respectively. For **3** in acetonitrile in the range of 10−30 °C the free energy change $\Delta G = 13.5$ kJ mol^{-1}, the enthalpy $\Delta H = 1.4$ kJ mol^{-1}, and the enthropy $\Delta S = 11.2$ J mol^{-1} K^{-1} were obtained. The respective values in formamide are 9.4 kJ mol^{-1}, 18 kJ mol^{-1}, and 29 J mol^{-1} K$^{-1.}$

Photocoloration. The trans isomer concentration in equilibrium with the Sp form can be greatly increased upon irradiation at λ < 400 nm.

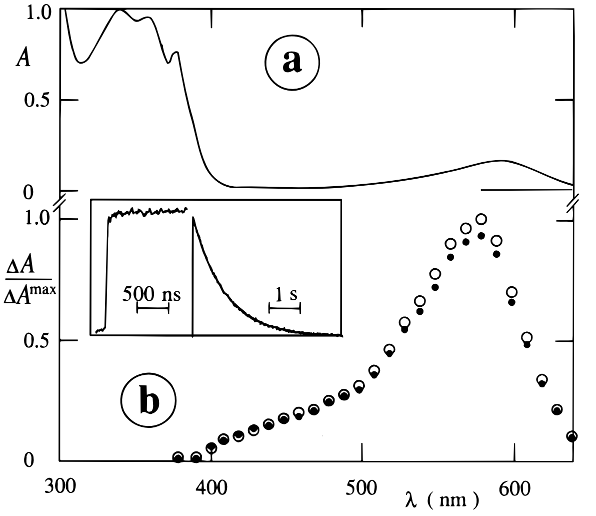


Figure 1. (a) Absorption spectrum of **4** in acetonitrile at 25 °C and (b) transient absorption spectra ($\lambda_{exc} = 354$ nm) of **1** in toluene at 50 ns (open) and 500 ns (full) after the 354 nm pulse; inset: kinetics at 593 nm.

TABLE 2: Molar Absorption Coefficient at λ_t and Quantum Yield of Sp → *trans*-Merocyanine Photocoloration from the Literature and the Relative Yields[a]

compd	solvent	ϵ_t (10^4 M^{-1} cm^{-1})	Φ_{col}	ref	$P_{col}{}^{rel\ b}$	$\Delta A_{col}{}^{rel\ c}$
1	cyclohexane	2.4	0.41	25	0.23	0.7
	MCH	3.8	0.41	28	0.36	
	toluene	3.1	0.23	18, 28	0.16	0.7
		3.1	0.33	25	0.23	
	acetone					0.7
	acetonitrile					0.6
	ethanol	6.1	0.32	28	0.45	0.7
		5.1	0.24	25	0.28	
3	cyclohexane					0.8
	MCH	4.2	0.55	28	0.53	
	toluene	3.2	0.42	24, 28	0.31	0.8
		3.2	0.74	25	0.54	
	acetone					0.85
	acetonitrile					0.95
	ethanol	6.7	0.65	28	1.0	1.0
4	cyclohexane					0.75
	MCH	5.1	0.49	28	0.57	
	toluene					0.8
	acetone					0.85
	acetonitrile					0.85
	ethanol	8.7	0.29	28	0.58	0.75

[a] At 25 °C using $\lambda_{exc} = 354$ nm. [b] $P_{col}{}^{rel} = (\epsilon_t\Phi_{col})/(\epsilon_t\Phi_{col})^{max}$. [c] Obtained in this work.

$$\mathrm{Sp} \xrightarrow{h\nu} {}^1\mathrm{Sp}^* \tag{2}$$

$${}^1\mathrm{Sp}^* \rightarrow\rightarrow \mathrm{trans} \tag{3}$$

The quantum yields of the Sp → *trans*-merocyanine photocoloration of the SOs are compiled in Table 2. For **1** in MCH and ethanol Φ_{col} is 0.41 and 0.32, respectively;[28] the largest value of $\Phi_{col}{}^{max} = 0.74$ has been reported for **3** in toluene.[25]

While the Sp form of **1** shows virtually no fluorescence even at −196 °C, that of **3** was reported to exhibit weak fluorescence.[39] A fluorescence of **1** at room temperature has been suggested to originate from a solvent-stabilized intermediate, which does not contribute significantly to photocoloration.[16,17] Interestingly, the weak fluorescence with maximum at 422 nm in ethanol at room temperature is more than 30-fold enhanced when **1** is present in microheterogeneous media, e.g., Triton X-100.[30]

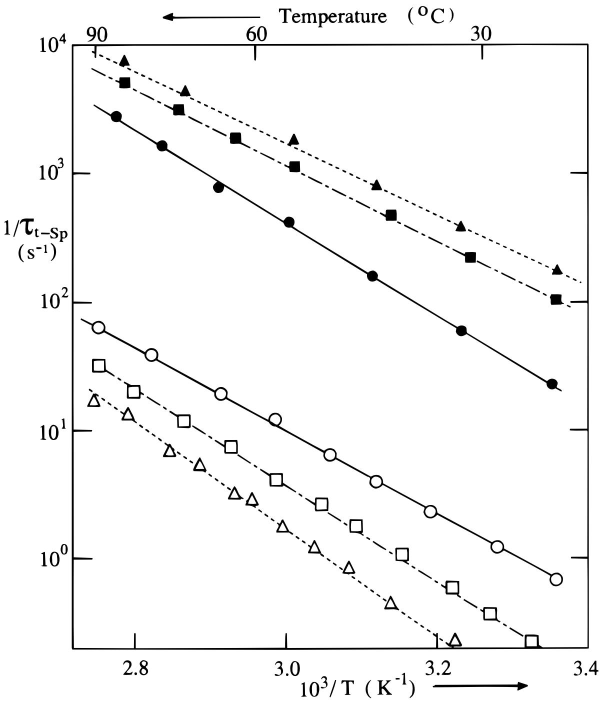


Figure 2. Arrhenius plots obtained from decoloration kinetics at 593 nm (after the 354 nm pulse) for **1** (circles), **3** (triangles), and **4** (squares) in toluene; full and open symbols refer to the shorter and longer lived component, respectively.

SOs (without nitro group) exhibit no phosphorescence;[36] the ring opening occurs in the S_1 state[26,37] and intersystem crossing either in their Sp or trans geometries does not take place. The energy of the triplet state of the Sp form is about 200 kJ mol^{-1}, as obtained by energy transfer to **1**.[25] This is in agreement with the phosphorescence of NO_2-SOs at −196 °C;[29,36] the quantum yield and lifetime of phosphorescence of the 6-nitro derivative of **1** in petroleum ether are 0.002 and 15 ms, respectively.[36]

The photocoloration of **1** in several solvents at room temperature ($\lambda_{exc} = 354$ nm) appears in a two-step process with a major component within 10 ns and a very minor second one with $t_{1/2} < 1$ μs (Figure 1b). This delayed coloration is not due to a triplet state as precursor since it appears even in oxygen-saturated solution. A similar behavior has also been reported previously.[18,37,40] The nature of this process is tentatively ascribed to a change in isomer distribution (see below). The relative absorption signals at λ_t (ΔA_{col}^{rel}) are compiled in Table 2. They are compared with the steady-state colorability values, $P_{col} = \epsilon_t \Phi_{col}$, taken from the literature and normalized with respect to **3** in ethanol. The ΔA_{col}^{rel} values are generally larger than the P_{col}^{rel} values and their changes with respect to polarity and variation of the structure are relatively small.

Relaxation Kinetics. It is well-known that the relaxation kinetics of the *trans*-merocyanine form follow first-order decay in solution at various temperatures.[18,20,24,27,28,39] First-order decay of the absorbance (e.g., at 593 nm) after preirradiation of Sp at 354 nm was also found in this work, e.g., at elevated temperatures. The log of the rate constant ($1/\tau_{t-Sp}$) is linearly dependent on $1/T$ throughout. From these Arrhenius plots (open symbols in Figure 2) the activation energy ($E_{t\rightarrow Sp}$) was determined. The relaxation time at 25 °C is in the order of $\tau_{t-Sp} = 0.5-10$ s, and the activation parameters are in agreement with those in the literature (Table 3). The $E_{t\rightarrow Sp}$ values show a remarkable variation with substitution and solvent, but a clean trend on polarity can be ruled out.

TABLE 3: Activation Energies and Rate Constants for Thermal Decoloration[a]

compd	solvent	$E'_{t\rightarrow Sp}$ (kJ mol^{-1})	$1/\tau'_{t-Sp}$[b] (s^{-1})	$E_{t\rightarrow Sp}$ (kJ mol^{-1})	$1/\tau_{t-Sp}$[b] (s^{-1})	ref[c]
1	cyclohexane				0.75	18, 20
	MCH	78	18	65	0.7	
				71	0.24	28
	toluene	69	20	62	0.7	
		61	35	56	0.54	20
	MTHF		10		1.3	
	acetone		*d*	79	1.5	
	acetonitrile		*d*	80	1.5	
					1.85	18, 20
				70	1.1	39
	ethanol		*d*	85	0.7 (0.9)[e]	
				69	0.7	20
				81	0.23	27, 28
				86	0.6	39
2	toluene			68	0.3	
	acetonitrile		*d*	75	0.5	
	ethanol				(0.3)	
3	MCH			88	0.04	28
	toluene	54	200	75	0.053	
				64	0.035	27
	acetone		150	76	0.5	
	acetonitrile		220	65	0.6	
	ethanol		100		3 (3)	
				41	0.58	27, 28
				58	1.9	39
4	MCH	63	160	60	0.08	
				79	0.07	28
	toluene	56	120	70	0.17	
				66.5	0.14	27
	MTHF		120		0.22	
	acetone		60	79	1.1	
	acetonitrile		60	60	2.4	
	ethanol		40	70	4 (3.9)	
				66	3.2	27, 28

[a] Using $\lambda_{exc} = 354$ nm. [b] Measured at 25 °C using $\lambda_{obs} = 593$ nm; major component: $1/\tau_{t-Sp}$, minor component: $1/\tau'_{t-Sp}$. [c] From this work unless indicated. [d] No fast component detectable. [e] Values in parentheses refer to naphthalene-sensitized excitation in argon-saturated ethanol.

Closer inspection of the relaxation kinetics at shorter times, however, reveals a second minor (5−20%) component in most cases (Figure 3). Its inverse relaxation time ($1/\tau'_{t-Sp}$) also follows an Arrhenius dependence (filled symbols in Figure 2). The values of $\tau'_{t-Sp} = 5-50$ ms at 25 °C may be compared with $\tau_{t-Sp} = 0.5-5$ s (Table 3). The activation energy ($E'_{t\rightarrow Sp}$) is comparable with the $E_{t\rightarrow Sp}$ value of the major relaxation component. A biexponential thermal decoloration of SOs has already been reported by Pottier et al.[20] Since a fully established equilibrium between two photoisomers cannot account for the observed biexponential relaxation, we suggest two separate steps leading to the ring closure.

The thermodynamic activation parameters, obtained from the kinetic data of the major component, have already been discussed.[27] For example, values in ethanol at 25 °C of $\Delta H^\ddagger = 78.6$ kJ mol^{-1}, $\Delta G^\ddagger = 76.5$ kJ mol^{-1}, and $\Delta S^\ddagger = 6.7$ J mol^{-1} K^{-1}, and $\Delta H^\ddagger = 63.1$ kJ mol^{-1}, $\Delta G^\ddagger = 69.9$ kJ mol^{-1}, and $\Delta S^\ddagger = -23$ J mol^{-1} K^{-1} were reported for **1** and **4**, respectively. The activation entropy ranges from close to zero when the barrier is large to $\Delta S^\ddagger = -120$ J mol^{-1} K^{-1} when $\Delta H^\ddagger$ is smaller.[27] For the minor component of **1** and **4** in toluene, we calculated $\Delta S^\ddagger = 17$ and -19 J mol^{-1} K^{-1}, respectively.

Indoline spiropyrans and their photomerocyanine are separated by an energy barrier; for NO_2-BIPSs the activation energy of thermal coloration is $E_{Sp} = 80-110$ kJ mol^{-1}.[1,4] There is a general agreement that cleavage of the C−O bond in the

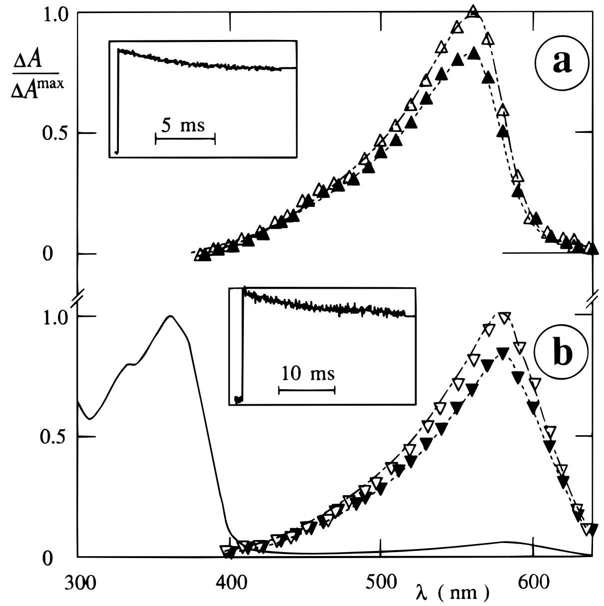
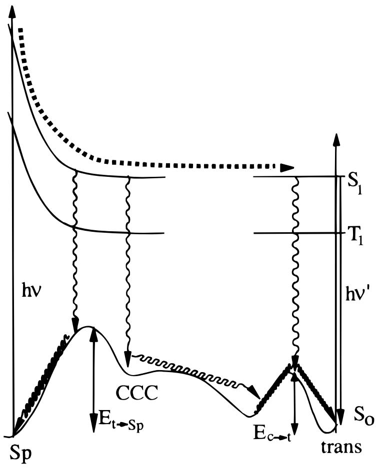


Figure 3. Transient absorption spectra of **3** in (a) cyclohexane and (b) ethanol at <1 ms (open) and 50 ms (full) after the 354 nm pulse; ground state, full line; insets: kinetics at 580 nm.

SCHEME 1



benzopyran portion leads initially to the CCC (cis−cis−cis) structure and subsequently to one or several trans isomers.[7] For several NO_2-BIPSs (albeit not all)[8] at room temperature it has been shown that τ_{t-Sp} increases with the solvent polarity.[5,6] This is due to the zwitterionic character of the merocyanine isomers[1−12] which is probably much smaller for BIPS itself.

The structure of the involved merocyanine in the case of SOs is still the subject of some controversy.[26,32,40] Cleavage of the C−O bond should lead to the CCC isomer and subsequently to the stable isomers with trans geometry. ^{1}H NMR measurements and MO calculations indicate that the TTC (trans−trans−cis) isomer has the lowest energy.[31] The small effect of solvent polarity on the A_t/A_{Sp} ratio and τ_{t-Sp} for **1** and **2** at room temperature (Tables 1 and 3) may be due to the quinoide character of the merocyanine isomers and the results for **3** and **4** indicate a more pronounced zwitterionic character. Nevertheless, this point has not unambiguously been settled as yet.[35,39,41]

The potential energy surface of the relevant S_1 state, leading from the Sp form via the CCC to the TTC isomer or essentially a trans isomer, is illustrated in Scheme 1. The kinetics of ring opening are very fast,[16,17,21,26] which favors the efficiency of photocoloration, in agreement with the rather high quantum yield. A strong decline of the potential energy of the S_1 state is expected on going from the Sp form to the most stable merocyanine. To account for the results that Φ_{col} is well below unity, there should be a $S_1 \rightarrow S_0$ pathway left from the maximum of the $E_{t\rightarrow Sp}$ barrier. Whether or not the potential energy surface at the position of the CCC isomer has a minimum remains open. The potential energy surface of the ground state along the reaction coordinate should have at least one major maximum (referring to $E_{t\rightarrow Sp}$) and at least one minor barrier.

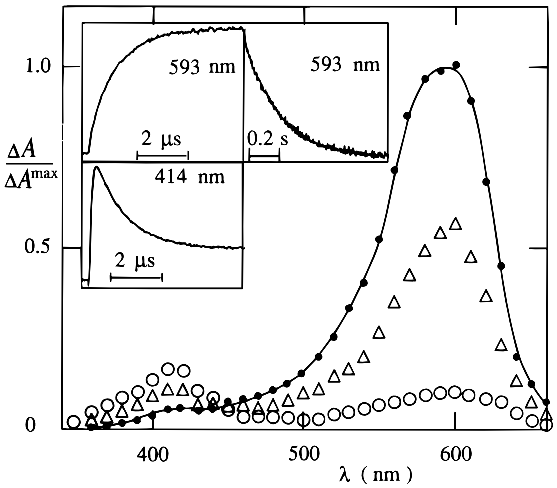


Figure 4. Transient absorption spectra of **4** in argon-saturated ethanol upon naphthalene-sensitized excitation at 100 ns (○), 1 μs (△) and 10 μs (●) after the 308 nm pulse; inset: kinetics at 414 and 593 nm.

Sensitized Coloration. Coloration is enhanced in the presence of high-energy donors.[25,29] In order to test for the triplet pathway, the method of sensitized coloration was applied using naphthalene as sensitizer in argon-saturated ethanol and $\lambda_{exc} = 308$ nm. The decay of the triplet state of the donor (^{3}D*), e.g., at 415 nm, is reduced in the presence of **1**−**4**. The SO concentration was adjusted such that the decay of ^{3}D* was 2−5 times faster. Under appropriate conditions, e.g., using a high enough naphthalene concentration, the amount of direct excitation of the Sp form was 10% or less, as measured by the absorption increase at longer wavelengths. An example for **4** is shown in Figure 4. The ΔA_{600} value, which at the end of the pulse is ≤5% of the maximum value, increases with the same first-order rate constant as the decay of ^{3}D*. This shows that another way of photocoloration of SOs runs via triplet states, i.e., by reactions 4 and 5.

$$^3\mathrm{D}^* + \mathrm{Sp} \rightarrow \mathrm{D} + {}^3\mathrm{Sp}^* \qquad (4)$$

$$^3\mathrm{Sp}^* \rightarrow\rightarrow \mathrm{trans} \qquad (5)$$

For **4** the rate constant for energy transfer is $k_4 \approx 4 \times 10^9$ M^{-1} s^{-1}. This is in agreement with $k_4 = 5 \times 10^9$ M^{-1} s^{-1} for **1** or **3** in toluene using acetonaphthone as sensitizer.[25] The ϵ values at $\lambda_t = 600$, 615, 580, and 600 nm for **1**, **2**, **3**, and **4**, respectively, are ca. 5 times larger than that of the donor triplet. The rate constant of the major (slower) decay process was found to be practically the same as upon direct excitation (Table 3). It should be noted that the quantum yield of triplet-sensitized coloration is close to unity.[25,29]

Photoinduced Processes from the *trans*-Merocyanine. A weak fluorescence signal of **1** in polar solvents at room temperature ($\Phi_f \leq 10^{-6}$) has been reported to originate from the merocyanine form.[38] Under steady-state conditions, the trans

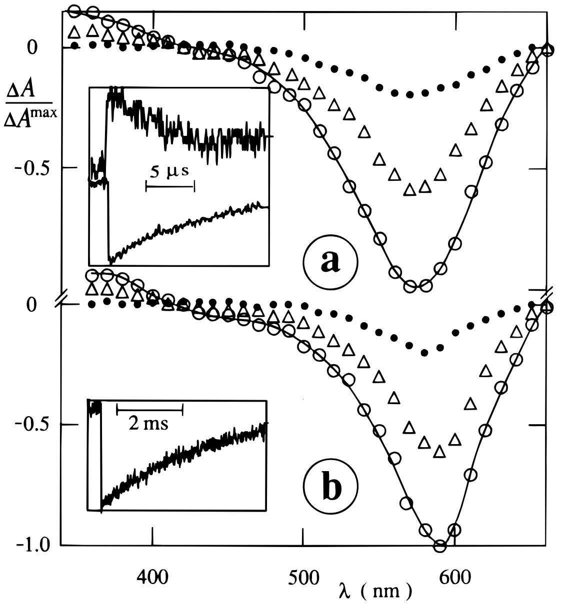


Figure 5. Transient difference spectra of *trans*-**1** in MTHF at (a) −12 °C and (b) −80 °C; (a) at the end of the 530 nm pulse (○) and after 5 μs (△), and 20 μs (●) and (b) after <0.1 ms (○), 3 ms (△) and 10 ms (●); insets: kinetics at 360 nm (absorption) and ≈580 nm (bleaching).

isomer of a SO shows virtually no fluorescence in fluid solution, e.g., at temperatures between −20 and −130 °C using λ_{exc} = 500−560 nm. However, weak fluorescence from the *trans*-merocyanine was recorded for **1**−**4** in MTHF at −196 °C; the maxima are at 660−670 nm, indicating a value of about 180 kJ mol^{-1} for the level of the ^{1}trans* state.

After UV irradiation of a SO in a given solvent at temperatures below −10 °C, the color remains stable within the time of the measurement (<10 s). Upon excitation of the *trans*-merocyanine at 530 nm, a strong bleaching over the whole vis spectrum and a weak transient absorption below 400 nm was observed. Examples for **1** in MTHF are shown in Figure 5. The kinetics of bleaching recovery and absorption decay are first order and practically identical (inset in Figure 5). The behavior is similar in most cases, but for **1** or **4** in polar solvents, such as acetonitrile or ethanol, the bleaching is much smaller (2−5 times) and almost no recovery could be observed. In solvents of low and moderate polarity, however, the rate constant ($k_{c\to t}$) decreases with temperature. Where the scatter is low enough, the plot of log $k_{c\to t}$ depends linearly on 1/*T* (Figure 6). The activation energies ($E_{c\to t}$) are compiled in Table 4. The lifetime, extrapolated to 25 °C, is in the 0.5−5 μs range. For comparison, the lifetime of the observed cis isomer of NO$_2$-BIPSs at room temperature is generally longer and varies from 2 μs to 1.4 ms.[9]

In those cases where τ_{t-Sp} is long enough, the spectral and kinetic measurements were also possible under continuous irradiation at room temperature, using either the whole analyzing light of the setup or a part after passing through an interference filter. These results (Table 4) can be directly compared with those obtained by Scaiano and his group[22,23] who applied the two-pulse two-color technique at room temperature. Essentially the same reversible spectral changes in solvents of low and moderate polarity on the one hand and almost no or a nonreversible bleaching in polar solvents on the other were observed by their and our methods. Nevertheless, for **1** in butyronitrile, which is almost as polar as acetonitrile, the major bleaching in the temperature range from 25 to −100 °C (Figure 6) was found to be reversible. The lifetime at 25 °C is as short as ca. 130 ns, but the activation energy is similar to those in solvents of lower polarity (Table 4).

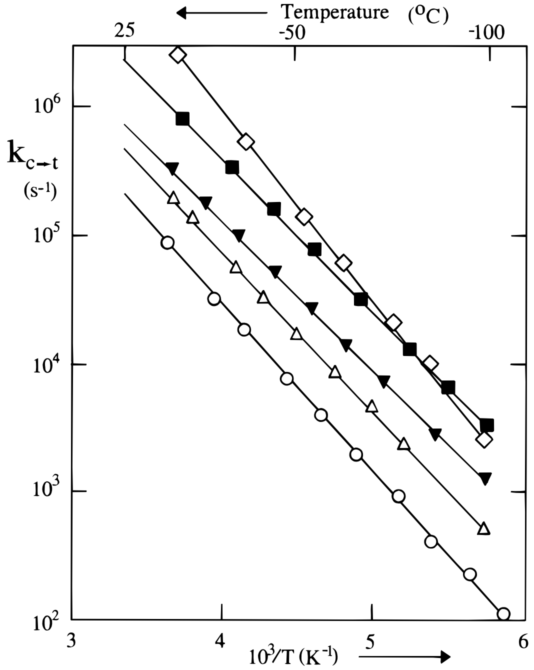


Figure 6. Arrhenius plots obtained from kinetics of bleaching recovery (560−600 nm) after 530 nm pulsing of **1** in MCH (○), MTHF (△) and butyronitrile (◇), **3** in MTHF (▼) and **4** in MCH (■).

TABLE 4: Preexponential Factor, Activation Energy, and Rate Constant for Isomerization[a]

compd	solvent	*A* (s^{-1} × 10^{10})	$E_{c\to t}$ (kJ mol^{-1})	$k_{c\to t}$[b] (s^{-1} × 10^5)
1	cyclohexane			2.4 2.3[c]
	heptane		27	2.3[c]
	MCH	0.5	25	2
	toluene	0.4	21	2
	MTHF	3	23	(4)[d]
	acetone	30	25	(20)
	butyronitrile	50	28	70
2	cyclohexane			8
	MTHF	2	27	(4)
3	cyclohexane			1.8
	toluene			17
	MTHF	0.7	22	(7)
	acetone			2
4	cyclohexane			20
	MCH	1.3	22	(20)
	toluene			24[e]
	MTHF	0.7	25	(3.2)

[a] Using λ_{exc} = 530 nm. [b] Measured directly at 25 °C. [c] Taken from ref 23. [d] Values in parentheses: extrapolated to 25 °C. [e] Major component.

The reversible bleaching is now attributed to fast (<10 ns) photoisomerization from the relaxed trans isomer into a mixture containing at least one cis isomer which has a larger ϵ value only below 400 nm. An alternative intermediate, where a four-membered ring with a bond between N and O is formed,[23] seems less likely in view of activation energies of ca. 40 kJ mol^{-1} for several NO$_2$-BIPSs.[9] The $E_{c\to t}$ and $k_{c\to t}$ values of the major reversible component are suggested to be due to back-isomerization. Note that $E_{c\to t}$ is significantly smaller than the $E'_{t\to Sp}$ and $E_{t\to Sp}$ values. To account for the two relaxation pathways (see above) one could imagine that the reaction coordinate in Scheme 1 should be better expanded in two directions according to two different stereoisomers, the structure of which is yet to be established.

Conclusions

A major longer-lived and a minor shorter-lived relaxation time for the four SOs at various temperatures indicate two distinctly different photomerocyanines and separate pathways for the thermal back reaction to the closed Sp form. A third, more twisted, stereoisomer was spectroscopically and kinetically observed on irradiation of the most stable photomerocyanine preferentially in solvents of low and medium polarity. Replacing the naphtho- by the phenanthrooxazine has no influence on the overall pattern and only minor effects on the various thermal and photochemical parameters. This is also the case for **3**, containing the bulky piperidine substituent.

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