View Article Online / Journal Homepage / Table of Contents for this issue

J. Chem. Soc., Faraday Trans 1, 1989, **85**(6), 1469–1483

Published on 01 January 1989. Downloaded by University of Birmingham on 30/10/2014 23:33:09.

trans → *cis* Photoisomerization of 1-Styrylnaphthalene and its 4′-Bromo- and 4′-Chloro-derivatives

A Fluorimetric and Laser Flash Photolytic Study

Fausto Elisei and Ugo Mazzucato*
Dipartimento di Chimica, Università di Perugia, I-06100 Perugia, Italy

Helmut Görner
Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim a. d. Ruhr, Federal Republic of Germany

The *trans* → *cis* photoisomerization of 1-styrylnaphthalene (1-StN) and two *para*-halogen-substituted derivatives (Cl- and Br-1-StN) have been studied in solution by laser flash photolysis and by fluorimetric and photochemical methods. Measurements of the fluorescence lifetime (τ_F) and quantum yield (ϕ_F), the corresponding triplet data (τ_T, ϕ_T), and the *trans* → *cis* photoisomerization quantum yield ($\phi_{t\rightarrow c}$) in a large temperature range are reported as well as the effects of solvents, quenchers and sensitizers. The temperature dependences of these parameters suggest that twisting around the central double bond in the lowest excited singlet state competes successfully with fluorescence and intersystem crossing for the three 1-StNs at elevated temperatures. At room temperature, twisting in the lowest triplet state contributes to a minor degree for 1-StN but markedly for Br-1-StN while at lower temperatures this becomes the only pathway for *trans* → cis photoisomerization of the three 1-StNs.

The photoisomerization of *trans*-1- and *trans*-2-styrylnaphthalene (StN) to the corresponding *cis* isomers has been studied extensively in our and other laboratories.[1–8] The conformational equilibrium in solutions of *trans*-StNs has also been investigated by fluorimetric and flash photolytic techniques.[6–16] The rotamers of 2-StN have been extensively characterized whilst only one rotamer was detectable for 1-StN since the rather large difference in the enthalpy of the two species shifts the equilibrium towards the most stable one.

The temperature independence of the fluorescence quantum yield (ϕ_F) and lifetime (τ_F) of *trans*-1-StN in a large range (from 280 to *ca.* 90 K) has been taken as evidence of a triplet mechanism ($^1trans^* \rightarrow {}^3trans^*$ intersystem crossing (ISC), followed by $^3trans^* \rightarrow {}^3\text{perp}^*$ rotation around the ethylenic bond towards the perpendicular configuration from which $^3\text{perp}^* \rightarrow {}^0\text{perp}$ internal conversion and partitioning to the *trans* and *cis* ground states takes place).[6] Only at higher temperatures does the activated $^1trans^* \rightarrow {}^1\text{perp}^*$ rotation in the singlet manifold, the mechanism operating for stilbene,[17] become the main isomerization pathway of 1-StN. However, this interpretation cannot accommodate the recently reported low triplet yield ($\phi_T \approx 0.04$ in benzene).[18] For 2-StN ϕ_T is even smaller.[8,18,19]

In order to gain a better understanding of the singlet and triplet behaviour of *trans*-1-StN, we have studied over a wide temperature range the fluorescence (ϕ_F, τ_F), the photoisomerization ($\phi_{t\rightarrow c}$) and some properties of the triplet state (ϕ_T, τ_T) of the parent compound and its 4′-chlorine (Cl-1-StN) and 4′-bromine (Br-1-StN) derivatives. The latter offers an interesting reference compound since its heavy atom induced ISC should strongly enhance the contribution of the triplet pathway for *trans* → *cis* photo-

View Article Online

Published on 01 January 1989. Downloaded by University of Birmingham on 30/10/2014 23:33:09.

isomerization. For the 4′-nitro derivative (NO_2-1-StN) we have recently shown that at room temperature and lower, the triplet mechanism is operative.[20]

This paper extends and completes our insight into the photochemical properties of *trans*-1-StN[6] and confirms the previously advanced interpretation of the photoreaction mechanism. We suggest only minor revision concerning the role of the triplet state and the temperature range where the *trans* → *cis* photoisomerization changes from a singlet to a triplet mechanism.

Experimental

The three compounds investigated were prepared for previous work by standard methods.[1] The samples were handled under red light and purged with argon or nitrogen unless otherwise indicated. The solvents were spectro-grade commercial products and purified where necessary. Details of the fluorimetric, photochemical and flash photolytic measurements (in a few experiments $\lambda_{exc} = 308$ and 248 nm; unless indicated otherwise $\lambda_{exc} = 353$ nm) are given elsewhere.[6, 20–23] The experimental error is typically ± 10% for ϕ_F and $\phi_{t\to c}$ (±20% at low temperatures), ±10% for τ_T, and *ca.* 20% for ΔA. In the quenching experiments, the samples were irradiated either at 366 nm (window for ferrocene) where the absorption of the 1-StNs is rather small or at 313 nm. The $\phi_{t\to c}$ values were corrected for the absorption of the quencher.

Results

trans → *cis* Photoisomerization

Table 1 shows the quantum yield of *trans* → *cis* photoisomerization for the three 1-StNs in several solvents at room temperature. The $\phi_{t\to c}$ values show some variation (0.16–0.34) when the substituent and the solvent polarity are varied. Generally, the photostationary state favours the *cis* isomer, typically 75–85% *cis*. When ferrocene is added to 1-StN and Br-1-StN in acetonitrile, $\phi_{t\to c}$ is reduced. From the linear dependence of $\phi_{t\to c}^{-1}$ *vs.* [ferrocene], Stern–Volmer constants (K_{SV}) of *ca.* 100 and 150 $dm^3 mol^{-1}$, respectively, were estimated. These values may be compared with the corresponding values obtained from triplet quenching (see below).

The temperature dependence of $\phi_{t\to c}$ is illustrated in fig. 1–4 for some typical cases, *e.g.* in methylcyclohexane (MCH) or in a 8:3 mixture of 2,2-dimethylbutane and *n*-pentane (D–P), as examples for non-polar solvents, in 2-methyltetrahydrofuran (MTHF), and in ethanol. For 1-StN in D–P $\phi_{t\to c}$ decreases strongly on decreasing the temperature between 297 and *ca.* 200 K, only moderately between 200 and *ca.* 120 K, and decreases again strongly on further cooling. Correspondingly, the position of the photostationary state is shifted to the *trans* side at lower temperatures (table 2). A similar temperature dependence has already been reported for $\phi_{t\to c}$ of 1-StN in a 2:1 mixture of MCH and 2-methylpentane.[7] At high temperatures in MCH $\phi_{t\to c}$ approaches 0.5, *i.e.* it increases by a factor of about three on going from 297 to 363 K. A smaller change of log $\phi_{t\to c}$ *vs.* T^{-1} in the low temperature range compared to higher temperatures was also found in ethanol and, still less pronounced, in MTHF (fig. 2). For 1-StN in glycerol triacetate (GT) the total change of $\phi_{t\to c}$ is similar to the other three solvents (about a hundredfold) but in a much smaller temperature range (table 2).

For Br-1-StN in D–P the region where $\phi_{t\to c}$ changes slightly is larger than for the parent molecule, it extends from 220 to *ca.* 120 K, and $\phi_{t\to c}$ therein is significantly larger (*cf.* fig. 1 and 3). Similar temperature dependences of $\phi_{t\to c}$ were obtained for Br-1-StN in MTHF and ethanol (fig. 4). The behaviour of the chlorine derivative lies between the two other cases; it resembles more closely that of 1-StN (table 2).

View Article Online

Published on 01 January 1989. Downloaded by University of Birmingham on 30/10/2014 23:33:09.

Table 1. Fluorescence lifetime and quantum yields of fluorescence and *trans* → *cis* photoisomerization of 4′-substituted 1-StNs[a]

compound	solvent	τ_F/ns	ϕ_F	$\phi_{t\rightarrow c}$
1-StN	n-hexane	1.8	0.60[b]	
	MCH	1.8	0.72 (0.72)[d]	0.16[c]
	D–P	—	0.55 (0.9)	0.28
	MTHF	—	0.45 (0.8)	0.30
	GT	—	0.40	0.24
	acetonitrile	—	0.28	0.28
	ethanol	1.1	0.32 (0.6)	0.25
Cl-1-StN	n-hexane[c]	—	0.76	0.14
	MCH	1.7	0.70	0.18
	D–P	—	0.65 (0.8)	0.20
	MTHF	—	0.45 (0.7)	0.28
	GT	—	0.45	0.25
	ethanol	—	0.42	0.26
Br-1-StN	n-hexane[c]	—	0.47	0.22
	MCH	1.47	0.41	0.30
	D–P	—	0.45 (0.6)	0.34
	MTHF	—	0.38 (0.5)	0.26
	GT	—	0.35	0.22
	acetonitrile	1.1	0.35	0.28
	ethanol	—	0.33 (0.5)	0.30

[a] In argon-saturated solution at 297 K; λ_{irr} = 313 nm (355 nm for τ_F); MCH: methylcyclohexane, D–P: 2,2-dimethylbutane and n-pentane (8:3), MTHF: 2-methyltetrahydrofuran, GT: glycerol triacetate. [b] Taken from ref. (6). [c] Taken from ref (1). [d] values in brackets refer to 77 K.

Fluorescence Quantum Yield and Lifetime

Values for ϕ_F of the *trans* isomers in solution at room temperature are given in table 1. In non-polar solvents they are high (0.5–0.7) for 1-StN and Cl-1-StN and slightly smaller (0.4–0.5) for Br-1-StN. In solvents of medium and high polarity ϕ_F is markedly smaller. The values are roughly complementary to $\phi_{t\rightarrow c}$, *i.e.* $\phi_{t\rightarrow c}$ is enhanced at the expense of ϕ_F.

At 77 K ϕ_F is generally larger than at room temperature but still well below unity. For 1-StN in MCH, D–P and MTHF ϕ_F is larger than in the other cases, slightly smaller for the chlorine, and smallest for the bromine derivative (table 1). The temperature dependence of ϕ_F is shown for 1-StN in MCH, D–P and ethanol (fig. 1 and 2) and for Br-1-StN in non-polar media (fig. 3). Generally, ϕ_F is constant within the whole range between 77 and *ca.* 270 K and log ϕ_F approaches a linear dependence on T^{-1} only above 320 K. Activation energies (E_a), obtained from these high-temperature regions, are 7–10 kcal mol^{-1}† (table 3). For 1-StN in MCH the pre-exponential factor (A) and E_a are larger than in ethanol. A smaller barrier to ^{1}*trans** → ^{1}perp* rotation in polar solvents has already been reported.[6]

The fluorescence lifetime is short for the three compounds in non-polar media and becomes even shorter in polar solvents (table 1). As expected from the ϕ_F values, changing the temperature between 77 and 297 K has only a small effect on τ_F while it is reduced at elevated temperatures, *cf.* ref. (6).

† 1 kcal mol^{-1} = 4.184 kJ mol^{-1}.

View Article Online

Published on 01 January 1989. Downloaded by University of Birmingham on 30/10/2014 23:33:09.

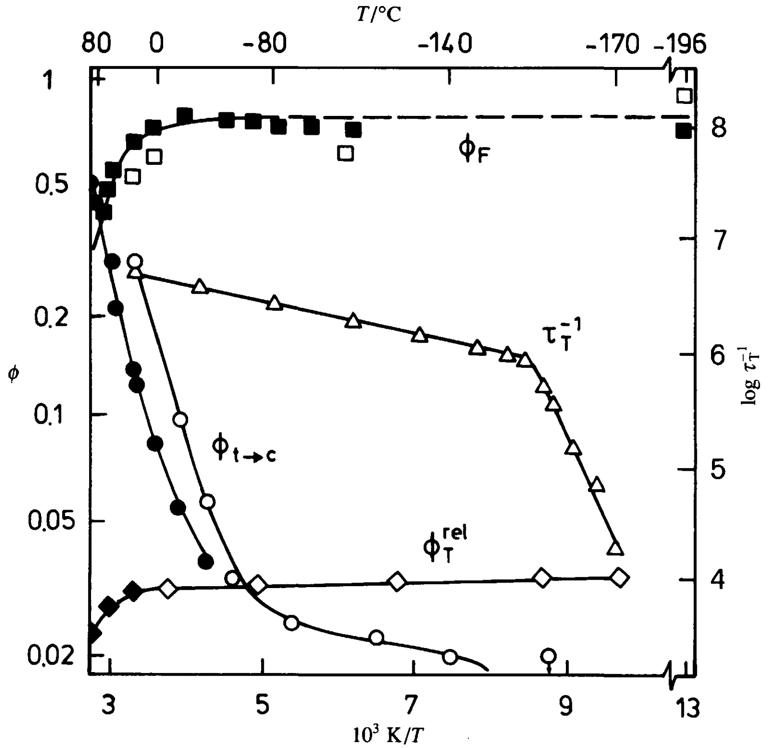

Fig. 1. Semilogarithmic plots of $\phi_{t\rightarrow c}$ (○, ●), ϕ_F (□, ■), ϕ_T^{rel} (◇, ◆) and τ_T^{-1} (△) *vs.* T^{-1} for 1-StN in D–P (open symbols) and MCH (full symbols).

Transient Absorption Spectra

The transient absorption spectrum of *trans*-1-StN in acetonitrile at 297 K exhibits three components, a short-lived species, a second one with a lifetime of *ca.* 1 μs, and a longer lived species [fig. 5(*a*)]. The short-lived transient, being observable only during the laser pulse width and showing maxima in the red spectral range, is assigned to an $S_1 \rightarrow S_n$ transition (the absence of a band at 500 nm which was recorded using ps laser pulses[24] can easily be explained by the distortion from the much stronger fluorescence signal under our conditions). The longer-lived transient which is rather weak and was also observed for Br-1-StN [fig. 5(*b*)] and Cl-1-StN is tentatively ascribed to a photoproduct of a side-reaction.

The main transient of *trans*-1-StN, showing two distinct absorption bands with maxima (λ_{max}) at 480 and 570 nm, is assigned to a triplet state. The assignment is based on the results that its lifetime is quenched by oxygen and ferrocene (see below) and that it is generated on sensitized excitation using xanthone as high-energy triplet donor [fig. 6(*a*)]. The xanthone triplet (λ_{max} = 630 nm) is generated within the laser pulse width and its lifetime is reduced on addition of 1-StN. Since at high concentrations (> 1 mmol dm^{-3}) 1-StN absorbs also at 353 nm, its $S_1 \rightarrow S_n$ absorption overlaps in the red spectral region with that of the xanthone triplet. The remaining longer-lived transient is practically identical to that observed on direct excitation at both 353 and 248 nm [fig. 5(*a*) and table 4], as expected for the 1-StN triplet. This is in agreement with a similar energy transfer experiment using fluorenone.[18]

In *m*-dibromobenzene at room temperature the T–T absorption spectra of the three 1-StNs are very similar with two maxima in the 460–500 nm range [table 4 and fig. 6(*b*)].

View Article Online

Published on 01 January 1989. Downloaded by University of Birmingham on 30/10/2014 23:33:09.

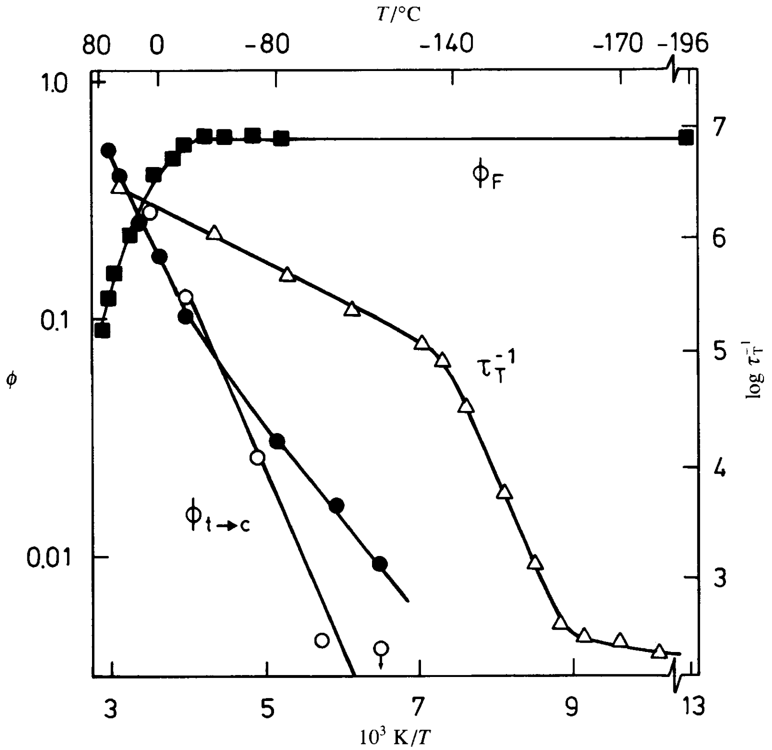

Fig. 2. Semilogarithmic plots of $\phi_{t\rightarrow c}$ (○, ●), ϕ_F (■) and τ_T^{-1} (△) *vs.* T^{-1} for 1-StN in MTHF (open symbols) and ethanol (full symbols).

In some solvents only the maximum around 490 nm was observed while in a few cases a further maximum or shoulder also appeared around 570 nm. The triplet nature of the latter was confirmed by the same lifetime at both maxima.

In glassy solvents at low temperatures (table 5) virtually the same T–T absorption spectra were recorded as at room temperature. Examples are shown for 1-StN and Br-1-StN in D–P at 77 K [fig. 7(*a*)] and for the latter in GT at 200 K [fig. 7(*b*)]. Our spectra of 1-StN are in agreement with those already observed using both laser flash photolysis at room temperature[18] and μs flash photolysis in alcoholic glasses.[11]

Triplet Yield

Since the shape and maxima of the T–T absorption spectra depend only slightly on the environment (nature of solvent, temperature and viscosity), the transient absorption (ΔA) at λ_{max} can be regarded as a measure of the relative triplet yield (ϕ_T^{rel}). At room temperature these values (table 4) show the following trend. For 1-StN in MCH, MTHF and acetonitrile the ΔA values are much smaller than in *m*-dibromobenzene, *i.e.* the maximum value of ϕ_{ISC} in the former solvents should be well below 0.1. A similar external heavy-atom effect has been reported by Wismontski-Knittel and Das using small amounts of ethyl iodide in benzene.[18] Similar results with slightly larger ΔA values were found for Cl-1-StN, while for Br-1-StN ΔA is substantial in all solvents.

No discernible change in ΔA was found for the three StNs in several solvents in the range 297–77 K (fig. 1, 3 and 8). Especially in the high viscosity range we could not observe a considerable enhancement of ΔA, in contrast to the case of *trans*-stilbene and

View Article Online

Published on 01 January 1989. Downloaded by University of Birmingham on 30/10/2014 23:33:09.

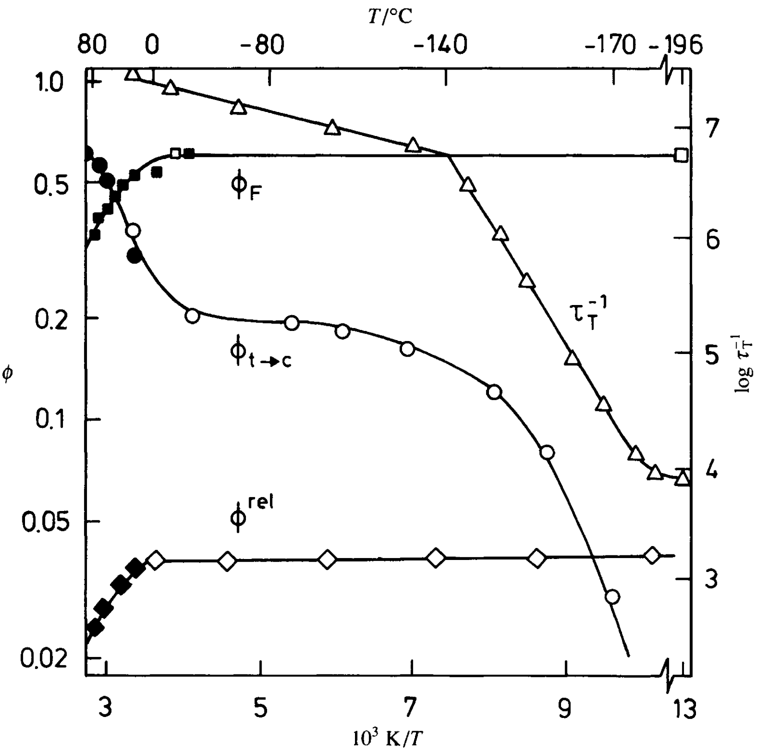

Fig. 3. Semilogarithmic plots of $\phi_{t\to c}$ (○, ●), ϕ_F (□, ■), ϕ_T^{rel} (◇, ◆) and τ_T^{-1} (△) *vs.* T^{-1} for Br-1-StN in D–P (open symbols) and MCH (full symbols).

its 4-F, 4-Cl and 4-Br derivatives[21] and azastilbenes.[22] On the other hand, ϕ_T^{rel} of 1-StN (fig. 1), Cl-1-StN (not shown) and Br-1-StN (fig. 3) in MCH decreases on going from 297 to *ca.* 363 K. Our measurements are accompanied by two complications: (1) ΔA of the 1-StN triplet is rather small even at room temperature and ΔA of the second, longer-lived transient seems to increase at higher temperatures. (2) For Br-1-StN ΔA is much larger even at 350 K but τ_T is too short to allow an accurate measurement of ϕ_T [keeping in mind that the high fluorescence intensity distorts the T–T absorption for the first 20–50 ns, *cf.* ref. (8)].

A second method to evaluate the intrinsic ISC yield is the estimation of the 'enhancement factor' which we define as the ratio of the ΔA value in the presence of a sensitizer (*e.g.* xanthone) relative to that for direct excitation. For 1-StN and Cl-1-StN in acetonitrile this factor is larger than 10. The concentration of the *trans* isomer was kept below 2 mmol dm^{-3}, corresponding to the lifetime for the xanthone triplet of *ca.* 100 ns. However, for Br-1-StN a concentration of 2 mmol dm^{-3} was insufficient for the triplet to be detected by sensitization because of its lifetime was too short (see table 4).

Triplet Lifetime

The decay of the triplet of the three StNs follows first-order kinetics at room temperatures (and in most cases also in the whole temperature range examined). For 1-StN and Cl-1-StN τ_T (reciprocal first-order decay rate constant: k_{obs}^{-1}) increases from *ca.* 200 ns in MCH up to *ca.* 1 μs in polar solvents. For Br-1-StN however, τ_T is significantly shorter in all solvents (table 4). This may be explained by the internal heavy-atom effect due to the bromine substituent. There is still a trend to longer lifetimes on increasing the solvent polarity.

View Article Online

Published on 01 January 1989. Downloaded by University of Birmingham on 30/10/2014 23:33:09.

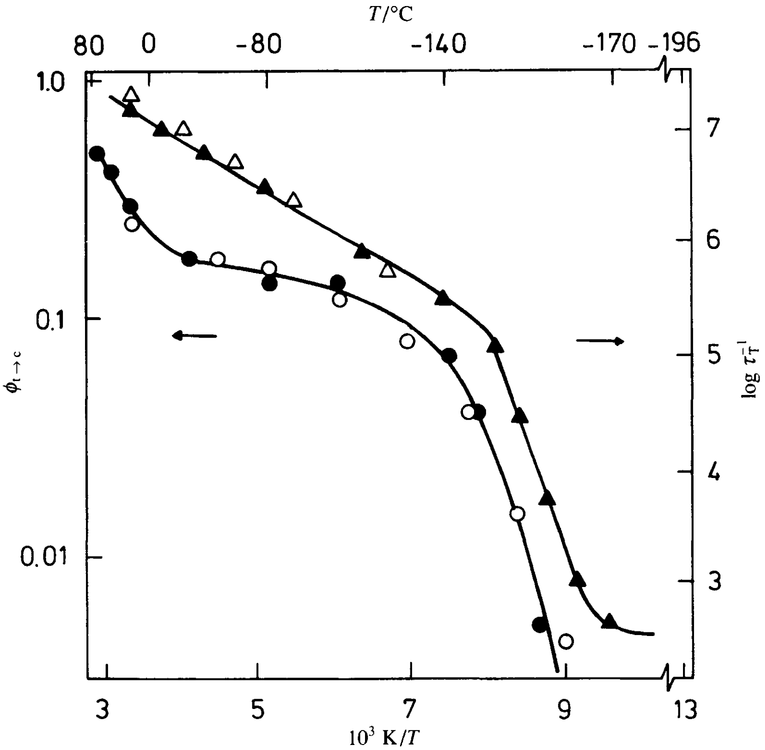

Fig. 4. Semilogarithmic plots of $\phi_{t\to c}$ (○, ●) and τ_T^{-1} (△, ▲) *vs.* T^{-1} for Br-1-StN in MTHF (open symbols) and ethanol (full symbols).

From the lifetime in argon-, air- and oxygen-saturated solutions the rate constant for quenching by oxygen (k_{ox}) was obtained. For Cl-1-StN in acetonitrile $k_{ox} = 5 \times 10^9$ dm^3 mol^{-1} s^{-1}, *i.e.* nearly diffusion controlled. For 1-StN in *m*-dibromobenzene $k_{ox} = 3 \times 10^9$ dm^3 mol^{-1} s^{-1} assuming $[O_2] = 1.5$ mmol dm^{-3} in air-saturated solution. For Br-1-StN k_{obs} is too large in most solvents to allow an accurate measurement of k_{ox}. As second quencher we used ferrocene. From linear plots of k_{obs} *vs.* [ferrocene] quenching rate constants (k_Q) of $(2\text{–}5) \times 10^9$ dm^3 mol^{-1} s^{-1} were obtained (table 4). For 1-StN and Br-1-StN in acetonitrile the product $\tau_T \times k_Q$ is approximately 5500 and 350 dm^3 mol^{-1}, respectively. This value for 1-StN is much larger than the corresponding Stern–Volmer constant K_{SV}, obtained from the steady-state method (see above).

The temperature dependence of the reciprocal triplet lifetime is shown in fig. 1–4 and 8. On decreasing the temperature $\tau_T{}^{-1}$ exhibits a decrease by three or four orders of magnitude in all cases examined. The plot of log $\tau_T{}^{-1}$ *vs.* T^{-1} can be divided into three segments which are described by two characteristic temperatures: T_v and T_0; they are the higher and lower temperatures, respectively, at which the 'quasi-linear' parts intersect. Almost linear dependences were found between T_0 and T_v on the one hand and above T_v on the other, the slope being significantly larger in the former than in the high-temperature range. A constant lifetime is generally approached on further cooling below T_0. Values of T_v decrease in the order X = H (116 K), Cl (119 K) and Br (132 K) in D–P, the most fluid medium at low temperatures; they are higher in MTHF and highest (247–260 K) in GT, the most viscous solvent. The second characteristic temperature T_0, generally displaced to lower temperatures, changes in the same order (table 5). This type of behaviour is well known from stilbenes,[21] especially nitrostilbenes,[25] and has recently been reported for NO_2-1-StN.[20]

View Article Online

Published on 01 January 1989. Downloaded by University of Birmingham on 30/10/2014 23:33:09.

Table 2. Temperature dependence of $\phi_{t\rightarrow c}$ and position of the photostationary state for 4′-substituted 1-StNs[a]

		1-StN		Cl-1-StN		Br-1-StN	
solvent	temp./K	$\phi_{t\rightarrow c}$	(% *cis*)$_s$	$\phi_{t\rightarrow c}$	(% *cis*)$_s$	$\phi_{t\rightarrow c}$	(% *cis*)$_s$
MCH	363	0.49	89	0.55	89	0.60	90
	333	0.32	84	0.45	86	0.50	88
	297	0.16	76	0.18	80	0.30	83
D–P	297	0.28	78	0.20	80	0.34	85
	223	0.044	43	0.06	50	0.20	77
	173	0.024	32	0.05	40	0.19	73
	133	0.020	22	0.03	30	0.14	65
	113	$\leqslant$ 0.008	$\leqslant$ 18	0.01	20	0.08	50
MTHF	273	0.23	78	0.30	83	0.22	80
	223	0.050	40	0.06	55	0.18	74
	173	0.006	10	0.02	25	0.14	70
	133	$\leqslant$ 0.002	$\leqslant$ 5	0.01	15	0.07	45
GT	363	0.45	86	0.60	89	0.42	80
	273	0.10	65	0.15	70	0.18	75
	203	0.01	15	0.01	$\leqslant$ 20	0.01	15
ethanol	343	0.46	85	0.52	87	0.50	87
	273	0.18	65	0.22	80	0.22	80
	223	0.050	40	0.05	50	0.17	70
	173	0.017	18	0.02	28	0.14	66
	133	$\leqslant$ 0.005	$\leqslant$ 8	0.01	15	10 0.07	40

[a] In argon-saturated solution, λ_{irr} = 313 nm.

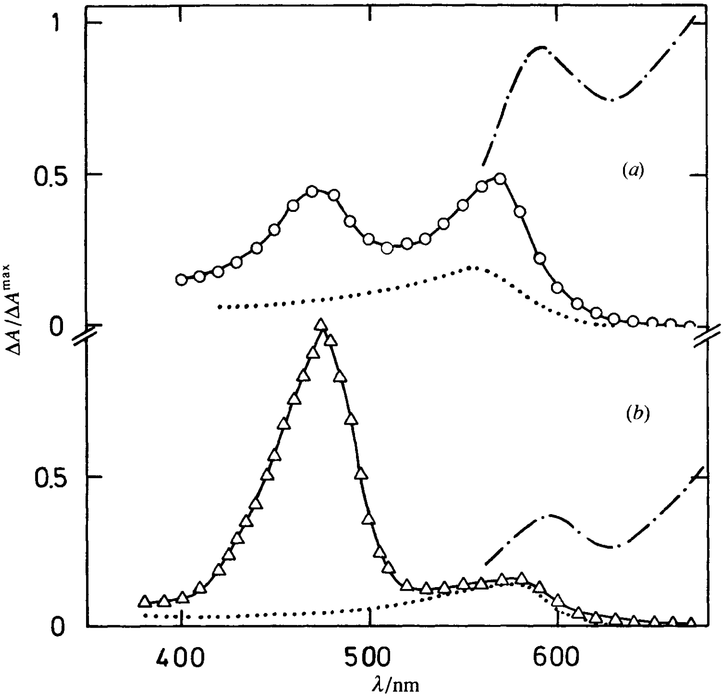

Fig. 5. Transient absorption spectra in acetonitrile at 297 K: (*a*) for 1-StN and (*b*) Br-1-StN; at 10 ns (----), 50 ns (○, △), and 2 μs (...) after the pulse; λ_{exc} = 353 nm.

View Article Online

Published on 01 January 1989. Downloaded by University of Birmingham on 30/10/2014 23:33:09.

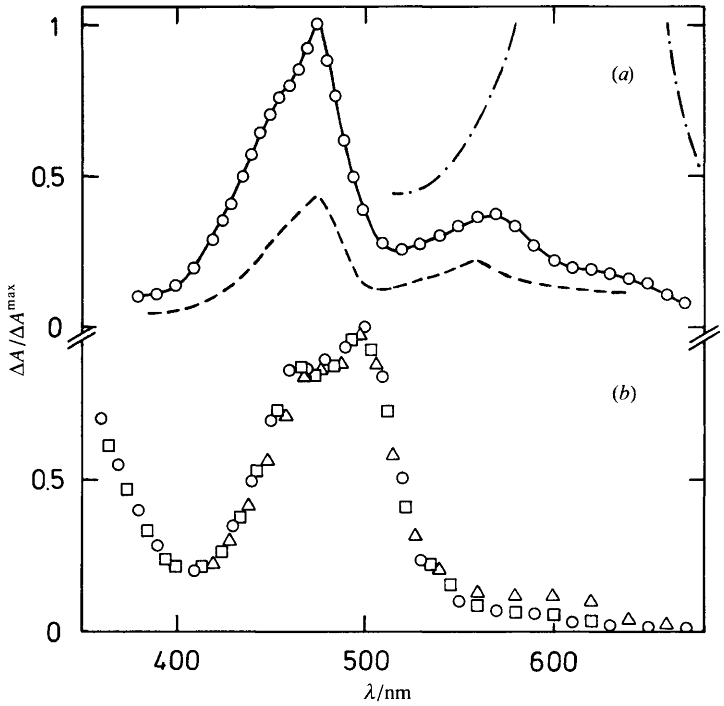

Fig. 6. T–T absorption spectra at 297 K: (*a*) 1-StN (1 mmol dm^{-3}) in acetonitrile in the presence of xanthone (10 mmol dm^{-3}) at 10 ns (-·-·-), 50 ns (○) and 800 ns (---) after the pulse; (*b*) 1-StN (○), Cl-1-StN (□), and Br-1-StN (△) in *m*-dibromobenzene; λ_{exc} = 353 nm.

Table 3. Arrhenius and kinetic parameters for the $^1trans^*$ deactivation of 1-StN and Br-1-StN in different solvents at 297 K

compound	solvent	$E_a{}^a$ /kcal mol^{-1}	A^a/s^{-1}	$k_F/10^{-8}$ s^{-1}	$k_{t\rightarrow p}/10^{-8}$ s^{-1}	$k_{ISC}/10^{-8}$ s^{-1}
1-StN	MCH	10.8	3.2×10^{15}	4.0	0.36	1.2
		7.8^b	3.2×10^{13}	4.0	0.58	0.97
	ethanol	7.3	1.0×10^{14}	2.9	4.24	1.95
Br-1-StN	MCH	10.0	5.7×10^{14}	2.8	0.25	3.75
		6.7^b	5.0×10^{12}	2.8	0.59	3.41
	ethanol	6.6	3.0×10^{13}	3.0	4.17	1.92

[a] From ln (ϕ_F^{lim}/ϕ_F-1) *vs.* T^{-1}. [b] From ln (τ_F^{lim}/τ_F-1) *vs.* T^{-1}.

Discussion

Pathways of Excited 1-StNs Competing with Fluorescence

Below 300 K fluorescence is the main deactivation pathway for the excited *trans* singlet state of 1-StN and its chlorine derivative and is a relevant process also for Br-1-StN (table 1). Above room temperature, ϕ_F and τ_F become smaller: both are coupled with $\phi_{t\rightarrow c}$ indicating that the fluorescent state isomerizes through activated $^1trans^* \rightarrow {}^1perp^*$ twisting, as does stilbene.[17, 26] If one takes as yield for this process $\phi_{t\rightarrow p} = \phi_{t\rightarrow c}/\beta$, where β is the fraction of relaxation of molecules in the perpendicular singlet configuration into the *trans* ground state, and assumes $\beta = 0.5$ (for stilbene β = 0.4–0.5),[17] one obtains

Published on 01 January 1989. Downloaded by University of Birmingham on 30/10/2014 23:33:09.

Table 4. T–T Absorption maximum, triplet lifetime, rate constants for quenching by ferrocene and transient absorbances of 4′-substituted 1-StNs[a]

compound	solvent	λ_{max}/nm	τ_t/ns	$k_Q{}^b/10^{-9}$ dm^3 mol^{-1} s^{-1}	ΔA^c
1-StN	MCH/D–P	480, 570sh	200	–	$\leqslant$ 0.03 (0.04)[d]
	m-dibromobenzene	470sh, 500	240	2.0	0.5 (0.40)
	MTHF	490	300	–	0.05
	GT	485	600	–	0.1 (0.09)
	acetonitrile	475, 570sh	1100	5	$\leqslant$ 0.03 (0.02)
		475, 570[e]			
Cl-1-StN	MCH/D–P	490	230	–	$\leqslant$ 0.08 (0.10)
	m-dibromobenzene	475sh, 500	250	1.8	0.6 (0.45)
	MTHF	495	500	–	
	GT	490	650	–	0.2 (0.15)
	acetonitrile	480, 570sh	600	5	$\leqslant$ 0.05
Br-1-StN	MCH/D–P	482	40	5	$\geqslant$ 0.4 (0.5)
	m-dibromobenzene	475sh, 500	50	$\geqslant$ 2	0.7 (0.6)
	MTHF	490	40	–	0.6
	GT	485	60	–	0.6 (0.6)
	acetonitrile	475	70	5	$\geqslant$ 0.4 (0.6)
		480[e]			
	dimethylformamide	460sh, 490	85	3.6	0.7 (0.8)
	ethanol	490	55	–	$\geqslant$ 0.4 (0.7)

[a] In argon-saturated solution at 297 K, λ_{exc} = 353 nm unless indicated otherwise. [b] Q: ferrocene. [c] Relative to T–T absorption of benzophenone in benzene, ΔA(520 nm) = 1. [d] Values in parentheses refer to λ_{exc} = 308 nm. [e] λ_{exc} = 248 nm.

Table 5. T–T Absorption maximum and triplet lifetime in rigid media and characteristic temperatures for triplet decay of 4′-substituted 1-StNs and related compounds[a]

compound	solvent	$\lambda_{max}{}^b$/nm	$\tau_T{}^b$/ms	T_v/K	T_0/K
1-StN	D–P	465sh, 495	> 1	116	< 95
	D–P	465, 495[c]			
Cl-1-StN	D–P	470sh, 495	$\geqslant$ 1	119	$\leqslant$ 97
Br-1-StN	D–P	465sh, 495	0.14	132	95
1-StN	MTHF	475, 500	5	135	109
Cl-1-StN	MTHF	475sh, 505	$\geqslant$ 1	140	$\leqslant$ 108
Br-1-StN	MTHF	470sh, 500	$\geqslant$ 2	143	118
NO_2-1-StN	MTHF		3	163	123
4-Br-stilbene	MTHF		0.5	*e*	104
1-StN	GT	490	3	247	206
Cl-1-StN	GT	490	0.8	260	215
Br-1-StN	GT	465sh, 495	0.12	260	218
NO_2-1-StN	GT		1	263	213
stilbene	GT		10	*e*	201
4-Br-stilbene	GT		0.4	*e*	207
4-NO_2-stilbene	GT			249	209
1-StN	EtOH/MeOH[d]	460, 490	3		
Br-1-StN	ethanol	465sh, 495	$\geqslant$ 2	125	105
stilbene	ethanol		13	*e*	105
4-Br-stilbene	ethanol		0.5	*e*	115

[a] In argon-saturated solution, λ_{exc} = 353 nm unless indicated otherwise; values for NO_2-StN and stilbenes taken from ref. (20), (21), (25). [b] At *ca.* 90 K in D–P, MTHF, and ethanol and 200 K in GT. [c] λ_{exc} = 248 nm. [d] Taken from ref. (11). [e] T_v not defined due to too low ϕ_T values.

Published on 01 January 1989. Downloaded by University of Birmingham on 30/10/2014 23:33:09.

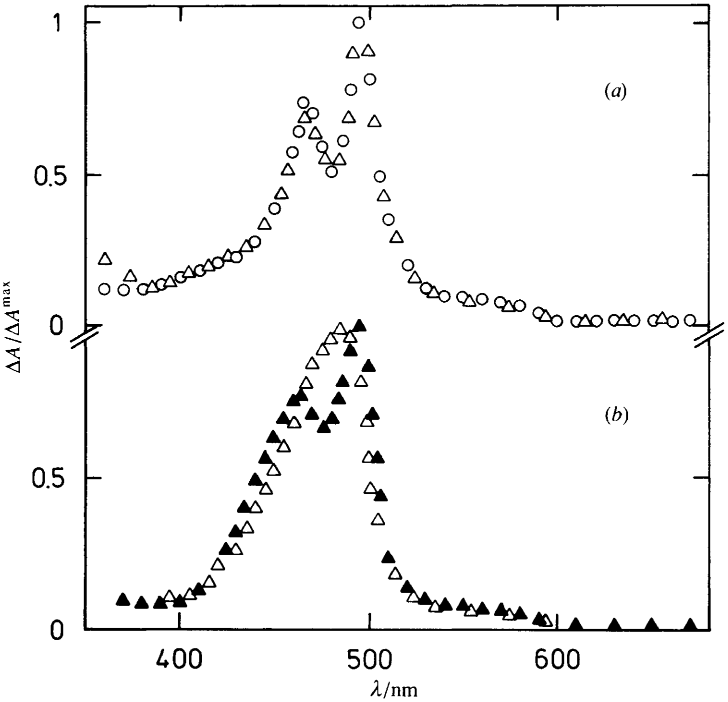

Fig. 7. T–T absorption spectra in rigid media: (*a*) 1-StN (○) and Br-1-StN (△) in D–P at 77 K and (*b*) Br-1-StN in GT at 297 (△) and 200 K (▲); λ_{exc} = 353 nm.

$\phi_{t\to p}+\phi_F \approx 1$. Thus, the yields of radiative and reactive deactivation pathways account for most or all of the absorbed quanta at room temperature and above.

The Arrhenius parameters measured in this temperature range (table 3) show that the activated step is a spin-allowed process ($A > 10^{13}$ s^{-1}) and that the energy barrier (E_a = 7–10 kcal mol^{-1} in non-polar and polar solvents)[6] is much higher than for stilbene (2–3 kcal mol^{-1}).[17, 21, 26] The two lowest excited singlet states have probably mixed ethylenic and naphthalenic character.[3–6] They are very close and their relative position may depend on the substituent and the nature of the solvent. The partial localization of the excitation in the aromatic group is certainly responsible for the high activation energy and relatively low $\phi_{t\to c}$ of these compounds.

The high barrier to twisting in S_1 opens the triplet pathway for *trans* → *cis* photoisomerization below room temperature. The independence of the T–T absorption spectrum from temperature and viscosity (fig. 7 and tables 4 and 5) shows that the observed triplet originates from the *trans* configuration, ^{3}*trans**. A contribution of the triplet mechanism is strongly suggested by the following. First, the temperature dependence of the triplet lifetime (fig. 1–4 and 8) shows that τ_T^{-1} decreases on cooling. It is reminiscent of the typical behaviour well established for stilbenes.[21, 25] The plots of τ_T^{-1} *vs.* T^{-1} are described by the characteristic temperatures T_v and T_0. Below the latter, triplet decay is only due to the ^{3}*trans** → ^{0}*trans* ISC transition and between T_v and T_0 by the ^{3}*trans** → ^{3}perp* rotation, whereas the back step in this high-viscosity range cannot successfully compete with ISC at the twisted configuration (^{3}perp* → ^{0}perp). Secondly, the temperature dependence above T_v is readily explained by an equilibrium between the two relevant triplet configurations. Similar to nitrostilbenes[25] the small dependence in non-polar solvents (fig. 1 and 3) indicates that the ^{3}*trans** $\rightleftharpoons$ ^{3}perp* equilibrium is displaced towards the twisted configuration whereas the larger temperature dependence of the triplet lifetime in slightly or strongly polar solvents (fig. 2 and 4) points to a shift

View Article Online

Published on 01 January 1989. Downloaded by University of Birmingham on 30/10/2014 23:33:09.

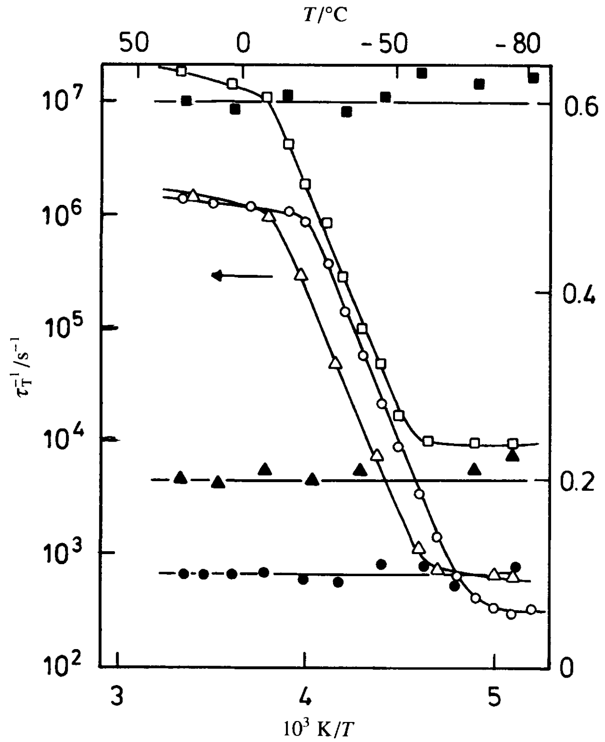

Fig. 8. Semilogarithmic plots of ϕ_T^{rel} (full symbols) and τ_T^{-1} (open symbols) *vs.* T^{-1} for 1-StN (circles), Cl-1-StN (triangles) and Br-1-StN (squares) in GT.

of this equilibrium towards the *trans* side. Thirdly, a shift to the *trans* side is also proposed to account for the longer lifetime of 1-StN and Cl-1-StN in polar solvents such as acetonitrile at room temperature (table 4). The markedly shorter triplet lifetime of Br-1-StN reflects an internal heavy atom effect for the ^{3}perp* → ^{0}perp ISC step. A corresponding effect for the ^{3}*trans** → ^{0}*trans* transition in highly viscous media was also found (fig. 8 and table 5).

Mixed Singlet and Triplet *trans* → *cis* Pathways of 1-StN

For 1-StN in non-polar solvents at or just below room temperature ϕ_F and τ_F remain constant whilst $\phi_{t\rightarrow c}$ continues to decrease with decreasing temperature (fig. 1). The fluorescence behaviour in the range 190–280 K indicates that the fluorescent state is no longer the reactive one and that the mechanism prevailing at lower temperatures involves only the triplet manifold for the initial twisting. Since the quantum yield for the anthraquinone-sensitized isomerization at room temperature has been reported to be 0.415,[1] the same value can be assumed for the partitioning factor to the *cis* and *trans* ground states after the ^{3}*trans** → ^{3}perp* twisting. From $\phi_{t\rightarrow c} \approx 0.1$ as measured just below room temperature in non-polar solvents an upper limit for ϕ_{ISC} of 0.2 can therefore be concluded.

On the other hand, the measured ϕ_{ISC} is generally quite small in solution at room temperature, as also reported by other authors (*ca.* 0.04).[18] In this work ϕ_T was obtained (i) from the relative Δ*A* values in comparison to the value in *m*-dibromobenzene (table 4), (ii) from the enhancement factor obtained with xanthone in acetonitrile ($\phi_T \leqslant 0.1$) and (iii) from the $\phi_{t\rightarrow c}$ values at low temperatures (see also below). Furthermore, the quenching experiments with ferrocene in acetonitrile show that ϕ_{ISC} is small.

View Article Online

Published on 01 January 1989. Downloaded by University of Birmingham on 30/10/2014 23:33:09.

Therefore, the fluorimetric results seem to indicate that the triplet mechanism begins to prevail already at room temperature (or 20–25 K below, in polar solvents) whilst the flash photolytic results indicate that ϕ_T is too small to account for the $\phi_{t\to c}$ values at, and just below, room temperature. The intervention of an upper excited triplet state would be an interesting explanation for the relatively high $\phi_{t\to c}$ values. However, this seems to be ruled out by the result that ϕ_T remains practically constant down to 77 K (fig. 1) when rotation is inhibited and $T_n \rightarrow T_1$ internal conversion should increase the T_1 population. An alternative but rather speculative possibility would be a reactive T_n (or S_n) state non-interacting with T_1 (or S_1) because of the too high barrier separating their energy minima.

As a matter of fact, there is no doubt that the *trans* → *cis* photoisomerization changes from the singlet to the triplet pathway on decreasing the temperature. The open question concerns the temperature region where the change in mechanism takes place. On the basis of the present measurements, it appears to occur at *ca.* 275 K for 1-StN in non-polar solvents and at lower temperatures ($\leqslant$ 240 K) in ethanol (fig. 2 and table 2) and acetonitrile where the energy barrier to twisting in S_1 is smaller. Thus, these temperatures are 20–30 K smaller than those reported previously.[6] The latter results indicated that in non-polar solvents the triplet mechanism begins to prevail already at room temperature, or just below, when it was found $k_{t\to p} \ll k_{ISC}$ and the fluorescence parameters (ϕ_F, τ_F) reached their maximum value, which remained practically constant down to 77 K.

The present flash photolytic results for 1-StN are in qualitative agreement with the fluorescence data showing that the relative ϕ_T values follow the same trend (see fig. 1) and reach their maximum constant value at practically the same temperature as do ϕ_F and τ_F. This is strong confirmation of the complementary role of S_1 and T_1 in the photoisomerization of 1-StN. However, ϕ_{ISC} cannot account for $\phi_{t\to c}$ in non-polar solvents (0.16) or in acetonitrile (0.28) at room temperature. This indicates that in the polar solvent (and probably also in MCH) the photoreaction at room temperature occurs predominantly *via* the singlet manifold.

These contrasting findings can be explained by the difficulties typical for these delicate measurements. In fact, if $k_{t\to p}$ from fluorescence data is estimated using a somewhat lower E_a and a higher A value, one could find $k_{t\to p} \gg k_{ISC}$ still at room temperature, the inequality becoming inverse only at lower temperatures, *e.g.* *ca.* 275 K in non-polar solvents and *ca.* 240 K in polar solvents. This could explain why the singlet mechanism is still prevailing at room temperature and the triplet mechanism becomes predominant only at lower temperatures, when ϕ_F, τ_F, ϕ_T are clearly constant and $\phi_{t\to c}$ decreases only slightly. In this lower temperature region, between 200 and 120 K in non-polar solvents, $\phi_{t\to c} \approx 0.03$ which requires $\phi_T \approx 0.06$ if the photoreaction occurs completely in the triplet manifold. The latter value is not too far from the measured one, if the uncertainty typical of the ϕ_T evaluation is taken into account.

On the other hand, the fact that $\phi_F + \phi_{t\to p} \approx \phi_F + 2\phi_{t\to c} \approx 1$ (table 1) indicates that internal conversion can be neglected at room temperature. Therefore, one should expect $\phi_{ISC} \approx 1 - \phi_F \approx 0.3$ at low temperatures. This estimation is rather larger than the ϕ_T values measured in the low-temperature region ($\leqslant$ 0.05) even considering a large experimental error. To explain these differences, one should assume that the internal conversion step ^{1}*trans** → ^{0}*trans* is enhanced at low temperatures. This assumption which appears to be somewhat speculative would imply that internal conversion, taking place from the quasi planar ^{1}*trans* form, is favoured at low temperatures when the activated twisting becomes inhibited.

Effect of Substitution

The behaviour of the Cl-derivative parallels that of the parent hydrocarbon with slightly higher ϕ_{ISC} (see tables 2 and 4). For Br-1-StN, however, the triplet mechanism contributes markedly already at *ca.* 300 K. Fluorescence and ISC are the main deactivation pathways of excited Br-1-StN, too, the sum of their yields being near unity.

View Article Online

Published on 01 January 1989. Downloaded by University of Birmingham on 30/10/2014 23:33:09.

Activated rotation in the singlet manifold contributes to a smaller extent for this compound. As expected, ϕ_T is relatively high at room temperature (*ca.* 0.5, table 4). Owing to the enhanced contribution of ^{1}*trans** → ^{1}perp* twisting, the singlet mechanism prevails above this temperature. $\phi_{t \to c}$ shows again three different steps as a function of temperature, corresponding again to the singlet (above room temperature) and the triplet (at lower temperatures) mechanisms and to the rigidity of the medium (low-temperature range). Also the trend of ϕ_T *versus* temperature fits with those of ϕ_F and τ_F, the three parameters remaining constant below *ca.* 280 K. The effect of temperature on fluorescence parameters (table 3) implies a small contribution of singlet mechanism at room temperature ($\phi_{t \to p} \approx 0.04$).

Compared to the parent molecule the change in ϕ_{ISC} of Br-1-StN is smaller on going from non-polar to polar solvents, assuming $\phi_{ISC} = 2 \times \phi_{t \to c}$ around 200 K (fig. 1–4). The contribution of the singlet mechanism at room temperature is well evident. A rough estimate of the quantum yields is $\phi_F = 0.3$–0.4, $\phi_{t \to p} \approx 0.3$ and $\phi_{ISC} \approx 0.2$–0.4. This enhancement of ϕ_{ISC} compared to the parent molecule is in line with the result that the Stern–Volmer constants, obtained from quenching of $\phi_{t \to c}$ and τ_T, are much closer for Br-1-StN in acetonitrile (*ca.* 150 and 350 dm^3 mol^{-1}, respectively) than for 1-StN (*ca.* 100 and 5500 dm^3 mol^{-1}, respectively).

p-Substitution of *trans*-1-StN by the nitro group brings ϕ_{ISC} at *ca.* 300 K close to the limit $1 - \phi_F$ which is virtually unity in MCH and *ca.* 0.8 in toluene.[20] Thus, the pure triplet pathway for *trans* → *cis* photoisomerization of 1-StN is best approached by NO_2-1-StN in non-polar solvents. The spectral properties (absorption of both isomers, fluorescence of the *trans* isomer and T–T absorption) of NO_2-1-StN are quite different from those of 1-StN and the chlorine and bromine derivatives. This is not surprising in view of the behaviour of the stilbenes.[21, 25] However, the temperature dependence of the triplet decay is similar for NO_2-1-StN and 1-StN (table 5). Here, the main exception is Br-1-StN, due to the internal heavy-atom effect, as also found for stilbenes.[21] For a given solvent, the two characteristic temperatures, T_v and T_o, exhibit close similarities for the four 1-StNs and even for stilbenes (table 5). The reason is the viscosity-induced barrier against twisting towards the ^{3}perp* configuration which is common for both systems.

Conclusion

The present data for *trans*-1-StN confirm the co-existence of singlet and triplet mechanisms in the room temperature photoisomerization, the former being the predominant mechanism above 240–280 K (where $\phi_{t \to c} \gg \phi_{ISC}$) and the second one becoming the only mechanism at low temperatures (220–260 K). These temperature ranges, indicated by the new photochemical and photophysical results, are 20–30 K lower than those previously reported.[6] The mixed singlet–triplet mechanism also accounts for the *trans* → *cis* photoisomerization of Cl-1-StN and Br-1-StN.

The authors are grateful to Professor D. Schulte-Frohlinde (Mülheim) for his generous support and thank Professor G. Bartocci (Perugia) for useful discussions, Professor G. Galiazzo (Padova) for samples of the compounds investigated and Mrs C. Hüsken and Mr L. J. Currell (Mülheim) for technical assistance.

References

1 P. Bortolus and G. Galiazzo, *J. Photochem.*, 1973/74, **2**, 361.
2 G. G. Aloisi, U. Mazzucato, J. B. Birks and L. Minuti, *J. Am. Chem. Soc.*, 1977, **99**, 6340.
3 U. Mazzucato, *Pure Appl. Chem.*, 1982, **54**, 1705 and references cited therein.
4 U. Mazzucato, *Gazz. Chim. Ital.*, 1987, **117**, 661.
5 G. S. Hammond, S. C. Shim and S. P. Van, *Mol. Photochem.*, 1969, **1**, 89.
6 G. Bartocci, F. Masetti, U. Mazzucato and G. Marconi, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 1093.

View Article Online

Published on 01 January 1989. Downloaded by University of Birmingham on 30/10/2014 23:33:09.

7 T. Wismontski-Knittel, G. Fischer and E. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1930.
8 H. Görner, D. W. Eaker and J. Saltiel, *J. Am. Chem. Soc.*, 1981, **103**, 7164.
9 E. Haas, G. Fischer and E. Fischer, *J. Phys. Chem.*, 1978, **82**, 1638.
10 E. Fischer, *J. Photochem.*, 1985, **28**, 139.
11 E. Fischer and N. Castel, *J. Mol. Struct.*, 1986, **145**, 367.
12 Yu. B. Sheck, N. P. Kovalenko and M. V. Alfimov, *J. Lumin.*, 1977, **15**, 157.
13 J. B. Birks, G. Bartocci, G. G. Aloisi, S. Dellonte and F. Barigelletti, *Chem. Phys.*, 1980, **51**, 113.
14 G. Bartocci, U. Mazzucato, F. Masetti and G. G. Aloisi, *Chem. Phys.*, 1986, **101**, 461.
15 J. Saltiel and D. W. Eaker, *J. Am. Chem. Soc.*, 1984, **106**, 7624.
16 I. Baraldi, F. Momicchioli and G. Ponterini, *J. Mol. Struct.*, 1984, **110**, 187.
17 J. Saltiel and J. L. Charlton, in *Rearrangements in Ground and Excited States*, ed. P. de Mayo (Academic Press, New York, 1980), vol. 3, pp. 25–89 and references therein.
18 T. Wismontski-Knittel and P. K. Das, *J. Phys. Chem.*, 1984, **88**, 2803.
19 R. S. Becker, personal communication.
20 H. Görner, F. Elisei, U. Mazzucato and G. Galiazzo, *J. Photochem.*, 1988, **43**, 139.
21 H. Görner and D. Schulte-Frohlinde, *J. Phys. Chem.*, 1979, **83**, 3107.
22 F. Elisei, U. Mazzucato, H. Görner and D. Schulte-Frohlinde, *J. Photochem.*, 1987, **37**, 87.
23 G. Bartocci, U. Mazzucato, F. Masetti and G. Galiazzo, *J. Phys. Chem.*, 1980, **84**, 847.
24 S. A. Krysanov and M. V. Alfimov, *Chem. Phys. Lett.*, 1983, **98**, 176.
25 D. Schulte-Frohlinde and H. Görner, *Pure Appl. Chem.*, 1979, **51**, 279.
26 J. Saltiel and J. T. D'Agostino, *J. Am. Chem. Soc.*, 1972, **94**, 6445 and references cited therein.

Paper 8/02615G; *Received* 30*th June*, 1988