Photophysics and Photochemistry of *trans*-4-Nitrostilbenes and *trans*-2,4-Dinitrostilbenes: Effect of Intramolecular Charge Transfer

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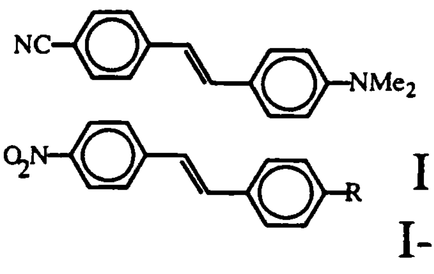
The photophysical and photochemical properties of *trans*-2,4-dinitrostilbene (**II**) and a series of *trans*-R-2′,4′-dinitrostilbenes (**II**-R, R: 2-NO_2, 3-NO_2, 4-Br, 4-F, 4-Me, 4-C_3H_7, 4-$OCH_2C_6H_5$, 3,4,5-$(OMe)_3$, 4-OEt, 4-NMe_2, 4-NEt_2) were studied in solution as a function of solvent polarity and temperature. The quantum yield of fluorescence (Φ_f) is very small for all **II**-R at 25 °C. At −196 °C Φ_f is moderate for several derivatives in 2-methyltetrahydrofuran (MTHF) but strongly enhanced for those bearing electron donating substituents. For the latter compounds the quantum yield of *trans*→*cis* photoisomerization is low, but for the other compounds $\Phi_{t\to c}$ is substantial (0.2–0.5 in toluene or MTHF at room temperature). The triplet state absorbs typically in a broad spectral range; its lifetime (τ_T) lies in the 20–200 ns range and is longer for R = 4-NEt_2; at −196 °C τ_T of all **II**-R approaches milliseconds. The results are compared with those of *trans*-4-R-4′-nitrostilbenes (**I**-R, R: NO_2, H, OMe, NH_2, NMe_2, NEt_2). Phosphorescence of singlet molecular oxygen was observed for several mono- and dinitrostilbenes at room temperature. Generally, the quantum yield of singlet oxygen formation is much smaller than that of intersystem crossing into the triplet state. The triplet mechanism accounts for *trans*→*cis* photoisomerization and the contribution of this pathway is lowered by intramolecular electron transfer to the nitro group(s). The similarities and differences between **I**-R and **II**-R type compounds and the effects of intramolecular charge transfer are discussed.

Introduction

Donor-acceptor substituted *trans*-stilbenes, where an electron donating and an electron withdrawing group interact through π-conjugation (so called push-pull stilbenes), have attracted much attention [1–44]. Introduction of a cyano group in stilbene does not change the singlet pathway for *trans*→*cis* photoisomerization [1–4]. If the electron donor is the dimethylamino group and the electron acceptor the cyano group, interesting fluorescence properties become apparent. However, the discussion concerning intramolecular charge transfer (ICT) for *trans*-4-cyano-4′-dimethylaminostilbene and the involvement of a twisted or "conformational relaxed" ICT state is still going on [3–18].



I R: NO_2
H
OMe
NH_2
I-R NMe_2
NEt_2

Substitution of stilbene by a nitro group [19-44] opens another pathway for *trans*→*cis* photoisomerization via the triplet state [26–32]. The known fluorescence properties of *trans*-4-R-4′-nitrostilbenes (**I**-R) seemed to be less spectacular as compared to *trans*-4-cyano-4′-dimethylaminostilbene. However, this is not so for certain 4′-donor substituted 4-nitrostilbenes and derivatives [19–22, 33–38]. The application potential of 4-dialkylamino-4′-nitrostilbenes is quite large, for example, *trans*-4-dimethylamino-4′-nitrostilbene (**I**-NMe_2) has been shown to be useful in non-linear optics [41–44].

In the pioneering papers of Lippert [19, 20], Schulte-Frohlinde [21], Fischer [22] and their co-workers, the question arose concerning the role of solvent polarity in the deactivation mechanism of excited *trans*-nitrostilbenes. Even today a satisfactory explanation has been given only for certain cases. It has been shown that the *trans*→*cis* photoisomerization of 4-nitro-, 4,4′-dinitro- and 4-methoxy-4-′nitrostilbene (**I**, **I**-NO_2 and **I**-OMe, respectively) involves an equilibrium of two triplet geometries [28–35]. The key intermediates of the triplet mechanism are the excited *trans* singlet state ($^1t^*$), the (lowest) *trans* triplet ($^3t^*$) and the perpendicular triplet conformation ($^3p^*$). After intersystem crossing at the *trans* side (quantum yield: Φ_{isc}) the initial twisting process around the C=C double bond populates the $^3p^*$ state. Further twisting occurs after the second intersystem crossing step into the perpendicular ground state (*perp*).

$$^1t^* \rightarrow {}^3t^* \rightleftarrows {}^3p^* \rightarrow perp \rightarrow cis + trans$$

Fluorescence, competing with *trans*→*cis* photoisomerization, is sensitive to the solvent properties, especially for **I**-OMe and **I**-NMe_2, where ICT is suggested to be involved [26–38]. For **I**-NMe_2 and the amino and diethylamino analogues (**I**-NH_2 ,**I**-NEt_2) the *trans*→*cis* photoisomerization occurs via different mechanisms, depending on the nature of the solvent [33–35]. Owing to a much larger dipole moment of the $^1t^*$ state than of the ground state, the excited state properties (energy, lifetime, rate constants for competing processes) depend on the polarity and polarizability of the medium. This is significant for **I**-OMe and stronger for the dialkylamino derivatives of **I**.

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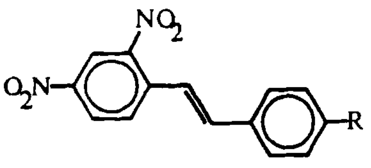
In this work *trans*-2,4-dinitrostilbene (**II**) and various *trans*-R-2′,4′-dinitrostilbenes (**II**-R) were studied by photochemical methods in fluid solution and rigid glasses. Previously, only **II**-NMe$_2$ and a monoaza-18-crown-6 derivative have been studied at room temperature [39, 40]. The photophysical and photochemical properties of the **II**-R are described and compared with those of the corresponding mononitrostilbenes (**I**-R). In particular, the features of the fluorescing $^1t^*$ state and the lowest triplet manifold were investigated by steady-state and time-resolved techniques, respectively. Moreover, formation of singlet molecular oxygen, $O_2(^1\Delta_g)$ [45–49], was observed and the quantum yield (Φ_Δ) measured for mono- and dinitrostilbenes. Some effects caused by the second nitro group in ortho position and those concerning ICT for **II**-R with substituents of different electron donating abilities are quantified.



II-R

2-NO$_2$
3-NO$_2$
4-Br
2,4-Cl$_2$
4-F
H
4-Me
4-C$_3$H$_7$
4-OCH$_2$C$_6$H$_5$
2-OEt
4-OEt
3,4,5-(OMe)$_3$
4-NMe$_2$
4-NEt$_2$

Experimental

The samples were the same as used previously (**I**-R with R=NO$_2$, H, NH$_2$, NMe$_2$ and NEt$_2$) [26–35] or purchased from Aldrich; they are *trans* isomers throughout and R refers to the 4-position (if not further specified). **II**-R and all derivatives were recrystallized from acetonitrile, except for R=OCH$_2$C$_6$H$_5$ (chloroform). Melting points (°C): 2-NO$_2$: 186–187, 3-NO$_2$: 171–175, F: 145–146, H: 137–138, Me: 179–181, C$_3$H$_7$: 176–177, OEt: 131–132, 3,4,5-(OMe)$_3$: 179–181, OEt: 131–132, NMe$_2$: 176–177, NEt$_2$: 155–156. Ferrocene (Merck) was recrystallized twice, azulene (Aldrich) and 9,10-diphenylanthracene (Ega) were used as received. The solvents (Merck) were purified by distillation, e.g. methylcyclohexane (MCH), 2-methyltetrahydrofuran (MTHF) or by passing through an aluminium oxide column (cyclohexane); the others, e.g. dimethylformamide (DMF), were checked for impurities and used without further purification, acetonitrile (Uvasol quality).

The absorption spectra were recorded on a Perkin Elmer 554 spectrophotometer. The molar absorption coefficients (in units of $10^4\ M^{-1}\ cm^{-1}$) of **II**-R in acetonitrile are: 2-NO$_2$: $\varepsilon_{340}=1.9$, 3-NO$_2$: $\varepsilon_{344}=2.2$, Br: $\varepsilon_{359}=2.6$, H: $\varepsilon_{358}=2.2$, Me: $\varepsilon_{372}=2.2$, C$_3$H$_7$: $\varepsilon_{374}=2.3$, OCH$_2$C$_6$H$_5$: $\varepsilon_{382}=2.4$, 2-OEt: $\varepsilon_{383}=2.0$, 4-OEt: $\varepsilon_{394}=2.3$, NMe$_2$: $\varepsilon_{475}=2.8$, NEt$_2$: $\varepsilon_{490}=2.6$. The initial decrease in absorption at the maximum, $A(\lambda_t)$, using a 1000 W Xe-Hg lamp and a monochromator, was taken as a measure of the quantum yield of *trans*→*cis* photoisomerization ($\Phi_{t\to c}$) which was determined with **I** in toluene as reference ($\Phi_{t\to c}=0.50$ [29]). The experimental error is about ±15% for $\Phi_{t\to c}$ values larger than 0.02. Typical absorbances were $A_{366}=2.0$ (1 cm pathlength), corresponding to *trans* isomer concentrations of 0.1 mM for **II** ($\varepsilon_{340}=1.9\times10^4\ M^{-1}\ cm^{-1}$ in benzene [39]) or 0.4 mM for **II**-NMe$_2$ ($\varepsilon_{366}=0.5\times10^4\ M^{-1}\ cm^{-1}$; $\varepsilon_{480}=2.4\times10^4\ M^{-1}\ cm^{-1}$ in benzene [39]) and $\varepsilon_{471}=2.45\times10^4\ M^{-1}\ cm^{-1}$ in methanol [40]).

Phosphorescence of singlet molecular oxygen at 1269 nm was detected after the pulse by using a cooled Ge detector (North Coast, EO 817FP), a silicon and an interference filter and one or two amplifiers (Comlinear, CLC-103) as described elsewhere [45]. The decay follows first-order kinetics in all cases and the lifetimes (τ_Δ) of $O_2(^1\Delta_g)$ were generally larger than 23 µs. Methanol, with a $O_2(^1\Delta_g)$ lifetime of 10 µs and because of fluorescence of **I**-R (R=OMe or dialkylamino) extending even to 1269 nm, was not suitable. The signals extrapolated to 0.1 µs after the pulse (I_Δ) were found to show linear dependences on the absorbed energy, which is proportional to $(1-10^{-A})$, and (for a given concentration) the incident laser intensity (I_L); the slope of the latter plot is denoted as q_Δ. The quantum yield of formation of $O_2(^1\Delta_g)$ was obtained from q_Δ values using optically matched solutions ($A=0.3$ or 0.6 at $\lambda_{exc}=354$ nm) and either acridine or 2-acetonaphthone in benzene as references ($\Phi_\Delta^{ref}=0.71$ and 0.84, respectively [46, 47]); the error is ±20%. For the values in other solvents a correction has to be carried out using the rate constant for radiative deactivation (k_r) with respect to benzene (k_r^0).

$$\Phi_\Delta = \Phi_\Delta^{ref}(q_\Delta/q_\Delta^{ref}) \times (k_r^0/k_r) \qquad (1)$$

The k_r/k_r^0 ratio is known to be 0.44, 0.96, 0.50 and 0.30 in cyclohexane, toluene, dichloromethane and acetonitrile [48]. The solutions were saturated with oxygen; air was only used in those cases where the difference in lifetimes of air- and argon-saturated solutions is larger than 95%, e.g. for the standards.

The fluorescence spectra were recorded on a Spex-Fluorolog (corrected spectra) or another spectrofluorimeter (Perkin Elmer LS-5); determination of Φ_f was performed by using optically matched solutions (A at λ_{exc} ca. 0.2) and 9,10-diphenylanthracene in ethanol as standard: $\Phi_f=0.68$ (deoxygenated) at 25 °C and 1.0 at −196 °C. The experimental error is typically ±15% and ±40% for Φ_f values of >0.1 and <0.01, respectively. Laser flash photolysis measurements were carried out using generally the third harmonic of a Nd-YAG laser ($\lambda_{exc}=354$ nm) and in some cases an excimer laser ($\lambda_{exc}=308$ nm, pulse width 20 ns). The temperature was varied between 25 and −

Table 1
Absorption and fluorescence maxima of the *trans* isomers and quantum yields of fluorescence and *trans*→*cis* photoisomerization[a])

Compound	Solvent	$\frac{\lambda_t}{(\text{nm})}$	$\frac{\lambda_f}{(\text{nm})}$	Φ_f	$\Phi_{t\to c}$
I-OMe[b])	Cyclohexane	368	500	<0.001	0.55
	Toluene	372	540	0.007	0.53[c])
	DMF			0.09	0.05
I-NEt$_2$[b])	Cyclohexane	427	509	0.34	0.18
	Toluene	438	589	0.50	0.002
	Acetone	441	830	<0.005	<0.002
II-NEt$_2$	Cyclohexane	475	560	<0.001	0.008
	Toluene	485	580	0.001	<0.001

[a]) In argon-saturated solution at room temperature, λ_{exc}=436 nm (366 nm for **I**-OMe).
[b]) Φ_f and $\Phi_{t\to c}$ from [31, 35].
[c]) In benzene.

196 °C and for **I**-NMe$_2$ in all solvents from 50 and –50 °C (where possible). For fast and slow detection transient digitizers (Tektronix, 7912 and 390AD) were used and data handling was performed with a computer (Arcon 540).

Results

Fluorescence of Mononitrostilbenes

The steady-state fluorescence properties of several *trans*-nitrostilbenes are well characterized [4, 19, 22, 35, 38] with a few exceptions. The absorption and fluorescence emission maxima (λ_t and λ_f, respectively) of **I**-OMe and **I**-NEt$_2$ are presented in Table 1. The Stokes shift ($\Delta\tilde{\nu}$ $1\lambda_t$–$1/\lambda_f$) depends strongly on the solvent polarity; as a measure, the normalized Dimroth E_T^N parameter [50, 51] was taken. Plots of $\Delta\tilde{\nu}$ versus E_T^N are shown in Fig. 1a. The quantum yield of fluorescence (Φ_f) is also sensitive to the solvent polarity, as shown in Fig. 1b. For **I**-OMe the semilogarithmic plot of Φ_f increases with increasing E_T^N, whereas for **I**-NH$_2$ the curve is essentially decreasing. In all these cases, including other *trans*-4-dialkylamino-4′-nitrostilbenes [35], Φ_f varies by two orders of magnitude or more when E_T^N is changed from 0 to about 0.6. The fluorescence lifetime (τ_f=Φ_f/k_f), in view of the large changes in Φ_f and relative small changes in k_f, should reveal more or less the same dependences on polarity and gradually on substituent, as Φ_f. However, the data is scarce [3]. For **I**-NMe$_2$ in solvents of low polarity (E_T^N=0.05–0.2), where Φ_f is large at room temperature, τ_f= 1–3 ns [25]; in the polar butyronitrile τ_f increases from <0.1 ns at 27 °C to 3.0 ns at –196 °C [37].

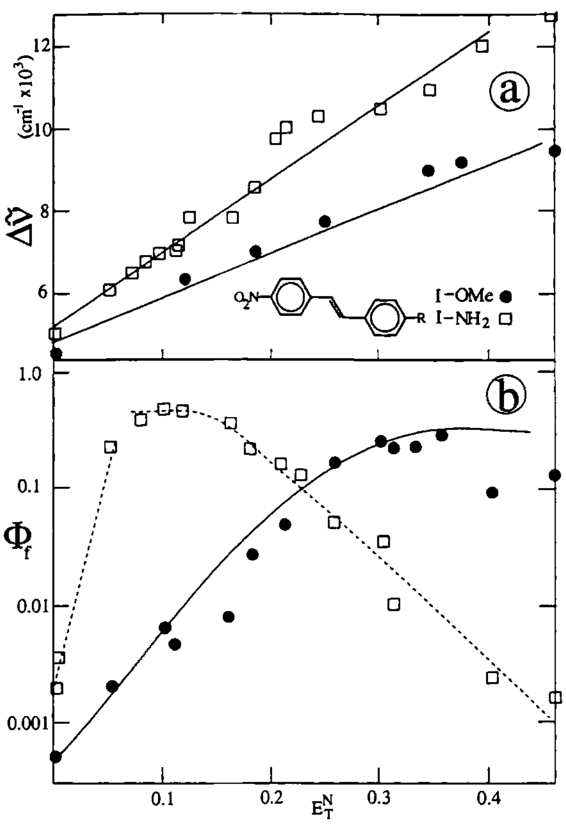


Fig. 1
(a) Plots of $\Delta\tilde{\nu}$ ($1\lambda_t$–$1/\lambda_f$) versus E_T^N [50, 51] for **I**-NH$_2$ (□) [35] and **I**-OMe (●) at 25 °C, λ_{exc}=366 nm. (b) Semilogarithmic plots of Φ_f versus E_T^N

Triplet Properties of Mononitrostilbenes

The features of the observed triplet state of dialkylamino substituted *trans*-**I**-R depend strongly on the nature of the solvent [21, 24, 25, 35]. Now the triplet decay properties of **I**–NMe$_2$ were studied more intensively. The T-T absorption maximum (λ_T) ranges from 600 nm in methanol to 830 nm in glycerol triacetate and the triplet yield decreases by a factor of 10–20 on going from cyclohexane to alcohols [28]. The lifetime shows a trend to increase on increasing E_T^N from ≈0.30 µs in non-polar solvents at room temperature to 7.5 µs in acetonitrile (Table 2); an exception is the strongly viscous glycerol triacetate with τ_T=20 µs. For **I** the inverse lifetime decreases only slightly with increasing E_T^N, this effect is much larger for **I**-NMe$_2$ and intermediate for **I**-OMe (Fig. 2).

For **I**-NMe$_2$ the plots of log $1/\tau_T$ versus $1/T$ were found to be linear (not shown) and from these Arrhenius dependences the activation energy (E_τ) and the pre-exponential factor (A_τ) were determined. Note that the linear dependence refers only to rather fluid media, whereas below ca. -100 °C diffusion is strongly reduced due to high viscosities. The E_τ values are in the 8–20 kJ mol^{-1} range and the corresponding A_τ-factors range from 2x10^6 s^{-1} in acetone or acetonitrile to ca. 10^9 s^{-1} in ethyl acetate. The values of E_τ and A_τ are coupled to a certain extent, but essentially independent of polarity and significantly larger only in the rather viscous glycerol triacetate (Table 2). Ferrocene or azulene (Q) and oxygen are known to be efficient triplet quenchers of (nitro)stilbenes [1, 3, 26, 29, 49). The rate constants for quenching the triplet moiety of **I**-NMe$_2$ in solution at room temperature by ferrocene or azulene (k_q) and oxygen (k_{ox}) are compiled in Table 2.

Table 2
Lifetime, pre-exponential factor and activation energy for triplet decay of **I**-NMe_2 and rate constants for quenching by ferrocene and oxygen[a])

Solvent	E_T^N [b])	$\frac{\tau_T}{(\mu s)}$	$\frac{A_\tau}{(10^7 s^{-1})}$	$\frac{E_\tau}{(kJ\,mol^{-1})}$	$\frac{k_q}{(10^9 M^{-1} s^{-1})}$ [c])	$\frac{k_{ox}}{(10^9 M^{-1} s^{-1})}$
Cyclohexane[d])	0.006	0.33			7.0 (7.3)	5.8
n-Pentane[d])	0.009	0.28			9.0 (8.0)	6.1
n-Hexane	0.009	0.32	7	7.9	8.2	4.9
MCH		0.40	7	8.0		
m-Xylene	0.080	1.2			5.5 (5.6)	
Toluene[d])	0.099	1.8	45	17	7.6 (7.0)	4.6
Benzene	0.111	0.85	8	11	6.2 (6.0)	2.6
Dioxane	0.164	2.8	73	19		3.6
MTHF	0.179	4.2	2.5	13		
Ethyl acetate	0.228	5	95	21		
Chloroform	0.259	3			5.1	3.3
Dichloromethane	0.309	5			4.0	3.5
Glycerol triacetate	0.336	20	2×10^3	32		
Acetone	0.355	4.6	0.2	6		
DMF	0.404	6	0.7	9	2.8	2.5
Acetonitrile	0.460	7.5	0.2	7	5.0	3.9
t-Butanol	0.389	3			1.8	2.7
2-Propanol	0.546	5			3.7	2.1
Ethanol	0.654	2			4.5	1.2
Methanol	0.762	1.4			6.9	1.0

[a]) In argon-saturated solution (τ_T, k_q) at 25 °C (k_{ox}, except A_τ, E_τ), $\lambda_{exc}=354$ nm.
[b]) See [50, 51].
[c]) Values in parentheses refer to azulene.
[d]) Taken from [33, 34].

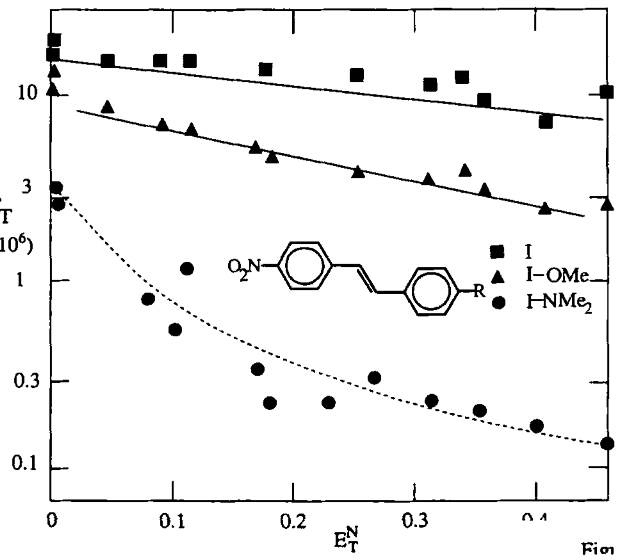


Fig. 2
Semilogarithmic plots of $1/\tau_T$ versus E_T^N for **I** (■), **I**-OMe (▲) [28] and **I**-NMe_2 (●) at 25 °C

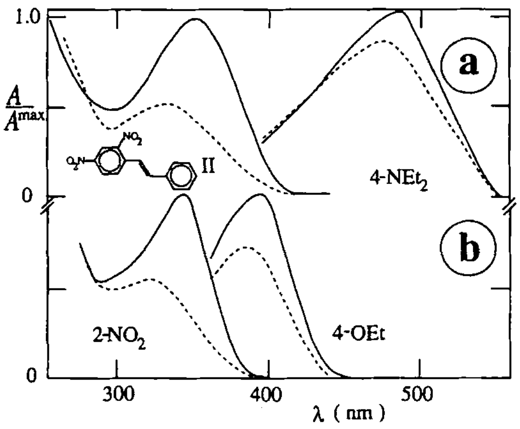


Fig. 3
Absorption spectra of **II**-R in toluene at 25 °C for (a) R=H (left) and 4-NEt_2 (right) and (b) 2-NO_2 (left) and 4-OEt (right) prior to (full lines) and after irradiation at 366 nm into the photoequilibrium (broken lines)

The k_q values are similar to those of **I** and **I**-OMe [32], i.e. they are close to the diffusion-controlled limit. On the other hand, the k_{ox} values show a trend to become smaller in polar solvents (see Discussion).

Trans→*cis* Photoisomerization of Dinitrostilbenes

The absorption maximum of **II** (Fig. 3a) and several derivatives with R=2-NO_2, 3-NO_2, Br, 2,4-Cl_2 or F is around 350 nm and increases up to λ_t=485 nm with increasing electron donating ability of the substituent (Table 3). Irradiation (λ_{irr}=366 nm) at room temperature leads to a decrease of the absorbance at λ_t due to *trans*→*cis* photoisomerization and eventually a photostationary state is approached (Fig. 3). The position of this photoequilibrium is indicative of the ratio of ε values of the *trans* and *cis* isomers at λ_{irr} and the quantum yield of *cis*→*trans* photoisomerization [21, 22]. In toluene $\Phi_{t\to c}$ is substantial for **II** and 2-NO_2, 3-NO_2, Br, F, Me and C_3H_7 derivatives, but low for those with polar substituents.

Table 3
Absorption and fluorescence maxima of *trans*-2,4-dinitrostilbenes and quantum yields of fluorescence and *trans*→*cis* photoisomerization[a])

R	$\frac{\lambda_t}{(\mathrm{nm})}$	$\frac{\lambda_f}{(\mathrm{nm})}$		Φ_f		$\Phi_{t\to c}$
Temp./(°C)	25	25	−196	25	−196	25
2-NO_2	338	<510	540	$<10^{-3}$	0.003	0.32
3-NO_2	344	<510	500	0.001	0.007	0.45
4-Br	355	<520	480	<0.001	0.003	0.38
2,4-Cl_2	350					0.4
4-F	346		470		0.002	0.4
H	355	<490	480	0.004	0.005	0.42
4-Me	374	495	485	0.005	0.02	0.28
4-C_3H_7	375	502	480	0.003	0.02	0.28
4-$OCH_2C_6H_5$	392	508	512	0.01	0.08	0.16
2-OEt	384					0.12
4-OEt	396	510	540	0.008	0.02	0.12
3,4,5-$(OMe)_3$	396	515	530	0.007	0.2	0.06
4-NMe_2[b])	480	570	603	0.001	0.4	<0.01
4-NEt_2	485	585	615	0.002	0.5	<0.01

[a]) In MTHF, argon-saturated at 25 °C and air-saturated at −196 °C, $\lambda_{exc}=366$ nm, unless otherwise indicated.
[b]) No difference using $\lambda_{exc}=366$ or 436 nm.

Table 4
Effect of solvent on the quantum yields for *trans*-2,4-dinitrostilbenes[a])

R	$\Phi_{t\to c}$ $(\Delta A/\Delta A^{max})$[b])		
	Cyclohexane	Toluene	Acetonitrile
2-NO_2	–[c])	0.40 (0.6)	0.26 (0.4)
3-NO_2	–[c])	0.48 (0.7)	0.30 (0.5)
H	0.48 (0.5)	0.43 (0.5)	0.32 (0.4)
4-Me	0.30 (0.6)	0.26 (0.5)	0.12 (0.3)
4-C_3H_7	0.40 (0.7)	0.35 (0.8)	0.15 (0.2)
4-$OCH_2C_6H_5$	–[c])	0.18 (0.7)	0.07 (0.5)
4-OEt	0.19 (1.0)	0.12 (0.8)	0.06 (0.5)
3,4,5-$(OMe)_3$	–[c])	0.08 (0.6)	0.03 (0.2)

[a]) In argon-saturated solution at room temperature, $\lambda_{exc}=366$ and 354 nm for steady-state and pulsed excitation, respectively.
[b]) Values in parentheses refer to relative triplet yields (ΔA values at λ_T) under optically matched conditions.
[c]) Too low solubility.

$\Phi_{t\to c}$ decreases with increasing solvent polarity, e.g. for R=Me or C_3H_7 (Table 4).

It is well-known that the nitro group in stilbenes strongly reduces the quantum yield of photocyclization, cf. [3]; likewise no indication of photocyclization was found for **II**-R compounds. For **II**-NMe_2 and a monoaza-18-crown-6 derivative in benzene, formation of the dinitroisatogen has been reported [39, 40]. Indeed, 2-(4-dimethylaminophenyl)-6-nitroisatogen, which has $\varepsilon_{420}=2.2\times10^4$ and $\varepsilon_{620}=0.6\times10^4$ M^{-1} cm^{-1} [39], is the only spectroscopically detectable photoproduct upon prolonged irradiation of **II**-NMe_2. Its formation depends on the **II**-NMe_2 concentration and is sensitive to solvent properties since it is clearly observable in benzene but not in toluene or acetonitrile. The mechanism is complex and has not unambiguously been established as yet [39].

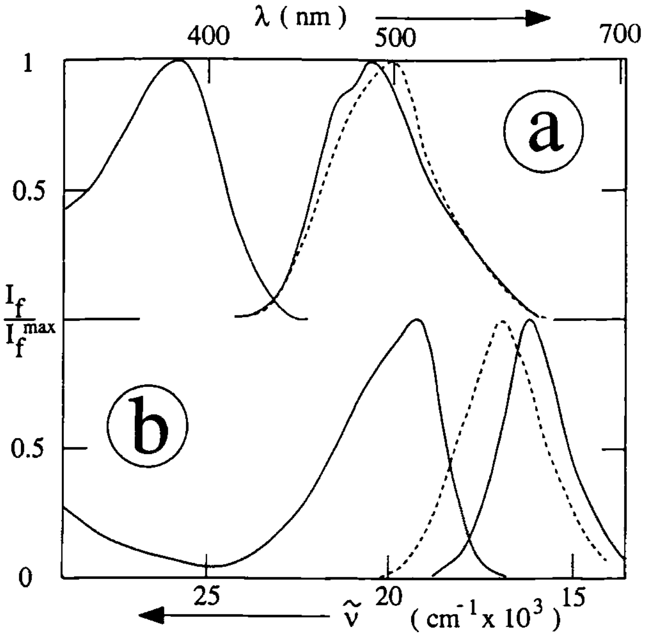


Fig. 4
Fluorescence emission (right) and excitation (left) spectra of **II**-R in MTHF at 25 and −196 °C (broken and full lines, respectively) for (a) R=4-Me and (b) 4-NEt_2, $\lambda_{exc}=366$ nm, $\lambda_f=500$ and 600 nm, respectively

Fluorescence of Dinitrostilbenes

At room temperature most **II**-R show only weak or moderate fluorescence (Tables 1 and 3). The fluorescence excitation spectra of those compounds where Φ_f is larger than 10^{-3}, coincide with the absorption spectra and are mirror images of the emission spectra (Fig. 4). The fluorescence emission maximum exhibits a red shift with respect to the electron donating ability of the substituent, e.g. from $\lambda_f \leq 490$ nm for **II** to $\lambda_f=585$ nm for **II**-NEt_2 in MTHF (Table 3). At −196 °C the fluorescence becomes detectable throughout. The fluorescence excitation and emission spectra of several **II**-R in glassy MTHF are shown in Fig. 4. The red shift is comparable to or larger than the λ_f values at room temperature, extending in MTHF up to $\lambda_f=615$ nm for R=NEt_2 (Table 3). The quantum yield covers a range from $\Phi_f=2\times10^{-3}$ for R=F to $\Phi_f=0.5$ for R=NEt_2 at −196 °C. For **II**-R at room temperature the solvent properties have generally no significant effect on Φ_f. This is in contrast to the behaviour of mononitro analogues with electron donating substituents.

Triplet Properties of Dinitrostilbenes

The T-T absorption spectrum of **II**-R in solution at room temperature appears within the duration of the laser pulse (15 ns, $\lambda_{exc}=354$ nm) and extends over a broad

Table 5
Triplet absorption maximum and lifetime of *trans*-2,4-dinitrostilbenes[a])

R Temp./(°C)	Solvent	$\frac{\lambda_T}{(nm)}$ 25	$\frac{\lambda_T}{(nm)}$ –196	$\frac{\tau_T}{(ns)}$ 25	$\frac{\tau_T}{(ms)}$ –196
2-NO_2	Toluene/MTHF	420–500	480	30	1.2
3-NO_2		400–550		50	
4-Br		500–600	500–600	15	0.6
2,4-Cl_2		400-520	520	40	>1
4-F		440–570	440–560	60	5
H	Cyclohexane	440–550		45	
	Toluene/MTHF	440–550	450–550	55	8
	Acetonitrile	440–550		60	
	Ethanol	430–550		55	3
4-Me	Toluene/MTHF	450–580	450–550	65	4.5
4-C_3H_7		450, $\underline{580}$	460, $\underline{580}$	70	6
4-$OCH_2C_6H_5$		640	550-650	200	2
2-OEt		440–570	450–550	80	3
4-OEt[b])		460, $\underline{630}$	640	180	10
3,4,5-$(OMe)_3$		480, $\underline{710}$	460, $\underline{680}$	550	2
4-NEt_2	Cyclohexane	540		2×10^4	
	Toluene	–[c])			

[a]) In argon-saturated solution at 25 °C and in MTHF at –196 °C, $\lambda_{exc}=354$ nm, unless otherwise indicated.
[b]) Same values with $\lambda_{exc}=308$ or 354 nm.
[c]) No transient.

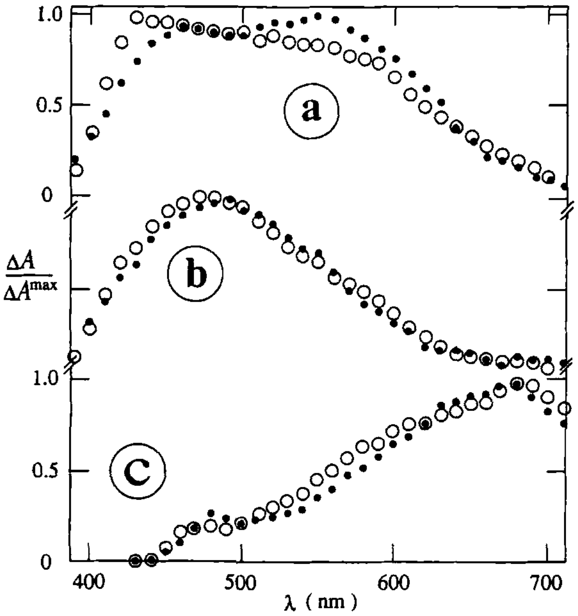


Fig. 5
T-T absorption spectra of **II**-R in MTHF at 25 and –196 °C (open and filled symbols, respectively) for (a) R=H, (b) 2-NO_2 and (c) 3,4,5-$(OMe)_3$, $\lambda_{exc}=354$ nm

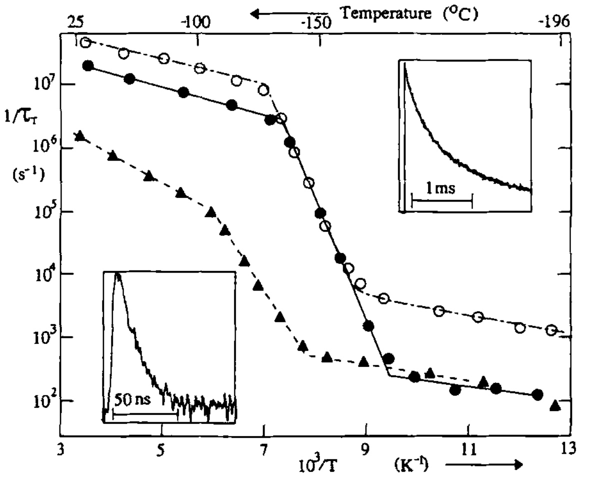


Fig. 6
Semilogarithmic plots of $1/\tau_T$ versus $1/T$ for **II**-R in MTHF for R=H (●), 4-Br (○) and 3,4,5-$(OMe)_3$ (▲), $\lambda_{exc}=354$ nm; insets: kinetics of **II**-Br at 25 and –185 °C, lower and upper, respectively

range with one or two bands, the maximum depends on the substituent (Table 5). Examples for R=H, 2-NO_2 and 3,4,5-$(OMe)_3$ in MTHF are shown in Fig. 5. For most **II**-R the T-T absorption spectrum depends only slightly on the solvent properties. The sensitivity of the T-T absorption spectrum towards changes in substituent can also be seen when the ethoxy group is introduced either in 2 or 4 position. The transient absorbance at λ_T (as a relative measure of Φ_{isc}) of **II**-R, which are substituted by a weak or moderately strong donor, shows a trend to decrease with increasing polarity (Table 4), which is similar to the effect of solvent on $\Phi_{t\rightarrow c}$. For a strong donor such as NEt_2, a weak T-T absorption spectrum was measured in cyclohexane, but none in toluene or more polar solvents, indicating that Φ_{isc} is low in a non-polar solvent and decreases with increasing polarity.

Decay of the triplet follows a first-order law; the triplet lifetime in argon-saturated toluene or MTHF at room temperature lies in the 20–200 ns range for most **II**-R (Table 5) except for those bearing a strong electron donor. For R=3,4,5-$(OMe)_3$ where $\tau_T=0.5$ μs it was verified that oxygen quenches the triplet state with rate constants of

Tabl 6
Quantum yields of singlet oxygen formation and intersystem crossing for *trans*-4-R-4′-nitrostilbenes and *trans*-4-R-2′,4′-dinitrostilbenes[a]

Compound	Φ_Δ (Φ_{isc})[b]				
Solvent	Cyclohexane	Toluene	Benzene	Dichloromethane	Acetonitrile
I-NO_2		0.19	0.18 (0.81)	0.22	
I	0.14	0.16	0.14 (0.86)	0.12	0.13
I-OMe	0.23 (0.89)	0.18	0.22 (0.93)	0.14	0.15
I-NH_2	0.18 (≥0.8)	0.2	0.17	–[c]	
I-NMe_2	0.23 (0.45)	–[c] (0.05)			<0.1
II	0.09	0.10	0.22	0.04	
II-2-NO_2			0.10		
II-3-NO_2			0.12		
II-$OCH_2C_6H_5$		0.12	0.12	0.06	
II-$(OMe)_3$		0.11	0.10	0.06	

[a] In oxygen-saturated solution at 25 °C, λ_{exc}=354 nm unless otherwise indicated.
[b] Values in parentheses are taken from Table 7.
[c] Too low emission from singlet oxygen as compared to the signal in the absence of oxygen.

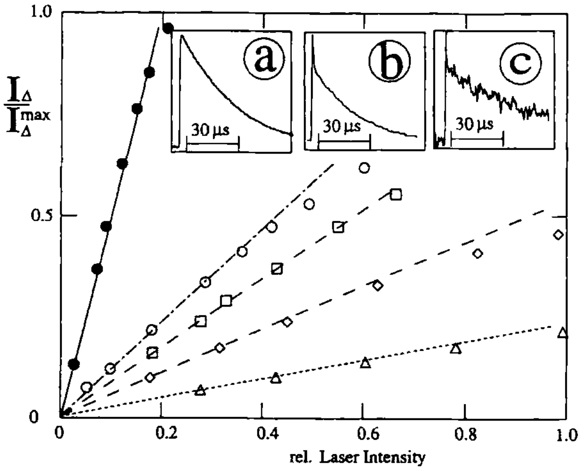


Fig. 7
Plots of the singlet oxygen signal (extrapolated to 0.1 µs after the pulse) versus I_L for I-OMe in oxygen-saturated cyclohexane (◇), toluene (□), benzene (○) and acetonitrile (△) and for 2-acetonaphthone in benzene (●) at 25 °C; insets: kinetics of (a) 2-acetonaphthone in benzene and I-OMe in (b) cyclohexane and (c) acetonitrile

$k_{ox}=(3–6)\times10^9$ M^{-1} s^{-1} in several solvents, e.g. 4×10^9 M^{-1} s^{-1} in toluene. Note that a reduced triplet lifetime in oxygen- versus argon-saturated solution could be observed in virtually all cases. In glasses at –170 to –196 °C the T-T absorption spectrum of **II**-R is similar to that in fluid solution in most cases (Table 5). This demonstrates that the absorption occurs at the *trans* geometry since for (nitro)stilbenes rotation into the perpendicular geometry is hindered in rigid glasses [3, 29].

The yield of the triplet state of most **II**-R is almost constant between 25 and –196 °C, whereas its lifetime increases with decreasing temperature in a characteristic way. The dependence of log $1/\tau_T$ on $1/T$ is shown in Fig. 6 for several cases. Generally, $1/\tau_T$ 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 which show *trans*→*cis* photoisomerization via the lowest triplet state [3, 29]. At –196 °C the lifetime of virtually all **II**-R approaches values which are in the ms range; the significantly shorter τ_T values for the bromo derivative, both at high and low temperatures (Table 5), are ascribed to the internal heavy atom effect.

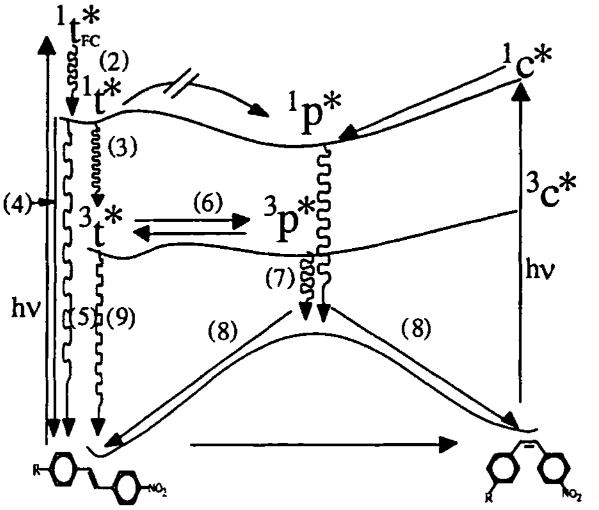
Singlet Molecular Oxygen

$O_2(^1\Delta_g)$ was detected upon excitation of *trans*-(di)nitrostilbenes in several oxygen-saturated solvents. Examples of formation and decay of $O_2(^1\Delta_g)$ are shown in Fig 7. Typical τ_Δ values are 25, 28, 30, 90 and 65 µs for cyclohexane, toluene, benzene, dichloromethane and acetonitrile, respectively, in agreement with the literature [46, 52]. The initial I_Δ signals of **I**-OMe in cyclohexane, toluene and benzene and of 2-acetonaphthone in benzene as reference depend linearly on the incident laser intensity (Fig. 7) or, for a fixed I_L, on the absorbed energy. The quantum yield ranges from $\Phi_\Delta=0.04$ for **II** in dichloromethane to 0.2 for **I**-NMe_2 in cyclohexane (Table 6). Kuhn et al. have earlier reported Φ_Δ values of 0.28, 0.24 and 0.24 for **I**, **I**-NO_2 and **I**-OMe in methanol, respectively using a steady-state method [53]. Upon sensitized excitation of *trans*-stilbene in benzene Gorman and Rodgers found $\Phi_\Delta=0.18$ [54]. On the other hand, for 2-anthrylethylenes in benzene Φ_Δ values are as large as 0.7–0.9 [55].

Discussion

Deactivation Pathways of Excited *Trans*-Mononitrostilbenes

For most *trans*-1,2-diarylethylenes in fluid solution at room temperature, $\Phi_{t\to c}$ is substantial, Φ_f is small or moderate and Φ_{isc} is very small [1–3]. Thus, deactivation of the excited *trans* isomers occurs via singlet states. For some cases at low temperatures, a pathway via an upper excited triplet state has been suggested, e.g. for 4-bromostilbene and to a smaller extent for stilbene itself [3]. Only little is known concerning the influence of solvent and temperature on Φ_{isc} and internal conversion at the *trans* side (quantum yield: Φ_{ic}) of stilbenes. *trans*-4-R-4′-nitrostilbenes, however, are suitable candidates to address questions concerning intersystem crossing and intramolecular charge transfer. Here, at least in some cases at room temperature, $\Phi_{t\rightarrow c}$ is closely related to Φ_{isc}. The reason is the triplet mechanism (Scheme 1):



Scheme 1

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

$$^1t^*_{FC} \longrightarrow {}^1t^* \tag{2}$$

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

$$^1t^* \xrightarrow{k_f, k_{ic}} trans \tag{4, 5}$$

$$^3t^* \rightleftarrows {}^3p^* \tag{6}$$

$$^3p^* \longrightarrow perp \tag{7}$$

$$perp \longrightarrow a\, trans + (1-a) cis \tag{8}$$

$$^3t^* \longrightarrow trans \tag{9}$$

Here, 1-*a* is the fraction for population of the *cis* form from the $^3p^*$ conformation.

The nearly linear dependence of the Stokes shift of E_T^N for the *trans*-nitrostilbenes shown in Fig. 1a demonstrates the strong solvent rearrangement (2) from the Franck-Condon state ($^1t^*_{FC}$) prior to fluorescence from the $^1t^*$ state (4). The slopes of the initial linear part of the plots of the Stokes shift versus E_T^N, which are a measure for the dipole moment in the $^1t^*$ state, are similar for **I**-NH$_2$, **I**-NMe$_2$ and **I**-NEt$_2$ [35] and rather large, compared to *trans*-4-cyano-4′-dimethylaminostilbene. For the latter, **I**-OMe and **I**-NMe$_2$ the dipole moments in the $^1t^*$ state are about 21,17 and 31–42 Debye, respectively [17, 19, 37, 38].

The initial twisting process around the C=C double bond from 0 to ca. 90° yields $^3p^*$ (reaction 6) and further twisting from ca. 90 to 0 or 180° (reaction 8) leads to the stable isomers. Intersystem crossing (9) at the *trans* side can be disregarded in fluid solution, but takes place when a rigid glass prevents rotation into the $^3p^*$ state [29]. For the triplet pathway the relationships between fluorescence, intersystem crossing and *trans*→*cis* photoisomerization are as follows.

$$\Phi_f = \frac{k_f}{(k_f + k_{isc} + k_{ic})} \tag{10}$$

$$\Phi_{isc} = \frac{k_{isc}}{k_f} \Phi_f \tag{11}$$

$$\Phi_{t\rightarrow c} = \frac{(1-a)k_{isc}}{(k_f + k_{isc} + k_{ic})} \tag{12}$$

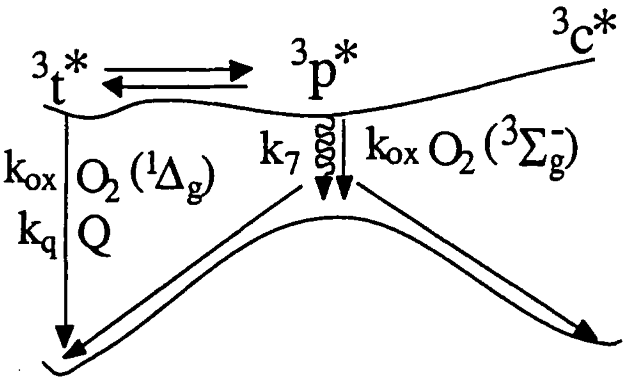
$$\Phi_{isc} = \Phi_{t\rightarrow c}/(1-a) \tag{13}$$

$$\Phi_{ic} = 1 - \Phi_f - \Phi_{isc} \tag{14}$$

Independent of the mechanism, fluorescence necessarily reduces *trans*→*cis* photoisomerization, unless the twisting process is initiated prior to population of the $^1t^*$ state, which is not the case for nitrostilbenes. For **I** Φ_f is small even at −196 °C because intersystem crossing at the *trans* side (3) is nearly as large as at room temperature [29]. This is different for **I**-R with OMe and dialkylamino substituents, where Φ_f, $\Phi_{t\rightarrow c}$ and Φ_{isc} are dependent on both solvent polarity and temperature [31, 35]. Note that 4-dialkylamino-4′-nitrostilbenes do not follow an exclusive triplet mechanism [33–35] (see below).

Fast establishment of equilibrium (6) is well-known for **I** and some derivatives [3, 26–32]. A shift from the $^3p^*$ configuration in non-polar solvents at room temperature to the *trans* side in polar solvents is indicated for **I**-OMe and **I**-NMe$_2$ (Fig. 2) since $\tau_T=(1+k_{-6}/k_6)\times 1/k_7$ [28], i.e. the triplet lifetime increases with k_{-6}, which is largest in polar solvents, whereas k_7 should be rather independent of polarity. The activation energy for **I**-NMe$_2$ in various solvents (Table 2) is not indicative of the position of equilibrium (6); only the A_τ-factor becomes lower when the *trans* side is favoured. Ferrocene or azulene react with the $^3t^*$ state of stilbene, whereas, due to energetic reasons, quenching of the $^3p^*$ state is not possible [1, 31] (Scheme 2).

On the other hand, quenching by oxygen occurs with both $^3t^*$ and $^3p^*$ states, the former by energy transfer yielding $O_2(^1\Delta_g)$ and the latter via a spin exchange mechanism yielding triplet oxygen, $O_2(^3\Sigma_g^-)$ [1, 28, 49]. This



Scheme 2

Table 7
Quantum yields of fluorescence, intersystem crossing and internal conversion for *trans*-(di)nitrostilbenes [a])

Compound	Solvent	Φ_f	Φ_{isc} [b])	Φ_{ic} [b])
I-NO_2	Benzene	<0.001	0.81	0.19
	Methanol	<0.001	0.69	0.31
I	Benzene	<0.001	0.86	0.14
	Methanol	<0.001	0.71	0.29
I-OMe	Cyclohexane	<0.001	0.89	0.11
	Benzene	0.006	0.93	0.06
	Methanol	0.009	0.28	0.71
	DMF	0.09	0.11	0.80
I-NH_2	Cyclohexane	0.002	≥0.8	≤0.2
	Benzene	0.50		
I-NMe_2	Cyclohexane	0.33	0.45	0.21
	Benzene	0.50	0.05	≥0.4
	Methanol	<0.001	0.04	>0.9
I-NEt_2	Cyclohexane	0.34	0.36	0.3
	Toluene	0.50	<0.05	0.55
	Acetonitrile	<0.002	<0.01	0.98
II	Cyclohexane	<0.001	>0.6	
	MTHF	<0.004	>0.8	<0.2
II-NEt_2	Cyclohexane	<0.02	<0.1	
	MTHF	0.002	<0.1	>0.9

[a]) In solution at room temperature, for **I**-R taken from [3, 29–35].
[b]) Calculated from $\Phi_{t\rightarrow c}$ and a using Eq. (13) and Φ_f and Φ_{isc} using Eq. (14).

triplet decay pattern has also been reported for 1-naphthylethylenes [56]. For **I**-NMe_2 in various solvents the k_{ox} value is significantly smaller when equilibrium (6) is shifted to the *trans* side (Table 2). The quantum yields of formation of $O_2(^1\Delta_g)$ of several **I**-R are much lower than the Φ_{isc} values, e.g. $\Phi_\Delta=0.1$–0.2 where $\Phi_{isc}=0.8$–0.9 (Table 6). The reason is the preferred perpendicular triplet geometry in most cases and thus quenching of $^3p^*$ yields triplet rather than singlet oxygen because of the too low energy gap (≤38 kJ mol^{-1} [53]) between the $^3p^*$ and *perp* states. The expected higher Φ_Δ values for R=OMe or NMe_2 in polar solvents are counterbalanced by significantly lower Φ_{isc} values.

Dipole moments for the triplet of **I**-NMe_2 have been determined by Warman and coworkers [24, 25] using the time-resolved microwave conductivity technique. In non-polar solvents a smaller dipole moment was found that in benzene and *trans*-decalin, while for the excited singlet state the dipole moment remains the same in these solvents. The authors proposed a thermal equilibrium between close lying (π,π^*) and (n,π^*) triplets, the latter being favoured in non-polar and the former in slightly polar solvents [25]. Alternatively, equilibrium (6) may be considered with a shift from the *perp* configuration in non-polar solvents to the *trans* side in polar solvents, as indicated by the solvent dependence of $1/\tau_T$ (Fig. 2). The electronic character of these configurations can be the same, but the dipole moments may differ. For comparison, the semilogarithmic plot of $1/\tau_T$ versus E_T^N is only slightly decreasing for **I** and intermediate for **I**-OMe.

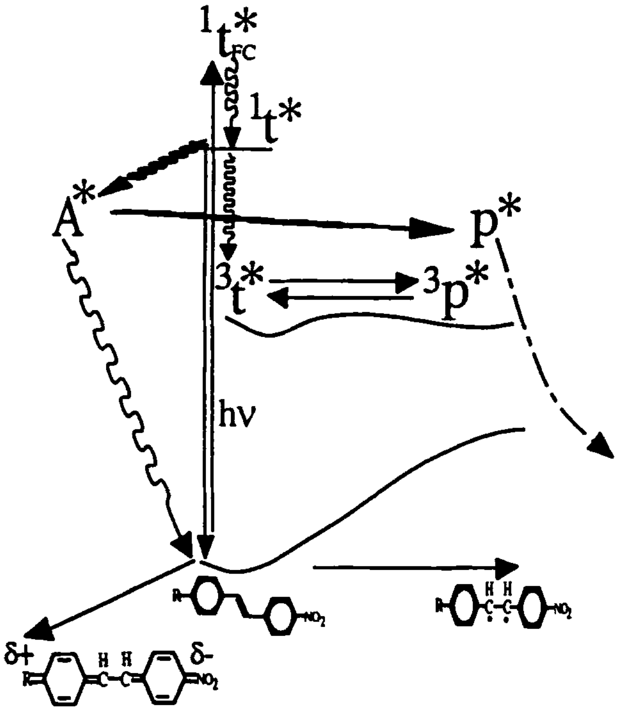
Which parameters have an important influence and to what degree is reaction (5) involved in the relaxation of nitrostilbenes? The results in Table 7 point to internal (e.g. substituent R) and external factors (e.g. solvent polarity). Fluorescence is negligible for R=H and NO_2, but for R=OMe Φ_f is gradually enhanced and for those stilbenes which show strong interactions of the donor and the nitro group (e.g. **I**-NMe_2) Φ_f can be large; the solvent polarity plays an important role (see below). In addition, Φ_{ic} can increase in polar solvents at the expense of Φ_{isc}.

For **I**-R bearing a dialkylamino group the *trans*→*cis* photoisomerization in non-polar solvents occurs via a mixed singlet-triplet mechanism [3, 33–35]. A doubly activated pathway, i.e. two subsequent thermally activated steps competing with fluorescence [33], has been suggested for **I**-NMe_2 in solvents of moderate polarity (e.g. toluene), whereas in polar solvents $\Phi_{t\rightarrow c}$ is virtually zero and this is not compensated by an increase in Φ_f. In these cases ICT bypassing the triplet state is involved in the relaxation [35]. In addition, Φ_{isc} is significantly smaller (sevenfold or more) in other than non-polar solvents [28]. Analogues, where the NMe_2 group is incorporated into a stiff dihydroindole ring, have been studied and show more or less similar effects [35]. Therefore, rotation around the C-N single bond cannot be the cause of the enhanced internal conversion at the *trans* side. Rotation around the C-C single bond between the nitrophenyl and ethylene parts is also excluded on the basis of fluorescence results for a corresponding bridged model compound of **I**-NMe_2; the nearly exponential decline of Φ_f versus E_T^N for **I**-NH_2 (Fig. 1b) and several analogues has been ascribed to the involvement of an excited ICT state (A*) [35].

$$^1t^* \longrightarrow A^* \qquad (15)$$

$$A^* \longrightarrow \textit{trans} \qquad (15')$$

A* has *trans* geometry, is even more polar than $^1t^*$ and should be associated with electron transfer from the (dialkylamino)stilbenyl moiety to the nitro group (Scheme 3).



Scheme 3

A lowering of the level of A* with increasing E_T^N increases the rate constant for the ICT transition (15) at the expense of reaction (4). Interestingly, also for the cyano analogue a low-lying non-emissive A* state has been proposed [10, 13]. Recently, Zachariasse and co-workers have given evidence that the relaxed CT state of *trans*-4-cyano-4′-dimethylaminostilbene, from which fluorescence and *trans*→*cis* photoisomerization start, is populated within 5 ps, i.e. ICT takes place in the subpicosecond time scale [17, 18].

For **I**-OMe, where the opposite effect results, a nearly exponential rise of Φ_f versus E_T^N (Fig. 1b), a mechanism different from that for **I**-NH_2 or **I**-NMe_2 has to be offered. It is conceivable that for **I**-OMe k_{isc} decreases with increasing E_T^N, because $\Phi_{t\rightarrow c}$ is almost proportional to Φ_{isc} (see Tables 1 and 5 in [27]). The main effect should be a lowering of the $^1t^*$ state level in polar solvents and therefore a strong increase in k_f and k_{ic} at the expense of k_{isc}. Corresponding findings are known for semi-flexible donor-acceptor systems studied by Verhoeven and his group [57, 58]. Internal conversion at the *trans* side of **I**-OMe is the major pathway in polar solvents (Table 7), but whether the effect can simply be described by reaction (5) or a more complex initial twisting mode in the excited singlet manifold remains open thus far.

Photophysical and Photochemical Properties of *Trans*-2,4-Dinitrostilbenes

The *trans*-2,4-dinitrostilbenes under examination show *trans*→*cis* photoisomerization as do the mononitrostilbenes. However, the second nitro group in ortho position reduces Φ_f to virtually zero and gives rise to significant changes in the Stokes shift $\Phi_{t\rightarrow c}$ and Φ_{isc}. For **II** itself, the major deactivation process is photoisomerization. If *a* can be assumed to be 0.5, the radiationless process via reactions (3) and (6–8) accounts for 80% of the excitation energy. In this respect, **II** is similar to **I**. The quantum yield of *cis*→*trans* photoisomerization of **I** is $\Phi_{c\rightarrow t}=0.35$ in several solvents [31]. For **II** in toluene $\Phi_{c\rightarrow t}$ is likely to be similar since $\Phi_{t\rightarrow c}$, the ratio of molar absorption coefficients at 366 nm and the percentage of *cis* in the photostationary state of **I** and **II** are also very similar.

The above photoprocesses, negligible fluorescence and efficient *trans*→*cis* photoisomerization (Table 3), are more or less the same for 3-NO_2, Br, F, and C_3H_7 derivatives of **II** in toluene. $\Phi_{t\rightarrow c}$ is gradually reduced for R=2-NO_2, Me and C_3H_7 and smaller than 0.1 in the presence of benzyloxy, (m)ethoxy and dialkylamino groups. In addition, for weakly or moderately donating substituents, $\Phi_{t\rightarrow c}$ decreases with increasing polarity. This is due to a corresponding decrease in Φ_{isc} since virtually the same change was observed in ΔA from T-T absorption (Table 4). For those **II**-R bearing a stronger electron donor, $\Phi_{t\rightarrow c}$ is ≤0.01 even in non-polar solvents. For comparison, for **I**-NEt_2, the mononitro analogue of **II**-NEt_2, $\Phi_{t\rightarrow c}=0.18$ in cyclohexane. Thus, when R is a stronger donor the nitro group in ortho position results in a marked reduction of $\Phi_{t\rightarrow c}$ due to internal conversion at the *trans* side (reaction 5), i.e. bypassing the common pathway of *trans*→*cis* photoisomerization. The Stokes shift of **II**-R is generally large, but less solvent dependent than for **I**-R with R=OMe or alkyl (no satisfactory explanation can be offered as yet).

At −196 °C Φ_f is small for most **II**-R, but moderate to large for those **II**-R with a stronger electron donor (Table 3). In the latter cases intersystem crossing is low since ΔA at λ_T is virtually independent of temperature and Φ_{isc} is probably comparable to $\Phi_{t\rightarrow c}$ at 25 °C which is ≤0.01. Therefore, internal conversion at the *trans* side (reaction 5) is operating even in rigid glasses where the transition from the Franck-Condon state to the CT state should be slowed down.

Similarities between **II** and **I** result from the behaviour of the triplet state. A short lifetime of $\tau_T \approx 0.1$ µs at 25 °C indicates that equilibrium (6) is shifted to the *perp* side. It follows that the rate constant for the intersystem crossing step (7) is approximately $1/\tau_T$, which is comparable to **I** with $k_7=(1\text{–}3)\times10^7\ s^{-1}$ and stilbene itself [29]. A longer triplet lifetime for several **I**-R [28, 32] and **I**-R is due to a shift of equilibrium (6) to the *trans* side. In this case, a reduction in $\Phi_{t\rightarrow c}$ may be due to a smaller Φ_{isc} and/or a larger *a* value, i.e. triplet decay at a geometry which is slightly shifted to the *trans* side with respect to the maximum in the ground state energy profile (Scheme 1). On the other hand, the rate constant for the intersystem crossing step (9), which can be taken from the triplet lifetime of **II** at −196 °C as $k_9 \approx 2\times10^3\ s^{-1}$, is also in the same order of magnitude as those for (nitro)stilbenes [3, 29].

The triplet decay pattern discussed above and the quenching effects of ferrocene or azulene (energy transfer from the $^3t^*$ state) and oxygen (energy transfer from $^3t^*$ yielding $O_2(^1\Delta_g)$ and spin exchange involving the $^3p^*$ state) are very similar for **I**-R and **II**-R. The rather large Φ_{isc} values contrast to the small Φ_Δ values (Table 6). Even in this respect **I** and **II** type stilbenes are similar.

Concluding Remarks

The following classification is proposed with respect to the deactivation processes (Scheme 3) which could be differentiated: (a) For **I** or **I**-NO_2 Φ_{isc} is large, therefore Φ_f small and the triplet mechanism is operative. The effect of ICT is also suggested to be small when R is moderately donating (R=OMe) in solvents of low or medium polarity and when R is strongly donating (R=dialkylamino) in non-polar solvents. The other extreme case (c) is R=dialkylamino and a polar solvent, where internal conversion at the *trans* side, reaction (5), is the major pathway. The intermediate cases (b) are: R is moderately donating in a polar solvent or strongly donating in a solvent of medium polarity. Here ICT and isomerization are both occurring. In the *trans*-4-R-2′,4′-dinitrostilbene series, case (a) is likely for **II** itself and **II**-R with electron withdrawing (R=2-NO_2, 3-NO_2, Br, F) and donating (R=Me or C_3H_7) substituents. Case (c) is proposed for **II**-R with stronger electron donating substituents.

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