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ARTICLES

Photoprocesses in Spiropyran-Derived Merocyanines

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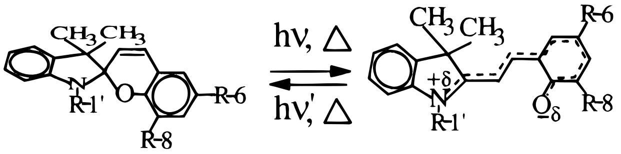
The photophysical and photochemical properties of a series of spiro[2*H*-1-benzopyran-2,2′-indoline] compounds (Sp-*n*)—five of them containing a nitro group in the 6-position of the benzopyran portion ($n = \mathbf{1}-\mathbf{5}$) while two ($n = \mathbf{6}, \mathbf{7}$) do not—were studied by nanosecond laser photolysis in solution. An intermediate, which is attributed to a photoisomer with cis structure, was observed for **1**−**5** upon excitation of either the spiropyran form or the trans isomer. The ground state properties of the spiropyran/trans isomer couple are characterized in a variety of solvents, and the activation parameters (e.g., activation energies of 38 and 49 kJ mol^{-1} for **1** and **5** in acetone, respectively) of the thermal cis → trans isomerization were determined. Relative quantum yields of the spiropyran → *trans*-merocyanine photocoloration and trans → cis photoisomerization ($\Phi_{Sp\rightarrow t}$ and $\Phi_{t\rightarrow c}$, respectively) were obtained. $\Phi_{Sp\rightarrow t}$ is substantial for **1**−**5** in solvents of low polarity but reduced in polar solvents. For **1**−**5** a short-lived transient (maximum at 420−440 and 560−590 nm, lifetime ≤ 10 μs) was observed and identified as a triplet state. It is suggested that this is the triplet of the trans isomer in equilibrium with the perpendicular triplet conformation. The nitro group strongly enhances the quantum yield of intersystem crossing for the spiropyran, thereby changing the singlet pathway of photocoloration for **6** or **7** into a triplet pathway for **1**−**5**. The trans → cis photoisomerization for **1**−**5**, despite the presence of the triplet state, is suggested to occur essentially via the singlet state.

Introduction

Spiropyrans have been investigated intensively by several groups over many years.[1−32] This class of photochromic compounds has attracted much attention because of the wide application potential, e.g., in information processing.[1,2,26] In solvents of low-polarity spiropyrans, in particular indoline spirobenzopyrans, exist in their colorless, closed form, which can be photoconverted reversibly into the colored merocyanine open form(s).



In polar solvents certain spiropyrans in equilibrium with their *trans*-merocyanine forms were found.

Introduction of a nitro group at the 6-position of the benzopyran moiety shifts the equilibrium toward the open form(s).[4,5,32] The equilibrium constant depends on the medium, increasing with solvent polarity. In virtually all solvents UV irradiation causes a shift toward the open form(s), which decreases to the equilibrium concentration after the light is removed. In some cases a back-reaction can be induced by visible light.[1,5] Spironaphthopyrans,[33−35] piperidinospiropyran type compounds,[36−38] and spiroxazines[38−44] behave similarly. The number of photochromic cycles is limited by photodegradation processes. Spiroxazines and chromenes are more photostable.[38−47] The photochromism of the spiropyran/*trans*-merocyanine couple has been reviewed previously.[1−3] Concerning the photophysics and photochemistry of the open form(s) and the mechanisms of isomerization, however, only little is known. The merocyanine form of nitro-substituted spirobenzopyrans was found to exhibit fluorescence at room temperature and phosphorescence at −196 °C.[13,28] For a spironaphthopyran no back-reaction to the colorless form occurs upon picosecond excitation at 547 nm, but a short-lived transient has been observed that was assigned to a $S_1 \rightarrow S_n$ transition.[34] For nitro-substituted piperidinospiropyrans, a short-lived photoisomer has been observed.[37] This raises the question of the pathway of *trans*-merocyanine → spiropyran and in particular of the role of triplet states in photodecoloration. A second question focuses on the pathways of formation of isomers in photocoloration of spiropyrans. Although this was the subject of many studies,[1−3,48] no agreement has been reached on the excited singlet or triplet pathways in the photocoloration.

A nitro group in spiropyrans could strongly enhance the quantum yield of intersystem crossing, thus changing the reaction pathway(s), as was shown for spironaphthopyran[35] and methoxy- and nitro-substituted piperidinospiropyrans.[36,38] One group of researchers[12,18,19] favors the excited singlet pathway to the merocyanine form(s) of nitro-substituted spirobenzopyrans, and another group[5,10,15,27] favors the triplet pathways. Besides, a better understanding of the photoprocesses of the merocyanine form(s) should be helpful for increasing the fatigue resistance of spiropyrans. The specificity of the photoprocesses for a particular indoline merocyanine might be caused by the existence of several transoid isomers that convert sequentially into the most stable one.[1,17,21,22,25,33,48] Another peculiarity of merocyanines is the ability to form dimers and higher aggregates.[4,8,12,15,20]

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In this paper we present spectroscopic and kinetic results obtained essentially by nanosecond flash photolysis measurements on seven spiropyrans (Sp-*n*). Five of them (termed NO_2−BIPSs) contain a nitro group in the 6-position of the benzopyran portion. Attention is directed to the photochemistry of their merocyanine form, which, when studied by UV−vis spectroscopy, is present as one (rather stable) trans isomer. We now give evidence that both Sp-*n* and *trans-n* (*n* = **1**−**5**) can, in solution at room temperature, be photochemically converted into one cis isomer with submillisecond lifetime. This raises the question of the pathway(s) of trans → cis photoisomerization as well as of the quantum yield ($\Phi_{t\rightarrow c}$) in photomerocyanines of spiropyrans.

	R-1′:	R-6:	R-8:
1	CH_3	NO_2	H
2	CH_3	NO_2	$CH_2CH{=}CH_2$
3	CH_3	NO_2	OCH_3
4	C_2H_4OH	NO_2	OCH_3
5	C_6H_5	NO_2	OCH_3
6	CH_3	H	OCH_3
7	CH_3	OCH_3	H

Experimental Section

Compounds Sp-*n* (*n* = **1**−**7**) have been synthesized according to methods described elsewhere.[49] Sp-**1**, the so-called 6-nitro-BIPS, Sp-**3**, and Sp-**7** were the same as used previously.[14] Note that **2** contains an 8-allyl group. The compounds were compared with authentic material by thin layer chromatography and checked by elementary analysis. Ferrocene was from Fluka. The solvents (Merck) were of the purest spectroscopic quality available, e.g., acetonitrile (Uvasol), glycerol triacetate (GT), and butyronitrile were from Fluka, and methylcyclohexane (MCH), 2-methyltetrahydrofuran (MTHF), butyronitrile, and methanol were purified by distillation.

Emission spectra were recorded on spectrofluorometers (Spex-Fluorolog and Perkin-Elmer LS-5). The quantum yield (Φ_f) was determined using cresyl violet in ethanol as reference ($\Phi_f = 0.54$ in methanol at 24 °C,[50] $\lambda_{exc} = 530{-}600$ nm) and optically matched samples having absorbances of 0.1 or 0.2 at λ_{exc}. No correction for the refractive index in other solvents was made. The transient absorption measurements were carried out by means of 10−20 ns flash photolysis (pathlength: 1.0 cm quartz cells).[51] Most experiments were performed with the second or third harmonic from a Nd laser (JK lasers) with λ_{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.[51] Absorbances of 0.5−5 were typically used for λ_{exc} = 354 nm, corresponding to NO_2−BIPS concentrations of 0.1−1 mM, whereas for λ_{exc} = 530 nm, the absorbances (0.1−1) and trans isomer concentrations (3−30 μM) were lower. Although an even lower trans isomer concentration of <5 μM is advantageous for bleaching, the triplet state becomes better resolved using much higher concentrations. The kinetics of cis → trans isomerization at elevated temperatures were measured with a Tektronix 390 AD digitizer. The absorption spectra were recorded on spectrophotometers (Perkin-Elmer 540, Bruins/Omega). The kinetics of decoloration were measured after preirradiation at 313 or 366 nm (response time of 1−2 s). *A*′ in Figure 1 refers to the difference $A_t - A_{end}$, where A_{end} is the absorbance after reaching the equilibrium.

The increase in absorbance at λ_{TT} (end of pulse) for optically matched conditions (e.g., $A_{354} = 1.0$) is nearly linear with the laser intensity (I_L). The slope is taken as the relative quantum yield for triplet population (Φ_T). Likewise, the slope of the increase in absorbance at the maximum and after longer times, e.g., 10 ms (for optically matched conditions, A_{354} = 0.5, 1.0, or 2.0) vs I_L was taken as the relative quantum yield for the spiropyran → trans photoconversion. Absolute $\Phi_{Sp\rightarrow t}$ values of 0.59[1,3] or 0.85[31] for **3** in toluene were taken from the literature. The values for $\Phi_{t\rightarrow c}$ were determined analogously from the relative absorbance at λ_c^{max} using normalized conditions, e.g., A_{530} = 0.1, 0.3, or 0.6). For determination of the three quantum yields of the NO_2−BIPSs, Φ_T, $\Phi_{Sp\rightarrow t}$, and $\Phi_{t\rightarrow c}$, we did not correct for changes in the molar absorption coefficients of the ^{3}trans* state and the Sp, trans, and cis states with respect to variation of the substituent and solvent. This increases their otherwise much smaller errors to ca ±30%, which is, nevertheless, significantly smaller than the effect of solvent polarity as the dominant parameter. Unless otherwise indicated, the measurements were performed at 24 °C.

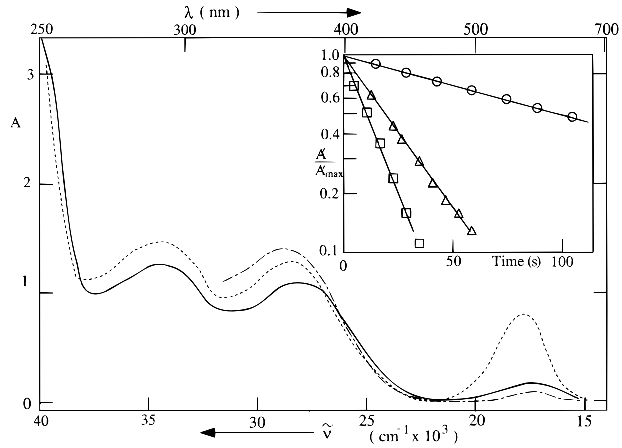


Figure 1. Absorption spectra of Sp-**4** in acetone (−•−), acetonitrile (−), and ethanol (- - -) in equilibrium with the trans isomer. Inset shows the kinetics of decoloration after irradiation at 313 nm of Sp-**1** (○), Sp-**3** (△), and Sp-**5** (□) in acetonitrile.

Results

Ground State of *trans*-Merocyanine. The absorption spectrum of the Sp form of each of the five NO_2−BIPSs in solution at ambient temperature has a maximum at 240−250 nm and contains a second weaker band with maximum at 330−365 nm (Table 1). The molar absorption coefficient in this UV range is typically (0.5−1) × 10^4 M^{-1} cm^{-1}.[1,2] The whole spectrum is significantly and slightly shifted to shorter wavelengths for Sp-**6** and Sp-**7**, respectively. In addition, a band with a maximum at $\lambda_t \approx 580$ nm appears in various cases, as shown in Figure 1 for **4** in three polar solvents. This band is attributed to *trans-n* in equilibrium with Sp-*n*.

$$\mathrm{Sp} \underset{\Delta}{\overset{\Delta}{\rightleftarrows}} \mathrm{trans} \qquad (1)$$

Equilibrium 1 depends, owing to the zwitterionic character of the open forms, on the solvent polarity, for which we used the Dimroth E_T^N parameter as a measure.[52] The relative absorbance at λ_t = 530−600 nm shows a decreasing trend with decreasing E_T^N parameter in some cases (Table 1); the molar absorption coefficient at λ_t is typically (3−5) × 10^4 $M^{-1}cm^{-1}$.[1,2] In particular, $\epsilon_{604} = 3.25 \times 10^4$ M^{-1} cm^{-1} for **3** in toluene.[31] For Sp-**6** and Sp-**7** virtually no coloration could be achieved even in polar solvents.

For NO_2−BIPSs the trans isomer concentration can be greatly increased upon irradiation of the Sp form (λ_{irr} = 313 or 366 nm).[3,5]

TABLE 1: Absorption Maxima of the Sp and Trans Forms, Ratio of These Absorbances, and the Lifetime of the Trans Isomer[a]

compd	solvent	E_T^N [b]	λ_{Sp} nm	λ_t nm	A_t/A_{Sp} [c]	$\tau_{t\rightarrow Sp}$ [d] s
1	toluene		340	600[d]	<0.001	9
	acetone		350	565	0.03	80
	acetonitrile		340	560	0.05	160
	ethanol		335	535	0.08	>1000
2	toluene		350 sh	600[d]	<0.001	10
	acetone		352	598	0.12	60
	acetonitrile		358	595	0.3	50
3	cyclohexane	0.006	336	605[d]	<0.001	
	toluene	0.099	340	605[d]	<0.001	20[e]
	MTHF	0.179	340	595	0.03	
	acetone	0.355	350	580	0.06	25
	DMF	0.404	350	585	0.05	80
	butyronitrile		350	575	0.05	≤100
	acetonitrile	0.494	352	580	0.15	35
	ethanol	0.654	348	558	0.4	140
	methanol	0.762	350	550	0.3	
4	acetone		350	594	0.06	15
	acetonitrile		355	583	0.15	20
5	acetone		355	605[d]	0.01	12
	acetonitrile		352	595	0.02	15
	ethanol		352	570[d]	≤0.005	
6	ethanol		290 sh		<0.001	
7	acetone		320		<0.001	

[a] From ground state measurements in aerated solution at room temperature. [b] Dimroth parameter. [c] Ratio of $A(\lambda_t)$ to $A(\lambda_{Sp})$ values for nonirradiated solution. [d] After irradiation at 313 or 366 nm. [e] A value of 172 s at 10 °C has been reported.[31]

TABLE 2: Fluorescence Maxima and Quantum Yield of the Trans Isomer[a]

compd	solvent	λ_f^{ex}, nm	λ_f, nm	Φ_f
1	acetone		645	0.005
	acetonitrile		645	0.008
	ethanol	545 (520)	642 (590)	0.012
2	acetone		685	0.01
	acetonitrile		685	0.01
	ethanol	590 (536)	685 (605)	0.012
3	MTHF	590 (555)	650 (605)	0.005
	acetone		670	0.01
	butyronitrile	590 (536)	~640 (605)	0.004
	acetonitrile		670	0.01
	ethanol		660 (600)	0.016
4	acetone		650	0.01
	acetonitrile		660	0.02
	ethanol	560 (580)	660 (603)	0.002
5	ethanol	580 (530)	670 (620)	<0.005

[a] In aerated solution at 24 °C (values in parentheses refer to −196 °C). λ_{exc} = 530−560 nm. λ_f = 620−660 nm.

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

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

It is well-known that the relaxation of the colored form, after preirradiation of Sp, follows first-order decay kinetics.[1−3,5] The lifetime is generally believed to be shorter in solvents of lower polarity.[4,21,32] For the five NO_2−BIPSs the values at 24 °C ($\tau_{t\rightarrow Sp}$) show a great variation with substitution (inset of Figure 1), e.g., $\tau_{t\rightarrow Sp}$ = 10−80 s in acetone or 15−160 s in acetonitrile (Table 1). There is a rough tendency to longer lifetimes with increasing E_T^N value for **1** or **3** but not for **5**.

Photoinduced Processes from *trans*-Merocyanine. The trans isomer of each NO_2−BIPS, using λ_{exc} = 500−560 nm, shows weak fluorescence in solution at room temperature with maxima (λ_f) around 640−680 nm (Table 2). Examples are shown for **1** and **4** in ethanol (Figure 2). Typical Φ_f values are 0.01. The excitation spectrum coincides with the absorption spectrum; the maximum (λ_f^{ex}) is around 550−590 nm. At −196 °C in butyronitrile or ethanol both the fluorescence emission and excitation maxima are blue-shifted. For **1** and **3** in ethanol the absorption band undergoes a similar blue-shift on going to −196 °C, thus excluding an impurity or other species as the origin.

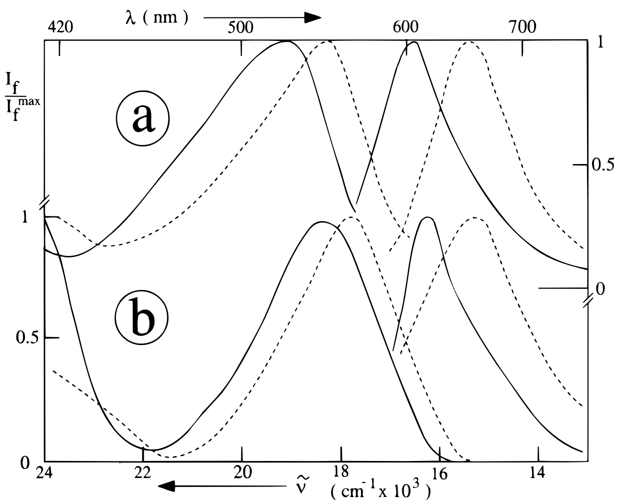


Figure 2. Fluorescence excitation (left) and emission (right) spectra at 24 °C (dashed lines) and −196 °C (full lines) of (a) *trans*-**1** and (b) *trans*-**4** in ethanol; λ_{exc} = 550 nm and λ_f = 650 nm.

Upon excitation at 530 nm of *trans*-**3** two transients were observed. One was recorded at the end of the 15 ns pulse. It is short-lived and exhibits a weak band with a maximum at $\lambda_{TT} \approx 440$ nm. Absorption of this initial species is overlapped by that of a longer lived one with maxima at 430 and ~635 nm and with bleaching around 570 nm. Formation of the band in the 600−660 nm range is delayed, since the short-lived transient has a lower absorption coefficient. The short-lived transient, which decays by first-order kinetics and which is efficiently quenched by oxygen for all NO_2−BIPSs, has been ascribed to a triplet state.[53] We further assign it to the triplet of the trans isomer (^{3}trans*)[53] and suggest that the excited singlet state of the trans isomer decays initially by intersystem crossing.

$$\mathrm{trans} \xrightarrow{h\nu} {}^1\mathrm{trans}^* \tag{4}$$

$$^1\mathrm{trans}^* \rightarrow {}^3\mathrm{trans}^* \tag{5}$$

The T−T absorption maximum is typically at λ_{TT} = 440 nm, and the triplet lifetimes are τ_T = 5−10 μs. Further properties of this ^{3}trans* state, which was more selectively detected upon excitation at 354 or 308 nm, i.e., without bleaching, are described below.

Similar spectra, kinetic properties, and the effect of oxygen were found for the five NO_2−BIPSs in several solvents. The longer lived transient of *trans-n* with a bleaching and an absorption maximum (λ_c^{max} and λ_c^{min}, respectively, Figure 3 and Table 3) is ascribed to one of the possible rotamers with essentially cis isomer structure termed: *cis-n*. This is based on the reversibility of the spectral changes, the independence of the decay kinetics from the oxygen concentration, and the effect of temperature (next section). The nature of the solvent has virtually no effect on the spectral properties, and apart from alcohols, it has a relatively small effect on the quantum yield $\Phi_{t\rightarrow c}$ (Table 3). In virtually all cases examined, $\Phi_{t\rightarrow c}$ was found to be independent of the oxygen concentration. Production of the cis isomer occurs via reaction 6 (bypassing ^{3}trans*) or 7:

$$^1\mathrm{trans}^* \rightarrow\rightarrow \beta\ \mathrm{cis} + (1-\beta)\mathrm{trans} \tag{6}$$

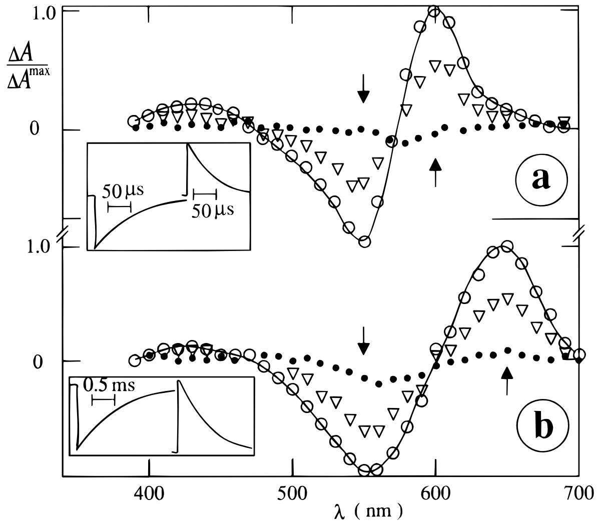


Figure 3. Transient absorption spectra of (a) *trans*-**1** in argon-saturated acetone at the end of the 530 nm pulse (○) and after 30 (▽) and 100 (●) μs and (b) *trans*-**5** in argon-saturated acetonitrile after <0.02 (○), 0.3 (▽), and 2 (●) ms. Insets show the kinetics at 550 and 600 or 650 nm.

$$^3\text{trans}^* \rightarrow\rightarrow \alpha\ \text{cis} + (1 - \alpha)\text{trans} \qquad (7)$$

Here, α and β are the fractions of triplet or excited singlet that decay into the cis isomer, respectively.

When ferrocene, having a triplet energy of ~163 kJ mol^{-1}, is used as a quencher, the triplet lifetime of **1**−**5** is strongly reduced, corresponding to rate constants of (4−6) × 10^9 M^{-1} s^{-1} in acetone, whereas the yield of the cis isomer remains rather constant in most cases. This is explained by energy transfer from ^{3}trans* to ferrocene yielding both isomers. In ethanol or methanol a bleaching was found, but for **1** and **2**, differing from **3** and **4**, virtually no transient absorption around 600 nm was recorded. Instead, the bleaching appeared to be permanent. Since the colored band of **1** and **2** in alcohols can be removed on irradiation at $\lambda_{irr} > 500$ nm and re-formed on irradiation at $\lambda_{irr} = 313$ nm, the main photoprocess is photoconversion from the trans isomer into the Sp form:

$$^1\text{trans}^* \rightarrow\rightarrow \text{Sp} \qquad (8)$$

Thermal Cis → Trans Isomerization. The decay kinetics of the observed cis isomer follow a first-order law in solution at room temperature and are the same in the area of bleaching and absorbance (insets of Figure 3). Thus, this main route is ascribed to a cis → trans isomerization: Additionally, a

$$\text{cis} \xrightarrow{\Delta} \text{trans} \qquad (9)$$

nonreversible side reaction was observed; its contribution is only significant in alcohols.

The lifetime of the cis isomer ($\tau_{c\rightarrow t}$) in moderately and strongly polar solvents at room temperature ranges from 2 μs for **3** in methanol to 1.4 ms for **5** in acetone (Table 4). The presence or absence of oxygen has no discernible effect on $\tau_{c\rightarrow t}$. First-order decay of the absorbance at 600−660 nm was also found at elevated temperatures. (Note that decoloration occurs in various cases at higher temperatures, e.g., at 60 °C.) The log of the rate constant ($1/\tau_{c\rightarrow t}$) is linearly dependent on $1/T$.[53] From these Arrhenius plots the activation energy ($E_{c\rightarrow t}$) and the pre-exponential factor were determined. Note that the scatter was too great to allow reproducible results in toluene at elevated temperatures. In particular, $E_{c\rightarrow t} = 42$ kJ mol^{-1} and $A = 7 \times 10^{10}$ s^{-1} or 49 kJ mol^{-1} and 2×10^{11} s^{-1} in acetone for **3** and **5**, respectively.

TABLE 3: Absorption Maximum and Minimum of the Cis Isomer and Its Relative Yield[a]

compd	solvent	λ_c^{min}, nm	λ_c^{max}, nm	$\Phi_{t\rightarrow c}$ [b]
1	toluene	580	640	0.9
	acetone	545	600	0.6
	acetonitrile	545	605	0.4
	ethanol	530	585	<0.1
2	acetone	590	645	0.9
	acetonitrile	590	640	0.8
	ethanol	560[c]		<0.1
3	toluene	580	660	1.0
	MTHF	565	640	0.8
	GT	575	645	
	acetone	570	635	0.6
	DMF	565	630	0.6
	acetonitrile	560	625	0.4
	ethanol	535	605	0.1
4	acetone	560	635	0.3
	acetonitrile	550	630	0.2
5	acetone	570	650	0.6
	acetonitrile	565	640	0.6

[a] In argon-saturated solution at room temperature. $\lambda_{exc} = 530$ nm. [b] Relative value. [c] Bleaching due to T−T absorption. No formation of cis.

TABLE 4: Activation Parameters for Thermal Cis → Trans Isomerization and Lifetime of the Cis Isomer[a]

compd	solvent	$E_{c\rightarrow t}$, kJ mol^{-1}	A, 10^{12} s^{-1}	$\tau_{c\rightarrow t}$,[b] μs
1	toluene			~2500
	acetone	40	0.1	55
	acetonitrile	39	0.9	16
2	acetone	38	0.16	20
3	toluene			~8000
	acetone[c]	42	0.07	280
	acetonitrile[c]	40	0.11	70
	methanol	38	2.1	2.1
4	acetone	46	0.5	160
	acetonitrile	38	0.1	50
5	acetone	49	0.24	1400
	DMF	41	0.03	400
	butyronitrile	44	0.07	500
	acetonitrile	39	0.7	500

[a] In aerated or argon-saturated solution using $\lambda_{exc} = 530$ nm. [b] At 24 °C. [c] Same values using $\lambda_{exc} = 530$ or 354 nm.

The data in Table 4 reveal some similarities on changing either substitution or solvent polarity and, to a certain extent, some differences, e.g., the small effect of polarity and the longer lifetimes for **5** in comparison to those for **1**−**4**. The larger $\tau_{c\rightarrow t}$ values are partly due to a larger pre-exponential factor. In addition, $E_{c\rightarrow t}$ tends to decrease with increasing value of the $E_T{}^N$ parameter. This might be caused by stronger solvation of the trans compared to the cis isomer due to a larger dipole moment of the former ground state.

Deactivation of the Excited Spiropyran. The seven Sp-*n*s in solution at ambient temperature show no fluorescence upon excitation in the 300−400 nm range, but phosphorescence (not shown) becomes observable at −196 °C.

The transient absorption spectrum of Sp-**1** in argon-saturated cyclohexane shows maxima at $\lambda_{TT} = 440$ and 580 nm at the end of the 354 nm pulse (Figure 4a). This absorption is overlapped by that of the longer lived species. Similar spectra were recorded in other cases (Table 5). The decay at 440 nm obeys first-order kinetics. The rate constant ($1/\tau_T$) matches the increase in the 540−660 nm range. The initial transient is the precursor of the secondary, as illustrated in Figure 4a for Sp-**1** in cyclohexane at different wavelengths. We assign them to the ^{3}trans* state and the cis and trans ground state mixture,

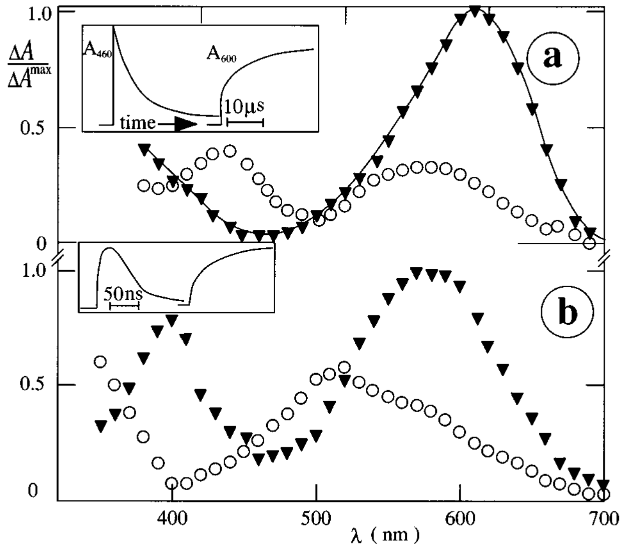


Figure 4. Transient absorption spectra (a) of Sp-**1** in cyclohexane under argon at <0.1 (○) and 30 (▼) μs after the pulse and (b) of Sp-**6** in argon-saturated acetonitrile in the presence of benzophenone at 0.1 (○) and 10 (▼) μs after the 354 nm pulse. Insets show the decay at 460 nm and the increase at 600 nm under argon (upper traces) and oxygen (lower traces).

TABLE 5: T−T Absorption Maxima, Triplet Lifetime and Yield, Absorption Maximum of the Isomer Mixture, and Yield of Formation of the Trans Isomer from Sp[a]

compd	solvent	λ_{TT}, nm	τ_T, μs	Φ_T [b]	$\lambda_{c,t}^{max}$,[c] nm	$\Phi_{Sp\to t}$ [d]
1	cyclohexane	440, 580	6	0.9	385, 605	0.8
	toluene	440, 580	6	0.8	390, 610	0.6
	acetone	440, 585	5	0.3	390, 590	0.22
	acetonitrile	440, 590	8	0.05	390, 580	0.07
2	toluene	440, 590	4	0.2	<400, 615	0.3
	acetone	430, 570	5	0.1	400, 600	0.06
	acetonitrile	430, 570	5	0.05	<400, 590	0.04
3	cyclohexane[e]	430, 565	5	1.0	<400, 610	0.85
	toluene	430, 560	7	0.7	410, 615	0.59[f]
	MTHF	440, 570	8	0.4	410, 610	0.35
	acetone[g]	440, 556	5	0.12	410, 605	0.16
	DMF	440, 565	10	0.18	<410, 595	0.17
	acetonitrile	430, 560	8	0.08	410, 595	0.18
	ethanol	440, 555	5	0.04	400, 560	0.07
4	acetone	430, 565	6	0.15	410, 600	0.22
	acetonitrile	430, 565	6	0.08	410, 600	0.12
5	toluene	420, 580	4	0.9	<410, 620	0.65
	acetone	430, 570	4	0.15	410, 620	0.22
	acetonitrile	430, 570	8	0.06	410, 620	0.09
6	toluene				*h*	<0.05
	acetone				<410, 570[i]	<0.05
7	toluene				<400, 550	<0.05

[a] At room temperature (under argon, $\lambda_{exc} = 354$ nm, unless otherwise noted). [b] Relative values. [c] Maximum in oxygen-saturated solution referring to the isomer mixture after 0.01−0.1 ms. [d] Relative values after 1 ms. [e] Same λ_{TT} and τ_T using $\lambda_{exc} = 308$ nm. [f] Absolute value: 0.59 taken from ref 3. [g] Same $\lambda_{c,t}^{max}$ using $\lambda_{exc} = 308$ nm. [h] No absorption in the visible measurable after preirradiation at 313 nm. [i] Upon xanthone- or benzophenone-sensitized excitation.

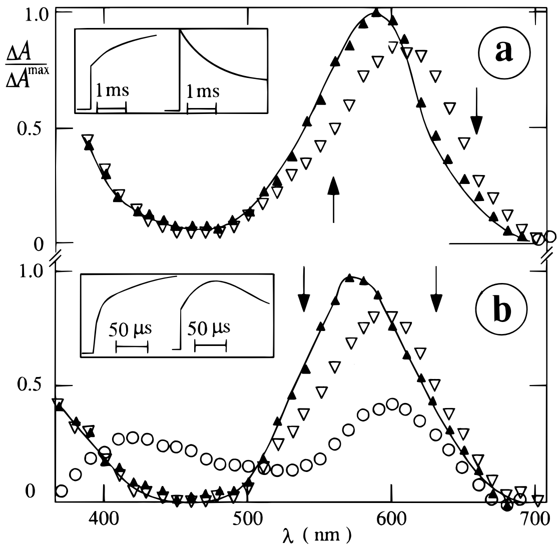


Figure 5. Transient absorption spectra of Sp-**1** (argon-saturated) in (a) toluene at <0.01 (▽) and 2 (▲) ms after the 354 nm pulse and (b) acetone at <1 (○), 10 (▽), and 100 (▲) μs after the pulse. Insets show the kinetics as indicated.

respectively. The properties of the triplet, e.g., λ_{TT} and τ_T, are compiled in Table 5. The identity of the triplet on excitation of the Sp or trans forms is suggested by similar lifetimes using either $\lambda_{exc} = 530$ or 354 nm.

Oxygen accelerates both the decay at $\lambda_{TT} = 420-450$ nm and the rise in the 560−680 nm range (inset of Figure 4a), whereas the yield of the second spectrum, measured after complete decay of the first, is not significantly changed. Rate constants of $(0.5-2) \times 10^9$ M^{-1} s^{-1} for triplet quenching by oxygen were determined in several solvents. The quantum yield of triplet population (Φ_T) decreases with increasing solvent polarity (Table 5).

To study the features of the cis and trans mixture, i.e., to separate the spectrum from that of T−T absorption, the samples were either saturated with oxygen or the kinetics were observed in the millisecond time range. In those cases in which $\tau_{c\to t}$ is sufficiently long, there is a further change at longer times, as illustrated in Figure 5. The secondary process is attributed to thermal cis → trans isomerization (reaction 9). This is supported by similar lifetimes of the cis isomer using either $\lambda_{exc} = 530$ or 354 nm. Moreover, upon excitation of Sp ($\lambda_{exc} = 354$ nm) in several cases, e.g., **5** in acetone and acetonitrile, we found the same activation parameters as with $\lambda_{exc} = 530$ nm (Table 4).

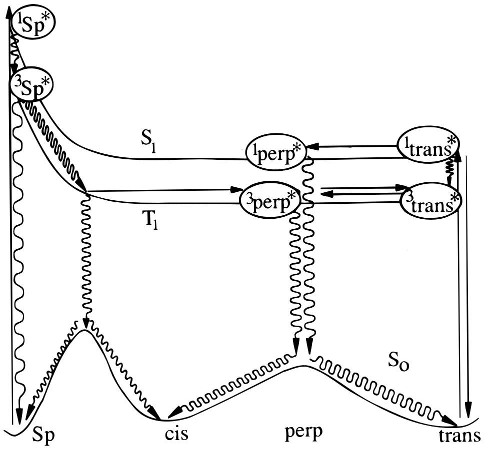
The $\Phi_{Sp\to t}$ values for the five NO_2−BIPSs are generally substantial in solvents of low polarity and decrease with increasing E_T^N values (Table 5). For **6** and **7** in all solvents examined, however, the $\Phi_{Sp\to t}$ values are much smaller. A similar effect has been reported for spironaphthopyran in comparison with two of its 6-nitro-substituted derivatives.[35] In order to test for a possible singlet route for **6** and **7** under direct excitation, we carried out sensitized excitation measurements. In fact, on naphthalene-sensitized excitation ($\lambda_{exc} = 308$ nm) of **7** in argon-saturated acetonitrile the yield of the colored form increased at least 10-fold with respect to that of direct excitation. To reduce the amount of absorption by the energy acceptor, $\lambda_{exc} = 354$ nm was successfully applied with several energy donors (D) such as xanthone, benzophenone, and 9-bromophenanthrene. They have triplet energies of 310, 287, and 255 kJ mol^{-1}, respectively. An example is shown for **6** in acetonitrile in the presence of benzophenone (Figure 4b). The enhanced photocoloration can be ascribed to energy transfer reaction 10 followed by relaxation step 11:

$$^3D^* + Sp \rightarrow D + {}^3Sp^* \qquad (10)$$

$$^3Sp^* \rightarrow \rightarrow \text{trans} \qquad (11)$$

It should be added that the method of sensitized coloration can also be successfully applied to NO_2−BIPSs in polar solvents, i.e., where $\Phi_{Sp\to t}$ is small. This indicates that one way of photocoloration runs via triplet states. Note that this is no proof for a triplet route under conditions of direct excitation, as

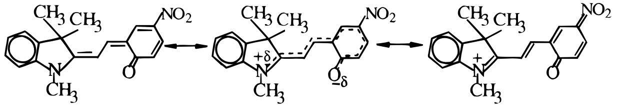
SCHEME 1



Bercovici et al. have already emphasized in their pioneering work on NO_2−BIPSs.[5]

Discussion

Ground State Properties. It is well-known that indoline spiropyrans and their colored merocyanine forms are separated by an energy barrier. For Sp-**1** the activation energy for thermal coloration is 81, 101, and 112 kJ mol^{-1} in benzene, propanol, and ethanol, respectively.[4,5] The activation energy for the thermal decoloration is slightly smaller, 69, 92, and 103 kJ mol^{-1}, respectively.[4,5] There is agreement that cleavage of the C−O bond in the benzopyran portion leads initially to a cis−cisoid zwitterionic structure and subsequently to one or several trans isomers.[1−5] The thermodynamics of spiropyrans have been extensively studied,[1,2] whereas the structure of the stable or metastable merocyanine in the case of the NO_2−BIPSs is still the subject of some controversy.[12,17,22] The mesomeric structures of *trans*-**1** are:



The "longest-living" merocyanine form, which is characterized by the A_t/A_{Sp} ratio in the "dark", i.e., at sufficiently long times after weak preirradiation (Figure 1) and its lifetime after irradiation (Table 1), is assigned to the most stable trans isomer. Concerning the energy content of the various isomers, no agreement has been reached as yet.[22,25] Our spectroscopic and kinetic results with ∼15 ns time resolution for the five NO_2−BIPSs in solution at room temperature indicate (i) a triplet state, (ii) the trans isomer, and (iii) only one additional merocyanine ground state species, which we assigned to a cis isomer. The observed cis isomer is photochemically generated either from the ^{1}Sp* or from the ^{1}trans* state. The isomers are separated by an activation barrier (Table 4), and the level of the cis ground state is above that of the trans isomer.

Two conceivable possibilities are considered: the observed cis isomer is the cis−cisoid or another isomer that is not formed in the pathway from ^{1}Sp* to trans. The latter possibility is not required for an interpretation of our results for the five NO_2−BIPSs in fluid media at room temperature. The potential energy surface of the ground state along the reaction coordinate should have at least two maxima. The maximum between the spiropyran and the cis isomer, E_{Sp}, should be significantly larger than the maximum between the two isomers, $E_{c\rightarrow t}$ (Scheme 1). This picture, however, may be too simple. A possible reason for the permanent bleaching upon heating is the existence of an equilibrium between two cisoid isomers; one (already termed cis) gives rise to a color and the other, having the initial perpendicular configuration of the spiro and pyran parts, does not. Thus, heating probably shifts this equilibrium toward the second species.

Excited Singlet State Properties. Concerning the energies of the S_1 level of the five NO_2−BIPSs, the absorption spectra indicate values of about 290 and 190−210 kJ mol^{-1} for ^{1}Sp* and ^{1}trans*, respectively. The latter values, showing a slightly decreasing trend in the order **1**, **4**, **3**, **2**, can be taken from the fluorescence spectra (Figure 2 and Table 2).

The potential energy surfaces of the two relevant states, S_1 and T_1, leading from the closed form via the cis−cisoid to the trans isomer, are proposed in Scheme 1. The absence of any fluorescence from the ^{1}Sp* state indicates very fast intersystem crossing and/or ring opening. This is supported by rather high quantum yields of cleavage and photocoloration.[3,23] In any case, a strong decline of the potential energy surface along the reaction coordinate is expected. An open question is that of the course of the surface between ^{1}trans*, ^{1}perp*, and ^{1}cis* and the respective triplet conformations. To account for both photocoloration and photodecoloration (reaction sequences 3 and 8, respectively), a pathway from ^{1}trans* to Sp has to be offered. This can be described more easily by a flat surface between ^{1}trans* and ^{1}cis*.

The properties of the ^{1}trans* state are summarized as follows. The fluoresence lifetime of *trans*-**1** in ethanol at room temperature is 0.2 ns.[13] This is in agreement with a rather low Φ_f for *trans*-**1** and similar or smaller values for the other NO_2−BIPSs in fluid solution, where fluorescence is only a minor deactivation route (Table 2). A strong increase in Φ_f on going to rigid media at −196 °C[54] indicates that other relaxation pathways, in particular rotation around a double bond, are hindered. High Φ_f values under these conditions are typical for many cyanine dyes for the same reason.[51]

Triplet State Properties. From phosphorescence measurements, the level of ^{3}Sp* is known to be ∼240 kJ mol^{-1}.[9,18,19] At −196 °C, where the quantum yield of phosphorescence of **1** in EPA is as high as 0.22,[18] the ring opening is probably retarded.[23] The energy of ^{3}trans* may be placed at 170−190 kJ mol^{-1}. For **3** in acetone or ethanol at −196 °C a broad, nonstructured emission with a lifetime in the 0.05−0.1 s range and a phosphorescence maximum at ∼665 nm has been reported.[28] These emission characteristics are in rough agreement with the literature.[1] Thus, at the trans geometry the T_1 level should be only slightly below that of S_1.

If ^{3}Sp* were long-lived enough and efficiently populated at room temperature, one could possibly assign the observed initial species (using $\lambda_{exc} = 354$ or 308 nm) to ^{3}Sp*. However, because of efficient quenching of ^{3}Sp* by oxygen, which could only lead to the spiropyran ground state, practically no trans isomer is expected in oxygen-saturated solution. This is not compatible with the experimental results (see, for example, the inset of Figure 4a). We therefore suggest that ^{3}Sp* is too short-lived to be accessed by oxygen and assign the observed triplet to ^{3}trans*. The yield of the observed triplet is substantial for the five NO_2−BIPSs in cyclohexane and toluene and much smaller in acetonitrile and ethanol (Table 5). Furthermore, the dependence of $\Phi_{Sp\rightarrow t}$ on solvent polarity is similar, indicating that the observed triplet is an intermediate in photocoloration.

Mechanistic Implications. For the trans formation (via the triplet state) from ^{1}Sp*, in principle two routes are conceivable: (a) via intersystem crossing in the spiropyran geometry followed by ring opening and (b) via first ring opening in the S_1 state and then intersystem crossing in the merocyanine moiety. The striking differences of the features of the two Sps without a nitro group (**6** and **7**) and the five NO_2−BIPSs point to the inefficiency of intersystem crossing in the former case and the first route (a) for the latter case. If this is valid for excitation of Sp, then the same transients should, in principle, be populated on excitation of the trans isomer. In fact, the changes in the microsecond to millisecond time domain, which are ascribed to cis → trans isomerization, are also observed from $^1Sp^*$ (Figure 5). Here, the same kinetics result in a blue-shift of the cis plus trans mixture to neat trans.

Apparently, there is a puzzle with the effects of oxygen on the triplet decay and the yield of the cis isomer upon excitation of the five NO_2−BIPSs either at 354 or 530 nm. The latter yield is not much influenced by oxygen, whereas the observed triplet is practically completely quenched; ~98% of the lifetime is quenched in oxygen-saturated solution. Population of the cis isomer occurs either via the singlet route ($\alpha = 0$, $0 < \beta < 1$) or via the triplet route ($0 > \alpha > 1$, $\beta = 0$). In the latter case one could expect that quenching by oxygen populates both isomers in nearly the same ratio as in the absence of oxygen. Reaction 7 as the major pathway, however, is unlikely because the triplet yield increases significantly on going to rigid media, e.g., for **3** at −180 °C in MTHF or at −70 °C in GT.[54] The proposed model for trans → cis photoisomerization is therefore the singlet route (Scheme 1). This is typical for many cyanines,[51] which, however, do not contain a nitro group.

On the other hand, the proposed model for the Sp → trans photocoloration is the triplet route (see above). To account for the results that ^{3}trans* is quenched by oxygen to the cis and trans isomers by different amounts, this pathway requires a modification. We propose an equilibrium between two triplets, ^{3}trans* and the perpendicular conformation (or even the ^{3}cis* state):

$$^3\text{trans}^* \rightleftharpoons {}^3\text{perp}^* \qquad (12)$$

Triplet decay (in the absence of oxygen) occurs essentially at the perpendicular conformation:

$$^3\text{perp}^* \rightarrow \text{perp} \rightarrow \alpha\ \text{cis} + (1-\alpha)\text{trans} \qquad (13)$$

Triplet quenching by oxygen enhances the ^{3}perp* → perp intersystem crossing transition without changing the branching ratio α significantly. Such a ^{3}trans*−^{3}perp* equilibrium is well-known from sensitized cis−trans isomerization of stilbenes.[55]

The common scheme for photocoloration of NO_2−BIPSs so far involves a state X representing the cis−cisoid isomer configuration, an X* state, and several B_n states representing merocyanine isomers.[1,2,5] The results in the literature[12,15,18] and in this work are similar to a certain extent, but their interpretations are definitely different. Possible reasons for this discrepancy are the lack of kinetic data upon excitation of the trans isomer, namely, the $\tau_{c\rightarrow t}$ values, and an overlapping of two effects, decay of the observed triplet state and cis → trans thermal isomerization. The proposed main effect of the nitro group on the photochemistry is the enhancement of the triplet route for reaction sequence 3. This is supported by energy transfer results (Figure 4b).

Effects of Solvent and Structure. The ground state behavior limits the access of the trans isomer to be investigated in polar solvents (without preirradiation). However, data in Table 1 indicate that there is no simple rule for the establishment of eq 1. It is well-known that the absorption maximum of the trans isomer exhibits negative solvatochromism.[1,21] For the five NO_2−BIPSs λ_t is blue-shifted on increasing the solvent polarity, in agreement with the literature.[1,21,32] From the steady-state absorption and fluorescence spectra of the trans isomer in polar solvents at room temperature (at a rather low NO_2−BIPS concentration) we found no indication for formation of dimers or higher aggregates.

A pronounced solvent dependence was found for both Φ_T and $\Phi_{Sp\rightarrow t}$ of **1**, **3**, and **5** (Table 5). The decrease of the $\Phi_{Sp\rightarrow t}$ values with increasing solvent polarity is in agreement with the literature,[3] but an explanation has not been offered as yet. We suggest that the pathway to the cis and trans isomers occurs via the lowest triplet manifold and that the reactive state is the n,π triplet state of Sp, i.e., intersystem crossing in the spiropyran geometry is followed by ring opening. Because of the expected increase of this $^3(n,\pi)^*$ energy level of Sp with increasing E_T^N, the $^3(\pi,\pi)^*$ state should become the lowest in polar solvents. This leads to an enhanced $^3Sp^*$ → Sp intersystem crossing and thus to smaller Φ_T and $\Phi_{Sp\rightarrow t}$ values. At least an efficient pathway from $^1Sp^*$ to Sp to operate at a Sp geometry (left from the maximum in S_0) has to be postulated in polar solvents. This channel is probably enhanced by the allyl group in **2**, where both Φ_T and $\Phi_{Sp\rightarrow t}$ are significantly smaller.

The small A_t/A_{Sp} ratio for **5** with respect to those of **1**−**4** seems to be an exception, and an explanation for this effect of the phenyl ring in the 1′-position cannot be offered. The markedly longer lifetime of the cis isomer is another peculiarity of **5** (Table 4). Again, introduction of the phenyl ring in the 1′-position has a special influence, i.e., essentially a lowering of the pre-exponential factor. A pronounced difference between **1**−**4** and **6** or **7** is that the spiropyrans without a nitro group are essentially noncolored even in polar solvents (Table 1). The offered hypotheses are that either the activation barrier E_{Sp} is lowered by the nitro group or the free energy change for equilibrium 1 becomes more negative.

The essential features of the proposed model are as follows. The above discussed arguments are in favor of the triplet route for photocoloration. The cis and trans ground states are populated at the perpendicular geometry (via the ^{3}perp*−^{3}trans* equilibrium). Quenching by oxygen affects the ^{3}trans* triplet state in most cases, but in a few cases the formation of the cis isomer from $^1Sp^*$ in the presence of oxygen implies that oxygen also quenches the ^{3}perp* triplet state. In a first extension of this, one could assume a triplet route also for trans → cis photoisomerization for the five NO_2−BIPSs. However, the relatively small triplet yield excludes this possibility. We suggest that formation of the observed ^{3}trans* triplet state is only a side reaction, whereas the main pathway occurs in singlet states:

$$^1\text{trans}^* \rightarrow {}^1\text{perp}^* \rightarrow \text{perp} \rightarrow \beta\ \text{cis} + (1-\beta)\text{trans} \qquad (14)$$

A cis isomer was observed upon excitation of either the Sp or the trans forms of five NO_2−BIPSs in solution at ambient temperature. It is formed by trans → cis photoisomerization and acts as a trap for the excitation energy absorbed by the *trans*-merocyanine, thereby reducing the photodecoloration. A radiationles deactivation process at the Sp geometry suppresses the photocoloration of NO_2−BIPSs in polar solvents.

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