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Photoprocesses in 4-nitro- and 2,4-dinitro-substituted *trans*-1-styrylnaphthalene, *trans*-9-styrylanthracene and related systems

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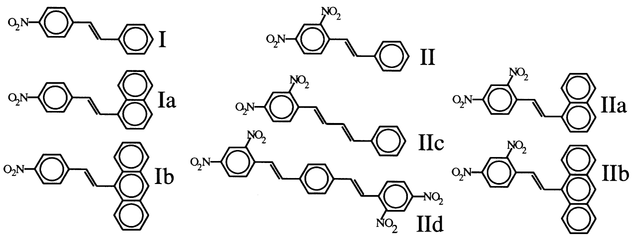
Abstract

The photophysical and photochemical properties of four *trans*-1-(R)-2-(2,4-dinitrophenyl)ethylenes (R: 1-naphthyl: **IIa**, 9-anthryl: **IIb**, styryl: **IIc** and 4-(2',4'-dinitro)-*trans*-stilbenyl: **IId**) were studied in solution. The quantum yield of fluorescence (Φ_{f}) is small for **IIa**–**IId** in 2-methyltetrahydrofuran (MTHF) at room temperature, but enhanced on going to −196°C. Phosphorescence of singlet molecular oxygen was observed in several solvents and its quantum yield is substantial. The properties of the triplet state (T–T absorption spectra and triplet lifetimes) of **IIa**–**IId** at 25 and −196°C are described. The quantum yield of *trans* → *cis* photoisomerization ($\Phi_{t\to c}$) is small with the exception of **IIc**, where $\Phi_{t\to c} \approx 0.3$. *Trans* → *cis* photoisomerization occurs via the triplet mechanism, but its contribution to the overall deactivation is reduced by intramolecular electron transfer to the nitro group. The results for **IIa** and **IIb** are compared with those of two mononitro analogues, R: 1-naphthyl (**Ia**) and 9-anthryl (**Ib**). The Stokes shift and Φ_{f} of **Ia** and **Ib** depend strongly on the solvent polarity. The effects of intramolecular charge transfer in mononitro- and dinitro-arylstyrenes are discussed. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Fluorescence; Triplet state; Singlet oxygen; *Trans* → *cis* photoisomerization; Intramolecular charge transfer

1. Introduction

Trans-1,2-diarylethylenes featuring an electron donating group and an electron withdrawing group that interact through π-conjugation have been the subject of intense investigations [1–26]. These donor–acceptor substituted (push–pull) polyenes can be considered as model compounds for intramolecular charge transfer (ICT). Certain photophysical and photochemical properties of *trans* isomers of 1,2-diarylethylenes are drastically altered if the electron acceptor is a nitro group in *para* position, especially in the cases of 4-nitro-4'-dimethylaminostilbene (**I**-Me_2) [3–9,12]. Related photoprocesses have been reported for styrylnaphthalenes [15] and styrylanthracenes [16–20]. The deactivation pathways for *trans* isomers of 1-(R)-2-(4-nitrophenyl)ethylenes, where R=1-naphthyl (**Ia**) and R=9-anthryl (**Ib**), are complex and only partly understood. The *trans* → *cis* photoisomerization occurs via different mechanisms, depending on the structure and the solvent. Fluorescence and other deactivation processes, competing with *trans* → *cis* photoisomerization, are sensitive to the solvent properties and temperature, especially for *trans* isomers of **Ia** and **Ib** [15–20].



In the present work the photophysical and photochemical properties of four 1,2-diarylethylenes (**IIa**–**IId**) containing a *trans*-2,4-dinitrostyryl subunit were studied and in the cases of **IIa** and **IIb** were compared with those of the corresponding mononitro compounds (**Ia** and **Ib**). In addition, formation of singlet molecular oxygen, $O_2(^1\Delta_g)$, was studied. The effects of substituents with different electron donating abilities and of the second nitro group (in *ortho* position with respect to the arylethylene moiety) concerning ICT are outlined.

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2. Experimental details

The *trans* isomers of 1-(1-naphthyl)-2-(4-nitrophenyl) ethylene (**Ia**) [15] and 1-(9-anthryl)-2-(4-nitrophenyl) ethylene (**Ib**) [19] were the same as used previously. The other compounds were purchased from Aldrich and recrystallized from acetonitrile, (**IIb**, **IIc**) or chloroform (**IIa**, **IId**). Melting points (in °C) are: **IIa**: 226–228, **IIb**: 167–168, **IIc**: 137–138 and **IId**: >256. The molar absorption coefficients at the maxima in acetonitrile are: $\varepsilon_{386} = 1.7 \times 10^4$, $\varepsilon_{424} = 0.55 \times 10^4$ and $\varepsilon_{407} = 2.2 \times 10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ for **IIa**, **IIb** and **IId**, respectively. The solvents (Merck) were purified by distillation, e.g. 2-methyltetrahydrofuran (MTHF), or by passing through an aluminium oxide column (cyclohexane); the others were used without purification, e.g. acetonitrile or D_2O (Uvasol quality), toluene or ethanol (p.A.).

Laser flash photolysis measurements were carried out using generally the third harmonic of a neodymium laser ($\lambda_{exc} = 354$ nm, pulse width 10–15 ns) and in some cases an excimer laser ($\lambda_{exc} = 308$ nm, pulse width ca. 20 ns). For fast and slow detection transient digitizers (Tektronix, 7912AD and 390AD) were used and data handling was performed with a computer (Archimedes 540). The quantum yield of *trans* → *cis* photoisomerization was determined using 4-nitrostilbene (**I**) in toluene as reference ($\Phi_{t\to c} = 0.50$ [8]). The absorption spectra were recorded on a Perkin–Elmer 554 spectrophotometer, typical absorbances were $A_{366} = 1$–2 (1 cm pathlength), corresponding to concentrations of 0.05–0.1 mM. The fluorescence spectra were recorded on a Perkin–Elmer LS-5 spectrofluorimeter or a Spex-Fluorolog (corrected spectra). Φ_f was measured using optically matched solutions (A at λ_{exc} ca. 0.2) and 9,10-diphenylanthracene (Ega, 99%) as standard; the experimental error was below 30%.

Phosphorescence of singlet molecular oxygen at 1269 nm [27–33] was detected after the pulse (intensity I_Δ) by using a cooled Ge detector (North Coast, EO 817FP), a silicon and an interference filter and two amplifiers (Comlinear, CLC-103) [14]. The lifetimes of $O_2(^1\Delta_g)$ in most solvents were >20 µs; due to strong fluorescence extending even to 1269 nm, methanol, where the lifetime is ca. 10 µs, was not suitable in several cases. At a fixed laser intensity (I_L) the I_Δ signal was found to show a linear dependence on either the absorbed energy, being proportional to $(1–10^{-A})$, or on I_L with a curvature at higher intensities; the slope of the latter plot is denoted as q_Δ. The quantum yield of for- mation of $O_2(^1\Delta_g)$ was obtained from the linear dependencies of the signal at the pulse end using optically matched solutions ($A = 0.3$ or 0.6 at $\lambda_{exc} = 308$ or 354 nm) and 2-acetonaphthone in benzene as reference ($\Phi_\Delta = 0.85$ [27]). For the values in other oxygen-saturated solvents a correction has to be applied using the rate constant for radiative deactivation of $O_2(^1\Delta_g)$ (k_r) relative to that in benzene (k_r^{o}).

Table 1
Absorption maximum of the *trans* isomer and quantum yield of *trans* → *cis* photoisomerization[a]

Compound	Solvent	λ_t (nm)	$\Phi_{t\to c}$
Ia[b]	Cyclohexane	357	0.45
	Toluene	366	0.35
	Acetone	368	0.16
	Acetonitrile	368	0.08
IIa	Cyclohexane	382	0.08
	Toluene	385	0.06
	Acetone	380	0.02
	Acetonitrile	386	<0.02
Ib[b]	Cyclohexane		<0.001
	Toluene	410	0.20
	Acetonitrile		<0.001
IIb	Toluene	435	0.02[c]
	Acetone	438	0.02
	Acetonitrile	434	<0.02
II[b]	Toluene	353	0.43
IIc	Cyclohexane	350	0.32
	Toluene	352	0.28
	Acetonitrile	354	0.2
IId	Toluene	398	0.05[d]
	Acetonitrile	407	<0.05[d]

[a] In argon-saturated solution at 25°C, $\lambda_{exc} = 366$ nm, unless otherwise indicated.

[b] Taken from the literature [14,15,19,20].

[c] No difference using $\lambda_{exc} = 366$ or 436 nm.

[d] Initial value, no unimolecular reaction.

$$\Phi_\Delta = \Phi_\Delta^{\mathrm{ref}} \times \frac{q_\Delta}{q_\Delta^{\mathrm{ref}}} \times \frac{k_r^{o}}{k_r} \qquad \text{(I)}$$

The k_r/k_r^{o} ratios were taken from the literature [28–32].

3. Results

3.1. Trans → cis photoisomerization

The absorption maximum (λ_t) of the *trans* isomer of **IIc** is similar to that of parent **II** [14] and is red-shifted in the order **IIa**, **IId** and **IIb** (Table 1). Upon irradiation ($\lambda_{irr} = 366$ nm) of **IIc** in several solvents the absorbance at λ_t decreases due to *trans* → *cis* photoisomerization and approaches a photostationary state (Fig. 1). For **II** and **IIc** $\Phi_{t\to c}$ is substantial in cyclohexane or toluene and smaller in polar solvents (Table 1). A similar trend and much smaller $\Phi_{t\to c}$ values were obtained for **IIa**, whereas for **IIb** and **IId** the $\Phi_{t\to c}$ values are even smaller. A maximum $\Phi_{t\to c}$ value in a non-polar solvent and a decreasing trend with increasing the polarity has been reported for **Ia** [15]. For **Ib** $\Phi_{t\to c}$ is virtually zero in cyclohexane, is highest in a solvent of low polarity, such as toluene, and smaller in polar solvents [19].

3.2. Fluorescence

The *trans* isomers of **IIa**–**IId** in solution at room temperature show only weak fluorescence, the fluorescence maxima

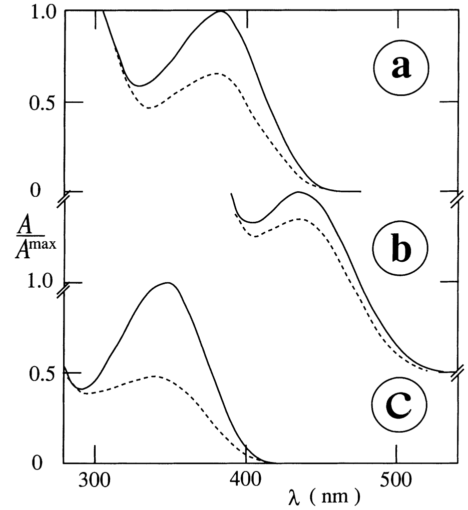

Fig. 1. Absorption spectra of (a) **IIa**, (b) **IIb** and (c) **IIc** in toluene at 25°C prior to (full lines) and after irradiation at 366 nm (broken lines).

Table 2
Maximum, quantum yield and lifetime of fluorescence of the *trans* isomers[a]

Compound	Solvent	λ_f (nm)	Φ_f	τ_f[b] (ns)
Ia[c]	Cyclohexane	496	0.0007(0.1)[d,e]	<0.1
	Toluene	520	0.002	
	MTHF	516 (490)	0.009 (0.15)[d]	0.3
	Acetone	576	0.23	
	Acetonitrile	610	0.18	
	Ethanol	645	0.002 (0.2)	
IIa	Toluene	495	0.001	0.6
	MTHF	500 (508)	0.001 (0.05)	
	Acetone	520	<0.001	
Ib	Cyclohexane	505	0.27	1.8
	Toluene	550	0.19	2.2
	Dioxane	580	0.10	1.0
	Dichloromethane	620	0.04	0.5
	Acetonitrile	>700	<0.002	
IIb	MTHF	505 (550)	0.003 (0.4)	
II[c]	MTHF	<500 (480)	0.004 (0.005)	
IIc	MTHF	510 (510)	<0.001 (<0.001)	
IId	MTHF	505 (470,500)	<0.001 (0.3)	

[a] In argon-saturated solution at room temperature, λ_{exc} = 366 and 436 nm for **IIa** and **IIb**, respectively.
[b] In air-saturated solution.
[c] Φ_f taken from [14,15,19].
[d] Values in parentheses refer to −196°C.
[e] In 2,2-dimethylbutane : n-pentane (8 : 3).

(λ_f) are compiled in Table 2. For the naphthyl or anthryl derivatives of *trans*-2,4-dinitrostilbene, the solvent properties have no significant effect on λ_f and Φ_f. This is in striking contrast to the mononitro analogues **Ia** and **Ib**, where both Φ_f and the Stokes shift ($\Delta\tilde{\nu} = 1/\lambda_t - 1/\lambda_f$) are sensitive to the solvent polarity. The $\Delta\tilde{\nu}$ values depend linearly on the Dimroth E_T^N parameter [34] with a larger slope for **Ib** (Fig. 2). For **Ia** the plot of log Φ_f increases linearly with increasing E_T^N from 0 to 0.3, whereas for **Ib** the curve between E_T^N = 0.2–0.4 is essentially decreasing (Fig. 3).

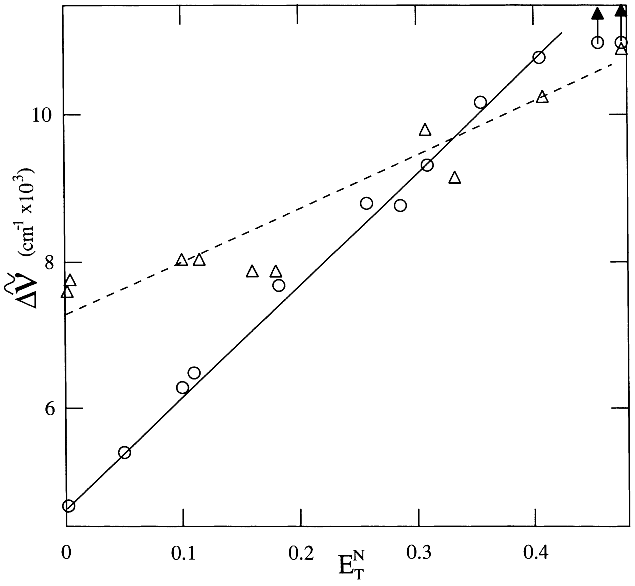

Fig. 2. Plots of the Stokes shift versus E_T^N for **Ia** (Δ) and **Ib** (o) at 25°C.

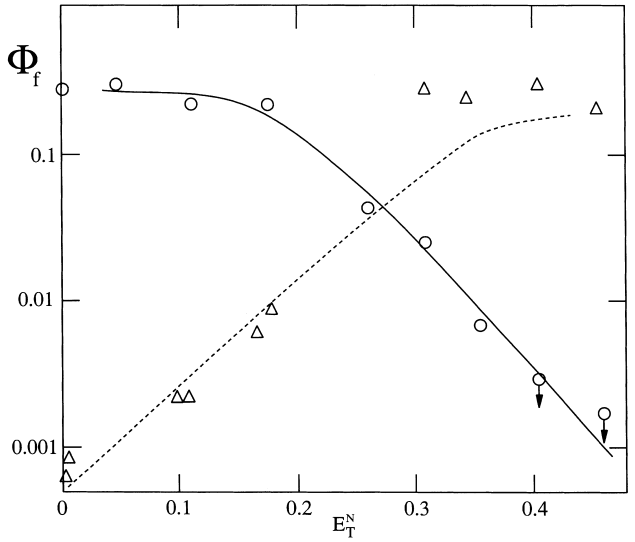

Fig. 3. Semilogarithmic plots of Φ_f versus E_T^N for **Ia** (Δ) and **Ib** (o) at 25°C.

At −196°C Φ_f becomes generally larger. The fluorescence excitation spectrum of **IIa** or **IIb** is a mirror image of the emission spectrum and similar to the absorption spectrum at room temperature. The quantum yield covers a range from $\Phi_f < 1 \times 10^{-3}$ at 25°C to 0.3–0.4 for **IId** or **IIb** in MTHF at −196°C. For **IIa** Φ_f is significantly smaller and virtually no fluorescence was observed for **IIc**.

The fluorescence lifetime ($\tau_f = \Phi_f/k_f$) of **Ia** in fluid and glassy MTHF is 0.3 and 3.2 ns, respectively [15]. The fluorescence lifetime, in view of the large changes in Φ_f and relative small changes in k_f, should reveal more or less the same dependencies on polarity, and gradually on substituent, as Φ_f. This is the case for **Ib** with τ_f = 2 ns and Φ_f = 0.2–0.3 in solvents of low polarity [19,20] and smaller τ_f and Φ_f values in more polar solvents (Table 2).

Table 3
T–T absorption maximum, lifetime and triplet yield of the *trans* isomer[a]

Compound	Solvent	λ_T (nm)	τ_T (μs)	Φ_{isc}
Ia[b]	Cyclohexane	475, 560	0.4	0.8
	MTHF	480, 580	0.9 (3)[c]	0.6
	Acetonitrile	480, 590	1.2	0.3
IIa	Toluene	470–590	0.8	
	Acetone	480, 580	2	
Ib[d]	MCH/Cyclohexane	350, 560	26–35 (0.5)	0.38
	Acetonitrile	350, 560	35–70	<0.05
	Ethanol	<400, 560	40 (0.5)	0.04
IIb	Toluene	360, 580	15	
	MTHF	580	15	
II[e]	Cyclohexane	440–550	0.04	
	MTHF	440–550	0.06 (8)	> 0.8
	Acetonitrile	450–550	0.06	
	Ethanol	430–520	0.06 (3)	
IIc	MTHF	440, 520	0.05 (5)	
IId	MTHF	640 (640)	4.0 (1.5)	

[a] In argon-saturated solution at 25°C, $\lambda_{exc} = 354$ nm.
[b] Taken from [15].
[c] Values in parentheses refer to -170°C, (lifetime in units of ms).
[d] Taken from [19,20].
[e] Taken from [14].

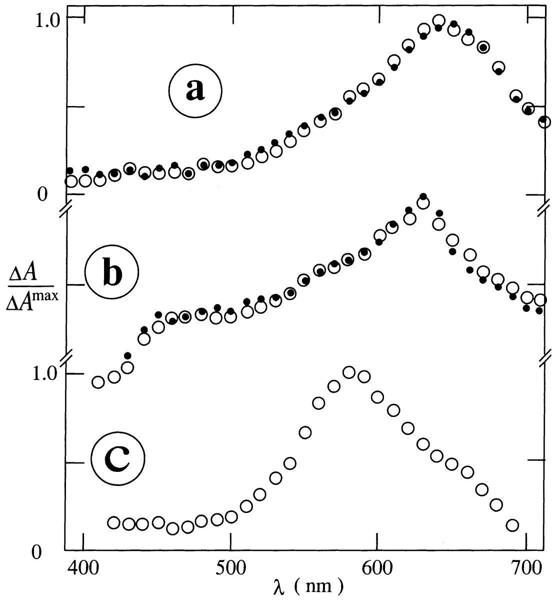

Fig. 4. T–T-absorption spectra in argon-saturated MTHF at 25 and −196°C (open and filled symbols, respectively) for (a) **IId**, (b) **IIa** and (c) **IIb**; $\lambda_{exc} = 354$ nm.

3.3. Triplet properties

On excitation ($\lambda_{exc} = 354$ nm) of the *trans* isomers of **II** and its derivatives in solution at room temperature, the triplet state appears within the duration of the laser pulse (15 ns). The T–T absorption spectra of *trans*-2,4-dinitrostilbenes are rather broad with one or two maxima (λ_T) depending on the substituent and only slightly on the solvent properties (Table 3). Examples are shown in Fig. 4. Decay of the triplet follows a first-order law; the triplet lifetime ($\tau_T = 1/k_{obs}$) in argon-saturated toluene at room temperature ranges from 50 ns for **IIc** to the 10–30 μs range for **IIb** (Table 3), but for the latter the ΔA value is low. Oxygen quenches the observed triplet state; the rate constant for **IId** in several solvents is $(3–8) \times 10^9\ M^{-1}\ s^{-1}$.

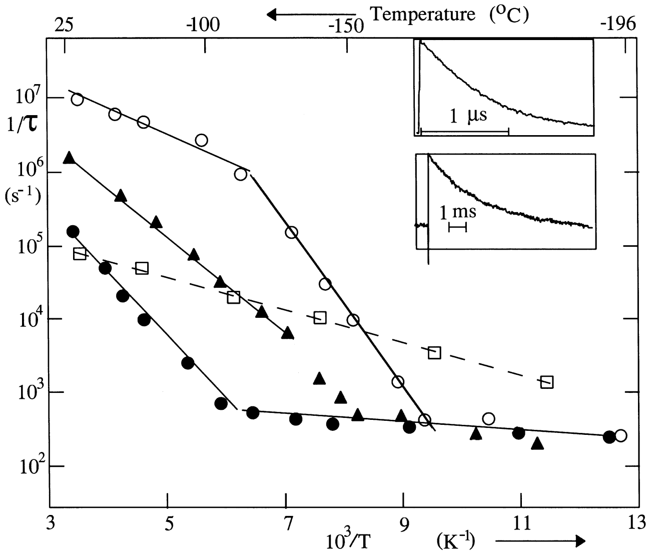

Fig. 5. Semilogarithmic plots of $1/\tau_T$ versus $1/T$ in MTHF for **IIa** (▲), **IIb** (□), **IIc** (o) and **IIb** (●), $\lambda_{exc} = 354$ nm; insets: **IIc** at 25°C (upper) and −170°C (lower).

The T–T absorption spectra of **IIa**–**IId** in glassy MTHF at −170 to −196°C are similar in most cases to those in fluid solution (Table 3). Thus, the absorption at room temperature refers to the *trans* geometry since rotation into the *perp* geometry is hindered in rigid glasses [12,13,15]. The yield of the triplet state is almost constant between 25 and −196°C, whereas its lifetime increases with decreasing temperature. The dependence of $\log 1/\tau_T$ as a function of $1/T$ is shown in Fig. 5 for several cases. For **IIc** (as for **II**) $1/\tau_T$ decreases only slightly with decreasing temperature in the upper range, decreases strongly in an intermediate small temperature range (e.g. −140 to −160°C in MTHF) and levels off below this. This overall pattern is typical for 1,2-diarylethylenes showing *trans* → *cis* photoisomerization via the lowest triplet state [13,15]. No characteristic temperature ranges were observed for **IIb** for which *trans* → *cis* photoisomerization is negligible. The triplet lifetime of **IId** and **IIa**, having small $\Phi_{t\to c}$ values at room temperature, is also relatively long.

3.4. Singlet molecular oxygen

Examples of formation and decay of $O_2(^1\Delta_g)$ upon excitation in air-saturated toluene are shown in Fig. 6. The signals at the end of the pulse (I_Δ) of **Ia** in cyclohexane, toluene and acetonitrile and 2-acetonaphthone in benzene as reference depend linearly on the incident laser intensity. The quantum yield ranges from $\Phi_\Delta = 0.02$ for **Ib** in acetonitrile to 0.4–0.5 for **Ia**, **Ib** or **IIa** in solvents of low polarity (Tables 4 and 5).

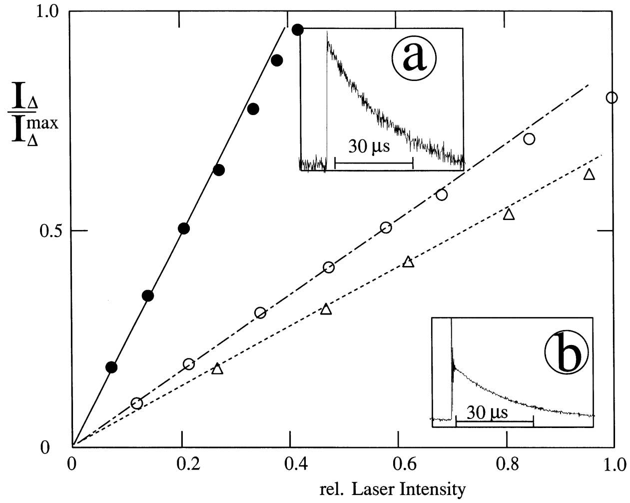

Fig. 6. Plots of the singlet oxygen signals after the 308 nm pulse versus the incident laser intensity in air-saturated solution for acetophenone in benzene (●), **IIa** (o, inset a) and **Ia** (Δ, inset b) in toluene.

Table 4
Relative radiative rate constant and quantum yield of formation of singlet oxygen of **Ia** in solvents of different polarity[a]

Solvent	E_T^N	$(k_r/k_r^o)^b$	Φ_Δ
Cyclohexane	0	0.44	0.42
Carbon tetrachloride	0.05	0.62	0.40
Toluene	0.10	0.96	0.50
Benzene	0.11	1.0	0.48
Dioxane	0.16	0.37	0.42
Chloroform	0.26	0.75	0.38
Dichloromethane	0.31	0.50	0.33
Acetone	0.36	0.39	0.29[c]
Acetonitrile	0.46	0.30	0.22
Methanol	0.76	0.21	–[d]

[a] In oxygen-saturated solution at 25°C, $\lambda_{exc} = 308$ nm unless otherwise indicated.

[b] Rate constant for radiative decay of $O_2(^1\Delta_g)$ in the given solvent versus benzene.

[c] $\lambda_{exc} = 354$ nm.

[d] Too low signal, emission not distinguishable from oxygen-free solution.

Table 5
Quantum yield Φ_Δ of singlet oxygen formation[a]

Solvent	**II**[b]	**Ib**	**IIa**	**IIb**	**IIc**	**IId**
Cyclohexane	0.14	0.38	0.40			
Toluene	0.16	0.22	0.33	0.22	0.11	0.24
Dichloromethane	0.12			0.06		
Acetonitrile	0.13	0.02				

[a] In oxygen-saturated solution at 25°C, $\lambda_{exc} = 354$ nm.

[b] Taken from [14].

4. Discussion

4.1. Deactivation pathways via the triplet state

For *trans*-4-nitrostilbene (**I**) and their 4' OMe or NMe$_2$ substituted derivatives [3–8] as well as their 2,4-dinitro derivatives [14] the influence of solvent and temperature on Φ_{isc} and internal conversion at the *trans* side (yield: Φ_{ic}) has been studied previously. For **I** and 2,4-dinitrostilbene (**II**) at room temperature $\Phi_{t\rightarrow c}$ is closely related to Φ_{isc}. This is a consequence of the triplet mechanism which is briefly expressed by:

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

$${}^1trans^*_{FC} \rightarrow {}^1trans^* \tag{2}$$

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

$${}^1trans^* \xrightarrow{k_f} trans \tag{4}$$

$${}^1trans^* \xrightarrow{k_{ic}} trans \tag{5}$$

$${}^3trans^* \rightleftharpoons {}^3perp^* \tag{6}$$

$${}^3perp^* \rightarrow perp \tag{7}$$

$$perp \rightarrow \alpha\, trans + (1-\alpha)\, cis \tag{8}$$

The initial twisting process about the C=C double bond (0 to ca. 90°) yields $^3perp^*$ and the second part (ca. 90 to 180°) the two isomers, where, $1-\alpha$ is the fraction for population of the *cis* form from the $^3perp^*$ conformation. Intersystem crossing from the $^3trans^*$ state to the *trans* ground state does not play a role in fluid media, but takes place when a rigid glass prevents rotation into the $^3perp^*$ state [13,14]. Ferrocene or azulene react with the $^3trans^*$ state of stilbenes, whereas, due to energetic reasons, quenching of the $^3perp^*$ state is not possible [8,13]. On the other hand, both triplet conformers are quenched by oxygen. Triplet oxygen is converted by energy transfer into singlet oxygen involving the $^3trans^*$ state, whereas the $^3perp^*$ state is quenched via a spin exchange mechanism [33].

The quantum yield of formation of $O_2(^1\Delta_g)$ is 0.1–0.5 for the compounds under examination (Table 5). $\Phi_\Delta = 0.12$–0.16 for **I** and 0.04–0.22 for **II** [14], i.e. lower than Φ_{isc}. One reason for this effect is formation of the perpendicular triplet geometry in those cases where *trans* → *cis* photoisomerization is efficient. Quenching of $^3perp^*$ yields triplet rather than singlet oxygen, as reported for 1,2-diarylethylenes [13,33]. In this respect mononitro and dinitro *trans*-isomers are similar.

The above photoprocesses, negligible fluorescence and efficient *trans* → *cis* photoisomerization, are common to **I** and **II** and several derivatives. However, when the substituent in 4' position is a strong electron donor, the second nitro group in *ortho* position gives rise to a marked reduction of $\Phi_{t\rightarrow c}$ due to ICT-induced internal conversion at the *trans* side (k_{ic}), bypassing the common pathway of *trans* → *cis* photoisomerization [14]. At −196°C Φ_f is small for most *trans*-**II**, but moderate to large for those with a stronger electron donor. In the latter cases intersystem crossing is low. This is based on the finding that ΔA at λ_T is virtually independent of temperature and that Φ_{isc} is probably comparable to $2 \times \Phi_{t\rightarrow c}$ which is <0.01 at 25°C. Therefore, ICT at the *trans* side is operating. This occurs even in rigid glasses where the transition from the Franck–Condon state to the CT state should be slowed down.

4.2. Photochemical properties of **IIc** and **IId**

Deactivation of the $^1trans^*$ state of the bis-styryl derivative **IId** occurs mainly at the *trans* geometry, as indicated by the small $\Phi_{t\to c}$ value (Table 1). While *trans* → *cis* photoisomerization is strongly retarded by introduction of the second styrene group, intersystem crossing is efficient, as indicated by similar Φ_Δ values for **IId** and **II** (Table 5). The relatively long triplet lifetime (Table 3) can be ascribed to a decay transition of the observed triplet at a geometry which is *transoid* with respect to the *perp* conformer. If a triplet equilibrium is established, it is shifted to the *trans* side since otherwise τ_T is expected to be much shorter, e.g. <100 ns as for **II** and some derivatives. The relatively large Φ_f value of **IId** at −196°C (Table 2) is remarkable since the much smaller value for **II** was taken as an indication for ICT at the *trans* side. Thus, the contribution of ICT in the case of **IId** is probably smaller than in the case of **II**.

The photochemical properties of the diphenylbutadiene derivative **IIc** (Tables 1, 2 and 3) are comparable to those of derivatives of **II** bearing no or a weakly polar substituent, even though the phenyl rings are separated by two double bonds. For **IIc** the photoisomerization is effective and occurs via the triplet state and fluorescence plays no role even in rigid glasses.

4.3. Photochemical properties of trans-(di)nitrostyrylnaphthalene

What are the major changes when the phenyl ring not containing a nitro group in **I** and **II** is replaced by the naphthyl group? *Trans* → *cis* photoisomerization of 1-styrylnaphthalene occurs via the singlet pathway at ambient temperatures with a contribution of the triplet pathway at low temperatures [15]. The presence of a 4-nitro group in **Ia** opens the triplet pathway at room temperature and results in negligible fluorescence in non-polar solvents and opposing effects for Φ_f (Fig. 2) and $\Phi_{t\to c}$ (Table 1) as a function of the parameter E_T^N. A decrease versus solvent polarity was also found for Φ_Δ (Table 4) and Φ_{isc} [15]. The reason may be a lowering of the $^1trans^*$ level in polar solvents, as suggested for **I**-OMe [14]. In addition, an enhancement of internal conversion at the *trans* side of **Ia**, at least in polar solvents such as acetonitrile, becomes apparent. The slope in Fig. 2 is slightly smaller than for 4-cyano-4’-dimethylaminostilbene for which the dipole moment in the $^1trans^*$ state is about 23 Debye [23].

The presence of the second nitro group in the styrylnaphthalene derivative gives rise to strong reductions in both Φ_f and $\Phi_{t\to c}$ in solvents of low and large polarity (Tables 1 and 2). ICT-induced internal conversion at the *trans* side is suggested to be the major deactivation mechanism for **IIa**. Once the triplet state of **Ia** or **IIa** is populated, deactivation is suggested to occur via sequence (6) to (8) as suggested by the rather short triplet lifetime (Table 3), despite the finding that $\Phi_{t\to c}$ is small for **IIa**. In this respect triplet decay of the nitrostyrylnaphthalene is different from that of the anthracene derivative.

4.4. Photochemical properties of trans-(di)nitrostyrylanthracene

What is changed when the phenyl ring in **I** and **II** is replaced by the anthryl group? The deactivation routes of excited *trans*-9-styrylanthracene in solvents of low, medium and large polarity at room temperature are fluorescence and intersystem crossing, whereas $\Phi_{t\to c}$ is nearly zero [16,17,20]. For **Ib** with one nitro group, *trans* → *cis* photoisomerization takes place in slightly polar solvents such as toluene, where ca. 35% of the $^1trans^*$ state relaxes into the *cis* isomer, but the contribution from this pathway is <1% in both non-polar and polar solvents [19]. The slope for **Ib** in Fig. 2 is between those of **I**-OMe and **I**-NMe$_2$ [14], corresponding to a dipole moment of about 36 Debye.

The proposed reason for the strong decrease of Φ_f for **Ib** in polar solvents (Fig. 3) is the presence of a *transoid* ICT state (A*) and the lowering of this level with increasing E_T^N, i.e. k_9 increases with respect to k_f.

$$^1trans^* \xrightarrow{k_9} A^* \tag{9}$$

$$A^* \rightarrow trans \tag{10}$$

The rate constant for the radiative decay is $k_f = 1.3 \times 10^8\,s^{-1}$ in MCH at room temperature [20]. Such a *transoid* ICT state has previously been suggested for **I**-OMe and **I**-NMe$_2$ to account for the temperature dependence of Φ_f [12,14]. For donor–acceptor systems, where the dialkylamino group acts as donor and various arylvinyl groups as acceptor (e.g. 1- or 2-naphthalene), Verhoeven et al. [35] have shown that the polarity region, where Φ_f is large, depends significantly on the nature of the electron acceptor. When the acceptor is weak, this region is the polar one, whereas the region is shifted to non-polar solvents, when the acceptor is strong. Another relevant system where Φ_f decreases with polarity is a rigidified *para*-nitrostilbene: 2-nitro-5,11-*trans*-diethyl-5,6,11,12-tetrahydrochrysene-8-ol [36].

For **IIb** with two nitro groups, fluorescence and *trans* → *cis* photoisomerization are inefficient (Tables 1 and 2), whereas intersystem crossing and internal conversion at the *trans* side contribute to the deactivation mechanism. This indicates the presence of a *transoid* ICT state also for **IIb**. In toluene, where for **Ib**, due to rotation in the singlet state, $\Phi_{t\to c} = 0.2$ [19], the value for **IIb** is only 0.02. On the other hand, the Φ_Δ values of **Ib** and **IIb** are comparable (Table 5), i.e. intersystem crossing contributes under these conditions also for **IIb**.

5. Conclusions

The relative contribution of the distinguishable deactivation processes is as follows: Φ_f is small and Φ_{isc} large for *trans*-2,4-dinitrostilbene, several derivatives (Br, F or Me) and **IIc**. Therefore, the triplet mechanism is operating. The other extreme case is where CT-induced internal conversion at the *trans* side is the major deactivation pathway, reducing Φ_f and Φ_{isc}. This is the case for the anthryl derivatives **Ib** and **IIb** in polar solvents. For the naphthyl derivatives where *trans* → *cis* photoisomerization is operating the parallel singlet-triplet routes leading to *cis*-**Ia** are changed to a triplet pathway with a major contribution of ICT for **IIa**.

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