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Effect of the nitrogen heteroatom on the photophysics and photochemistry of *trans*-1-styrylnaphthalene and *trans*-9-styrylphenanthrene in different solvents

Giampiero Bartocci, Ugo Mazzucato and Anna Spalletti

Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy (Received March 7, 1995)

Abstract. The effect of the nitrogen heteroatom on the excited state properties of *trans*-1-styrylnaphthalene (1-StN) and *trans*-9-styrylphenanthrene (9-StPh) has been investigated by fluorimetric and photochemical techniques. The relaxation processes of two aza analogues of each of these diarylethylenes, bearing the nitrogen atom in the mono- and polycyclic aryl group, respectively, were studied in different solvents and over a large temperature range. The aza derivatives have smaller radiative and large reactive decay yields compared with the parent hydrocarbons. The polar solvent reduces the torsional energy barrier and favours the *trans* \rightarrow *cis* photoisomerization while intramolecular hydrogen bonding may slow down the rate of the reactive deactivation.

Introduction

The insertion of one or more heteroatoms in the phenyl group(s) of trans-stilbene (S) markedly affects its photophysical and photochemical behaviour^{1,2}. The effect of the nitrogen atom has been mainly investigated for the trans isomers of the three isomeric styrylpyridines (n-StP) and the three symmetrical 1,2-di(n-pyridyl)ethenes (n-DPE), with n = 2, 3, 4^{1,3-5}. It has been shown that the N atom in the ortho or para position with respect to the ethene bridge (n = 2 and 4) leads to a decrease of both the fluorescence and *trans* \rightarrow *cis* photoisomerization quantum yield (the latter being particularly low for DPEs) in non-polar solvents compared with stilbene and the aza derivatives with N in meta position (n = 3). This behaviour has been attributed to concurrent internal conversion (IC) to the ground state induced by the vibronic coupling between the closely located ${}^{1}(n,\pi^{*})$ and ${}^{1}(\pi,\pi^{*})$ states. All these trans isomers were found to be characterized by a very small yield of intersystem crossing (ISC)⁶ similar to the case of the parent hydrocarbon, trans-stilbene⁷. Therefore, as for stilbene, the isomerization proceeds in the singlet manifold by a ¹trans * \rightarrow ¹perp * twisting to the perpendicular configuration from which IC to the ground state $^{1}perp$ and partitioning (almost 50:50) to the trans and cis ground-state isomers takes place⁸. The ground-state conformational equilibria of these N-positional isomers of trans-azastilbene have also been investigated^{9,10}. Similar studies of the effect of the position of the styryl substituent on photoisomerization and rotamerism have also been reported for styrylquinolines and isoquinolines¹¹.

Since we have previously investigated several series of stilbene-like molecules where one (or both) phenyl group(s) were replaced by larger polycyclic aryl groups¹², it was interesting to study the N-atom effect in some *trans*-1,2-diarylethene analogues bearing the heteroatom in the phenyl or in the polycyclic group, respectively. Preliminary measurements on the *n*-pyridyl (n = 2, 3, 4) derivatives of the *n*-naphthyl-¹³ and *n*-phenanth-

rylethenes¹⁴ have shown that when the nitrogen is introduced into the phenyl ring, its effect differs in the ortho and para positions compared with the meta position, in a similar fashion to that observed in azastilbenes. As an example, in both series of the 1-(1-naphthyl)-2-(npyridyl)ethene (1,n-NPE) and 1-(9-phenanthryl)-2-(npyridyl)ethene (9, n-PhPE) isomers, we found that the meta compound (n = 3) behaved similarly to the corresponding hydrocarbons, 1-styrylnaphthalene $(1-\text{StN})^{12,15}$ and 9-styrylphenanthrene (9-StPh)¹⁶, while the *ortho* (n = 2) and para (n = 4) compounds showed a substantial reduction in the yield of radiative deactivation but a parallel increase of the yield of the reactive pathway. Similar behaviour has been observed when the nitrogen atom is in the polycyclic group and in the same ring as the styryl substituent¹⁷. On the other hand, when the N atom is in a ring of the polycyclic group different from that bearing the styryl substituent, its effect was much less important, the photochemistry and photophysics being similar to that of the corresponding hydrocarbon^{11,17}. To analyze these effects, systematic research was carried out on two aza analogues of both 1-StN and 9-StPh. The study of the temperature and solvent effects on the spectral properties and on the photophysical and photochemical parameters of the molecules investigated, and a comparison with the known behaviour of StPs and DPEs, allowed a clear description to be given of their excited state properties.

Experimental

The *trans* isomers of the following compounds were investigated: 1-styrylnaphthalene (1-StN) and its aza analogues 1-(1-naphthyl)-2-(4-pyridyl)ethene (1,4-NPE) and 4-styrylquinoline (4-StQ), 9styrylphenanthrene (9-StPh) and its aza analogues 1-(9-phenanthryl)-2-(4-pyridyl)ethene (9,4-PhPE) and 10-styryl-1-azaphenanthrene ^a

^a IUPAC name: 5-styrylbenzo [f] quinoline

Trans isomer	Solvent	Absorption $\bar{\nu}_{max}$ (cm ⁻¹)	Fluorescence $\bar{\nu}_{max}$ (cm ⁻¹)
1-StN	MCH/3MP (9/1)	31150 [2.0]	27100-25770-24690 ^s
	PrCN	30770 [2.2]	26810-25580-24150 ^s
	EtOH	30860 [2.3]	26950-25640-24510 ^s
1,4-NPE	MCH/3MP (9/1)	30770 [1.8]	26810-25640-24270
,	PrCN	30490 [1.9]	24570
	EtOH	30120 [1.9]	24040
4-StQ	MCH/3MP (9/1)	31250 [1.9]	26670 ^s -25380-24040
	PrCN	30770 [2.2]	24570
	EtOH	30300 [2.1]	23700
9-StPh	MCH/3MP (9/1)	31150 [2.2]	26600-25190-23920 ^s
	PrCN	30680 [2.4]	26320-24880-23530 ^s
	EtOH	30860 [2.5]	26390-25000-23750 ^s
9,4-PhPE	MCH/3MP (9/1)	30770 [1.8]	26320-24880-23590
	PrCN	30490 [1.9]	23980
	EtOH	30030 [1.8]	23530
10-St-1-APh	MCH/3MP (9/1)	29410 [2.4]	26110-24750-23470 ^s
	PrCN	29410 [2.5]	24390
	EtOH	29410 [2.3]	23530

Table I Absorption and emission maxima of trans-1-StN, trans-9-StPh and some of their aza analogues in MCH / 3MP (dielectric constant, D 2.0), PrCN (D 24.8) and EtOH (D 24.6) at room temperature. Values in parentheses refer to the molar extinction coefficient, ε (10⁴ M⁻¹·cm⁻¹).

(10-St-1-APh). The *cis* isomers, needed for the spectrophotometric measurements of the photoreaction yield, were obtained by photoisomerization of the *trans* isomers on preparative scale. All compounds had been prepared previously^{13,14}. Their purity was checked by HPLC analysis using a Waters apparatus equipped with an Erbasil C_{18} column and a UV detector (eluent: MeCN/H₂O 80/20 v/v).

The solvents acetonitrile (MeCN), butyronitrile (PrCN), methylcyclohexane (MCH) and 3-methylpentane (3MP), all from Carlo Erba RP, were purified by standard procedures before use.

The trans $\rightarrow cis$ photoisomerization quantum yield ($\phi_{1\rightarrow c}$, mean deviation, ca. 7%) was determined by irradiation of an olefin solution ($10^{-3}-10^{-4}$ M) at 313 or 366 nm using an Osram HBO 200 W mercury lamp coupled with Balzers interference filters. The conversion percentage, measured spectrophotometrically (Perkin-Elmer, Lambda 5) and by HPLC, was held at below 10% to avoid competition from the back-photoreaction.

The fluorescence spectra and quantum yields ($\phi_{\rm F}$) were measured with a SPEX Fluorolog-2 F112AI spectrofluorometer. The quantum yield determinations (mean deviation of three independent experiments, ca. 5%) were carried out in dilute solutions (absorbance ≤ 0.1 at the excitation wavelength) using 9,10-diphenylanthracene in cyclohexane ($\phi_{\rm F}$ 0.93)¹⁸ as standard. The fluorescence lifetimes ($\tau_{\rm F}$, mean deviation of three independent experiments, $\leq 5\%$) were measured by an Edinburgh Instrument 199S fluorescence spectrofluorometer.

A cryostat (Oxford Instruments DN 1704) was used to control the temperature in the 77–350K range. For measurements of ϕ_F as a function of temperature, the value at room temperature was used as a reference, taking into account the changes in absorbance and refractive index with temperature. The ϕ_F and τ_F values at 77K were measured in fast cooling experiments by direct immersion in pure nitrogen.

The solutions were deoxygenated by purging with nitrogen.

Results and discussion

Spectral properties

Table I shows the absorption and fluorescence properties of the six *trans* isomers investigated in different solvents. They show a strong unstructured absorption in the region 280-360 nm, characteristic of a "stilbenic" system. The phenanthrenic derivative with the N atom in the polycyclic group, 10-St-1-APh, shows a marked red shift (*ca.* 1700 cm⁻¹) with respect to the parent hydrocarbon, 9-StPh, probably due to intramolecular hydrogen bonds favouring more planar geometries. In fact, theoretical calculations have indicated an angle $\varphi = 20^{\circ}$ around the arene-ethene bond for the equilibrium conformation of 9-StPh in the ground state¹⁶. No sign of $n \to \pi^*$ transitions was observed, these being hidden by the intense S_0 - S_1 ($\pi \to \pi^*$) transition. The fluorescence spectra show a structured band in the non-polar solvent in the region 370-420 nm with vibronic interval $\Delta \nu \approx 1300 \text{ cm}^{-1}$ for the aza derivatives of 1-StN and $\Delta \nu \approx 1400 \text{ cm}^{-1}$ for those of 9-StPh, characteristic of the naphthyl and phenanthryl chromophores, respectively. In polar solvents, a red shift was observed for both the absorption and emission spectra indicating that the lowest emitting state has an ionic nature $({}^{1}L_{a}{}^{-1}B_{u})$, as already found for the parent hydrocarbons and in agreement with the theoretical description¹². Moreover, a loss of vibronic structure was found in the emission band for the aza derivatives. No significative changes in the spectral shape



Scheme 1. Trans isomers investigated.



Figure 1. Absorption and fluorescence (normalized at unitary area) spectra of trans-10-St – 1-APh in a non-polar solvent as a function of temperature.

were observed between PrCN and EtOH thus indicating that intermolecular H bonds do not play an important role.

Decreasing temperature and increasing viscosity produced substantial changes in the spectral shape. In particular, a red shift of the bands and the appearance of a vibronic structure (with an intensity increase in the vibronic components at lower energies) and an increase in the vibrational interval was found (Figure 1). This behaviour, similar to that already observed for *trans*-stilbene¹⁹ and StPs⁵, has been explained on the basis of excitation of different distributions of non-planar conformations in these flexible molecules, due to different twist angles around the arene-ethene quasi-single bonds in the ground state. In the emission spectra one can distinguish between two

cases: (i) when the emission originates from a relaxed geometry in S_1 , the spectrum is already structured at room temperature and (*ii*) when the emission comes from Franck-Condon states, the spectrum only shows a vibronic structure in rigid matrices (see Figure 2).

Photophysics and photochemistry

Table II shows the fluorescence quantum yields, lifetimes and kinetic parameters and the photoisomerization quantum yields of the *trans* compounds investigated in three low-viscosity solvents of different polarity and proticity at room temperature. These values are in a reasonable agreement with those previously reported, when available in the same or similar solvents^{13–16}.

The results of Table II in the non-polar solvent show that the n,π^* states introduced by the heteroatom have a much smaller effect compared to that found for azastilbenes³⁻⁵. This is probably due to reduced proximity and then to smaller interaction of the lowest ${}^{1}(\pi,\pi^*)$ state of



Figure 2. Absorption and fluorescence (normalized at unitary area) spectra of trans-4-StQ in PrCN as a function of temperature.

arylic or ethenic character with the upper (n, π^*) states. In this solvent, the presence of the heteroatom causes a decrease in the emission yield of the hydrocarbon (small for 10-St-1-APh but particularly high for 4-StQ) and an increase in the photoreaction yield (not observed for 10-St-1-APh but high for the 4-pyridyl derivatives). The polar solvents, both aprotic and protic, lead to a decrease in $\phi_{\rm F}$ (not observed for 10-St-1-APh) and to an increase of $\phi_{t \to c}$ in the hydrocarbons and 4-StQ while a small decrease and a substantial decrease were found in the APh derivative and in the two pyridyl derivatives, respectively. These different effects on the yields can be better understood if one looks at the kinetic parameters. The $k_{\rm F}$ values are of the same order of magnitude for all the compounds and solvents investigated, thus indicating that the nature of the emitting state is the same in all cases, namely a ${}^{1}(\pi,\pi^{*})$ state of ${}^{1}L_{a} - {}^{1}B_{u}$ character, as suggested by the spectral properties. The increase in reactivity of 1-StN and 9-StPh in polar solvents had been ascribed to a decrease in the activation energy of the ${}^{1}trans^{*} \rightarrow {}^{1}perp^{*}$ twisting process ^{15,16}. The fluorescence lifetime is drastically reduced in polar solvents (except that of 10-St-1-APh which increases slightly) in agreement with the faster twisting generally measured. This is probably due-as said above-to the reduced torsional barrier in polar solvents, which stabilize the intermediate $^{1}perp^{*}$ configuration of zwitterionic character more than the $^{1}trans^{*}$ form²⁰. Table III shows the photophysical parameters measured

in a rigid matrix of MCH/3MP and EtOH. The study was here limited to two solvents (the non-polar and protic ones) because of the difficulty in obtaining transparent glass matrices with PrCN. The results show that $\phi_{\rm F}$ never reaches unity, thus indicating that non-radiative and nonreactive processes (ISC and/or IC) are competitive with the radiative pathway in the relaxation of S₁. The lifetime becomes longer in these matrices, as expected from the

Table II Effects of the solvent on the photophysical and photochemical parameters of trans-1-StN, trans-9-StPh and some of their aza analogues at 293K.

	MCH/3MP			PrCN			EtOH				
$\phi_{\rm F}$	$\phi_{\iota \to c}$	$\tau_{\rm F}$ (ns)	$k_{\rm F} (10^8 {\rm s}^{-1})$	$\phi_{\rm F}$	$\phi_{t \rightarrow c}$	$\tau_{\rm F}$ (ns)	$k_{\rm F} (10^8 { m s}^{-1})$	$\phi_{\rm F}$	$\phi_{\iota \rightarrow c}$	$\tau_{\rm F}$ (ns)	$k_{\rm F} (10^8 {\rm s}^{-1})$
1-StN 0.72 1,4-NPE 0.10 4-StQ 0.01 9-StPh 0.69 9,4-PhPE 0.15	0.15 0.58 0.26 0.14 0.47	$ \begin{array}{c c} 1.8 \\ 0.22 \\ \leq 0.2 \\ 4.0 \\ 0.73 \\ \end{array} $	4.0 4.6 ≥ 0.55 1.7 2.1	0.39 0.038 0.006 0.42 0.051	0.27 0.51 0.41 0.24 0.39	$ \begin{array}{r} 1.0 \\ \leq 0.2 \\ \leq 0.2 \\ 3.0 \\ \leq 0.2 \end{array} $	$3.9 \ge 1.9 \ge 0.3 \\ 1.4 \ge 2.6$	0.38 0.027 0.009 0.40 0.031	0.28 0.48 0.53 0.21 0.38	$ \begin{array}{r} 1.1 \\ \leq 0.2 \\ \leq 0.2 \\ 2.9 \\ \leq 0.2 \end{array} $	$3.6 \ge 1.4 \ge 0.45 \ 1.4 \ge 1.6$

Table III Fluorescence quantum yield, lifetime and rate constant of trans-1-StN, trans-9-StPh and some of their aza analogues in rigid matrices of MCH / 3MP and EtOH at 77K.

Trans isomer	MCH/3MP			EtOH			
	$\phi_{\rm F}$	$\frac{\tau_{\rm F}}{(\rm ns)}$	$(10^{8} \text{ s}^{\text{F}^{-1}})$	$\phi_{\rm F}$	$\tau_{\rm F}$ (ns)	$\binom{k_{\rm F}}{(10^8 {\rm s}^{-1})}$	
1-StN 1,4-NPE 4-StQ 9-StPh 9,4-PhPE 10-St 1-APb	0.75 0.76 0.17 0.70 0.72 0.75	1.8 1.7 1.7 2.2 1.7	4.2 4.5 1.0 3.2 4.2 3.3	0.69 0.71 0.58 0.63 0.75	1.8 2.1 1.7 3.7 1.9	3.8 3.4 3.4 1.7 4.0	

inhibition of the activated torsional process. In EtOH, no significant changes in the ϕ_F values were found with respect to MCH/3MP, except for 4-StQ whose yield increased markedly in the protic solvent.

Compared with the $k_{\rm F}$ values measured at room temperature, the values in matrices are *ca.* 15% higher for 1-StN and its aza derivatives, as expected from the refraction index effect. On the other hand, for 9-StPh and its aza derivatives, the $k_{\rm F}$ values are *ca.* twice those at room temperature. This "anomalous" result could be due to a viscosity-induced change of non-planar equilibrium geometries in S_1 towards more planar conformations, as observed for StPs⁵.

The temperature effect on ϕ_F was explored in MCH/3MP and EtOH in the 77–350 K range using the equation

$$\ln\left[\left(\phi_{\rm F}^{\rm lim}/\phi_{\rm F}\right) - 1\right] = \ln\left({}^{1}\!{\rm A}\tau_{\rm F}^{\rm lim}\right) - {}^{1}\!\Delta E/(R \cdot T) \qquad (1)$$

where the superscript 1 refers to the singlet manifold and the superscript lim refers to the values measured at low temperature when the activated process(es) is(are) inhibited. An example is shown in Figure 3 for 9,4-PhPE in ethanol. Table IV shows the Arrhenius parameters and the rate constants for the activated process thus obtained. The high values of the *A* parameter (~ $10^{11}-10^{13}$ s⁻¹), characteristic of a spin-allowed process, and the large increase of ${}^{1}k_{act}$ in polar solvent, indicate that the ${}^{1}trans^{*}$ $\rightarrow {}^{1}perp^{*}$ torsional process is the activated pathway in the deactivation of the S_{1} state. Only for 4-StQ, can a contribution of the IC process in the ${}^{1}k_{act}$ value not be excluded in inert solvent on the basis of the low quantum



Figure 3. Fluorescence quantum yield of trans-9,4-PhPE in ethanol as a function of temperature. The inset shows the corresponding Arrhenius plot (Eqn. 1).

yields of both fluorescence and isomerization (see Tables II and III). Except for 10-St-1-APh, the activation energy decreases strongly for the aza derivatives compared with the corresponding hydrocarbons and also decreases in polar solvents. The small $\phi_{t \rightarrow c}$ value (*ca.* 0.14) of 10-St-1-APh measured in non-polar and polar solvents is probably due to a high torsional barrier in both S_1 and T_1 caused by intramolecular hydrogen bonding, as already reported for 1-styrylisoquinoline in inert solvents²¹. In agreement with the spectral results, the formation of such bonds forces the molecule into a "transoid" conformation which leads to an increase in the torsional barrier in T_1 too, even if smaller than that in S_1 .

Since the lifetimes at room temperature in polar solvents were generally shorter than the resolution time of our apparatus (ca. 0.2 ns), they were also estimated by the following indirect methods:

(i) From the lifetime measured at 77K (where the twisting was inhibited) and the quantum yields measured at low and room temperature, assuming that $k_{\rm F}$ did not vary in the 77–350K range (Eqn. 2).

$$F_{\rm F}^{293} = \phi_{\rm F}^{293} \cdot \tau_{\rm F}^{77} / \phi_{\rm F}^{77}$$
(2)

Table IV Arrhenius parameters and rate constants of the activated process(es) at 293K for trans-1-StN, trans-9-StPh and some of their aza analogues in MCH/3MP and EtOH.

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Trans isomer	MCH/3MP			EtOH			
	${}^{1}\Delta E$ (kcal·mol ⁻¹)	(10^{12} s^{-1})	$\begin{array}{c c} {}^{1}k_{act} \\ (10^{8} {\rm s}^{-1}) \end{array}$	$\frac{{}^{1}\Delta E}{(\text{kcal}\cdot\text{mol}^{-1})}$	^{1}A (10 ¹² s ⁻¹)	$\binom{{}^{1}k_{\rm act}}{(10^8{ m s}^{-1})}$	
1-StN 1,4-NPE 4-StQ 9-StPh 9,4-PhPE 10-St-1-APh	9.2 3.8 1.5 9.8 4.2 > 12	250 2.6 0.10 100 1.7	0.34 38 76 0.049 12.5	7.2 3.6 2.4 7.3 3.5 > 12	100 5.7 2.9 25 4.5	4.2 117 470 0.90 110	

Table V Experimental and calculated fluorescence lifetimes (τ_F/ns) of trans-1-StN, trans-9-StPh and some of their aza analogues in MCH/3MP and EtOH (data in parentheses refer to cases where k_F was temperature-dependent, see text).

Trans isomer		MCH/3MP		EtOH			
	Exper.	From Eqn. 2	From Eqn. 3	Exper.	From Eqn. 2	From Eqn. 3	
1-StN 1,4-NPE 4-StQ 9-StPh 9,4-PhPE 10-St-1-APh	$ \begin{array}{c c} 1.8 \\ 0.22 \\ \leq 0.2 \\ 4.0 \\ 0.73 \\ 3.1 \end{array} $	$ \begin{array}{c} 1.7 \\ 0.22 \\ 0.11 \\ (2.2) \\ (0.35) \\ (1.7) \end{array} $	1.5 0.24 0.13 (3.6) (0.33)	$ \begin{array}{c} 1.1 \\ \leq 0.2 \\ \leq 0.2 \\ 2.9 \\ \leq 0.2 \\ 4.6 \end{array} $	$ \begin{array}{r} 1.0\\ 0.080\\ 0.026\\ (2.3)\\ (0.078)\\ (2.6) \end{array} $	1.1 0.083 0.021 (2.8) (0.088)	

Table VI Photophysical and photochemical parameters for trans-1-StN and two aza analogues in MCH / 3MP and EtOH at 293K.

Parameters	N	MCH/3N	1P	EtOH			
	1-StN	1,4-NPE	4-StQ	1-StN	1,4'-NPE	4-StQ	
$ \phi_{\rm F} \phi_{\rm t \to c} \phi_{\rm T} (10^8 {\rm s}^{-1}) k_{\rm rr} (10^8 {\rm s}^{-1}) {}^1k_{\rm t \to p} + k_{\rm ISC} (10^8 {\rm s}^{-1}) {}^1k_{\rm act} (10^8 {\rm s}^{-1}) $	0.72 0.15 1.8 4.0 1.7 1.8 0.34	0.10 0.58 0.22 4.5 41 45 a 38	0.011 0.26 0.12 0.92 82 43 76	0.38 0.28 1.1 3.6 5.6 5.1 4.2	0.027 0.48 0.082 3.3 118 117 117	0.009 0.53 0.023 3.9 431 435 a 470	
$\begin{bmatrix} k_{\rm IC} (10^8 {\rm s}^{-1}) \\ k_{\rm ISC} (10^8 {\rm s}^{-1}) \end{bmatrix}$	< 0.01 ≤ 1.6	< 0.01 $ \le 1.4$	39 ≤ 4.9	$ \le 0.5 \\ \le 1.7$	$\begin{array}{c} < 0.01 \\ \le 1.4 \end{array}$	< 0.01 ≤ 2.4	

^a In the application of Eqn. 7 to these compounds, a maximum value of unity was assigned to the ratio $\phi_{t \to c} / \alpha$.

(ii) From the parameters for the non-radiative processes at 293K, using Eqn. 3 where the sum $k_{IC} + k_{ISC}$, assumed to be temperature-independent, was estimated by the ratio $(1 - \phi_F)/\tau_F$ measured at 77K.

$$\tau_{\rm F} = \phi_{\rm nr} / k_{\rm nr} = (1 - \phi_{\rm F}) / ({}^{1}k_{\rm act} + k_{\rm ISC} + k_{\rm IC})$$
(3)

The latter method seems to be more reliable in the present case since the change in the distribution of twisted conformations with temperature, as indicated by the spectra, can lead to changes in the radiative kinetic parameter on going from 77K to higher temperatures, which should have less effect on the parameter derived by Eqn. 3. Anyway, when a comparison was possible between the values derived by Eqns. 2 and 3 and the value directly measured at 298K, the three parameters were in reasonable agreement. Table V shows the experimentally measured lifetimes and those derived through Eqns. 2 and 3. For phenanthrene and its aza derivatives, the derived values are in parentheses since the assumption of a temperature-independent $k_{\rm F}$ (present in both methods) can no longer be valid for the reasons mentioned above. When the experimental lifetime was shorter than 0.2 ns, averages of the values derived by the two methods, when available, are given in Table V. These lifetimes allowed the kinetic parameters for the competitive relaxation processes of S_1 at room temperature to be obtained through the usual relationships in Eqns. 4 and 5.

$$k_{\rm F} = \phi_{\rm F} / \tau_{\rm F} \tag{4}$$

$$k_{\rm nr} = (1 - \phi_{\rm F}) / \tau_{\rm F} \tag{5}$$

The isomerization quantum yield is the sum of the singlet and triplet contributions and then:

$$\phi_{t \to c} = {}^{1}\phi_{t \to c} + {}^{3}\phi_{t \to c}$$
$$= {}^{1}k_{t \to p} \cdot \alpha \cdot \tau_{F} + k_{ISC} \cdot \tau_{F} \cdot {}^{3}k_{t \to p} \cdot \alpha \cdot \tau_{T}$$
(6)

1

where α is the partitioning factor (assumed to be 0.5 in both the singlet and triplet state)^{8,12} when ^{1,3}perp decay to

the *trans* and *cis* ground-state isomers; since for these molecules the *trans* \rightarrow *perp* twisting is the fastest decay process in the triplet manifold $({}^{3}k_{t} \rightarrow p \equiv 1/\tau_{T})^{12}$, Eqn. 6 reduces to Eqn. 7.

$${}^{1}k_{\iota \to p} + k_{\rm ISC} = \phi_{\iota \to c} / (\alpha \cdot \tau_{\rm F})$$
⁽⁷⁾

Moreover:

$${}^{1}k_{\text{act}} = {}^{1}A \cdot \exp\left[-{}^{1}\Delta E/(R \cdot T)\right]$$
(8)

$$k_{\rm IC} = k_{\rm nr} - \left({}^{1}k_{\rm t \to p} + k_{\rm ISC}\right) \tag{9}$$

$$k_{\rm ISC} \le \left(1 - \phi_{\rm F}^{77}\right) / \tau_{\rm F}^{77} \tag{10}$$

In the latter relationship, one has to consider that the term on the right contains $k_{\rm IC}^{77}$ and to assume that $k_{\rm ISC}$ is temperature-independent.

Tables VI and VII collate the photophysical and photochemical parameters for the six compounds. The kinetic parameters show that the twisting process (singlet and/or triplet mechanism) predominates among the other nonradiative processes $(k_{nr} \cong {}^{1}k_{t \rightarrow p} + k_{ISC})$. This indicates that the $S_1 \rightarrow S_0$ IC process does not compete in the deactivation of S_1 , except for 4-StQ in the non-polar solvent, for which a substantial IC contribution (*ca.* 50% of the non-radiative processes) was evaluated. The latter behaviour is probably due to a smaller energy gap between the lowest ${}^{1}(\pi,\pi^*)$ and ${}^{1}(n,\pi^*)$ states and a consequent larger S_1-S_0 vibronic coupling. For the other compounds, k_{IC} was always very small, generally much smaller than k_{ISC} .

Contrary to the case of the parent hydrocarbons^{15,16}, in the aza derivatives the ${}^{1}k_{act}$ values are close to the $({}^{1}k_{1} \rightarrow p + k_{ISC})$ values, thus indicating that isomerization proceeds by a prevalent singlet mechanism induced by a smaller torsional barrier in S_1 (see Table IV). The k_{ISC} values are generally small, the ISC process becoming competitive with the radiative one only at low temperatures in media of high viscosity.

In the case of 10-St-1-APh, for which evidence of intramolecular H-bond formation was mentioned above, the sum ${}^{1}k_{t \rightarrow p} + k_{ISC}$ is close to k_{ISC} indicating that the twisting is mainly operative in the triplet manifold because of the too high torsional barrier caused by the H bonds.

In the polar and protic solvent, the ${}^{1}k_{act}$ generally increases and the k_{1C} of 4-StQ decreases. This behaviour is due to the decrease of the torsional barriers, as mentioned above, and to a larger energy gap between the ${}^{1}(\pi,\pi^{*})$ and ${}^{1}(n,\pi^{*})$ states. The 10-St-1-APh compound is peculiar in this respect. In fact, its relaxation processes are practically independent of the solvent since the H bond, still present in EtOH (in contrast to 1-styry-lisoquinoline where intermolecular H bonds have been reported to prevail in alcohols²¹), maintains high torsional barriers in both S_1 and T_1 . In this case, the *trans* $\rightarrow cis$ photoisomerization proceeds through a triplet mecha-

Table VII Photophysical and photochemical parameters for trans-9-StPh and two aza analogues in MCH / 3MP and EtOH at 293K.

Parameters	MCH/3MP			EtOH			
	9-StPh	9,4-PhPE	10-St-1-APh	9-StPh	9,4-PhPE	10-St-1-APh	
$\phi_{\rm F} \\ \phi_{\rm t \to c} \\ \tau_{\rm F} ({\rm ns}) \\ k_{\rm F} (10^8 {\rm s}^{-1}) \\ k_{\rm nr} (10^8 {\rm s}^{-1}) \\ {}^1k_{\rm t \to p} + k_{\rm ISC} (10^8 {\rm s}^{-1}) \\ {}^1k_{\rm act} (10^8 {\rm s}^{-1}) \\ k_{\rm IC} (10^8 {\rm s}^{-$	$\begin{array}{c} 0.69\\ 0.14\\ 4.0\\ 1.7\\ 0.78\\ 0.70\\ 0.049\\ < 0.07\\ < 0.8\end{array}$	0.15 0.47 0.73 2.1 12 13 12.5 < 0.01	0.55 0.14 3.1 1.8 1.4 0.9	$0.40 \\ 0.21 \\ 2.9 \\ 1.4 \\ 2.1 \\ 1.5 \\ 0.90 \\ \leq 0.6 \\ \leq 1.2$	0.031 0.38 0.09 3.5 110 86 110 24	0.56 0.10 4.6 1.2 0.96 0.43	
$k_{\rm ISC}$ (10° s °)	≤ 0.8	≤ 1.0	≤ 1.1	≤ 1.2	≤ 1.3	≤ 0.94	

nism. The slight decrease of $\phi_{t \rightarrow c}$ in EtOH could depend on the fact that the deactivation processes of S_1 originates from Franck-Condon states (see spectral properties), namely from distorted geometries for which the IC process can become competitive with the radiative and reactive ones³.

Conclusions

The present study of the heteroatom and solvent effects on the excited state properties of 1-StN and 9-StPh, even if limited to few compounds and few solvents, gave most informative results.

In the two parent hydrocarbons, the high activation energy to twisting in S_1 leads to a mixed singlet and triplet mechanisms, the latter prevailing at low temperatures and in non-polar solvents. An increase of the singlet contribution is generally found in their aza derivatives. However, two cases have to be distinguished. When the N atom is introduced in the phenyl ring (1,4-NPE and 9,4-PhPE) or in the same ring of the polycyclic group bearing the styryl substituent (4-StQ), the reduction in activation energy leads to a prevalence of the singlet mechanism in all solvents. The behaviour is similar to that found for styrylpyridines: as in that case, the presence of the n,π states leads to a decrease of the torsional barrier but can have a deactivating role, inducing IC at the expense of the radiative and reactive pathways. On the other hand, when the N atom is in a ring different from that bearing the styryl group (10-St-1-APh), the activation energy in S_1 remains high (in this case, also because of the presence of the intramolecular H bonds) and the trans compound is forced to isomerize in the triplet manifold where the stabilizing effect of the polar solvent becomes negligible. A study of the triplet state of these compounds and of the quantum yields of the T_1 production would aid discrimination between the two series of aza compounds.

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