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Involvement of the upper excited state S_2 in the photophysics of *trans*-1,2-diarylethenes due to slow internal conversion to S_1 [1]

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Abstract

The fluorescence decay of some styrylarenes bearing naphthyl, phenanthryl, anthryl, pyrenyl and pyridyl groups has been measured by both the single photon counting and phase-modulation techniques in the nanosecond and picosecond regions. Generally, two decay components were observed. The most abundant and longer component (in the 1–10 ns range) corresponded to the typical $S_1 \rightarrow S_0$ emission of these molecules. A second weaker component (in the 100–800 ps range) was practically coincident with the short component recently observed for some of these compounds by absorption measurements using laser flash photolysis. It was assigned to the emission from an upper excited singlet state, S_2, directly populated at high excitation energies. An investigation of the effect of the exciting and monitoring wavelengths on the fluorescence decay showed that the abundance of the short component increased with the excitation energy. Preliminary quantum-chemical calculations supported the relatively slow internal conversion from S_2 to S_1, so that other relaxation pathways, such as fluorescence from S_2 by-passing S_1 or intersystem crossing or twisting towards the cis isomer, can become competitive and play a role in the deactivation pathways of these flexible molecules. © 1997 Elsevier Science S.A.

Keywords: Diarylethenes; Fluorescence; Upper excited state; Internal conversion

1. Introduction

Examples can be found in the literature where an anti-Kasha behaviour of upper excited states has been occasionally invoked to explain unusual experimental observations in the study of the relaxation properties of specific compounds [1]. In previous works, we proposed such behaviour to explain a dual fluorescence observed for a rotamer of *trans*-2-styrylanthracene (2-StAn) [2] and some results on the absorption and emission properties of other styrylarenes recently obtained by pulsed techniques in the sub-nanosecond time-scale [3].

The fluorescence and geometrical photoisomerization of stilbene-like molecules with a phenyl group replaced by a polycyclic aromatic group strongly depends on the nature of the larger aryl group and the position of the styryl group [4]. Cases were found where the measured fluorescence and photo-isomerization quantum yields were not easily understandable on the basis of the properties of the lowest singlet and triplet excited states [5,6]. The intervention of upper excited states (S_n or T_n), decaying through pathways different from S_1 and T_1, respectively, offered a speculative explanation of the obtained results in spite of the absence of direct experimental evidence.

With the aim of obtaining a direct evidence of the involvement of upper excited states in the decay processes of diarylethenes (DAEs), fluorescence and flash photolysis measurements in the nanosecond and picosecond time domain have been recently undertaken [3]. For styryl derivatives of naphthalene, phenanthrene and anthracene, transient absorption spectra in the 400–800 nm range were recorded in solvents of different polarity and viscosity. In all cases, the decay kinetics were fairly well described by a bi-exponential fitting with τ_S (the short-lived component) < 1 ns and τ_L (the longer lived component) > 1.5 ns. Fluorescence lifetimes were also measured by both single photon counting and phase-shift methods in various experimental conditions and confirmed the results obtained by absorption measurements. While the longer lived component was clearly due to $S_1 \rightarrow S_n$ absorption transitions and $S_1 \rightarrow S_0$ emission, respectively, the shorter one, in the picosecond range, was tentatively assigned to $S_2 \rightarrow S_n$ and $S_2 \rightarrow S_0$ transitions, respectively. To gain a

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deeper insight in the behaviour of the lowest excited singlet states of these molecules, the present work extends the previous fluorimetric investigation to some other compounds and solvents. A few new absorption measurements by ps laser flash photolysis were also performed. Moreover, a theoretical study of the internal conversion (IC) processes from S_2 and S_1 through quantum chemical calculations of the vibronic coupling was undertaken to support the assignment of the short-lived component to S_2 and the competition of its fast relaxation processes with the IC to S_1.

2. Experimental

The diarylethenes investigated are shown in Scheme 1. The trans isomers of *n*-styrylanthracene (*n*-StAn, with $n = 1$, 2 and 9), *n*-styrylphenanthrene (*n*-StPh, with $n = 1$, 2, and 9), 1-styrylpyrene (1-StPy) and 1-(1-naphthyl),2-(4′-pyridyl)-ethene (1,4′-NPE) were the same as used for previous works [7–10].

The solvents (Fluka, ACS grade) acetonitrile (MeCN), bromopropane (BrP), cyclohexane (CH), ethylene glycol (EtG) and *n*-hexane (*n*-H) were used without further purification.

The fluorescence lifetimes, τ_F, were measured in the nanosecond time domain by an Edinburgh Instruments 199S spectrometer, using the single photon counting (SPC) method (mean deviation of three independent experiments, ca. 5%) and in the picosecond time domain, by a Spex Fluorolog-τ2 system, which uses the phase-modulation technique (excitation wavelength, λ_{exc}, modulated in the 0.5–330 MHz range; time resolution ca. 10 ps; for uncertainties, see Tables 2 and 3). To avoid photodegradation of the samples, the intensity of the excitation light was reduced by neutral filters and, therefore, a broad band of the emission light (selected by a cut-off filter) was collected to increase the signal intensity. The study of the effect of the emission wavelength, λ_{em}, was carried out inserting a second monochromator on the emission arm and using a reduced filtration of the exciting light. Accurate measurements were then possible only with the non photoreactive *trans*-n-StAn [7]. The frequency-domain intensity decays (phase angle and modulation vs. frequency) were analysed with the Globals Unlimited™ (rev. 3) global analysis software [11].

A few picosecond flash photolysis experiments were carried out using the excitation wavelengths of 355 and 266 nm (pulse width ca. 30 ps and energy < 5 mJ per pulse) from a mode-locked Nd:YAG laser system (Quantel YG571) [3,12].

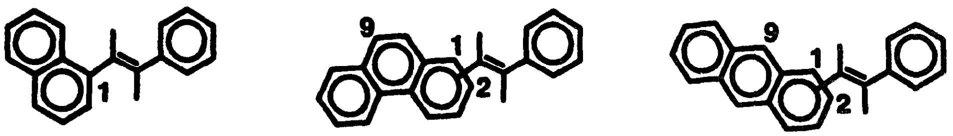
All measurements were carried out at 22 ± 2 °C unless otherwise indicated; the solutions of the *trans*-styrylarenes (concentrations ca. 10^{-4} M) were deaerated by bubbling with oxygen-free argon.

3. Results

3.1. Spectroscopic measurements

Fluorimetric measurements carried out with the SPC method gave fluorescence lifetimes in the nanosecond domain in good agreement with those previously measured for the compounds here investigated [7–10,13,14]. The only evidence for a short-lived component came from the poor fitting parameters found when using a mono-exponential treatment and from the slight improvement obtained by a bi-exponential decay function, indicating an uncertain contribution of a weak short component in the sub-nanosecond region. The better time resolution offered by the phase-shift technique (picosecond resolution) clearly showed that the experimental data were fitted by bi-exponential decay functions with two lifetimes in agreement, within the experimental error, with the values obtained from absorption flash photolysis in the sub-nanosecond region [3].

Fig. 1 shows, as an example, the results obtained for 9-StAn in EtG treating the frequency response by mono- and bi-exponential functions. One can clearly show the improvement obtained in the fit of the phase vs. frequency plot by using the bi-exponential function. The results are collected in Table 1, which includes new compounds



1-styrylnaphthalene (1-StN) n-styrylphenanthrene(n-StPh) n-styrylanthracene(n-StAn)

1-naphthyl,4′-pyridyl-ethene (1,4′-NPE) 1-styrylpyrene (1-StPy)

Scheme 1.

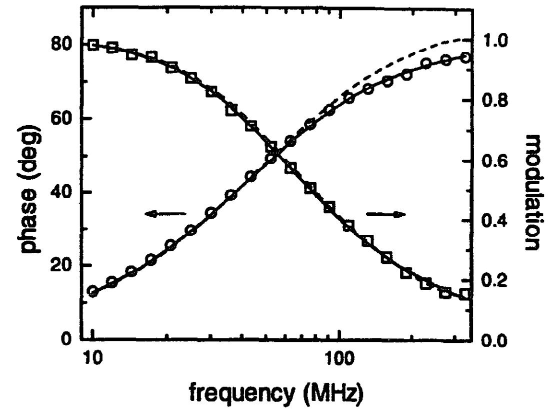


Fig. 1. Frequency response of 9-StAn in EtG fitted by mono-exponential (dashed line) and bi-exponential (full line) analysis respectively (λ_{exc} = 355 nm).

Table 1
Fluorescence lifetimes (τ_1 and τ_2) of diaryethenes in different solvents

Compound	Solvent	τ_1 (ns)	τ_2 (ns)
1-StAn	CH	0.89	5.90
	MeCN	0.84	6.31
2-StAn	CH		9.1/56.2
9-StAn	CH	0.68 [a]	3.48 [a]
	BrP		1.82
	MeCN	0.41 [a]	4.10 [a]
	EtG	0.41 [a]	3.67 [a]
1-StPh [a]	CH	0.29	8.5
	MeCN	0.78	7.0
2-StPh [a]	CH	0.26	33.7
	MeCN	0.47	29.1
9-StPh	CH	0.40 [a]	4.1 [a]
	BrP	0.20	1.26
	MeCN	0.32 [a]	1.79 [a]
	EtG	0.23	1.85
1-StPy	CH	0.38	4.30
	MeCN	0.24	4.40
1,4′-NPE	n-H	0.26	
	MeCN	0.15	

[a] From Ref. [3b].

(1-StAn, 2-StAn, 1-StPy and 1,4-NPE) and a new solvent (BrP) with respect to the previous work [3].

The data show that, with the exception of only three cases which will be analysed in Section 4, two components are generally present in the emission decay, the known long component, τ_2, corresponding to the $S_1 \rightarrow S_0$ emission measured by nanosecond fluorimetry, and a short component, τ_1, in the range of hundreds of picoseconds with an amplitude factor of a few percents or less, recently assigned to the $S_2 \rightarrow S_0$ transition [3].

The solvent effect was found to be relatively modest. The polar solvent MeCN has not a clear effect, sometimes shortening, sometimes increasing the lifetime. Its behaviour is probably the result of two opposite effects, namely a decrease of the torsional energy barrier (leading to an increase of the twisting rate for S_1) and a possible increase of the S_2–S_1 energy gap (leading to a slower IC). The other two solvents, BrP and EtG, led to shorter lifetimes: the effect of BrP was expected, due to the faster intersystem crossing (ISC), but the shortening effect of EtG is not obvious. A tentative explanation could be related to the role of conformations deviating from planarity, stabilized in the viscous solvent, which could favour relaxation from the Franck–Condon states reached by absorption with a consequent increase of the IC rate [3].

An accurate investigation of the effect of λ_{exc} and λ_{em} was only possible with *trans*-StAns, which do not isomerize to cis due to too high activation energies for twisting [7,14] in both singlet and triplet manifolds (see Section 2). Table 2 shows the results obtained with 9-StAn in MeCN varying λ_{exc}. While the lifetime of the two decay components remain practically constant (considering the uncertainty in these measurements), the pre-exponential factor of the short decay component increases at the higher excitation energies indicating an increase in the population of the upper excited state.

Table 3 shows an interesting effect of λ_{em} found with 9-StAn in MeCN when exciting at 355 nm. It is shown that monitoring at λ_{em} longer than 430 nm, the decay was mono-exponential. At slightly shorter λ_{em} (420–430 nm), an acceptable fit was only obtained by a bi-exponential decay (see also Fig. 2) with the amplitude of the short component substantially increasing up to 2.5%.

Table 2
Mono- and bi-exponential analysis of 9-StAn fluorescence in MeCN by the phase-shift method (λ_{em} = 420 nm)

λ_{exc} (nm)	τ [a] (ns)	χ^2 [a]	τ_1 [b] (ns)	τ_2 [b] (ns)	A_1 [b,c]	χ^2 [b]
340	3.96 ± 0.13	3.0	0.52 ± 0.20	4.05 ± 0.07	3.2	0.8
345	3.99 ± 0.13	4.7	0.53 ± 0.16	4.18 ± 0.07	3.5	0.9
350	3.94 ± 0.11	2.3	0.37 ± 0.11	4.06 ± 0.06	2	1.0
355	3.97 ± 0.17	4.0	0.35 ± 0.10	4.20 ± 0.07	2.5	0.6
360	3.96 ± 0.13	4.5	0.35 ± 0.20	4.12 ± 0.06	2.4	0.95
370	4.00 ± 0.09	2.6	0.35 ± 0.20	4.10 ± 0.05	1.5	0.82
380	3.91 ± 0.10	4.0	0.35 ± 0.20	3.97 ± 0.03	2	1.2
390	3.88 ± 0.09	4.9	0.35 ± 0.20	3.98 ± 0.05	2	1.2
400	4.08 ± 0.12	3.1	0.35 ± 0.20	4.19 ± 0.05	2.5	0.62

[a] Obtained from mono-exponential analysis.
[b] Obtained from bi-exponential analysis.
[c] Amplitude of the component with decay time τ_1 determined by a nonlinear least-squares fitting.

Table 3
Mono- and bi-exponential analysis of 9-StAn fluorescence in MeCN by the phase-shift method (λ_{exc} = 355 nm)

λ_{em} (nm)	τ [a] (ns)	χ^2 [a]	τ_1 [b] (ns)	τ_2 [b] (ns)	A_1 [b,c]	χ^2 [b]
450	4.10 ± 0.09	1.2				
440	4.00 ± 0.07	1.1				
435	4.09 ± 0.10	1.5				
430	4.11 ± 0.07	1.6	0.37 ± 0.12	4.13 ± 0.07	0.3	1.5
425	4.00 ± 0.10	1.9	0.33 ± 0.06	4.07 ± 0.06	1	1.0
420	3.97 ± 0.17	4.0	0.35 ± 0.10	4.20 ± 0.07	2.5	0.6

[a] Obtained from mono-exponential analysis.
[b] Obtained from bi-exponential analysis.
[c] Amplitude of the component with decay time τ_1 determined by a nonlinear least-squares fitting.

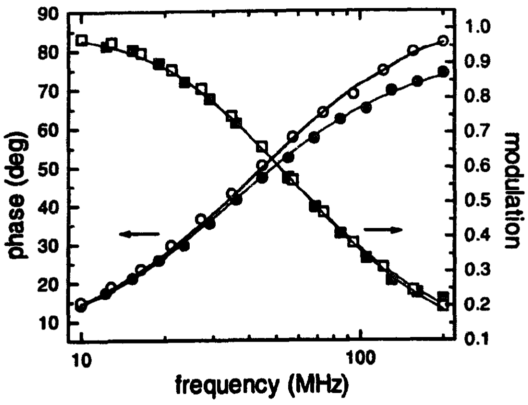


Fig. 2. Frequency response of 9-StAn in MeCN recorded at 450 nm (open symbols) and 420 nm (full symbols) fitted by mono-exponential and bi-exponential, analysis, respectively (λ_{exc} = 355 nm).

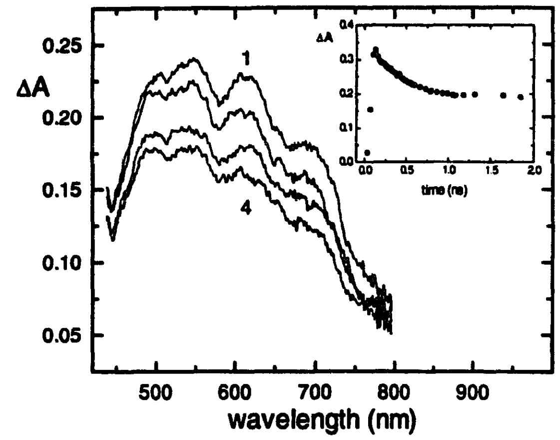


Fig. 3. Time-resolved absorption spectra of 1-StPh in MeCN recorded at "zero" time (1), and at 0.27 (2), 0.57 (3) and 1.80 (4) ns after the laser pulse; inset: decay kinetics recorded at 600 nm (λ_{exc} = 355 nm).

A few measurements by laser flash photolysis confirmed the results obtained by fluorimetry. Fig. 3 shows, as an example, the transient spectra of 1-StPh in MeCN. The kinetic analysis led to decay times of 0.42 ± 0.16 ns and 8.5 ± 0.1 ns, to be compared with the values of 0.78 ± 0.15 ns and 7.0 ± 0.2 ns reported in Table 1. Taking into account the difference in the techniques involved and the experimental uncertainty, the agreement is acceptable. Interestingly, the short decay component of 9-StAn in BrP, not observed by fluorimetry (probably due to the quenching by the heavy atom, which reduces further the small emission intensity from S_2, see before), was observable by absorption. The lifetimes thus obtained were τ_2 = 1.8 ± 0.08 ns (to be compared with 1.82 ± 0.03 ns in Table 1) and τ_1 = 0.40 ± 0.13 ns, a value shorter than those found by both absorption and fluorescence measurements in CH (0.77 ± 0.13 ns and 0.68 ± 0.30 ns, respectively).

3.2. Theoretical calculations

In order to gain insight into the dynamics of the deactivation processes of the states involved, a series of quantum mechanical calculations on the equilibrium energies (CNDO/S method), on the ground state frequencies (QCFF/PI method) and on the adiabatic and non-adiabatic vibronic coupling terms (orbital following method) was carried out for three specific compounds: 1-styrylnaphthalene (1-StN), 1-StPh and 9-StAn. These compounds were chosen in order to avoid complications by the presence of s-trans–s-cis conformational equilibria. In fact, 9-StAn has not conformers, while for 1-StN and 1-StPh at room temperature the equilibrium is almost completely shifted towards the most stable conformer [5]a, [13–16].

The close proximity of the two lowest excited singlets, as resulting from the calculations, joined to the experimental evidence of two decay components, point to a strong vibronic mixing of the relevant states. Therefore, a treatment analogous to that applied recently to a series of styrylpyridines and dipyridylethenes [17] appeared pertinent to the present case. Using the same method described in Ref. [17a], we found that the two lowest excited singlet states can be written as linear combinations of the type:

$$\Psi_{1,2}=a\Psi_E^\circ \pm b\Psi_A^\circ \qquad (1)$$

where Ψ_E° and Ψ_A° represent the zero order states of ethenic and arenic character and the coefficients a and b are related to the state mixing induced by adiabatic vibronic coupling. The coefficients so obtained, reported in the first two columns of Table 4, show a larger state mixing for the larger chromophores, reflecting a smaller energy gap for these compounds.

Once the composition of the two emitting states has been obtained, a calculation of the IC processes can be carried out using the expression:

$$k_{IC}=2\times10^{12}\beta_{el}^2\exp[-0.25\,\Delta E^{0.4332}] \qquad (2)$$

which appears appropriate to evaluate the rate of IC processes involving large energy gaps, such as $\Delta E(S_{1,0})$ and $\Delta E(S_{2,0})$, in the compounds examined [18]. Taking into account the calculated vibronic coupling terms β_{el} and the pertinent energy gaps, one obtains the results reported in Table 4

Table 4
Mixing coefficients of ethenic (a) and arylic (b) moieties in the S_1 state and internal conversion rate constants calculated by CNDO/S

Compound	a	b	$k_{IC}(S_1\rightarrow S_0)$ (10^7 s^{-1})	$k_{IC}(S_2\rightarrow S_0)$ (10^7 s^{-1})	$k_{IC}(S_2\rightarrow S_1)$ (10^7 s^{-1})
1-StN	0.82	0.57	3.3 (4.4)	1.4	0.6
1-StPh	0.53	0.84	6.2 (1.1)	1.1	0.9
9-StAn	0.44	0.89	9.7 (3.3)	2.4	1.4

(fourth and fifth columns), which appear in good agreement with the experiment (see discussion below). On the other hand, Eq. (2) does not appear appropriate for states very close in energy, such as S_2 and S_1. In this case, we carried out a direct calculation of the product $F\rho$ (Franck–Condon factor by density of states) taking into account the most important accepting modes, represented by the group of stretching modes with $\bar{\nu} \approx 1500\ \mathrm{cm^{-1}}$ and a group of low energy torsional modes. The calculation of the F factor was carried out using the formula proposed by Siebrand for displaced modes [19] (the γ values, which represent the adimensional displacement between the minima of S_2 and S_1, were obtained by using the QCFF/PI programme), whereas the density of states was estimated using the Haarhof's formula [20]. Comparison of the $F\rho$ product for typical S_2–S_1 energy gaps ($\approx 3000\ \mathrm{cm^{-1}}$) with that obtained for typical S_1–S_0 energy gaps ($\approx 25000\ \mathrm{cm^{-1}}$ with predominant CH stretching modes of $\approx 3000\ \mathrm{cm^{-1}}$) leads to a ratio $(F\rho)_{1,0}/(F\rho)_{2,1} \cong 7$, which, combined with the pertinent value of the electronic factor β_{el}, gives the k_{IC} values reported in the last column of Table 4. The results so calculated, although subject to the large uncertainty of the method, represent as a whole a suitable hint to understand the peculiar behaviour of the deactivation processes involved, showing possible competitiveness of the $S_2 \rightarrow S_1$ IC with respect to the other IC processes and a general trend in agreement with the experimental findings as far as the $S_2 \rightarrow S_0$ and $S_1 \rightarrow S_0$ processes are concerned. Generally speaking, the presence of small energy gaps joined to a sizeable vibronic coupling, points to a dynamic behaviour of these molecules within the so-called intermediate scheme, a behaviour which differs from the statistical limit for the fact that the $S_2 \rightarrow S_1$ IC is not an irreversible process and recurrence may occur on the same time scale of the fluorescence decay [21]. In this case, a decay characterized by a fast and a slow component has been detected in vapour phase for systems having S_2–S_1 energy gaps similar to those of our styrylarenes, such as pyrene [22]. However, more detailed and less approximate calculations on the potential energy curves as well as on the Franck–Condon factors involved are necessary in order to provide a more accomplished description of the complicate deactivation behaviour of these compounds.

4. Discussion

The results obtained by emission and absorption measurements in the picosecond time-scale show that the long lifetime of the S_2 state is a common phenomenon for styrylarenes.

Only a few cases of mono-exponential decay are shown in Table 1. For 9-StAn in BrP, the absence of the short component can be reasonably explained—as mentioned above—by the presence of the heavy atom in the solvent, which induces an increase in the yield of singlet–triplet ISC, thus reducing further the small yield of emission. This quenching effect on the emission intensity was confirmed by laser flash photolysis measurements indicating that the short lifetime (0.77 ns in CH) reduces to 0.40 ns in BrP. For 2-StAn, two decay components were observed in the nanosecond domain, similar to those previously reported by SPC emission measurements and assigned to the two rotamers (A and B) present in solutions of this compound [14,16]. A third fluorescence component of 2-StAn was reported for the B rotamer in certain experimental conditions ($T > 200$ K, $\lambda_{\mathrm{exc}} < 410$ nm) and assigned to emission from S_2 thermally equilibrated with the closely located S_1 [2]. Therefore, it is expected that S_2 emits with the same fluorescence lifetime as S_1. The third case showing a mono-exponential decay was that of *trans*-1,4′-NPE. The presence of n,π* states introduced by the heteroatom, more or less strongly mixed with the fluorescent π,π* state, is likely to produce an increase of IC to the ground state [17] for this pyridyl derivative with a consequent reduction in the fluorescence yield and lifetime, which probably makes undetectable the short component. In fact, absorption measurements for NPEs showed the presence of a short component living ca. 100 ps in *n*-H and MeCN.

The presence of a fast component in the fluorescence decay of the styrylarenes investigated, confirmed by parallel absorption measurements by laser flash photolysis (some of them are part of the present work), implies a relatively slow internal conversion to S_1, which thus allows other relaxation pathways from S_2 (fluorescence, twisting, intersystem crossing) to become competitive. The results of calculations show that this behaviour can be related to the quite different nature of the coupled states and to the small energy gap involved. Indeed, a different nature of the two states reflects both on the adiabatic coupling induced by the promoting modes and on the relative displacement of the states along the accepting modes. However, since the IC processes involved are estimated of the same order of magnitude, the influence of experimental conditions such as environment and temperature should be instrumental in addressing the molecule along a preferential deactivation channel. In previous works, quantum-mechanical (semiempirical) calculations on styrylarenes have indicated a quite different nature of the two states (prevalently ethenic and prevalently arenic, respectively, depending on the compound). Therefore, relatively small k_{IC} values could be predicted for S_2, in agreement with its relatively long lifetime. In fact, those calculations have shown that the two lowest excited singlet states of diarylethenes (of ethenic and arenic character) [4], [5a], [13,14] and their aza-analogues (of n,π* and π,π* character) [17] share a mixed nature and that the proximity effect can heavily influence their dynamic behaviour [17].

As said above, clear evidence for competition of non-communicating deactivation channels of S_1 and S_2 to the ground state S_0 has been already reported for 2-StAn, whose radiative relaxation from S_2 became observable when population of the upper state was favoured by temperature and/or excitation energy [2]. Recent results, mainly obtained by picosecond transient absorption photolysis on styrylnaphthalenes [3a] and other styrylarenes [3b], have also indicated that the S_2 state may have deactivation channels competitive with IC to S_1. One example is given by 9-StAn, whose $T_1 \rightarrow T_n$ absorption transient was shown to increase in intensity at the same rate of the decrease of that assigned to the $S_2 \rightarrow S_n$ transition [3b]. In two other cases, 1-StN [3a] and 2-StPh [3b], an interesting competition of the twisting towards the perpendicular configuration was evidenced by the increase of the photoisomerization quantum yield (and a parallel decrease of the fluorescence quantum yield) by increasing the excitation energy.

The present work, mainly concerned with the radiative deactivation, extends the result of a relatively long lifetime of the S_2 state to a larger series of styrylarenes. The effect of λ_{exc} and λ_{em}, mainly investigated for 9-StAn, shows that the population of S_2, which contributes, even if modestly, to the overall emission yield, increases at higher excitation energies and become undetectable when monitoring near the 0–0 band. While confirming the results and interpretation recently reported elsewhere [3], the present work also addresses a theoretical justification for the long lifetime of the upper excited singlet state.

It is interesting to compare the computed k_{IC} ($S_1 \rightarrow S_0$) values with those which can be roughly estimated from the experimental data. For 9-StAn, which does not isomerize under irradiation, the IC rate parameter can be evaluated from the relationship $k_{IC} = \Phi_{IC}/\tau_F = (1 - \Phi_F - \Phi_{ISC})/\tau_F$ using the experimental quantum yields and lifetime measured in non-polar solvents in previous works ($\Phi_F = 0.48$, $\Phi_{ISC} = 0.4$, $\tau_F = 3.6$ ns in methylcyclohexane [23]). A similar procedure can be used for the other two molecules, but in such cases the isomerization quantum yield must be considered. These molecules isomerize to cis by the same non-adiabatic pathway known for the model system *trans*-stilbene, namely by twisting from the lowest excited singlet state reached by absorption, ^{1}trans*, to the perpendicular configuration, ^{1}perp*, followed by crossing to the ground state ^{1}perp configuration and partitioning to ca. 50:50 cis and trans isomers [24]. In the case of stilbene, the isomerization takes place through a slightly activated twisting in the singlet manifold. Depending on the nature of the polycyclic group and the torsional barrier, the stilbene analogues can isomerize through singlet or triplet or mixed singlet–triplet mechanisms [4–6,13,25,26]. Since the activation energy is generally smaller in the triplet manifold compared with the singlet pathway, it can be considered that all molecules which populate the triplet manifold through ISC, are likely to twist and isomerize by an analogous non-adiabatic mechanism in T_1, with the same partitioning factor (ca. 0.5) [4,24,26]. Therefore, $k_{IC} = \Phi_{IC}/\tau_F = (1 - \Phi_F - 2\Phi_{t \rightarrow c})/\tau_F$. Using again the experimental data available ($\Phi_F = 0.60$ and 0.61, $\Phi_{t \rightarrow c} = 0.16$ and 0.14, $\tau_F = 1.8$ and 10 ns, for 1-StN [5a] and 1-StPh [27], respectively, in *n*-H), the experimental IC rate parameters were derived. Their values, reported in parenthesis in Table 4, are in a quite satisfactory agreement with the computed ones considering the uncertainty in the experimental values and the approximations involved in the calculations.

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