Effects of Alkyl Substituents in the Polymethine Chain on the Photoprocesses in Thiacarbocyanine Dyes

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The photophysical and photochemical properties of thiacarbocyanine (**1**) and three *meso*-substituted derivatives (9-Me, **2**; 9-Et, **3**, **4**) were studied in solvents of different polarity. Substantial differences in the absorption and fluorescence excitation spectra for **2**−**4** in polar solvents at room temperature indicate a shift of the equilibrium from the all-*trans* isomer in less polar solvents to a nonfluorescent mono-*cis* isomer in polar solvents. This shift is accompanied by a low yield of photobleaching, in contrast to those conditions where the thiacarbocyanines exist in the all-*trans* form, i.e., for **2**−**4** in solvents of low polarity and for **1** in all solvents. The recovery, which is due to thermal *cis* → *trans* isomerization, is characterized by its activation energy in the 55−65 kJ mol^{-1} range. The quantum yield of fluorescence (Φ_f) increases with decreasing temperature, and the limiting values of $\Phi_f \leq 0.6$ at −196 °C indicate internal conversion without twisting. The triplet state was observed upon sensitized excitation, but upon direct excitation intersystem crossing does not play a significant role in any of the compounds studied. The mechanism of deactivation of the excited all-*trans* form involves a mono-*cis* isomer as an observable intermediate in the microsecond to millisecond time scale for **2**−**4** in solvents of low polarity, whereas deactivation of the excited mono-*cis* isomer is radiationless, avoiding essentially *cis* → *trans* photoisomerization.

Introduction

Cyanine dyes still attract much attention because of their wide application mostly in conventional and nonconventional photographic processes[1,2] as well as in laser techniques as light pulse absorbers[3] and as photoinitiators in photopolymerization.[4−6] For photochemical studies cyanine dyes would appear to be very promising because of the occurrence of both *trans* → *cis* (*E* → *Z*) photoisomerization and electron transfer.[7−9] Normally, cyanine dyes are present in solution at room temperature as all-*trans* isomers in the ground state.[10−23] The main features of the excited singlet state are a substantial quantum yield of photoisomerization ($\Phi_{t\to c}$), a relatively low quantum yield of fluorescence (Φ_f), and a very low quantum yield of intersystem crossing (Φ_{isc}).[11−20] *Trans* → *cis* photoisomerization was found to occur in singlet states,[7,8] although involvement of the triplet state has also been reported.[21−23] *Cis* → *trans* photoisomerization of thiacarbocyanines was sudied by only a few groups.[16,19]

Cyanine derivatives substituted in the *meso* position of the polymethine chain are the subject of keen interest. The introduction of certain substituents (alkyl, alkoxy, nitro, or phenyl) in the *meso* position might, to some extent, result in steric hindrance for rotation around the polymethine chain.[7,10] As a possible consequence, *meso*-substituted cyanines exhibit substantial enhancement in Φ_{isc}, as was reported for thiacarbocyanines, which are substituted by 9-bromo,[8] 9-iodo,[24] 8,9-difluoro,[25] and 9-methoxy,[4] as well as for 10-fluoro-[25] and 10-bromo-substituted indodicarbocyanines.[26]

Φ_f and the fluorescence lifetime (τ_f) of cyanine dyes are known to decrease with increasing the solvent polarity.[27] Also, for *meso*-substituted thiacarbocyanines indication for such an effect has been reported.[28−30] Recent ^{1}H NMR studies by Noukakis *et al.* have revealed for 3,3′-bis(sulfopropyl)-5,5′-dichloro-9-ethyl-thiacarbocyanine triethylammonium (**5**) in solvents of moderate polarity at room temperature the existence of an equilibrium between the all-*trans* and the mono-*cis* configurations.[31] The first observation of a mixture of all-*trans* and mono-*cis* isomers for a *meso*-substituted thiacarbocyanine was based on absorption spectra at low temperatures.[32] In polar solvents the equilibrium in the ground state is shifted toward the mono-*cis* isomer[31] and depends also on the size of the substituent.[10]

In this paper we present data obtained by steady-state fluorescence and flash photolysis with thiacarbocyanine and three *meso*-substituted derivatives in solution. The counterion is ClO_4^- (**1**), I^-, or BF_4 (**1′**, so-called DTC) for the parent compound, Cl^- for **2**, and pyridinium for **3** and **4**. This work attempts to examine the possibility of enhancing Φ_{isc} for alkyl *meso*-substituted thiacarbocyanines because one could expect a retardation of $\Phi_{t\to c}$. Another purpose is to elucidate *cis* → *trans* photoisomerization. The essential results are low Φ_{isc} values and a decrease in Φ_f and $\Phi_{t\to c}$ with an increase of the solvent polarity. As a measure of polarity, we took the E_T^{30} values.[33]

Experimental Section

Compounds **1**−**4** have been synthesized according to methods described elsewhere.[34] Concerning the counterions, the compounds were used as for the silver halide emulsion coating. Their identity was verified by absorption spectroscopy and elemental analysis. The molar absorption coefficients of **1**−**4** in a polar solvent at the maximum are similar to that of **1′**, e.g., $\epsilon_{557} = 1.6 \times 10^5$ M^{-1} cm^{-1} in ethanol. The dye concentration was varied depending on the method, being in the 0.2−0.5 μM range for conventional flash photolysis and in the 1−10 μM range

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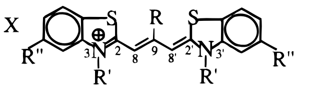
CHART 1



	R	R'	R''	X
1	H	Et	H	$I^{\ominus}$
1'	H	Me	H	$ClO_4^{\ominus}$
2	Me	C_2H_4OH	H	$Cl^{\ominus}$
3	Et	$C_3H_6SO_3^{\ominus}$	OCH_3	$C_5H_5NH^{\oplus}$

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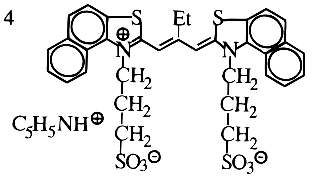


TABLE 1: Absorption Maximum, Fluorescence Excitation and Emission Maxima, and Quantum Yield of Fluorescence[a]

compound	solvent	λ_a (nm)	λ_f^{ex} (nm)	λ_f (nm)	Φ_f (×100)
1	dioxane	567	575	585	7.2
	MTHF	567	576	581 (577)[b]	5 (50)[b]
	acetone	558	562	574	4.5
	acetonitrile	553	557	576	4.0
1′	ethanol	559	557	575 (568)	3.8 (45)
2	dioxane	566	569	583	6.5
	MTHF	564	568	582 (579)	4.5 (55)
	dichloromethane	564	565	581	3.8
	acetone	557	563	577	1.7
	DMF	552	572	580	0.8
	acetonitrile	546	556	573	0.2
	ethanol	546	562	578 (570)	0.25 (60)
3	dioxane	583	586	599	10
	MTHF	562	577	582 (576)	6.1 (35)
	dichloromethane	566	592	598	1.8
	acetone	562	584	597	0.9
	DMF	570	592	606	0.9
	acetonitrile	560	580	591	0.4
	ethanol	560	588	598 (592)	0.3 (50)
4	dioxane	603	610	619	8.8
	MTHF	≈600	610	616	7.9
	dichloromethane	≤590[c]	610	614	1.0
	acetone	576	604	612	0.3
	acetonitrile	575	606	611	0.25
	ethanol	576	606	611 (607)	0.15 (40)

[a] In air-saturated solution at 24 °C unless otherwise indicated. **3** and **4** were first dissolved in acetone and then added (5%) to dioxane or MTHF. [b] Values in parentheses refer to −196 °C. [c] Significantly broader spectrum.

for fluorescence and laser-induced bleaching, and somewhat larger concentrations were used for T−T absorption. The solvents (Merck or Fluka) were used as received in most cases or purified by distillation, e.g., for 2-methyltetrahydrofuran (MTHF) or 1,4-dioxane. In some cases, **3** and **4** were first dissolved in acetone and then added (5%) to dioxane or MTHF.

Fluorescence emission and excitation spectra were recorded on spectrofluorometers (Shimadzu RF-5000, Spex-Fluorolog, and Perkin-Elmer LS-5), and for the absorption, spectrophotometers (Shimadzu UV-3100 and Perkin-Elmer 554) were used. Φ_f was determined using cresyl violet in ethanol as a reference, with $\Phi_f = 0.54$,[35] $\lambda_{exc} = 530$ nm, and optically matched samples having absorbances of 0.1 or 0.2 at λ_{exc} (path length of 1 cm). The experimental error in Φ_f (>0.01 and <0.01) was typically ±10% and ±30%, respectively. Oxygen was found to have only a negligible effect on the fluorescence intensity. This justifies a presentation of Φ_f values in air-saturated (rather than deoxygenated) solution.

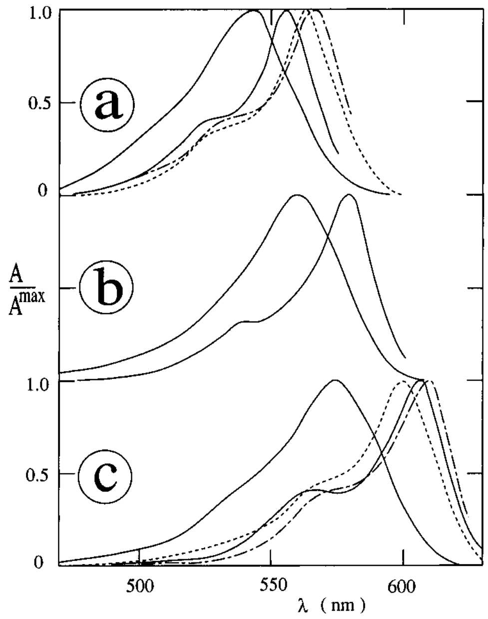


Figure 1. Absorption and fluorescence excitation spectra in acetonitrile (full lines, left and right, respectively) and in MTHF (broken and dotted-dashed lines, respectively) at 24 °C for (a) **2**, (b) **3**, and (c) **4**.

Transient absorption measurements were carried out by means of both 15 μs and 20 ns flash photolysis.[20] For conventional flash photolysis (half-peak width of 15 μs, energy of ≤150 J, quartz cell with a path length of 20 cm) at room temperature, appropriate cutoff filters were used. Most experiments were performed with the second harmonic from a Nd:YAG laser (J. K. Lasers, $\lambda_{exc} = 530$ nm, 1 cm cell). A dye laser (Lambda Physik, FL 2001/2 using rhodamine 6G), $\lambda_{exc} = 570$ nm, pumped by a 530 nm pulse, was used in some cases. For sensitized measurements, the 308 nm pulse of an excimer laser (Lambda Physik, EMG 200) or the 15 μs flash (e.g., for naphthalene-sensitized excitation) or the third harmonic of the Nd:YAG laser was used. Data acquisition and kinetic analyses were carried out on an Acorn computer (540).[20] The amount of ΔA at the maximum of bleaching under otherwise the same conditions (Φ_b^{rel}) depended linearly on the incident laser intensity (I_L) at lower I_L and approached saturation at higher I_L. For **1** in dimethylformamide (DMF) and acetonitrile, Φ_b was arbitrarily set to 1.0. The spectrum of the *cis* isomers of **2**, **3**, and **4** could be derived by using in each case the differential spectrum and the spectrum of the all-*trans* isomer and adjusting the ϵ_c values at λ_b and the two isosbestic points. It coincided with the steady-state absorption spectrum monitored in 2-propanol. The experimental error of ±5% in E_a was typically a factor of 3 in the pre-exponential factor. The calculations of the heat of formation for all possible isomers were carried out at the restricted Hartree−Fock (RHF) level PM3 semiemperical SCF MO method as implemented in the HyperChem program. All geometrical variables were optimized without any assumptions.

Results

Absorption. The absorption spectrum of parent compound **1** in a solvent of relatively low polarity, such as dioxane or MTHF, shows a band in the red spectral region with a peak at $\lambda_a = 567$ nm, which is blue-shifted up to 553 nm as the polarity is increased (Table 1). Also, for the derivatives **2**−**4**, λ_a is blue-shifted in polar solvents, but in a given solvent there is also a general red shift on going from **1** or **2** to **3** and **4**. In some cases a shoulder appears at a wavelength ca. 40 nm shorter than λ_a. Examples in MTHF and acetonitrile are shown in parts a−c of Figure 1 for **2**−**4**, respectively. Interestingly, the molar absorption coefficient of **2**−**4** at λ_a is larger in a solvent of lower polarity, e.g., about 2-fold in dichloromethane vs that in 2-propanol.

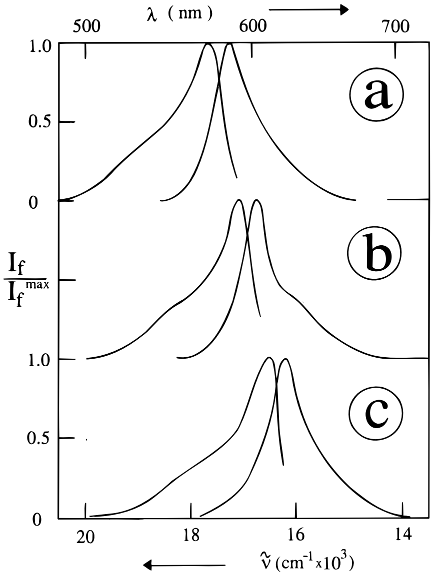


Figure 2. Corrected fluorescence excitation (left) and emission spectra (right) of (a) **2**, (b) **3**, and (c) **4** in acetone at 24 °C; $\lambda_{exc} = 530$ nm; $\lambda_f = 620{-}640$ nm.

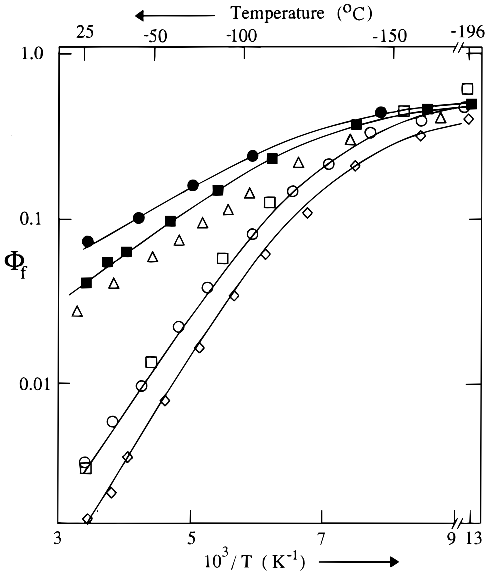


Figure 3. Semilogarithmic plots of Φ_f vs T^{-1} for **1** (triangles), **2** (squares), **3** (circles), and **4** (diamonds) in MTHF (full symbols) and ethanol (open symbols).

Fluorescence. The fluorescence emission exhibits a maximum (λ_f) ranging from around 575 nm for **1′** in ethanol to 619 nm for **4** in dioxane. Examples of the fluorescence spectra are shown in acetone at room temperature in parts a−c of Figure 2 for **2**−**4**, respectively. The fluorescence emission and excitation spectra show a mirror image behavior. The excitation maximum (λ_f^{ex}) is generally slightly larger than λ_a. This shift is relatively small for **1** in all solvents, for **2**−**4** in dioxane and MTHF, and for **2** in dichloromethane. The shift is somewhat larger for **2** in acetone, but in the other cases λ_f^{ex} is strikingly larger than λ_a (Figure 1 and Table 1).

Φ_f is substantial (0.04−0.07) for **1** in all solvents and for **2**−**4** in dioxane and MTHF (0.05−0.10), but for **2**−**4** it decreases strongly with increasing polarity (Table 1). Our Φ_f values of **1** are in good agreement with those in the literature.[15,16,18,20] For an analogue of **2** (R′ = $C_3H_6SO_3^-$) in methanol a value ($\Phi_f = 0.002$) similar to that for **2** in ethanol has been reported.[30] In general, Φ_f increases with decreasing temperature. For **1**−**4** in MTHF and ethanol at −196 °C Φ_f is markedly larger than at room temperature, the increase in ethanol being between 1 and 2 orders of magnitude. Plots of log Φ_f vs T^{-1} are shown in Figure 3. The activation energy of **2**−**4** in ethanol is 8−10 kJ mol^{-1}, i.e., slightly smaller than for **1**.

Photoconversion. The difference spectra for transient absorption and bleaching upon pulsed excitation at 530 nm are shown for **2**−**4** in dioxane at room temperature in parts a−c of Figure 4, respectively. Comparable spectra were recorded for **1** in all solvents and for **2** and **3** in dichloromethane and acetone. The bleaching maxima (λ_b), compiled in Table 2, roughly coincide with the λ_f^{ex} values; i.e., they show a trend to increase on going from **1** to **4**. For **2** and **3** λ_b is larger than λ_a in most solvents with the exception of those of low polarity, e.g., dioxane. The changes, a strong depletion of the ground state and formation of a weak band with a maximum around 500 nm for **1** in all solvents, are due to *trans* → *cis* photoisomerization (here, the *cis* isomer refers to a photoproduct after rotation about one of the bonds of the polymethine chain). This is in agreement with previous results for **1** in ethanol[16−20] and also for **2** and **3** in solvents of lower polarity and for **4** in dioxane. In some cases, however, the recovery is only partially due to photodecomposition, e.g., in chloroform. For **4** in acetone (inset of Figure 5), acetonitrile, and ethanol no bleaching, but a weak increase in ΔA around 600 nm, was measured. This laser-induced spectral change is suggested to be due to *cis* → *trans* photoisomerization in low yield (see below).

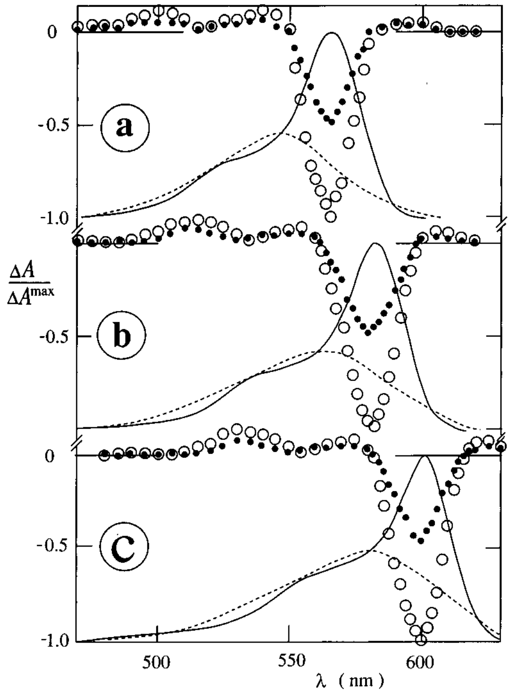


Figure 4. Difference absorption spectra of (a) **2**, (b) **3**, and (c) **4** in dioxane at 24 °C at the end of the 530 nm pulse (○) and (a) at 0.2 ms (●), (b) at 0.08 ms (●) and (c) at 0.06 ms (●) and absorption spectra of the all-*trans* and the observed *cis* isomer (full and broken lines, respectively).

The amount of ΔA at λ_b under otherwise the same conditions (Φ_b) is taken as a relative measure of the quantum yield $\Phi_{t\rightarrow c}$. Φ_b is large for **1** in almost all solvents and is only moderately reduced for **2**−**4** in solvents of lower polarity but is markedly smaller for **2**−**4** in polar solvents (Table 2). For **1′** the $\Phi_{t\rightarrow c}$ values change from 0.13 in dioxane at room temperature to 0.24 in dichloromethane[16] and decrease with decreasing temperature, e.g., from 0.25 in ethanol at 24 °C to 0.027 at −50 °C.[20] The activation energy, obtained from this temperature dependence, is consistent with that (ca. 12 kJ mol^{-1}) obtained from plots of log Φ_f vs T^{-1}.[20]

TABLE 2: Maximum and Relative Quantum Yield of Bleaching[a]

solvent	E_T^{30} (kcal mol^{-1})	λ_b (nm)				Φ_b^{rel}			
		1	**2**	**3**	**4**	**1**	**2**	**3**	**4**
dioxane	36.0	568	566	580	600	0.7	0.8	0.6	0.6
MTHF	36.5		568	*b*	*b*		0.9		
THF	37.4		572			>0.5	0.9		
chloroform	39.1		568	580	570		>0.7[c]		
dichloromethane	41.1	565	565	583		0.9	0.9	0.8	<0.05
acetone	42.2	560	560	578	(600)[d]	0.8	0.9	0.4	<0.05
DMF	43.8	566	565[e]	585		1.0	<0.1	0.2	
acetonitrile	46.0	558	565[e]	580	(600)[d]	1.0	<0.05	0.15	<0.05
2-propanol	48.6			580				0.05	
ethanol	51.9	560	565[e]	578	(600)[d]	0.8	<0.05	0.05	<0.05

[a] In air-saturated solution at 24 °C using a maximum value of 1.0, $\lambda_{exc} = 530$ nm (same maxima using $\lambda_{exc} = 570$ nm); recovery unless otherwise indicated. [b] Too low solubility. [c] Photodecomposition in addition. [d] Transient (positive) absorption but no bleaching, see text. [e] Here, λ_b as in dioxane was taken.

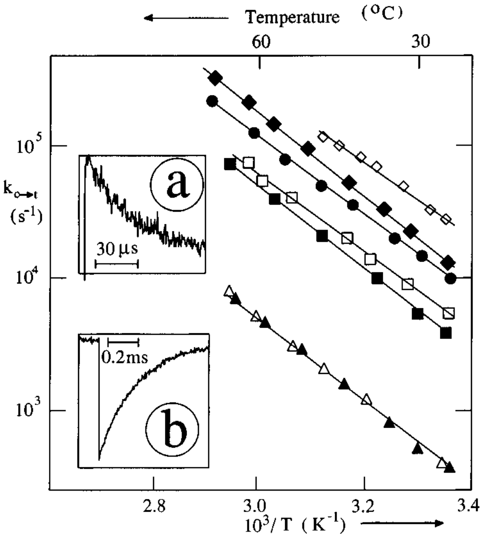


Figure 5. Semilogarithmic plots of the rate constant for the thermal back-reaction vs T^{-1} for **1** (triangles), **2** (squares), **3** (circles), and **4** (diamonds) in dioxane (full symbols) and acetone (open symbols); ◇ refers to **4** in ethanol). Insets refer to recovery for (a) **4** in ethanol at 600 nm and (b) **2** in dioxane at 565 nm.

TABLE 3: Activation Energy, Pre-exponential Factor, and Lifetime of the *Cis* Isomer[a]

compound	solvent	E_a (kJ mol^{-1})	A (s^{-1} × 10^{12})	$1/k_{c\to t}$ (ms)
1	dioxane	61 ± 3	12	3.0
1′	dichloromethane[b]	65 ± 5	6.3	
1	acetone	60 ± 3	8	2.9
	DMF	66 ± 3	120	2.2
	ethanol	59 ± 3	4	4
	methanol[b]	58 ± 1	2.0	
1′	ethanol[c]	64	20	6
2	dioxane[d]	60 ± 3	80	0.29
	dioxane−propanol[e]	58	43	0.27
	MTHF	55 ± 4	13	0.25
	acetone	57 ± 3	40	0.20
3	dioxane[d]	58 ± 3	100	0.11
	dioxane[e]	57		
	dioxane−propanol[e]	64	300	0.40
	acetone	65 ± 3	500	0.37
	acetonitrile	61 ± 3	200	0.18
4	dioxane	62 ± 3	680	0.08
	dioxane−propanol[e]	69	7000	0.13
	acetone[f]			0.05
	ethanol[f]	56 ± 4	120	0.04

[a] In air-saturated solution; $\lambda_{exc} = 530$ nm (unless otherwise indicated). The experimental error of $1/k_{c\to t}$ at 24 °C is typically ±5% for **1**−**3** and ±15% for **4**. [b] Taken from ref 16. [c] Taken from ref 20. [d] Two recovery components; for longer-lived one, see text. [e] Using conventional flash. Dioxane−propanol refers to a 4:1 mixture. [f] *Trans* → *cis* isomerization (no bleaching); see text.

Thermal Back-Isomerization. First-order kinetics of the ground-state recovery at λ_b were found for **1**−**3** in several solvents and for **4** in dioxane. At room temperature the lifetime of the observed *cis* isomer, i.e., the inverse rate constant of the thermal back-reaction ($1/k_{c\to t}$), decreases in the order **1**, **2**, **3**, and **4** (Table 3). The effect of temperature on the thermal *cis* → *trans* reaction was studied between 24 and ca. 70 °C for **1**−**4** in those cases where Φ_b is moderate or large. An Arrhenius-type behavior was obtained throughout (Figure 5) and the activation energy (E_a) and the corresponding pre-exponential factor are compiled in Table 3. Close inspection of the data reveals that for **2** and **3** in dioxane a second minor first-order recovery with virtually the same difference spectrum as the major decay component (parts a and b of Figure 4) is present. The lifetimes for **2** and **3** at 24 °C are significantly larger (ca. 30 and 0.4 ms, respectively) than that of the major component, and the activation energy is both about 64 kJ mol^{-1}. We suggest that two *cis* isomers are photochemically formed that convert independently back into the all-*trans* isomer.

Triplet-State Properties. In the absence of oxygen, a weak additional increase in ΔA at 600−750 nm, which is ascribed to triplet−triplet (T−T) absorption, could be detected, as has previously been reported for **1** in ethanol.[17,20] The triplet state of the four cyanine dyes in several solvents at room temperature was readily observed on naphthalene-sensitized excitation using both laser and conventional flash photolysis (Figure 6 and Table 4). The T−T absorption spectra show a major maximum in the red spectral range and a minor one below 530 nm. Decay of the triplet donor in acetonitrile matches the increase of the absorption of the acceptor, observed at 418 and 630 nm, respectively (insets of Figure 6b). Decay of the acceptor triplet occurs in the 10−50 µs range ($\lambda_{exc} = 530$ nm), but the triplet lifetime (τ_T) is much longer when conventional flash photolysis is used. This is a consequence mainly of the lower dye concentration, reducing self-quenching, and partly of the lower triplet concentration, avoiding T−T annihilation. This general behavior has been reported for related cases.[7,20,25] From such a long triplet lifetime for **1**−**4** in both dichloromethane (i.e., under conditions of efficient *trans* → *cis* photoisomerization) and 2-propanol, we conclude that the perpendicular conformation is not involved in the observed intersystem crossing process to S_0. Otherwise, τ_T should be much shorter. Consequently, rotation around partial double bonds and thus *trans* → *cis* photoisomerization does not take place in the T_1 state. Moreover, the energy level of T_1 should increase on going from *trans* and *cis* isomers to the perpendicular conformer (Schemes 1 and 2). Besides T−T absorption, a weakly absorbing, much longer-lived transient was observed for the four cyanine dyes in the 450−500 nm range, which we attribute to radical formation as a side reaction.

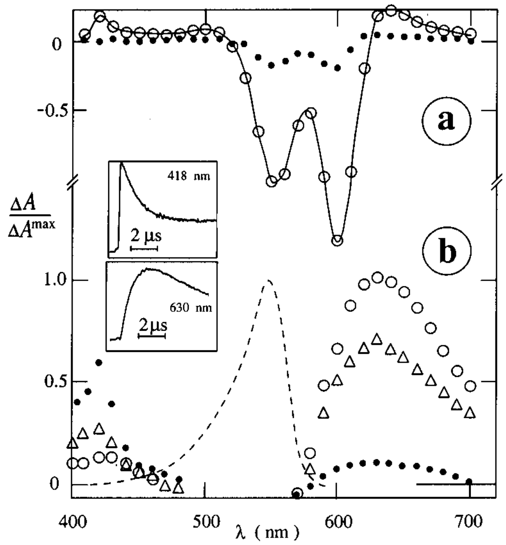


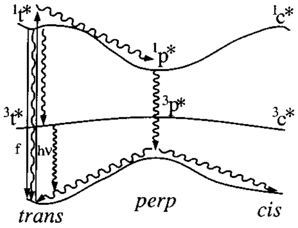
Figure 6. Difference absorption spectra in the presence of naphthalene at 24 °C for (a) **4** in degassed dichloromethane using conventional flash photolysis (at 0.3 ms (○) and 1.8 ms (●) after the pulse) and (b) **2** in argon-saturated acetonitrile (at ≤0.2 μs (●), 1 μs (△), and 2 μs (○) after the 308 nm pulse), where the broken line refers to the ground state. Insets show the decay at 418 nm (upper) and formation at 630 nm (lower).

TABLE 4: Maxima of T−T Absorption and Triplet Lifetime[a]

	λ_{TT} (nm)				τ_T (ms)			
solvent	1	2	3	4	1	2	3	4
dichloromethane	630	640	640	640	0.6	0.5	0.22	0.45
acetonitrile	620	630	650	650	<0.03	<0.03	<0.03	<0.03
2-propanol	620		650		1.0		0.18	0.23
ethanol[b]	610				2.5			

[a] Upon naphthalene-sensitized excitation at 24 °C, using conventional flash photolysis (in degassed dichloromethane, 2-propanol, and ethanol) or λ_{exc} = 308 nm (in argon-saturated acetonitrile). [b] Taken from ref 20.

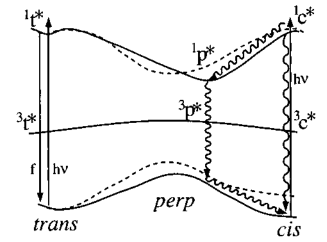
SCHEME 1: Potential Energy Surfaces of the S_1, T_1, and S_0 States (vs the Angle of Rotation about One of the Bonds of the Polymethine Chain) and the Photoprocesses of the All-*trans* Isomer, i.e., 1 in All Solvents and 2−4 in Solvents of Low Polarity



Direct triplet population using either conventional flash photolysis or the shorter pulse reveals the same T−T absorption maxima; the ΔA_{630} value is similar to that of **1** or is even lower (e.g., for **4**). From this we conclude that Φ_{isc} is not larger than 10^{-3}, the value that has been reported for **1**.[20] On the other hand, enhanced intersystem crossing was observed in mixtures with ethyl iodide (λ_{exc} = 530 nm). It should also be noted that for **1** in several solvents (but virtually not for **2**−**4** in acetone or ethanol) a transient absorption as short as the laser pulse could be detected in the 400−500 nm range, which is assigned to a $S_1 \rightarrow S_n$ transition.

Calculations. For **1**−**4** the most stable conformer is the all-*trans* (TTTT) form, where the configuration is defined from the chain of atoms 3-2-8-9-8′-2′-3′ as depicted in Chart 1. For **1** the next most stable conformer is 2,8-mono-*cis* (CTTT), which, however, is less stable for **2**. In this case 8,9-mono-*cis* (TCTT) is more stable than CTTT. The higher stability of TCTT for **2** arises from less steric hindrance for the rotation around the C8−C9 bond with respect to that for the C2−C8 bond. This is also supported by the larger torsion angle between N3−C2−C8−C9 (γ_1) than between C2−C8−C9−C8′ (γ_2). In contrast to **2** the next stable isomer for **3** and **4** is CTTT, but not TCTT, as claimed previously for related 9-alkyl-substituted thiacarbocyanines.[28] For **4** CTTT is less stable (by ca. 10 kJ mol^{-1}) than TCTT.

SCHEME 2: Photoprocesses of the Mono-*cis* Isomer, i.e., 2−4 in Solvents of Medium and Large Polarity (the Dashed Curves Refer to the S_1 and S_0 State in Scheme 1)



For **1** the third most stable conformer is 8,9-mono-*cis* (TCTT), which is ca. 2.5 kJ mol^{-1} above the 2,8-mono-*cis* (CTTT) isomer. For **2** CTTT is considerably less stable than TTTT (ca. 30 kJ mol^{-1}), whereas the difference in the heat of formation between TCTT and TTTT is ≪4 kJ mol^{-1}. The lower stability of CTTT is reflected in the torsion angle γ_1 for TTTT, TCTT, and CTTT, which is 178, 176, and 8°, respectively. The torsion is due to strong overlapping of the van der Waals radii of the 9-Me group with both sulfur atoms (S1 and S1′) and the CH_2 group of hydroxyethyl at N3 for CTTT. The latter overlap is not present for TCTT and TTTT. This is in contrast with the hypothesis of overlapping of the van der Waals radii of the 9-Me group with both sulfur atoms for TTTT.[34] The lower stability of CTTT is also indicated by a larger difference in distances (0.76 Å) between S1 and C9 and S1′ and C9; for TTTT and TCTT these differences are <0.1 Å. For **3** and **4** the third stable mono-*cis* isomer is CTTT (120 and 380 kJ mol^{-1}, respectively). The smaller stability might be influenced by the two SO_3^- groups.

Discussion

Effects of Solvent Polarity. The PM3 calculations reveal that for **1**−**4** the all-*trans* (TTTT) form is the most stable among all 10 isomers. We conclude from the spectroscopic results (Figure 1 and Table 1) that this holds true for **1** in various solvents and for **2**−**4** in solvents of low polarity. Thiacarbocyanine dyes **1** and **1′** are known to form ion pairs with counterions in solvents of low polarity.[6,37] In polar solvents the equilibrium between the ion pairs and the freely solvated ions is shifted toward free ions. Ion-pairing has also been characterized for other cyanine dyes in less polar solvents.[16,37] In analogy, ion pairs should exist for the three thiacarbocyanine derivatives with different substitutents in the *meso* position of the polymethine chain in dioxane or MTHF but virtually not in acetonitrile and ethanol. Ion-pairing may increase Φ_f and τ_f, as has been shown for indodicarbocyanine dyes and **5**,[4,31] and as a consequence, ion-pairing may decrease $\Phi_{t\rightarrow c}$.[25]

Generally, ion-pairing of cyanine dyes is indicated by a slightly broader absorption band than the free dye. However, this is only the case when the same all-*trans* isomer exists in solvents of both low and large polarity which is not so for **2**−**4**. For **5** it has been suggested that a broadening implies an equilibrium between the all-*trans* and a mono-*cis* isomer in the ground state and that this equilibrium is solvent dependent.[31]

This is also suggested for **2**−**4**. A comparison of the data for **2** and **3**, for example, may be instructive because they are present as anionic and cationic dyes, respectively. However, the results obtained from absorption, fluorescence, bleaching, and recovery measurements (Figures 1−5, Tables 1−3) show a steady trend on going from **1** to **4**, whithout any pronounced effect which could be ascribed to a difference between an anionic and a cationic dye.

The formation of one *cis* isomer which relaxes thermally to the all-*trans* isomer has been suggested for the parent compound.[16,18,20] One photoisomer was also observed for **2**, **3** (with the exception of dioxane), and **4**. While the A-factors are different for each combination of compound and solvents, the height of the activation barrier does not change strongly with substituent and solvent polarity (Table 3). The activation parameters for **1** in solvents of different polarity are in agreement with those reported previously.[16,20] In solvents of low polarity one may expect a decrease of the mobility around one of the polymethine C-C bonds. Thus, the ion-pairing could result in restriction of motion around a partial double bond, as has been indicated for indocarbocyanine dyes, and this could lead to an increasing energy barrier for the thermal *cis* → *trans* isomerization.[39] Based on decreasing E_a values for **1** and the oxacarbocyanine dye with increasing solvent polarity, Ponterini and Momicchioli[16] have proposed that the perpendicular configuration is better stabilized by a polar medium than the *cis* isomer. Such an effect, however, could not be confirmed in the present work (Table 3).

Deactivation of the Excited Singlet State of 1. The fluorescence properties of the parent compound in ethanol are $\tau_f = 0.3$ ns[14,16] and $\Phi_f = 0.04$ at 24 °C and are larger at −196 °C (Table 1). The reason for the increase in Φ_f in all cases on going from 24 to −196 °C is the hindrance toward rotation around one of the bonds of the polymethine chain in the first excited singlet state (S_1) upon excitation of the all-*trans* isomer. It is well-documented for cyanine dyes[16−20] that the activation barrier in S_1 cannot be overcome in a glassy medium at low temperatures, since the viscosity has increased by many orders of magnitude.

A model that describes the photophysical and photochemical features of **1** in solvents of weak and strong polarity and, to a certain extent, also for the other three thiacarbocyanine dyes in a solvent of low polarity is shown in Scheme 1. 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. The contributions of these processes depend on internal (structure of the molecule) and external (solvent polarity and temperature) factors.

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

$${}^1t^* \xrightarrow{k_f,\, k_{ic}} trans \tag{2}$$

$${}^1t^* \xrightarrow{k_{isc}} {}^3t^* \tag{3}$$

$${}^1t^* \xrightarrow{k_{rot}} {}^1p^* \rightarrow \alpha\, trans + (1-\alpha) cis \tag{4}$$

The fraction α of the perpendicular conformer in the S_1 state (${}^1p^*$) decaying into the all-*trans* form can be estimated to be 0.3 for **1** in polar solvents.[16] For **1** in ethanol at 24 °C, as already mentioned, $\Phi_f = 0.038$, $\Phi_{t\rightarrow c} = 0.25$, and $\Phi_{isc} = 0.001$. From similar Φ_b values in solvents of different polarity (Table 2) and $\Phi_f \leq 0.07$, we conclude that α is only slightly influenced by ion-pairing. It should be emphasized that most authors agree on the singlet mechansim for *trans* → *cis* photoisomerization of thiacarbocyanine[16−20] except for Serpone and Sahyun,[23] who argued for an analogue ($R' = C_{12}H_{25}$, $X^- = Br^-$) in favor of a triplet mechansim on the basis of a Φ_{isc} value of 0.55 in dichloromethane. The offered assignment of the difference spectrum after a few nanoseconds is the *cis* triplet state.[23]

Deactivation of the Excited Singlet State of 2−4. Excitation of the all-*trans* isomer in solvents of low polarity leads mainly to one isomer that should be mono-*cis* in nature (Scheme 1). Other possibilities, i.e., formation of a di-*cis* or tri-*cis*, are less likely, since this would require rotation around two or three bonds of the polymethine chain. Nevertheless, for thiadicarbocyanine in methanol a second photoisomer has been detected upon excitation at high laser intensity.[38] In fact, for **2** and **3** in dioxane, i.e., under conditions where parent **1** yields only the mono-*cis* isomer, we could also detect a second photoisomer.

In polar solvents the equilibrium in the ground state between the all-*trans* and the mono-*cis* isomer is shifted toward the mono-*cis* side. This follows from the absorption spectra which show a significant blue shift in polar solvents (Figure 1 and Table 1). The additional changes in the absorption spectra of **2**−**4**, e.g., broadening and decrease in molar absorption coefficient at the maximum, on going from a solvent of low to strong polarity are caused by partial loosening of the conjugation due to steric reasons. The mechanism for deactivation of the S_1 state of **2**−**4** in a solvent of medium or large polarity should, in principle, account for *cis* → *trans* photoisomerization (Scheme 2).

$$cis \xrightarrow{h\nu} {}^1c^* \tag{5}$$

$${}^1c^* \rightarrow cis \tag{6}$$

$${}^1c^* \rightarrow\rightarrow \beta\, trans + (1-\beta) cis \tag{7}$$

Reaction 6 is suggested to be radiationless, since the fluorescence results could only be interpreted by assuming that the excited *cis* isomer virtually does not fluoresce. For the photoisomer of **1** in (m)ethanol at room temperature, it has been estimated that $\Phi_f \leq 0.004$,[19] i.e., a value that is less than 10% of that of the all-*trans* isomer. For **2**−**4** the details of reaction 7 are unknown. In principle, deactivation of the ${}^1c^*$ state could occur via the ${}^1p^*$ state; then $\alpha = \beta$. Only for **4** in acetone (inset of Figure 5) and more polar solvents could we find a condition where β is larger than zero. This is in contrast to **1** where *cis* → *trans* photoisomerization occurs with $\Phi_{c\rightarrow t} = 0.16$.[19]

Conclusions

Alkyl substitution in the *meso* positon of the polymethine chain of thiacarbocyanine dyes results in a thermally maintained *cis*−*trans* equilibrium that is governed by solvent polarity. The expectations of both a retarded *trans* → *cis* photoisomerization and enhanced Φ_{isc} for **2**−**4**, due to steric hindrance for rotation in the S_1 state, were not confirmed. Instead, the triplet state does not play a discernible role in the deactivation of the excited singlet state of any isomer. For thiacarbocyanine dyes the singlet mechansim for *trans* → *cis* photoisomerization is operating and a Φ_{isc} value as high as 0.55, as reported by Serpone and Sahyun,[23] has to be revised. The excited *cis* isomer of **2** and **3** in polar solvents deactivates radiationlessly by strictly avoiding conversion into the *trans* isomer. This process occurs to a certain extent also for **4**.

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