Effect of pyridyl and thienyl groups on the excited state properties of stilbene-like molecules

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Abstract. The relaxation properties of the lowest excited states of singlet and triplet multiplicity of some *trans*-stilbene-like molecules with two-ring or three-ring polycyclic groups containing nitrogen and sulphur heteroatoms have been studied by stationary and pulsed fluorimetric and photolytic techniques. The kinetic parameters of the competitive relaxation processes, derived from the measured quantum yields and lifetimes, have been compared with the corresponding values of the hydrocarbon analogues to have information on the heteroatom effect on the photoisomerization mechanism. The n, π^* states introduced by the nitrogen atom can play a deactivating role, mainly through vibronic coupling and consequent internal conversion to the ground state. The heavy atom introduced with the thiophene ring favours the spin-orbit coupling and then the rate of intersystem crossing to the triplet manifold. In any case, the position of the heteroatom is an important factor affecting the nature of the lowest excited states and then the radiative and reactive behaviour of these compounds. The presence of polycondensed rings leads to a decrease in the quantum yield of photoisomerization to the *cis* isomers, as reported for the corresponding hydrocarbons, owing to an increase in the torsional energy barrier. The latter is drastically reduced in the polar solvents.

Keywords. Diarylethenes; pyridyl-derivatives; thienyl-derivatives; photophysics; photoisomerization.

1. Introduction

The stilbene analogues 1,2-diarylethenes (DAEs) have been the object of very extensive work in the last three decades (for review articles see [1-13]). Interest in stilbenoid systems arises from their role as models in the study of ultrafast kinetics and for their widespread applications in technology [14] and biology [15].

Since relatively less attention has been paid to hetero-analogues containing nitrogen and, particularly, sulphur atoms, it seems interesting to study the effect of these heteroatoms on the excited state behaviour of DAEs, taking *trans*-stilbene (S) as model compound. It is well known that S isomerizes in the singlet manifold by a slightly activated twisting to the perpendicular (90°) configuration (^{1}perp*), followed by internal conversion (IC) to the ground state ^{1}perp and then partitioning (almost 50:50) to the *trans* and *cis* isomers. The photoisomerization quantum yield, $\phi_{t \to c}$, is ≈ 0.45 in non-polar solvents at room temperature, with a small contribution of fluorescence ($\phi_F = 0.04$), a negligible $S_1 \to T_1$ intersystem crossing ($\phi_{ISC} < 0.01$) and no IC to the ground state. In fact, the fluorescence yield in a rigid matrix at 77 K (when the internal rotation is inhibited) reaches the value of unity [1,16].

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When a phenyl group of stilbene (S) (or both) is replaced by a larger polycyclic aryl group of low S_1 and T_1 energies, as in the styryl derivatives of naphthalene [17], phenanthrene [18] and anthracene [19], the excitation energy is more or less localized in the larger aryl group. Therefore, the nature of S_1 is more arylic than ethenic, fluorescence becomes the prevalent deactivation pathway and ISC can become competitive with twisting in S_1 so that isomerization can occur through a mixed singlet-triplet mechanism or even by a practically exclusive triplet mechanism [20].

We have re-visited recently the aza-analogues of S, in particular those containing the pyridyl group, such as styrylpyridines (StPs) and 1,2-dipyridylethenes (DPEs), which had been under study for a long time with special reference to the role of the nitrogen lone pairs [6,21-26]. The n, π^* states introduced by the pyridine rings can play a deactivating role, mainly through vibronic coupling. The proximity effect of the $^1(n, \pi^*)$ singlet state and the (generally) lowest $^1(\pi, \pi^*)$ state is responsible for the efficiency of the IC process [27,28]. S_1 loses the character of a pure ethenic state and undergoes IC to the ground state, particularly when the N atom is in *ortho* or *para* position with respect to the ethenic bridge. The deactivating effect is stronger on the radiative decay channel (ϕ_F of the order of 10^{-3} only). The reactive pathway becomes practically barrierless but its yield, only slightly reduced for 2-StP ($\phi_{t \to c} = 0.25$) and 4-StP (0.37) [29], is drastically reduced for the corresponding DPEs where the efficiency of IC is larger [24,26]. The photoisomerization mechanism is similar to that of S, namely it implies a slightly activated non-adiabatic pathway involving an absolute minimum in the perp configuration of the potential energy surface of S_1.
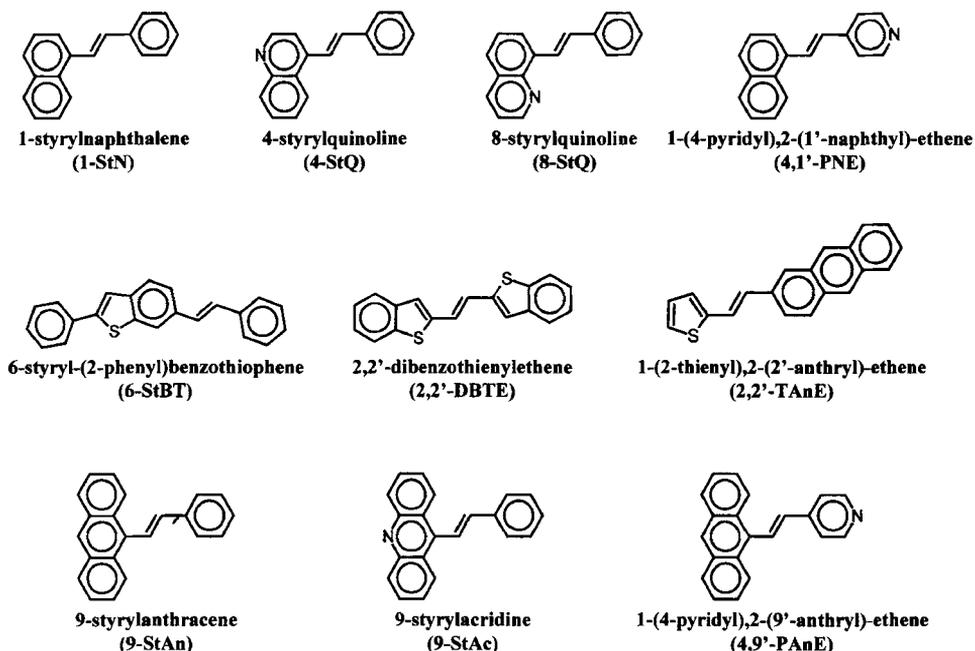
Much less information is available in the literature on the effect of the sulphur atom [30]. The simplest stilbene analogues, styrylthiophene (StT) and 1,2-dithienylethene (DTE) were recently investigated in this laboratory. For 2-StT, the isomerization in n-hexane proceeds by a singlet mechanism, as for S, with an even smaller ϕ_F (0.009) and a similar $\phi_{t \to c}$ (0.42). The presence of the heavy atom induces a higher ISC rate constant compared with S. However, the reactive triplet state is negligibly populated by ISC because of a fast twisting in the singlet manifold. For the symmetrical 2,2'-DTE, the heavy atom effect increases and a mixed singlet-triplet mechanism becomes operative [31].

The aim of the present work is to study further the role of the nitrogen and sulphur heteroatoms in stilbene-like molecules containing two-ring and three-ring polycyclic groups in order to have more general information on the excited state behaviour of this series of compounds.

2. Experimental

Most of the compounds investigated (scheme 1) had been prepared for previous work. The thienyl derivatives were gifts from E Fischer (StBT and TAnE) and R S Becker (DBTE) and were used with further purification when necessary. The solvents were benzene (B), cyclohexane (CH), 9/1 (v/v) methylcyclohexane/3-methylpentane (MCH/3MP), butyronitrile (BuCN) and acetonitrile (AcCN) from Carlo Erba SpA, RP grade. All of them were purified by standard procedures before use.

The quantum yields of photoisomerization and fluorescence and the fluorescence lifetimes were measured in non-polar (MCH/3MP) and polar (AcCN and BuCN) solvents by methods described elsewhere [31,32]. The sensitized yields were studied in B. The lifetimes were generally measured by the single photon counting technique but, for

1-styrylnaphthalene
(1-StN)

4-styrylquinoline
(4-StQ)

8-styrylquinoline
(8-StQ)

1-(4-pyridyl),2-(1'-naphthyl)-ethene
(4,1'-PNE)

6-styryl-(2-phenyl)benzothiophene
(6-StBT)

2,2'-dibenzothienylethene
(2,2'-DBTE)

1-(2-thienyl),2-(2'-anthryl)-ethene
(2,2'-TAnE)

9-styrylanthracene
(9-StAn)

9-styrylacridine
(9-StAc)

1-(4-pyridyl),2-(9'-anthryl)-ethene
(4,9'-PAnE)

Scheme 1.

the shorter ones in the subnanosecond region, the phase-modulation technique, having a better time resolution of $\approx 10\,\text{ps}$, was used.

The λ_{exc} of 347 nm from a ruby laser (J K, second harmonic) was used in nanosecond flash photolysis experiments (pulse width $\approx 20\,\text{ns}$ and energy $< 5\,mJ$ pulse^{-1})[31] in non-polar (CH) and polar (AcCN) solvents. All measurements were carried out at $22 \pm 2°\text{C}$; the solutions were saturated by bubbling with argon. The triplet lifetimes (τ_T), in the sub-μs time-scale, were measured at $\approx 1\,mJ/$pulse by direct excitation, when possible, or by sensitization. For the measurements of singlet oxygen production in aerated solvents, the phosphorescence of $O_2(^1\Delta g)$ was detected by a germanium diode[30]. At least ten decays were averaged for each kinetic measurement.

The uncertainty in the experimental parameters was about 5% for the fluorescence quantum yields and lifetimes, 15% for the triplet quantum yields and lifetimes and 10% for the photoisomerization quantum yields.

3. Results

In principle, the *aza-* and *thio*-derivatives investigated can exist in different conformations in solutions, but in most cases the conformational equilibria only slightly affect their photobehaviour so that one can neglect the complication of rotamers having different excited state properties[4,5,6,33]. Among the compounds investigated, the existence of rotamers becomes important and may affect the photobehaviour in the case of 2,2'-TAnE only. For this compound, conformational equilibria, due to the unfree rotation of the polycyclic group around the single bond with the ethenic carbon, led to a bi-exponential decay of fluorescence with two lifetimes similar to those found for the corresponding styryl-derivative, 2-StAn[19,34]. The fluorescence quantum yield
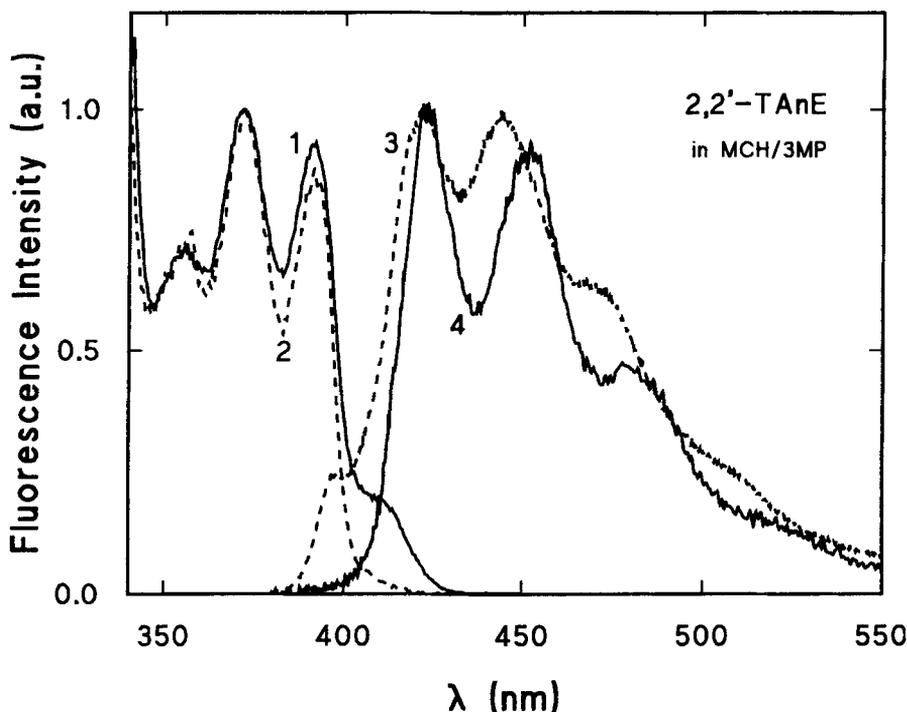
Figure 1. Corrected fluorescence excitation (1,2) and emission (3,4) spectra of 2,2′-TAnE in MCH/3MP at 293 K: curve 1 at $\lambda_{em} = 452\,nm$; curve 2 at $\lambda_{em} = 390\,nm$ (almost pure B rotamer); curve 3 at $\lambda_{exc} = 372\,nm$ and curve 4 at $\lambda_{exc} = 420\,nm$ (almost pure A rotamer).

of the rotamer mixture was roughly resolved into the separate contributions of the two rotamers by selective photoexcitation of the short-lived one on the tail of the absorption spectrum (figure 1). By exciting at 420 nm, one obtains the almost pure spectrum of the short-lived component A with a quantum yield of unity (spectrum 4 in figure 1). By monitoring the emission at 398 nm, where only the longer-lived B component practically emits, one gets the excitation spectrum reflecting the absorption spectrum of the almost pure B rotamer (spectrum 2 in figure 1). By measuring the emission decay kinetics at an isoemissive point and the fluorescence quantum yield as a function of λ_{exc}, the separate properties, fluorescence yields and lifetimes, of the two components were obtained using the method described elsewhere [33,35]. A third emissive component (see the shoulder at 390 nm in spectrum 3 of figure 1), it still under study.

The photophysical and photochemical properties of the compounds investigated are collected in tables 1 to 5. The data of the parent hydrocarbons, 1-styrylnaphthalene (1-StN) and 9-styrylanthracene (9-StAn), are also reported for comparison. The first four tables refer to non-polar and the last one to polar solvents.

Table 1 shows the fluorescence properties at room temperature and 77 K. The emission yield changes drastically with the nature of the aromatic groups going from $\approx 10^{-2}$ for 4-StQ to ≈ 1 for the rotamer A of 2,2′-TAnE at room temperature and for 8-StQ at 77 K. The fluorescence parameters of 4-StQ and 8-StQ were in agreement with those previously reported in different solvents [36]. In general, the fluorescence lifetimes

Table 1. Fluorescence quantum yield and lifetime at room temperature and in a rigid matrix at 77 K of some *aza-* and *thio*-derivatives of 1,2-diarylethenes in MCH/3MP together with the values for the corresponding hydrocarbons for comparison purposes.

Compound	ϕ_F	τ_F(ns)	ϕ_F^{77}	τ_F^{77}(ns)
1-StN[a]	0·72	1·8	0·75	1·8
4,1'-pPNE[b]	0·10	0·22	0·76	1·7
4-StQ[b]	0·011	0·07	0·17	1·7
8-StQ	0·67	2·6	0·98	2·4
6-StBT	0·71	0·94		0·90
2,2'-DBTE[c]	0·34	0·44	0·37	0·59
9-StAn[d]	0·44	3·6	0·49	2·8
4,9'-PAnE	0·49	3·6	0·47	2·4
9-StAc	0·36	5·0	0·50	5·6
2,2'-TAnE(A)	1·0	12·1		14·0
2,2'-TAnE(B)	0·6	94		91

References. [a] 17, [b] 32,45, [c] 31, [d] 19

Table 2. Triplet properties and quantum yields of singlet oxygen production (ϕ_Δ) of some *aza-* and *thio*-derivatives of 1,2-diarylethenes, in non polar solvents at room temperature.

Compound	λ_{max}(nm)	$\tau_T(\mu s)$	$\varepsilon_T(10^3 \, M^{-1} cm^{-1})$	ϕ_T	ϕ_Δ
1-StN[a]	470	0.24		< 0·02	
4,1'-PNE	500[a]	0·15[a]		≤ 0·01[a]	≤ 0·01
4-StQ	500	≤ 0·1			≤ 0·02
8-StQ	520	1·7	12	0·07	0·08
6-StBT	510	0·10		0·10	≤ 0·02
2,2'-DBTE[b]	440	0·63	15·7	0·70	0·56
9-StAn[c]	445	40	19	0·40	
4,9'-PAnE	450	50	14	0·40	0·24
9-StAc	500	30	26	0·07	
2,2'-TanE	430,460,506,620	23	24[d]	0·10	0·66

References. [a] 42, [b] 31, [c] 43
[d] Value obtained at 460 nm

followed the same trend as the quantum yields thus indicating similar values of the radiative rate constants (around $10^8 \, s^{-1}$) and then a similar π, π^* nature of the S_1 state. Measurements of the fluorescence yield in rigid matrices at liquid nitrogen temperature, where the photoreaction is inhibited, showed that, contrary to stilbene, ϕ_F^{77} remained substantially below unity in most cases, thus confirming a relevant competition of radiationless processes deactivating S_1.

The triplet properties are shown in table 2. The ISC pathway has been reported to be of scarce importance for *aza*-stilbenes (StPs and DPEs) whose triplet yield is very small, below 1%, as in the case of S itself[37]. The present laser flash photolysis experiments showed that the $T_1 \rightarrow T_n$ absorption is the dominant transient for compounds bearing
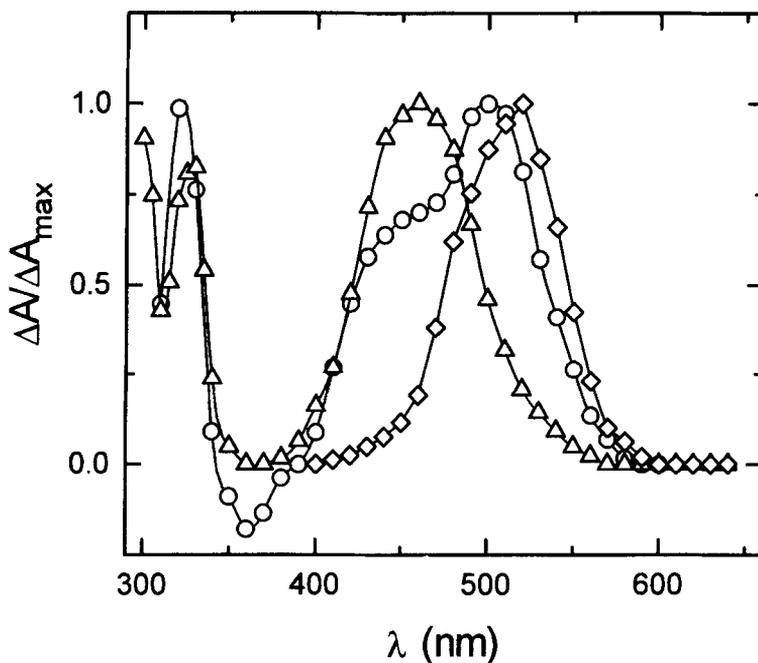
Figure 2. Triplet-triplet absorption spectra of 9-StAc ($\bigcirc$), 4,9'-PAnE ($\triangle$) and 8-StQ ($\diamondsuit$) in CH ($\lambda_{exc} = 347$ nm).

polycondensed rings (some examples for compounds not reported so far are shown in figure 2). The transients, which show broad bands in the region 400–600 nm, appear within the laser pulse and their decays follow first-order kinetics at low pulse intensities. The spectrum shifts towards the red when the transition character changes from a prevalently ethenic to a prevalently aromatic one. Energy transfer experiments were carried out with compounds not showing any transient by direct excitation. A comparison between the ΔA values at λ_{max} of optically matched solutions of DAEs and benzophenone in AcCN allowed the $\varepsilon_T \phi_T$ products to be obtained using $\varepsilon_T \phi_T = 6,500$ M^{-1} cm^{-1} for benzophenone at 520 nm. The values of the triplet-triplet molar extinction coefficient (ε_T) were evaluated using the energy transfer method from phenanthrene ($\varepsilon_T = 25,200$ M^{-1} cm^{-1} at 480 nm in CH) and benzophenone ($\varepsilon_T = 6,500$ M^{-1} cm^{-1} at 520 nm in AcCN) [38]. In two cases, the triplet quantum yield (ϕ_T) was calculated by the enhancement factor ($\Delta A_{dir}/\Delta A_{enh}$) obtained as ratio of the optical density change of direct and induced (by sensitizers for 4,1'PNE and heavy atoms for 6-StBT) experiments. Only for 4-StQ did the short τ_T prevent us from characterizing completely the T_1 state. The triplet properties measured for 6-StBT and 2,2'-TAnE in CH were in good agreement with those previously reported in different non-polar solvents [39,40].

Measurements of the singlet oxygen production were also carried out. Even if this indirect estimation of the triplet yield is very rough (particularly for compounds having very short triplet lifetime), since the fraction S_Δ of the triplet molecules which produces singlet oxygen is unknown, the ϕ_Δ values in table 2 parallel those of ϕ_T, thus indicating that they reflect the trend of the triplet yields. The higher values found for ϕ_Δ of

Table 3. Direct ($\phi_{t\to c}^{dir}$) and sensitized ($\phi_{t\to c}^{sens}$) *trans → cis* photo-isomerization quantum yields, relative triplet mechanism contribution ($^3\phi_{t\to c}$) and Arrhenius parameters of the activated processes of some *aza-* and *thio*-derivatives of 1,2-diarylethenes in non-polar solvents at room temperature.

Compound	$\phi_{t\to c}^{dir}$	$\phi_{t\to c}^{sens}$	$^3\phi_{t\to c}$	$^1\Delta E_{act}(kJ\,mol^{-1})$	$\log^1 A_{act}$
1-StN[a]	0·16	0·46	< 0·01	38·9	14·4
4,1'-PNE	0·58[b]	0·43	⩽ 0·005	15·9[b]	12·4[b]
4-StQ	0·26[b]	0·43		6·3[b]	11·0[b]
8-StQ	0·14	0·40	0·03	> 50	
6-StBT	0·034	0·35	0·035	⩾ 50	
2,2'-DBTE[c]	0·20	0·45	0·30	> 50	
9-StAn[d]	< 0·001	< 0·001	< 0·0004	> 50	
4,9'-PAnE	0·006	0·014	0·0056	35	12·7
9-StAc	0·011	0·026	0·0018	23	12·0
2,2'-TAnE	0·004	0·013	0·0013	30[e]	11·1[e]

References: [a] 17, [b] 32,45, [c] 31, [d] 19.
[e]Arrhenius parameters determined by the temperature effect on the *B* rotamer lifetime.

2,2'-TAnE with respect to ϕ_T is very probably due to oxygen sensitization by the long-lived S_1 state (around 100 ns!).

The yields and lifetimes are markedly dependent on the structure. Table 2 shows a very low ϕ_T for 4,1'-PNE, a yield of 7–10% for 8-StQ, 9-StAc, 6-StBT and 2,2'-TAnE and a more substantial yield for 2,2'-DBTE and 4,9'-PAnE. The lifetime is strongly dependent on the barrier to twisting in the T_1 surface. Generally the latter is very small, the twisting to ^{3}perp* is practically barrierless and the lifetime is very short, below $1\mu s$. On the other hand, when twisting in T_1 is highly activated (as in the case of the anthryl derivatives [19], τ_T becomes longer (20 to 50 μs).

Table 3 shows the direct and sensitized (by biacetyl) *trans → cis* photoisomerization quantum yields. Only the naphthyl analogue, 4,1'-PNE, has a high reaction yield under direct irradiation, while the two quinoline derivatives and the dibenzothienyl derivative have a markedly reduced yield and the anthryl analogues, as well as 6-StBT, a negligible yield of 1% or less. A common behaviour of DAEs is the generally high reactivity of their lowest triplet state which leads to high values (≈ 0.5) for the photoisomerization quantum yield sensitized by triplet donors, $\phi_{t\to c}^{sens}$. This means that, when T_1 is populated by ISC, its prevalent relaxation pathway is a practically barrierless twisting along the isomerization channel. For our compounds, we found $\phi_{t\to c}^{sens} = 0.45 \pm 0.05$ for the 1-StN analogues (except for 6-StBT, which has a smaller yield of 0·35), but more than one order of magnitude smaller for the anthryl derivatives whose activation energy in the triplet manifold is high enough to inhibit photoisomerization. By the knowledge of the triplet yields and sensitized reaction yields, it was possible to deduce the contribution of the triplet mechanism to photoisomerization as $^3\phi_{t\to c} = \phi_{t\to c}^{sens} \times \phi_T$. This contribution is relevant for 6-StBT, 2,2'-DBTE and the anthryl analogues.

The temperature effect on ϕ_F and/or τ_F (see an example for 9-StAc in figure 3) allowed the Arrhenius parameters for the activated process to be calculated (table 3) by methods
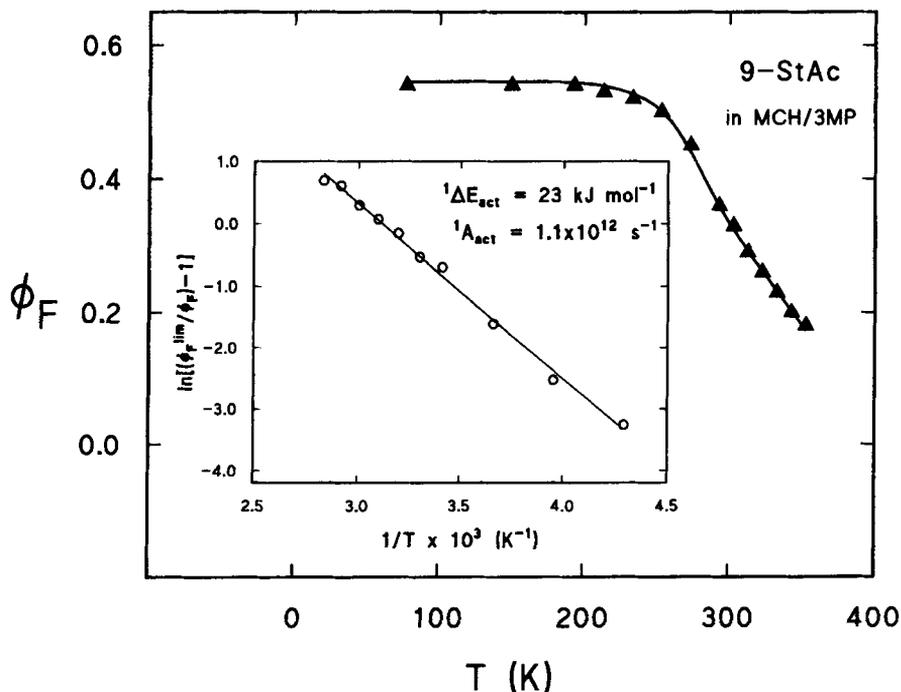
Figure 3. Temperature effect on the fluorescence quantum yield of 9-StAc in MCH/3MP. The inset shows the corresponding Arrhenius plot (ϕ_F^{lim} represents the fluorescence quantum yield measured at low temperature where the activated process is inhibited).

already described [32]. The frequency factor is high in all cases indicating that the activated twisting is a spin-allowed process. The activation energy goes from the very small value of 4-StQ to high values for 8-StQ, 6-StBT and 2,2′-DBTE.

In table 4, the derived rate constants of the competitive relaxation processes are reported. As in previous papers, they were obtained by assuming that the quantum yield for rotation around the double bond in S_1 ($^1\phi_{t\rightarrow p}$) is twice that for isomerization ($^1\phi_{t\rightarrow c}$), as in the case of S [3], namely a partitioning factor of $\alpha = 0.5$ was assumed for the decay from the ^{1}perp configuration to the two ground-state geometrical isomers [32]. Therefore, the kinetic parameters were derived by $k_F = \phi_F/\tau_F$ for the radiative deactivation, $k_{ISC} = \phi_T/\tau_F$ for ISC, $^1k_{t\rightarrow p} = 2\,^1\phi_{t\rightarrow c}/\tau_F$ for the ^{1}trans* $\rightarrow$ ^{1}perp* internal rotation in S_1 and $k_{IC} = 1/\tau_F - (k_F + k_{ICS} + \,^1k_{t\rightarrow p})$ for the $S_1 \rightarrow S_0$ IC. The rate parameters allow, better than the quantum yields, the prevailing relaxation process to be evidenced and then lead to a better characterization of the photoreaction mechanism. The results of table 4 show that IC is generally negligible compared to other processes with the notable exceptions of 4-StQ and 9-StAc, which have k_{IC} higher (much higher, in the case of 4-StQ) than the radiative parameter and competitive with twisting in S_1.

Table 5 shows some experimental parameters (quantum yields and lifetimes) measured for the compounds investigated in polar solvents (AcCN or BuCN) at room temperature. The main effect of these solvents is a general decrease in the twisting barrier leading to a much faster isomerization rate in S_1 and a drastic decrease in the

Table 4. Kinetic parameters (k in $10^8\,\mathrm{s}^{-1}$) of the S_1 relaxation processes of *aza-* and *thio-*derivatives of 1,2-diarylethenes in non-polar solvents at room temperature.

Compound	k_F	k_{ISC}	$^1k_{act}$	$^1k_{t\to p}$	k_{IC}	prevalent mechanism
1-StN	4·0	< 0·1	0·34	1·4	—	mixed
4,1'-PNE	4·5	≤ 0·45	38	45	—	singlet
4-StQ	1·6		76	74	67[a]	singlet
8-StQ	2·6	0·27	—	—	1·0	mixed
6-StBT	7·5	1·1	—	—	2·0	triplet
2,2'-DBTE	7·7	15·9	—	—	—	triplet
9-StAn	1·2	1·1	—	—	0·5	
4,9'-PAnE	1·4	1·1	0·03	0·002[b]	0·3	triplet
9-StAc	0·72	0·14	0·67	0·04[b]	1·1	mixed
2,2'-TAnE(A)	0·83	—	—	—	—	
2,2'-TAnE(B)	0·064	> 0·01	0·0064	0·0004[b]	< 0·03	mixed

[a] Value estimated assuming $\phi_{ISC} \cong 0$.
[b] Values estimated neglecting the contribution of adiabatic mechanism.

fluorescence yields and lifetimes and in the triplet population compared to the hydrocarbon analogues. As an example, the following Arrhenius parameters were obtained for 9-StAc in BuCN: $^1\Delta E_{act} = 11\,\mathrm{kJ\,mol}^{-1}$, $^1A_{act} = 2\cdot3 \times 10^{11}\,\mathrm{s}^{-1}$. With only one exception (2,2'-TAnE), the yields of singlet oxygen production are in a very good agreement with the triplet yields. The behaviour of this anthryl derivative is probably due to oxygen sensitization by the long-lived S_1 state, as observed in non-polar solvents.

4. Discussion

4.1 *Aza-derivatives in non-polar solvents*

The main effects on the photophysics and photochemistry of DAEs due to the introduction of the N heteroatom can be thus summarized:

(i) k_{ISC} is practically unchanged, indicating that the n,π^* states are not implied in the ISC process. The ISC rate parameters are generally smaller than the twisting rate in S_1, $^1k_{t\to p}$, for the *aza-*derivatives of 1-StN (except for 8-StQ) and their isomerization proceeds by a singlet mechanism. In the *aza-*derivatives of 9-StAn is $k_{ISC} \gg {}^1k_{t\to p}$, thus opening a triplet pathway to isomerization. The presence of adiabatic channels in the lowest singlet or triplet states ($^{1,3}trans^* \to {}^{1,3}cis^*$) and vice versa cannot be excluded, as already found for *n*-StAn ($n = 1,2$ and 9)[40]. However, a knowledge of the excited state properties of the *cis* isomers should be needed for an analysis of such specific mechanism.

(ii)   The experimental activation energy $^1\Delta E_{act}$ generally decreases compared with the hydrocarbons. This behaviour, which could be related to an increase in the zwitterionic

Table 5. Photophysical and photochemical parameters of some *aza*- and *thio*-derivatives of 1,2-diarylethenes in aprotic polar solvents at room temperature.

Compound	ϕ_F	τ_F(ns)	$k_F(10^8\,s^{-1})$	$\phi_{t\to c}^{dir}$	ϕ_T	$\tau_T(\mu s)$	$k_{ISC}(10^8\,s^{-1})$	ϕ_Δ
1-StN	0·39[a]	1·0[a]	3·9	0·27[a]	<0·03[b]	1·1[b]	<0·3	
4,1'-PNE	0·038[a]	0·10[a]	3·8	0·51[a]	<0·01	0·7	<1	≤0·01
4-StQ	0·006[a]	0·014[a]	4·3	0·41[a]		≤0·3		≤0·02
8-StQ	0·55	3·8	1·4	0·14	0·08	0·8	0·2	0·07$_5$
6-StBT	0·55	1·1	5·0	0·09	0·06	0·25	0·55	≤0·02
2,2'-DBTE[c]	0·12	0·27	4·4	0·44	0·24	0·63	8·9	0·13
9-StAn[d]	0·49	4·1	1·2	<0·001	0·27	45	0·69	
4,9'-PAnE	0·020	0·26	0·77	0·40	<0·01	>40	<0·4	≤0·02
9-StAc	0·027	0·36	0·75	0·27	<0·01	30	<0·3	≤0·02
2,2'-TAnE	0·63	7·0–20·0		0·03	0·09	14		0·39

References [a] 32,45, [b] 48, [c] 31, [d] 43

character of the ^{1}perp* configuration in the presence of the N heteroatom, leads to a decrease in the fluorescence quantum yield and lifetime and to higher $^1k_{t \to p}$ values. (iii) k_{IC} depends on the position of the heteroatom and on the nature (ethenic, arenic) of S_1 and mainly on the proximity effect [27,28] of the n, π^* state to the lowest fluorescent state of π, π^* nature. The IC process is particularly important for 4-StQ whose k_{IC} is much larger than k_F and competitive with $^1k_{t \to p}$. It is also present to a non negligible extent in 9-StAc.

The behaviour of the *aza*-analogues of 1-StN and 9-StAn in non-polar solvents (see tables 1 to 4) depends strongly on where the N atom is located, as pointed out in a previous paper on styryl-substituted naphthalenes and phenanthrenes [32]. When the N atom is in the styryl moiety (a pyridyl group replaces the phenyl group, as in the case of 4,1'-PNE and 4,9'-PAnE), the IC process, differently from 4-StP and 4,4'-DPE, is slowed down and does not compete with the radiative and/or reactive pathways. This behaviour is probably related to the arenic character of the S_1 state (naphthalenic and anthracenic, respectively), which could produce a larger energy gap between the n, π^* and π, π^* states. A general effect is the decrease of the torsional barriers with respect to the hydrocarbons. As seen above, this induces a decrease in the fluorescence quantum yield and lifetime and an increase in the isomerization quantum yield. The triplet yields are similar to those of the styryl counterpart, being negligible for the naphthyl derivative and high for the anthryl derivative [42,43]. The *trans → cis* quantum yield reaches the high value of 0·58 for the naphthalenic compound. On the other hand, the anthryl derivative behaves as 9-StAn with similar fluorescence and triplet quantum yields [19]. The corresponding hydrocarbon does not isomerize from *trans* to *cis* because of high activation energies in both S_1 and T_1 (*'one way'* photoisomerization [9,10]) whereas the pyridyl derivative shows a very low but detectable reactivity. It is not easy to prove the state responsible for such reactivity. The triplet contribution to the reaction yield accounts for the experimental (overall) $\phi_{t \to c}$ thus indicating, that a triplet mechanism prevails. However, the long $\tau_T (50 \, \mu s)$ and the very low reaction yield in the presence of triplet donors indicate that the torsional barrier is high in the T_1 state too, so that a singlet contribution is partially operative, at least above room temperature where the yield increases substantially ($\phi_{t \to c} = 0.027$ at 354 K to be compared with 0·006 at 295 K).

When N is in the polycyclic group, namely in the styryl derivatives of quinoline and acridine, the excited state properties depend whether N is in the ring bearing the styryl substituent or not. In the first case (4-StQ and 9-StAc), the behaviour depends on the nature of the lowest excited singlet state S_1, whether it is more aromatic or ethenic in character. In 4-StQ, the ethenic character prevails and its behaviour is reminiscent of that found for the pyridyl derivatives. In fact, it resembles 4-StP [25,29,44], having non-detectable ISC, little fluorescence and significant isomerization and IC yields. On the other hand, for 9-StAc, which is more aromatic in character (but with a torsional barrier reduced by the heteroatom), the behaviour is similar to 9-StAn, even if with a reduced triplet yield (0·07) and a small but detectable isomerization (0·011). The high isomerization barrier in both the lowest excited states, characteristic of compounds with an anthracene skeleton, leaves the yield of *cis* production very small despite the sizeable triplet yield. Since the derived triplet contribution accounts for $\approx 20\%$ of the experimental photoisomerization yield, one can conclude that a mixed singlet-triplet mechanism is probably operative.

When the N atom is not in the same ring as the styryl substituent, as in the case of 8-StQ, it does not have large effects compared with the corresponding hydrocarbon.

The fluorescence is high for this molecule and isomerization is relatively small due to its high torsional barrier, but a relevant contribution of triplet is present in non-polar solvents, whose yield is of the order of 7%. This sizeable triplet yield is accompanied by a slightly higher isomerization yield of 0·14 (indicating a mixed singlet-triplet mechanism).

The compounds bearing an anthracenic skeleton, 4,9′-PAnE and 9-StAc, deserve a particular comment since, for these compounds, the non-adiabatic process of S is no longer the best model. In fact, in their potential energy surfaces, the deep minimum (funnel) at the ^{1}perp* configuration can be replaced by a shallow minimum or a maximum [45] and twisting can proceed adiabatically from one excited isomer to the other with $\phi_{t \to c}$ (corresponding to $\phi_{t \to p}$ if the mechanism is only adiabatic) that can reach the value of unity, or even more in concentrated solutions when a chain mechanism can become operative [9,10,11]. While from ^{1,3}cis* to ^{1,3}trans* the torsional barrier has been found to be relatively small for some pyrenyl and anthryl derivatives [41,46], it becomes practically insuperable from ^{1,3}trans* to ^{1,3}cis* at room temperature. This means that, even if twisting from the *trans* side takes place, the twisted excited molecule relaxes fast to the quasi-planar *trans* configuration.

4.2 *Sulphur derivatives in non-polar solvents*

The main effect of a thienyl group in a DAE skeleton is the increase of the triplet population when ISC has a low yield in the hydrocarbon analogue, 1-StN. However, when the triplet yield is substantial in the hydrocarbons with larger polycyclic groups (e.g., in 9-StAn), the thienyl group does not change the competition of the relaxation processes of S_1 substantially. The fluorescence quantum yield is markedly high for these polycyclic derivatives compared to those of the simple thienyl compounds [31] because of the higher activation barriers for twisting in S_1 due to localization of the excitation energy in the aromatic groups. The fluorescence lifetime, which is short for the 1-StN analogues but unusually long for the anthryl derivatives, does not change at 77 K indicating the absence of activated processes in the relaxation of S_1.

For 6-StBT, where the sulphur atom is not in the same ring as the styryl substituent, the excited state properties are different from those of 1-StN. In fact, the main deactivation pathway is fluorescence ($\phi_F = 0.71$), but the triplet yield is not negligible (0·1) and accounts for the very small photoisomerization yield (0·034). For 2,2′-DBTE, the yield of the radiative process is 0·34 and ϕ_T reaches the high value of 0·70. Considering also the high energy of its activated process in S_1, the triplet state appears to be responsible for the photoisomerization quantum yield (0·20).

For 2,2′-TAnE we found a very high fluorescence yield, a modest triplet yield and a very small but detectable isomerization yield. As reported in a previous paper [47], this 2-StAn analogue with a phenyl group replaced by a thienyl group does isomerize to *cis*, even if with a small yield (0·4% in non-polar solvents). As mentioned above for the *aza*-derivatives, a contribution of adiabatic mechanism to isomerization appears to be improbable for this anthryl derivative.

4.3 *Effect of polar solvents*

The radiative parameter k_F remains unchanged in polar solvents indicating the same nature of the emitting state as in non-polar solvents. A slight decrease was observed in the k_{ISC} values, when a comparison was possible. The most important effect is the

generally large increase in the photoisomerization yield due to a smaller torsional barrier. Only for 8-StQ and 4,1'-PNE, is the $\phi_{t \to c}$ value not affected by the solvent. The activation barrier of 4,1'-PNE is already small in non-polar solvents, while, for 8-StQ, the absence of solvent effect[35] can be related to a twisting in S_1 which is probably slowed down by intramolecular hydrogen bonding of the nitrogen atom with the hydrogen of the ethenic bridge, as proposed for the 10-styryl-1-azaphenanthrene[31]. The increase in reactivity is huge for 9-StAc whose $^1k_{t \to p}$ goes from 0·04 to 15 (10^8 s^{-1}) on passing from MCH/3MP to BuCN. In general, ϕ_T is smaller in polar solvents since the lower torsional barrier favours twisting in S_1 and reduces the ISC quantum yield, thus increasing the contribution of singlet mechanism to photoisomerization. A typical example is offered by 4,9'-PAnE whose isomerization yield was found to be negligible in non-polar solvents (table 3). Only when decreasing the barrier in S_1 with a polar solvent does the isomerization yield reach the high value of 40%. The decrease in the torsional barrier in polar solvents is expected to be operative in the triplet manifold too. This was confirmed for 9-StAc whose $\phi_{t \to c}^{sens}$ changes from 0·026 in B to 0·2 in AcCN. However, the compounds having an S_1 state of aromatic character (8-StQ, 2,2'-TAnE and the two benzothienyl derivatives) maintain high radiative parameters, similar to the 1-StN and 9-StAn analogues[16,18] and relatively high torsional barriers even in polar solvents. The triplet yields also remain sizeable for these four compounds in polar solvents, thus leading to a prevalent triplet mechanism of photoisomerization.

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