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Journal of Photochemistry and Photobiology A: Chemistry 105 (1997) 261–267

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Singlet versus triplet photoprocesses in indodicarbocyanine dyes and spiropyran-derived merocyanines

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Received 7 August 1996; accepted 11 December 1996

Abstract

The photophysical and photochemical properties of the indodicarbocyanine **1** and three derivatives (**2**–**4**, the substituents in the *meso*-position of the polymethine chain being R: Br, CN and 1,3,3-trimethylindoline-2-ethenyl, respectively), as well as of three spiropyrans containing a nitro group in 6-position at the benzopyran portion (Sp-**n**, **n** = **5**–**7**), were studied by time resolved spectroscopy. The quantum yield of *trans* → *cis* photoisomerization is substantial for **2** and small for **1** and **3**; the lifetime of the observed *cis* form is in the sub-ms range at room temperature. The triplet state plays a role only for **2**. The *trans*-isomers of **1**–**4** and **5**–**7** (merocyanine form) exhibit weak and strong fluorescence in ethanol at 24 °C and −196 °C, respectively. An intermediate, which is ascribed to a photoisomer with *cis* structure, was observed for **5**–**7** at room temperature upon excitation of either the spiropyran or the *trans*-isomer. The activation energies of the thermal *cis* → *trans* isomerization were determined for **1**–**7**. The quantum yield of the spiropyran → *trans*-merocyanine photocoloration is substantial in solvents of low polarity but reduced in polar solvents. The nitro group strongly enhances the quantum yield of intersystem crossing for the spiropyran, leading to a triplet pathway for photocoloration. The *trans* → *cis* photoisomerization, however, is suggested to occur essentially via the singlet state. © 1997 Elsevier Science S.A.

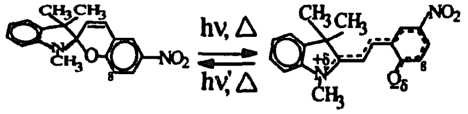
Keywords: Cyanine dyes; Spiropyrans; Photoisomerization

1. Introduction

Cyanine dyes are widely used because of their practical importance in spectral sensitization and color photography [1]. They generally reveal relatively weak fluorescence (Φ_f), a very low quantum yield of intersystem crossing (Φ_{isc}) and *trans* → *cis* photoisomerization via the excited singlet state in substantial yield ($\Phi_{t\rightarrow c}$) [2–11]. For covalently linked *bis*-cyanine dyes, however, due to a restriction of the flexibility, $\Phi_{t\rightarrow c}$ is reduced and Φ_f and Φ_{isc} are enhanced in comparison to sterically non-hindered cyanines [12]. For indodicarbocyanine dyes Φ_{isc} is also low, but one may expect an increase in Φ_{isc} when heavy atoms or a bulky group are introduced in *meso*-position of the polymethine chain. Such an enhancement was observed for thia(mono)-carbocyanines with 9-iodine, 9-methoxy and 8,9-difluoro substituents in the polymethine chain [2,6,7].

Spiropyrans belong to a class of photochromic compounds which have been intensively studied [13–26] because of their powerful application potential, e.g. in information processing. Spiropyrans exist in their colorless, closed form which can be photoconverted reversibly into the colored, open merocyanine form. In polar solvents spiropyrans, in particular indoline spirobenzopyrans (Sp), are in equilibrium with their open form which is shifted towards the *trans*-merocyanine when a nitro group is substituted in 6-position [13–18, 25,26].

	R-8:
5	H
6	$CH_2CH{=}CH_2$
7	OCH_3



In this paper we address the question of the relationship between the quantum yields Φ_f, Φ_{isc} and $\Phi_{t\rightarrow c}$ and the reaction pathway(s). The results are presented for parent 1,1′,3,3,3′,3′-hexamethylindodicarbocyanine perchlorate (**1**), derivatives which are substituted in *meso*-position by Br, CN or a bulky group (**2**–**4**, respectively), as well as for three 6-nitro substituted spiropyrans (so called 6-NO_2-BIPSs). We now give evidence that both forms, Sp-**n** and *trans*-**n** (**n** = **5**–**7**), can be converted photochemically into a *cis* isomer with sub-ms lifetime at ambient temperature. This

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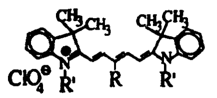
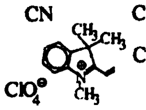
PII S1010-6030(96)04604-7

raises the question as to the pathways of photocoloration (Sp → *trans* + *cis*) and *trans* → *cis* photoisomerization.



Comp.	R:	R':
1	H	CH_3
2	Br	C_4H_9
3	CN	CH_3
4		CH_3

2. Experimental details

Compounds **1–4** [27] and Sp-**n** (**n** = 5–7) [28] have been synthesized according to methods described elsewhere. The solvents (Merck) were of the purest spectroscopic quality available (e.g. Uvasol) or purified by distillation, e.g. 2-methyltetrahydrofuran (MTHF) and methanol. Φ_f was determined using cresyl violet in ethanol as reference ($\Phi_f = 0.54$ at 24 °C [29], $\lambda_{exc} = 530$–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 [12]. The transient absorption measurements were carried out by means of 10–20 ns flash photolysis using transient digitizers (Tektronix 7912AD and 390AD). Most experiments with **1–4** were performed with a dye laser (Lambda Physik, FL 2001/2 using rhodamine B or the DCM styrene dye), pumped by the 308 nm line of an excimer laser (Lambda Physik, EMG 200) and most experiments with **5–7** were performed with the second or third harmonic from a Nd-laser (JK Lasers), $\lambda_{exc} = 530$ or 353 nm, respectively [12]. The relative absorbances at the bleaching maximum, using normalized conditions, e.g. $A_{530} = 0.3$, were taken as a measure for $\Phi_{t\to c}$, thereby neglecting substituent dependent changes in the $\epsilon(\lambda_{trans})/\epsilon(\lambda_{cis})$ ratio. The absolute $\Phi_{t\to c}$ value was obtained for **2** in ethanol from the ratio of transient absorbances using $\epsilon_{680} = 1.9 \times 10^5$ M^{-1} cm^{-1} for the *cis* isomer of **2** [30] and methylene blue as reference ($\Phi_{isc} = 0.54$, $\epsilon_{420} = 1.4 \times 10^4$ M^{-1} cm^{-1} [31]). For $\lambda_{exc} = 353$ nm, typical absorbances of 0.5–5 were used, corresponding to Sp concentrations of 0.1–1 mM, whereas for $\lambda_{exc} = 530$ nm, absorbances were lower, corresponding to 3–30 μM *trans* isomer (< 5 μM of *trans* isomer is advantageous for bleaching, whereas the triplet state becomes better resolved at much higher concentration). For Φ_{isc} of the indodicarbocyanine dyes we used optically matched conditions and assumed the same ε value (5.2×10^4 M^{-1} cm^{-1}) for T–T absorption at the maximum. The relative $\Phi_{Sp\to t}$ ($\lambda_{exc} = 353$ nm) and $\Phi_{t\to c}$ ($\lambda_{exc} = 530$ nm) values were obtained with optically matched solutions.

3. Results and discussion

3.1. Indodicarbocyanine dyes

The four dyes show an intense absorption band in the red spectral region, e.g. with a peak at 641 nm for parent **1** in ethanol at room temperature. Their fluorescence emission exhibits maxima at about 665 nm and a shoulder at 700–720 nm; only for **3** the maximum is blue-shifted by ≫ 30 nm. Φ_f ranges from 0.012 for **4** to 0.25 for **3** (Table 1). Our value for the parent **1** is in good agreement with those from literature [8,11]. In all cases Φ_f and the fluorescence lifetime (τ_f) are much larger at − 196 °C than at room temperature. In general, Φ_f increases steadily with decreasing temperature. The reason for the increase in Φ_f in all cases on going from 24 to − 196 °C is the hindrance toward rotation about one of the three central double bonds in the first excited singlet state (S_1).

The transient absorption and bleaching spectra ($\lambda_{exc} = 610$ nm) are shown in Fig. 1 for **2** in ethanol. The spectra for the other cases are similar except for **3** which has a further band at shorter wavelengths (Fig. 2). The changes, depletion of the ground state and formation of a new band with a maximum around 685 nm for **2** and 645 nm for **3**, are due to *trans* → *cis* photoisomerization. $\Phi_{t\to c}$ is largest for **2** in ethanol and much smaller for **1** and **3** (Table 2).

Table 1
Quantum yield and lifetime of fluorescence [a]

Compound	Φ_f 24 °C	τ_f (ns)	Φ_f − 196 °C	τ_f (ns)
1	0.21	0.98	0.89	2.4/6.2 [b]
2	0.19	0.43	0.70	3.2
3	0.25	0.80	0.66	2.6
4	0.012	<0.2	0.75	3.6
5	0.012		0.7	
6	0.012		0.8	
7	0.016 (0.005)		0.6 (0.7) [c]	

[a] Obtained in aerated ethanol, $\lambda_{exc} = 353$ nm for τ_f and 620 and 560 nm for Φ_f of **1–4** and **5–7**, respectively.
[b] Two components, integrated ratio 1:10.
[c] Values in parentheses refer to MTHF.

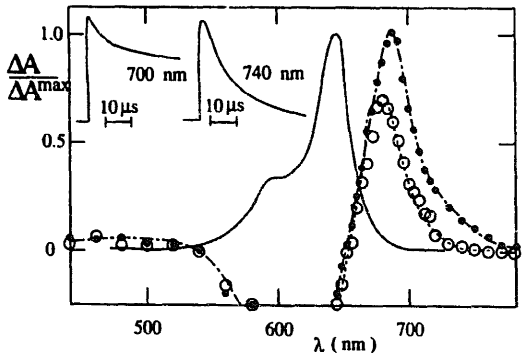


Fig. 1. Transient absorption spectra of **2** at 24°C in argon-saturated ethanol at 0.1 μs (●) and 10 μs (○); $\lambda_{exc} = 640$ nm. Insets: decay (normalized signals) at 700 and 740 nm.

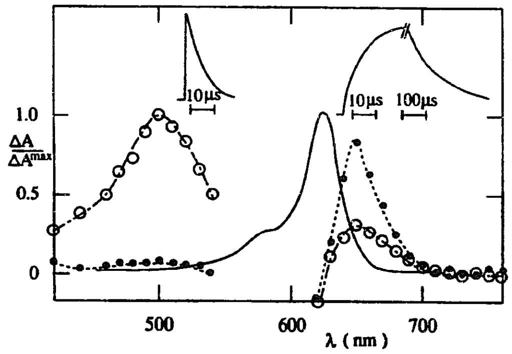


Fig. 2. Transient absorption spectra of 3 in ethanol at 24 °C (end of pulse, open symbols) and at 20 µs (●) after the 610 nm pulse; insets: decay at 500 nm (left) and formation and decay at 640 nm (right).

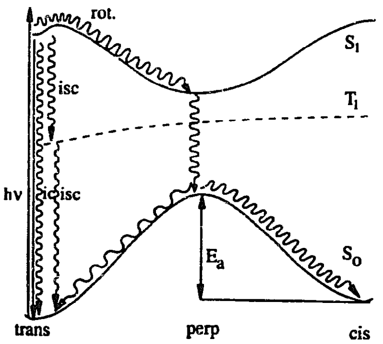
Table 2
Quantum yields of *trans* → *cis* photoisomerization and triplet formation [a]

Compound	$\Phi_{t\rightarrow c}$	Φ_{isc}
1	0.038	<0.003
2	0.19	0.17
3	<0.06	<0.006
4	0.13	0.006

[a] In argon-saturated ethanol at 24 °C; $\lambda_{exc}=610$ and 620 nm for Φ_{isc} and $\Phi_{t\rightarrow c}$, respectively.

In the absence of oxygen, a weak additional increase in ΔA at 680–750 nm, which is ascribed to triplet–triplet absorption, could be detected for 2 (Fig. 1). It has a maximum at $\lambda_{TT}=690$ nm; ΔA_{690} increases concomitant with the laser pulse and the decay follows first-order kinetics. The triplet lifetime lies in the 50–500 µs range [30] and is strongly reduced by oxygen. From these rather long triplet lifetimes we conclude that intersystem crossing to S_0 does not take place at the perpendicular conformation and that the energy level of T_1 should increase on going from the *trans* to the perpendicular form. The markedly higher level of ^{3}*perp** with respect to ^{3}*trans** has already been concluded for polymethine dyes on the basis of theoretical work [4]. The T–T absorption spectra of the indodicarbocyanine dyes show a red shift of λ_{TT} by 10–20 nm (except for 2) with respect to the maximum of the *cis* isomer, a long wavelength edge from 720 to about 760 nm and the appearance of a very weak transient absorption in the 400–530 nm region. The absolute triplet yield of $\Phi_{isc}=0.17$ for 2 was obtained from the absorption signal at 690 nm (inset of Fig. 1) using the absorption coefficient of the triplet as $\epsilon_{690}=5.2\times10^4$ M^{-1} cm^{-1} [30] together with $\Phi_{t\rightarrow c}=0.19$.

A model which describes the photophysical and photochemical features of the cyanine dyes is shown in Scheme 1 (here, the *cis* isomer refers to a photoproduct after rotation about one of the three double bonds). Excited all-*trans* molecules can be deactivated by fluorescence, internal conversion at the *trans* side, intersystem crossing and rotation, i.e. the initial step for *trans* → *cis* photoisomerization in the S_1 state; the rate constants are k_f, k_{ic}, k_{isc} and k_{rot}, respectively. In order to account for the rather small value of $\Phi_{t\rightarrow c}=0.038$ for 1 (Table 2), we propose that the minimum in the S_1 state is displaced toward the *trans* side with respect to the maximum in the S_0 state. This explains why less than 5% of the 80% excitation energy available for rotation populate the *cis* isomer, i.e. there is initial rotation around one double bond in S_1 and a branching from the ^{1}*perp** conformation (via internal conversion) into the *cis* and *trans* isomers.



Scheme 1.

The internal heavy-atom effect due to bromine substitution in 2 is reflected in fast intersystem crossing, $k_{isc}\approx0.4$ ns^{-1} in comparison to $k_{isc}<0.005$ ns^{-1} for 1, whereas Φ_f is virtually not reduced. From the Φ_f, Φ_{isc} and $\Phi_{t\rightarrow c}$ values for 2 in ethanol at 24 °C and the enhancement of Φ_f at −196 °C (Tables 1 and 2) it follows that internal conversion at the *trans* side does not play a significant role for deactivation of the ^{1}*trans** state. For 4 with a 1,3,3-trimethylindoline-2-ethenyl substituent Φ_f is smallest and $\Phi_{t\rightarrow c}=0.13$, i.e. four times larger than for the parent compound. This is surprising and indicates that the major effect due to steric hindrance does not reduce *trans* → *cis* photoisomerization; instead k_{rot} is substantially enhanced (>4 ns^{-1}). In principle, this substituent could also cause a change in the level of the S_1 state. However, neither the absorption nor the fluorescence maxima of 4 differ markedly from those of 1 [30].

The fraction of ^{1}*perp** decaying into the *cis* isomer is small for 1 and 3, where $\Phi_{t\rightarrow c}$ is small and $\Phi_f=0.21$ and 0.25, respectively, but significantly increased for 2 and 4. For 3 we propose that intramolecular electron transfer in S_1 is involved and that this enhances internal conversion at the *trans* side. Thus the contributions of the deactivation pathways of the ^{1}*trans** state are gradually changed on variation of the substituents because of electronic changes in the S_1 potential.

First-order kinetics of the ground state recovery and the decay of the absorption around 680–700 nm were found for 1 and 4, i.e. the decay coincides with the recovery. At room temperature the lifetime of the *cis* isomers ($1/k_{c\rightarrow t}$: inverse rate constant of thermal back-reaction) increases on going from 4 to 1 (Table 3). For 2 the decay to the all-*trans* ground state is composed of two identical spectra with differing first-order components. They are produced in parallel, with a higher absorption coefficient for the faster one. Fast and slow components were also observed for 3, but the spectra are quite different. The faster component has an absorption band

Table 3
Activation energy, pre-exponential factor and lifetime of the observed *cis* isomer(s) at room temperature [a]

Compound	Solvent	E_a (kJ mol^{-1})	A (s^{-1}×10^{12})	$1/k_{c\to t}$ (24 °C) (ms)
1	Ethanol	53	1.7	0.9
2		50	2.0	0.23
2 [b]		55	2.4	1.4
3		45	4.4	0.015
3 [b]		48	1.2	0.15
4		37	0.16	0.016
5	Toluene			>2
	Acetone	40	0.1	0.055
	Acetonitrile	39	0.9	0.016
6	Acetone	38	0.16	0.020
7	Acetone [c]	42	0.07	0.28
	Acetonitrile [c]	40	0.11	0.070
	Ethanol	39	1.5	0.005
	Methanol	38	2.1	0.002

[a] In argon-saturated solution, λ_{exc} = 610 and 530 nm for **1–4** and **5–7**, respectively.
[b] Longer-lived component, see text.
[c] Same data upon excitation of Sp at 353 nm [33].

in the 400–550 nm range while the slower absorbs around 650 nm (Fig. 2).

The activation energy (E_a) and the A-factor, obtained from the Arrhenius plot, are compiled in Table 3. Formation of one photoisomer which relaxes thermally to the all-*trans* isomer is suggested for parent **1**, where E_a is in agreement with the literature value of 47 kJ mol^{-1} [11]. The activation parameters show little dependence on the substituent, except for **4**, where E_a is about 10 kJ mol^{-1} lower. This may be due to the presence of the bulky group or the second positive charge in the ion. The suggested reason for the two first-order kinetics of **2** without a measurable spectral difference is a simultaneous formation of two *cis* isomers and thermal conversion into the all-*trans* isomer: *cis*(1) → all-*trans* and *cis*(2) → all-*trans*. For **3** the reason is likewise the formation of two *cis* isomers, but *cis*(1) with λ_{max} = 500 nm is the precursor of *cis*(2) with λ_{max} = 650 nm (Fig. 2), i.e. *cis*(1) → *cis*(2) → all-*trans*. The relatively small differences in activation parameters (Table 3) are contrasted by large spectral changes, i.e. a significant blue shift of the absorption of isomer *cis*(1). The finding that *cis*(1) absorbs similarly to the radical observed after electron transfer in the presence of an electron donor [32] indicates a so far unknown intramolecular process in the S_1 state of the cyano derivative, e.g. charge or electron transfer.

3.2. Spiropyran – *trans*-merocyanine couple

The absorption spectrum of the Sp form of **5–7** has a maximum around 245 nm and a second weaker band at 335–360 nm. In polar solvents a band with maximum at 560–600 nm appears which is due to the fact that Sp-**n** is in equilibrium with *trans*-**n**. Owing to the zwitterionic character of the merocyanine form the Sp ⇌ *trans* equilibrium depends on the solvent polarity; the *trans* isomer concentration can be greatly increased upon UV irradiation [13–17]. The *trans* isomers of **5–7** show only weak fluorescence in solution at room temperature with a maximum around 640–680 nm. The excitation spectrum coincides with the absorption spectrum. On going to a rigid glass (MTHF or ethanol at −196 °C) Φ_f increases strongly (Table 1).

Two transients were observed for *trans*-**7** in argon-saturated acetone (Fig. 3) or in other solvents upon excitation at 530 nm. One is short-lived and exhibits a weak band around λ_{TT} = 440 nm. Absorption of this initial species is overlapped by that of a longer lived one with absorption maxima at 430 and ≈635 nm and a bleaching area around 570 nm. The short-lived transient, owing to efficient quenching by oxygen (inset of Fig. 3), is assigned to a triplet state. It decays by first-order kinetics and the triplet lifetime is 5–10 μs. We further assign this transient to the ^{3}*trans** state [33]. Formation of the 600–660 nm band is delayed, because the triplet has a lower absorption coefficient. The longer lived transient of *trans*-**n** with a bleaching and absorption maximum is ascribed to one of the possible conformers with essentially

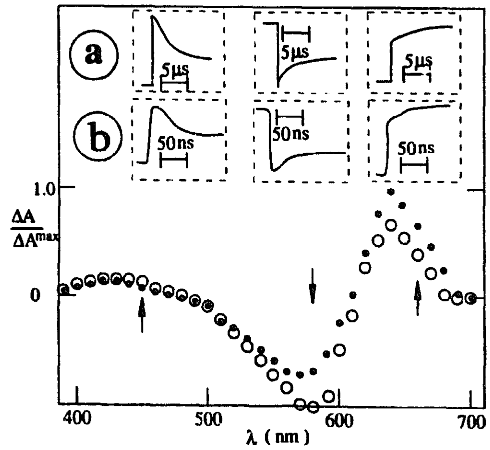


Fig. 3. Difference absorption spectra of *trans*-**7** in argon-saturated acetone at 0.1 μs (○) and 20 μs (●); λ_{exc} = 530 nm; insets: kinetics under (a) argon and (b) oxygen as indicated.

cis isomer structure, simply termed: *cis*-**n**. This identification is based on the reversibility of the spectral changes and the independence of the decay kinetics from the oxygen concentration. The nature of the solvent has virtually no effect on the spectral properties and, apart from alcohols, it has a relatively small effect on $\Phi_{t\to c}$ which is virtually not affected by oxygen.

Decay of the observed *cis* isomer follows first-order kinetics which are the same in the area of bleaching and absorbance. This is ascribed to thermal *cis* → *trans* isomerization. Oxygen has no discernible effect on the lifetime at room temperature which ranges from 2.1 μs for **7** in methanol to ≥ 2 ms for **5** in toluene (Table 3). In all cases the log of $k_{c\to t}$ is linearly dependent on $1/T$. The activation parameters in Table 3 reveal only small changes on variation of either substitution or solvent polarity; the larger lifetimes are partly due to a larger A-factor.

3.3. Deactivation of the excited spiropyran

Indoline spiropyrans and their merocyanine forms are separated by an energy barrier. The activation energy for thermal coloration of **5** is 101 and 112 kJ mol^{-1} in propanol and ethanol, respectively and that for the thermal decoloration is slightly smaller, 92 and 103 kJ mol^{-1}, respectively [13,14]. Cleavage of the C–O bond in the benzopyran-8-portion leads initially to a *cis–cisoid* zwitterionic structure and subsequently to the *trans* isomer(s) [13–17,19,24,25]. The spiropyrans are non-fluorescent, but they show phosphorescence at −196 °C [15,34].

The transient absorption spectrum of Sp-**7** in argon-saturated acetone shows maxima at $\lambda_{TT} = 440$ and 565 nm at the end of the 353 nm pulse (Fig. 4). Absorption of this initial species is overlapped by that of the longer lived species; the absorption coefficient of the short-lived transient is similar to that of the longer lived at 420 nm, but smaller in the 500–680 nm range. The decay at 440 nm obeys first-order kinetics; the rate constant matches the increase at 540–660 nm (insets of Fig. 4). We assign the initial transient (precursor) and the secondary species to the ^{3}*trans** state and the *cis* and *trans* ground state mixture (Table 4), respectively [33]. Oxygen accelerates both the decay and the rise; rate constants of (0.5–2) × 10^9 M^{-1} s^{-1} were determined in several solvents for triplet quenching by oxygen. The increase in absorbance at λ_{TT} (end of pulse) for optically matched conditions is nearly linear with the laser intensity and the slope is taken as the relative yield for triplet population. The Φ_{isc} values decrease with increasing solvent polarity (Table 4). The identity of the triplet on excitation of the Sp or *trans* forms is suggested by similar lifetimes using excitation at either 353 or 530 nm [33].

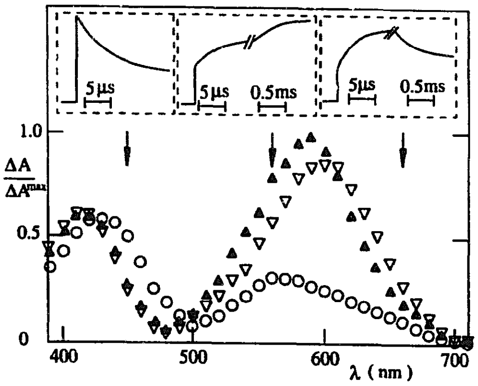


Fig. 4. Transient absorption spectra of Sp-5 in argon-saturated acetone at 1 μs (○), 10 μs (▽) and 1 ms (▲) after the 353 nm pulse; insets: kinetics as indicated.

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 saturated with air or oxygen and first-order kinetics were observed in the ms time range. In those cases, in which $1/k_{c\to t}$ is sufficiently long, this change can also be detected in the absence of oxygen, as illustrated in Fig. 4. The secondary process is attributed to thermal *cis* → *trans* isomerization. This is supported by similar lifetimes of the *cis* isomer using

Table 4
Absorption maximum of the isomer mixture and yields of formationof the *trans* isomer and the triplet state from Sp [a]

Compound	Solvent	$\lambda_{c,t}^{max}$ [b] (nm)	$\Phi_{Sp\to t}$ [c]	Φ_{isc} [d]
5	Cyclohexane	385, 605	0.8	0.9
	Toluene	390, 610	0.6	0.8
	Acetone	390, 590	0.22	0.3
	Acetonitrile	390, 580	0.07	0.05
6	Acetone	400, 600	0.06	0.1
7	Cyclohexane	<400, 610	0.85	1.0
	Toluene	410, 615	0.59	0.7
	MTHF	410, 610	0.35	0.4
	Acetone	410, 605	0.16	0.12
	Acetonitrile	410, 595	0.18	0.08
	Ethanol	400, 560	0.07	0.04

[a] Obtained at 24 °C in the presence of oxygen, $\lambda_{exc} = 353$ nm.

[b] Max. of the mixture after ≈ 10 μs.

[c] Absolute values obtained after ≈ 1 ms.

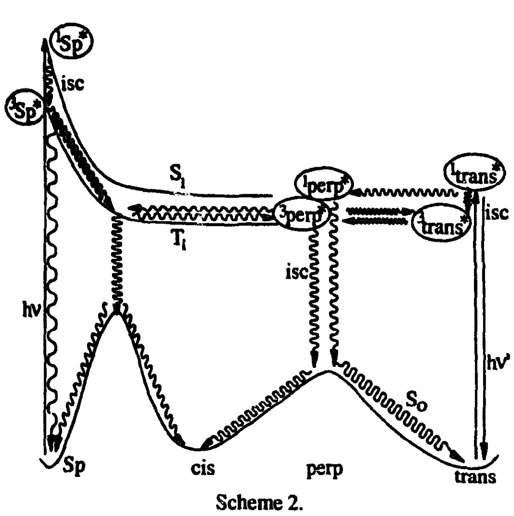
[d] Relative values.

either λ_{exc} = 530 or 353 nm. Moreover, for **7** in acetone and acetonitrile, we found the same activation parameters upon excitation of Sp or the *trans* isomer (Table 3). The increase in absorbance at the maximum and after longer times, e.g. 1-10 ms, for optically matched conditions is nearly linear with the laser intensity, the slope is taken as relative yield for the spiropyran → *trans* photoconversion. The absolute $\Phi_{Sp \to t}$ value of 0.59 for **7** in toluene was taken from literature [16]. The $\Phi_{Sp \to t}$ values generally decrease with increasing the solvent polarity (Table 4).

Our spectroscopic and kinetic results with ≈ 15 ns time resolution for the three NO_2-BIPSs in solution at room temperature indicate (i) a triplet state, (ii) the *trans* isomer and (iii) only one further merocyanine ground state species which we assigned to a *cis* isomer. This *cis* isomer can photochemically be generated from either ^{1}Sp* or ^{1}*trans** states; in both cases it converts into the more stable *trans* isomer. A barrier between the two observable isomers and a higher energy content of *cis* with respect to the *trans* isomer account for the activation parameters in Table 3. It should be noted that resonance Raman studies with **7** have indicated that among the eight stereoisomeric conformations (with respect to the three C–C partial double bonds) three or four are in equilibrium [19]. The observed *cis* isomer is either the *cis–cisoid* or another isomer which is not formed on the pathway from ^{1}Sp* to *trans*. For an interpretation of our spectroscopic and kinetic data, the latter possibility seems not to be required. We therefore propose that the potential energy surface of the ground state, along the reaction coordinate, should have at least two maxima, whereby that between the spiropyran and the *cis* isomer should be significantly larger than that (E_a) between the *cis* and the *trans* isomers (Scheme 2).

3.4. Excited singlet and triplet state properties

The absence of fluorescence indicates either very efficient intersystem crossing from the ^{1}Sp* state or rapid geometrical changes due to ring opening. In both S_1 or T_1 states a strong decline of the potential energy surface along the reaction coordinate is expected (Scheme 2). This is supported by rather high quantum yields of cleavage and photomerocyanine formation in several cases [16,23]. Rather flat curves between ^{1}*cis** and ^{1}*trans** as well as ^{3}*cis** and ^{3}*trans** are likely, taking into account that a pathway from ^{1}*trans** to Sp has to be offered, in order to account for the photodecoloration [14–17]. Fluorescence is only a minor deactivation route of ^{1}*trans** at room temperature, as concluded from low Φ_f values (Table 1) and a fluorescence lifetime of 0.2 ns for *trans*-**5** in ethanol [22]. The strong increase in Φ_f on going to − 196 °C indicates the ability of the *trans*-merocyanine to rotate around a double bond in fluid solution and the inability in rigid media. High Φ_f values under these conditions are typical for many cyanine dyes due to the same reason [11,12].



Scheme 2.

The ^{3}Sp* level is known to be ≈ 250 kJ mol^{-1} (239 kJ mol^{-1} for **5** in EPA [20]), the quantum yield of phosphorescence is as high as 0.22 [15]. If ^{3}Sp* would be long-lived enough and efficiently populated at room temperature, one could possibly assign the observed initial species (λ_{exc} = 353 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. Since this is not compatible with the experimental results, we suggest that ^{3}Sp* is too short-lived to be accessed by oxygen and assign the observed triplet to ^{3}*trans**. The triplet yield is substantial for **5** or **7** in cyclohexane and toluene and much smaller in acetonitrile and ethanol (Table 4). Furthermore, there is a similar dependence of $\Phi_{Sp \to t}$ on solvent polarity, indicating that the observed triplet is an intermediate in photocoloration.

3.5. Mechanistic consequences

The initial step of photocoloration (^{1}Sp* → *trans*) is probably intersystem crossing in the spiropyran geometry followed by ring opening, albeit the reverse order cannot be excluded. Upon excitation of Sp the same transients, in principle, should be populated as on excitation of the *trans* isomer. In fact, the changes in the μs–ms time domain which are ascribed to *cis* → *trans* isomerization are also observed from ^{1}Sp* (Figs. 3 and 4); here the same kinetics result in a blue shift of the *cis* plus *trans* mixture to yield the *trans* isomer. To account for the result that ^{3}*trans** is quenched by oxygen into the *cis* and *trans* isomers, this pathway requires a modification. We propose an equilibrium between the planar and perpendicular triplet conformations. Triplet decay (in the absence of oxygen) occurs essentially via ^{3}*perp**. Quenching by oxygen enhances the ^{3}*perp** → *perp* transition, thereby changing the branching ratio, i.e. the fraction of ^{3}*perp** decaying into the *cis* isomer, only slightly. Such a ^{3}*trans** ⇌ ^{3}*perp** equilibrium is well-known from *trans* → *cis* isomerization of (nitro)stilbenes [35].

A pronounced solvent dependence was found for both Φ_{isc} and $\Phi_{Sp \to t}$ which show a trend to decrease with increasing the solvent polarity (Table 4). This finding is in agreement with literature [16], but an explanation has not been offered as yet. A likely reason is that the pathway into the *cis* and *trans* isomers occurs via the lowest triplet manifold and that the reactive state is the n,π triplet state of the Sp geometry, i.e. intersystem crossing is prior to ring opening. Because of the increase of this $^3(n,\pi)^*$ energy level of Sp with increasing solvent polarity, the $^3(\pi,\pi)^*$ state should become the lowest in polar solvents, thus leading to lower Φ_{isc} and $\Phi_{Sp\rightarrow t}$ values. At least an efficient pathway from $^1Sp^*$ to $^1Sp^*$ has to be postulated in polar solvents to operate at an Sp geometry (left from the maximum in S_σ). The main effect of the nitro group concerning the photochemistry is proposed to open up the triplet route for photocoloration.

The common scheme for photocoloration of NO_2-BIPSs so far involves a state X, representing the *cis–cisoid* isomer configuration, an excited X* state and several isomers (B_1, B_2, B_3) [14–18]. To a certain extent, the results in literature [18–20,24] and in this work are rather similar, whereas the interpretation differs. One of the main reasons for this discrepancy is the lack of kinetic data upon excitation of the *trans* isomer, namely the $1/k_{c\rightarrow t}$ values. The second is an overlapping of two effects, decay of the observed triplet state and *cis* → *trans* thermal isomerization. For example, for **6** in acetonitrile, where the triplet lifetime is 5 μs [34], $1/k_{c\rightarrow t} = 8$ μs, i.e. the two processes cannot easily be separated. The essential features of the proposed model (Scheme 2) are a triplet route for photocoloration:

$$^1Sp^* \rightarrow {}^3Sp^* \rightarrow {}^3cis^* \rightarrow {}^3perp^* \rightleftharpoons {}^3trans^*$$

followed by

$$^3perp^* \rightarrow perp \rightarrow cis + trans$$

and a singlet route for *trans* → *cis* photoisomerization:

$$^1trans^* \rightarrow {}^1perp^* \rightarrow perp \rightarrow cis + trans$$

We suggest that formation of the observed $^3trans^*$ triplet state is only a side reaction [33].

The two systems discussed, *trans* merocyanines derived from spiropyrans and all-*trans* indodicarbocyanine dyes, differ considerably in structure and substituents, but they show certain similarities concerning the features of fluorescence, intersystem crossing and photochemical *trans* → *cis* isomerization and even thermal back isomerization. On the other hand, as yet not all of the factors influencing the photoprocesses in each system have been examined in detail.

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