Excited State Behavior of Diarylethenes in the Subnanosecond Timescale: The Role of an Upper Singlet

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Received June 3, 1996[⊗]

Abstract: Picosecond absorption measurements of the *trans* isomers of 9-styrylanthracene (9-StAn), *n*-styrylnaphthalene (*n*-StN, with *n* = 1 and 2), and *n*-styrylphenanthrene (*n*-StPh, with *n* = 1, 2, and 9) were carried out in a number of solvents at room temperature. In all cases, a short-lived transient (with $\tau_S = 0.1 \div 0.8$ ns) was produced monophotonically within the laser pulse. This transient, which absorbs in a wide wavelength range (400−750 nm), was assigned to the S_2 state. At longer delay time, the $S_1 \rightarrow S_n$ absorption (with lifetime τ_L) replaced that of S_2, its assignment being strongly supported by the comparison between τ_L and the fluorescence lifetime of these diarylethenes. The $S_1 \rightarrow S_n$ absorption of two distinct rotamers was detected for 2-StN in solvents of different polarity, while for the other compounds only one longer-lived transient was detected. Complementary fluorimetric measurements by phase-modulation technique confirmed the presence of a second decay component in the picosecond region with a lifetime corresponding to the τ_S values measured by laser flash photolysis. The effect of temperature studied in both picosecond and nanosecond regions suggests that the $S_2 \rightarrow S_1$ internal conversion is not the only decay pathway of S_2. In particular, for 9-StAn, it is shown that both S_1 and S_2 are involved in the singlet−triplet intersystem crossing, and, at least in the cases of 1-StN and 2-StPh, the S_2 state (or both S_1 and S_2) is (are) involved in the *trans* → *perp* decay process. An investigation of the effect of excitation wavelength on the fluorescence and *trans* → *cis* photoisomerization quantum yields was found to support such hypothesis of the role played by upper excited states in the relaxation processes of some of the styrylarenes investigated.

1. Introduction

The *cis*−*trans* photoisomerization of stilbene-like molecules where one (or both) phenyl groups are replaced by larger polycyclic aryl groups has been studied extensively for almost two decades.[1−5] In our laboratory, particular attention has been given to compounds bearing one naphthyl,[6,7] phenanthryl,[8] or anthryl group.[9,10] Quite different photochemical and photophysical behaviors were observed for these compounds depending on the nature of the larger arene and the position of the styryl group. Recently, the importance of the nature of the lowest excited singlet state (S_1) of *trans*-1,2-diarylethenes (DAEs) in determining the rates of the competitive reactive (*trans* → *cis*) and physical relaxation processes was reported.[5] The relative energies of the ethenic and arenic states and of the L_a and L_b components of the latter are particularly important in favoring the isomerization process or radiative decay. From this point of view, it is interesting to obtain information on the nature not only of S_1 but also of the nearby located upper excited states.

In the past, we dealt with cases where the quantum yields of the reactive and radiative channels of relaxation were not easily understandable only on the basis of the properties of the lowest excited states of singlet and triplet multiplicity. The intervention of upper excited states S_n or T_n, having deactivation channels bypassing S_1 and T_1, respectively, offered an interesting explanation of the observed behavior, even if such a hypothesis could be considered to be rather speculative in the absence of direct experimental evidence.

A typical example has been reported with 1-StN,[7] known to isomerize in the singlet manifold near room temperature with a high activation energy. The fluorescence (ϕ_F) and photoisomerization ($\phi_{t \rightarrow c}$) quantum yields were found to be coupled and complementary above *ca*. 300 K. When the temperature decreased below 300−270 K (the value depends on the solvent), ϕ_F remained practically constant down to the liquid nitrogen temperature, with its value remaining below unity. In contrast, $\phi_{t \rightarrow c}$ decreased due to thermal and viscosity barriers and was inhibited in rigid matrices. The constancy of ϕ_F in the low temperature region seemed to indicate that the fluorescent state

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⊗ Abstract published in *Advance ACS Abstracts,* October 1, 1996.
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was not the only reactive one. However, the $S_1 \rightarrow T_1$ intersystem crossing (ISC) quantum yield remained very small even at low temperature, and T_1 could not account for all the reactive quanta. A reactive upper state S_n or T_n has been invoked to explain such behavior, but this explanation is not without question since neither the fluorescence nor the T_1 absorption increased in rigid matrices when the isomerization was inhibited.

A somewhat clearer case is represented by 2-StPh,[8,11−13] for which a prevailing triplet mechanism has been hypothesized. The fact that ϕ_F was independent of temperature indicated that an activated twisting is not operative in S_1. On the other hand, T_1 was not detectable by direct excitation in fluid solutions. The T_1 spectrum became clearly observable only in rigid matrices at low temperatures, where isomerization was hindered. This behavior was tentatively attributed to fast twisting in an upper excited triplet state. However, the T_1 yield at low temperature should be known to have a complete picture of the relaxation mechanism and to compare the ISC efficiency with the quanta involved in the isomerization at room temperature. A similar behavior was observed for 1- and 3-StPh but only in a polar solvent.[12]

The object of the present paper is the study of the transient absorption and the fluorescence decay in the picosecond region of some widely studied styrylarenes, bearing a naphthyl, phenanthryl, or anthryl group, in order to have direct information about the possible role of higher excited states in their photochemistry and photophysics. The photokinetic behavior of the observed transients and the effects of temperature and excitation energy provided interesting evidence about the implication of higher excited states in the reactive deactivation of some of these compounds.

2. Experimental Section

The *trans* and *cis* isomers of 9-styrylanthracene (9-StAn), *n*-styrylnaphthalene (*n*-StN, with $n = 1$ and 2), and *n*-styrylphenanthrene (*n*-StPh, with $n = 1$, 2, and 9) were the same as used for previous works.[10,14,15] Anthracene (Baker Chem. Co.) and phenanthrene (Ph, Aldrich 99.5+%) were used without further purification.

The solvents (Fluka, ACS grade) acetone (Me$_2$CO), acetonitrile (MeCN), bromopropane (BrP), cyclohexane (CH), 1,2-dichloroethane (DCE), ethanol (EtOH), ethylene glycol (EtG), ethyl acetate (EtAc), 1-hexanol (HeOH), methanol (MeOH), *n*-hexane (*n*-H), and propanol (PrOH) were used without further purification.

Picosecond laser flash photolysis studies were carried out with the third ($\lambda_{exc} = 355$ nm, pulse width 30 ps and energy < 5 mJ) and fourth ($\lambda_{exc} = 266$ nm, pulse width 30 ps and energy < 2 mJ) harmonics of a mode-locked Nd:YAG laser system (Quantel YG571). The basic features of the pump-probe double-diode array spectrography and the single-wavelength kinetic setup have been already described.[16] Unless otherwise indicated, an excitation wavelength of 355 nm was used. The "zero" time was assumed to be the time just after the laser pulse when the maximum of singlet−singlet absorbance was reached. Decay kinetics were recorded up to 4 ns after the laser pulse.

Nanosecond flash photolysis experiments were performed with a Q-switched Nd:YAG laser, which was tripled and quadrupled to give single 7-ns pulses at 355 and 266 nm, respectively (energy < 10 mJ/

pulse).[16,17] The effect of temperature on the decay rate constant was determined employing a variable-temperature cell similar to that designed by Wardman.[18] A deconvolution program was used to obtain singlet lifetimes from this setup.

Typical statistical errors in the lifetimes are ±20% (for τ < 1 ns) and ±10% (for longer-lived singlets). To avoid photodegradation, the solutions were circulated in a flow through cell.

Corrected emission spectra were recorded by a Spex fluorimeter (Fluorolog 112). The fluorescence quantum yields were measured (estimated error ±5%) as a function of the excitation wavelength (λ_{exc}) using anthracene in ethanol as reference ($\phi_F = 0.27$).[19] For each measurement, fresh deareated solutions with absorbance at λ_{exc} below 0.1 were used.

The fluorescence lifetimes, τ_F, were measured by a Spex Fluorolog-$\tau 2$ system, which uses the phase-modulation technique (excitation wavelength modulated in the 0.5−330 MHz range; time resolution *ca.* 10 ps). 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 frequency-domain intensity decays (phase angle and modulation *vs* frequency) were analyzed with the Globals Unlimited (rev. 3) global analysis software.[20]

Trans → *cis* photoisomerization quantum yields ($\phi_{t \rightarrow c}$) were measured (mean deviation of at least three independent experiments, approximately 7%) at various λ_{exc} using the lamp of the fluorimeter Spex Fluorolog 112 (bandwidth *ca.* 2 nm). The conversion percentage, measured spectrophotometrically, was held below 10% to avoid competition from the back photoreaction.

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. Transient Absorption. 9-Styrylanthracene. Upon picosecond laser excitation of 9-StAn, a structured absorption spectrum, with λ_{max} of *ca.* 430, 580, and 730 nm, was recorded just after the laser pulse in solvents of different polarity and viscosity as CH, MeCN, and EtG (see Table 1 and Figure 1, as an example). The change of absorbance (ΔA) decreased with time at wavelengths longer than 525 nm but rose between 420 and 525 nm, with an isosbestic point at 525 nm. The spectrum taken after 3.9 ns (curve 7 of Figure 1) shows a main maximum at 460 nm (which is reminiscent of the $T_1 \rightarrow T_n$ spectrum of 9-StAn recorded in previous works)[10,21,26] and a low signal at $\lambda > 525$ nm. The absorption maximum at about 650 nm, recorded only in a polar solvent, showed that the cation radical 9-StAn$^{\bullet +}$ [21] was produced within a few nanoseconds.

The decay kinetics recorded at $\lambda > 525$ nm were described quite well by a biexponential fitting with τ_S (the short-lived component) < 1 ns and τ_L (the longer-lived component) ≥ 2.6 ns. The inset of Figure 1 shows the decay kinetics at 575 nm and the growth of ΔA at 480 nm, which are clearly coupled. In fact, the two kinetics were well-fitted with the same rate constants (differences within the experimental error) and correlation coefficients larger than 0.99. The value of τ_S was affected by the solvent on going from 0.77 ns in MCH to 0.33 ns in the viscous EtG; the solvent effect on τ_L was much smaller.

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Table 1. Singlet−Singlet Absorption Maxima (λ_{max}) and Singlet Lifetimes (τ_S and τ_L) of Some DAEs in Different Solvents at Room Temperature Together with Their Fluorescence Lifetimes (τ_F)

compd	solvent	λ_{max} (nm)	τ_S (ns)	τ_L (ns)	τ_F (ns)
9-StAn	CH	≤430, 585, 720	0.77	3.9	3.6[a]
	MeCN	<450, 580, 660, 730	0.67	4.7	4.2[b]
	EtG	430, 580, 730	0.33	2.9	
1-StN	CH	515, 590, 770	0.59	1.7	1.8[c]
	MeCN	505, 580, >700	0.33	0.83	0.9[d]
	EtG	505, 585, >700	0.11	3.3	
2-StN	n-H	495	0.15	4.5, >10	5.2, 27.6[e]
	MeCN	490, >700	0.14	2.3, >10	3.2, 17.8[d]
	EtG	500, >700	0.16	2.0, >10	
1-StPh	CH	530, 610, 730	0.43	10[f]	10[g]
	MeCN	500, 550, 610, 675	0.42	8.5[f]	7.0[h]
2-StPh	CH	<430, 570, 620	0.40	32[f]	34[g]
	MeCN	550, 600	0.35	26[f]	26.2[h]
	EtG	<430, 570, 620	0.32	27[f]	
9-StPh	CH	500, 705	0.32	5.1	5.3[g]
	MeCN	510, 690	0.30	2.0	2.0[h]
	EtG	510, 695	0.13	3.6	
Ph	n-H	475, 575, 650		56[f]	57.5[i]

[a] In methylcyclohexane, from ref 5. [b] From ref 21. [c] From ref 7. [d] From ref 22. [e] From ref 23. [f] From nanosecond flash photolysis (λ_{exc} = 355 nm). [g] In n-hexane, from ref 24. [h] From ref 12. [i] From ref 25.
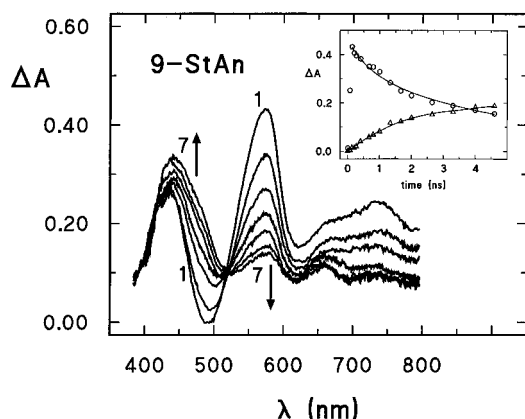

Figure 1. Time-resolved absorption spectra of 9-StAn in MeCN at "zero" time (1) and at 0.57 (2), 1.3 (3), 1.9 (4), 2.6 (5), 3.3 (6), and 3.9 (7) ns (λ_{exc} = 355 nm, air-equilibrated solution). Inset: kinetics recorded at 575 (○) and 480 (△) nm.

***n*-Styrylnaphthalene.** Rather different spectral and kinetic properties were found for the transients of the two *trans* isomers 1- and 2-StN, produced by 355 nm excitation. Preliminary measurements were recently reported elsewhere.[27]

In particular, Ar-saturated solutions of 1-StN, when irradiated with *ca.* 30 ps pulses, showed an instantaneously formed absorption spectrum (Table 1). The spectrum had three broad absorption bands with maxima near 515, 590, and 770 nm. All the bands decayed almost completely over 4 ns with biexponential decays (Table 1). The short-lived component τ_S was strongly affected by the solvent, being 0.59 ns in the nonpolar CH and 0.11 ns in the polar and viscous EtG. On the other hand, the longer-lived component τ_L was much longer in EtG (3.3 ns) than in the other solvents.

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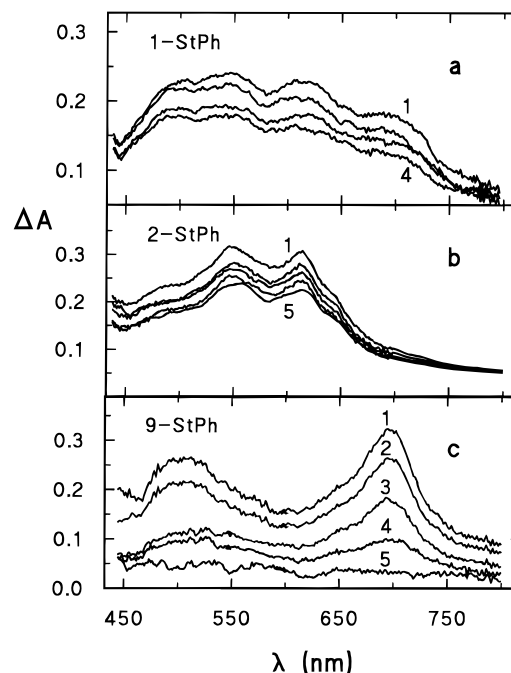
Figure 2. Time-resolved absorption spectra of 1-StPh in MeCN at "zero" time (1) and at 0.27 (2), 0.57 (3), and 1.8 (4) ns, 2-StPh in MeCN at "zero" time (1) and at 0.22 (2), 0.57 (3), 1.3 (4), and 1.8 (5) ns, and 9-StPh in MeCN at "zero" time (1) and at 0.17 (2), 0.57 (3), 1.3 (4), and 3.3 (5) ns (λ_{exc} = 355 nm, Ar-saturated solutions).

In the case of 2-StN, a main maximum (whose position was practically unaffected by the solvent) was present at about 500 nm together with a broad absorption band at λ > 600 nm. At least three transients were detected for this compound. In fact, the initial absorption, detected over the whole 450−700 nm range, decayed with a high rate constant (τ_S of *ca.* 0.15 ns in n-H, MeCN, and EtG) and was replaced by two longer-lived transients. The best fits of the decay kinetics recorded at 500 and 670 nm in MeCN were obtained by monoexponential plus residual (at 500 nm) and biexponential (670 nm) equations. In fact, τ_L values larger than 10 ns (rest absorption with ΔA constant over 2 ns) and of a few nanoseconds were obtained monitoring the absorption in the 500 nm region and at λ > 600 nm, respectively (see Table 1).

***n*-Styrylphenanthrene.** As shown for the previous compounds, a strong short-lived absorption was recorded in a wide wavelength range (see Figure 2) for n-StPh. This absorption decayed by a first-order kinetics with lifetime τ_S shorter than 1 ns (see Table 1).

The spectrum recorded in CH at "zero" time for 1-StPh (curve 1 of Figure 2a) was rather broad with three nonresolved maxima at about 530, 610, and 730 nm. In MeCN, the absorption was shifted at shorter wavelengths (λ_{max} of *ca.* 500, 550, 610, and 675 nm); τ_S did not change with the solvent (~0.43 ns). The longer-lived transient shown in Figure 2a (curve 4) replaced the short-lived component and decayed by a first-order kinetics of 10 ns (in CH) and 8.5 ns (in MeCN). These two lifetimes were measured by nanosecond laser flash photolysis experiments with λ_{exc} of 355 nm.

The behavior of 2-StPh was similar to that of isomer 1. The τ_S values (Table 1) did not change significantly with the position of the styryl group on the phenanthrene moiety. The main differences are due to the shape of the absorption spectra (λ_{max} of *ca.* 570 and 620 nm for the isomer 2) recorded after ps-pulses (Figure 2b) and to the lifetime of the longer-lived transient which was more than 26 ns (obtained by nanosecond flash photolysis).

Table 2. Solvent Effect on the Short-Lived (τ_S) and Longer-Lived (τ_L) Components of the Singlet Decay of 9-StPh

solvent	ϵ	η (mN s m^{-2})	τ_S (ns)	τ_L (ns)
n-H	1.89	0.313	0.37	5.0
CH	2.02	0.98	0.32	5.1
EtAc	6.02	0.455	0.71	3.0
BrP	8.09	0.539	0.11	0.8
DCE	10.36	0.887	0.67	1.8
HeOH	13.3	4.592	0.24	1.6
PrOH	20.33	2.237	0.18	0.9
Me$_2$CO	20.70	0.337	0.77	5.0
EtOH	24.55	1.078	0.23	0.9
MeOH	32.70	0.544	0.18	1.2
MeCN	37.5	0.375	0.30	2.0
EtG	38.66	21	0.13	3.6
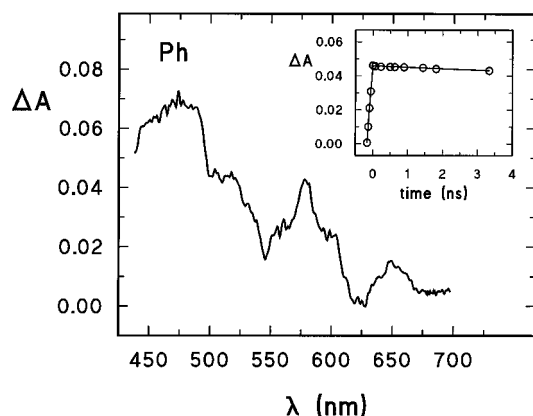
Figure 3. Time-resolved absorption spectra of Ph in *n*-hexane at "zero" time (λ_{exc} = 266 nm, Ar-saturated solution). Inset: decay kinetics recorded at 570 nm.

Picosecond-laser excitation of 9-StPh was performed in 12 solvents of different polarity and viscosity. In all cases, the spectrum showed two maxima (Figure 2c) at about 510 and 700 nm (Table 1). As obtained for the other compounds, two transients were produced in all the solvents. No clear trends of the measured lifetimes with the properties of the medium were found. The τ_S and τ_L values obtained by biexponential fittings are collected in Tables 1 and 2. The shortest values of τ_S were obtained in BrP and in the viscous EtG.

Phenanthrene. Picosecond excitation of Ph itself was performed in *n*-H in order to compare the behavior of the flexible styrylarenes described above with that of a polycyclic hydrocarbon, which does not bear the styryl group, under the same experimental conditions.

The results obtained are shown in Table 1 (last line) and Figure 3. The singlet–singlet absorption spectrum, recorded at "zero" time, shows three absorption bands (λ_{max} = 475, 575, and 650 nm) whose positions and intensities remained practically unchanged in the time-window accessible with our setup (4 ns). The kinetic profile, independent of the wavelength of analysis, is shown in the inset of Figure 3. For this compound, no evidence was found of short-lived transients over the whole wavelength range investigated (450–700 nm). A lifetime τ_L of 56 ns was determined by nanosecond laser flash photolysis. A comparison between τ_L and the fluorescence lifetime (τ_F = 57.5 ns)[25] of Ph in a nonpolar solvent, indicates that the absorption shown in Figure 3 is due to S$_1 \rightarrow$ S$_n$ transitions.

3.2. Fluorescence Lifetimes. To investigate the fluorescence lifetimes of DAEs in the subnanosecond time scale, the emission decays were recorded with a time resolution of *ca.* 10 ps (phase-shift method). Deaerated solutions of DAEs in CH and MeCN were excited at two wavelengths corresponding to the bathochromic maximum (300–330 nm) of the absorption

spectrum and to longer wavelengths (350–370 nm), closer to the 0-0 transition. In all cases, two decay components (τ_1 and τ_2) were detected, the fast one having small amplitudes of 1–4% or less with the exception of 1-StN (A$_1$ in the range 4–14%) (Table 3).

The frequency responses (phase and modulation) recorded for 2-StPh and 9-StPh in MeCN are shown, as examples, in Figures 4a and 5a, respectively. Treatments of the experimental data with a global analysis method[20] gave the results summarized in Table 3 for mono- and biexponential fitting functions. The analysis with a triexponential function (results not shown) gave one pre-exponential factor that was practically zero and/or two decay parameters that were very close to each other. χ^2 parameters greater than those given by biexponential fittings were obtained in all cases.

Generally, the monoexponential functions gave higher χ^2 parameters (Table 3) and worse residual distributions (see Figures 4b,c and 5b,c as examples) than the corresponding biexponential functions. In a few cases (1-StN in MeCN and 9-StPh in CH), at λ_{exc} around 350 nm, the fitting parameter did not improve by using a biexponential treatment thus indicating the absence of the short-lived component at low excitation energies. In the other cases, where two decay components were clearly observable, the amplitude of the short component generally increased with the excitation energy.

The longer-lived fluorescence component was found to be quenched by oxygen at nearly diffusion-controlled rate. Obviously, the short component was unaffected by the presence of oxygen.

The longer component was in reasonable agreement with the τ_F values (Table 1) previously measured by the single-photon counting method by monoexponential deconvolution. In that case, the time resolution (*ca.* 0.3 ns) and the different method of analysis, which had to take into account the source profile, did not allow the short component (with small amplitude) to be detected. In fact, the monoexponential fitting led to nonhomogeneous residual distribution in the short time range, while the biexponential function did not reach convergence.

The values of the fluorescence lifetimes (τ_1 and τ_2) obtained in this work can be compared with the lifetimes τ_S and τ_L measured by singlet–singlet absorption (Tables 1 and 2). If one takes into account the experimental error (larger in τ_1 due to its low pre-exponential factor), the lifetimes of the emission and those of the decay of the singlet–singlet absorption appear to be very close. The decay component in the subnanosecond time scale was not detected by fluorescence measurements for 2-StN. However, the system is here more complicated showing two-component decays with lifetimes longer than 3 ns (due to the emission of two conformers[23]). It must be noted that the large errors in τ_1 and τ_2, obtained by excitation of 2-StN at 320 nm in both solvents, seem to indicate that another component was present, but the triexponential function could not improve the fitting, probably due to the very small pre-exponential factor of the third component.

Frequency-domain intensity decays of anthracene (in CH and MeCN) and phenanthrene (in MeCN) were also recorded. In these cases, the best fitting of the frequency responses was obtained with a monoexponential equation with lifetimes not affected by λ_{exc} (for anthracene, τ_F = 5.1 and 4.7 ns in CH and MeCN, respectively, and for phenanthrene, τ_F = 54 ns in MeCN) and close to the literature data.[25]

3.3. Effects of Excitation Wavelength and Laser Energy. The emission measurements described in Section 3.2 showed that the lifetimes τ_1 and τ_2 were independent of λ_{exc}, while the

Table 3. Mono- and Biexponential Analysis of DAE Fluorescence by the Phase Shift Method[a]

compd	solvent	λ_{exc} (nm)	τ^b (ns)	$\chi^{2\ b}$	τ_1^c (ns)	τ_2^c (ns)	$A_1^{c,d}$	$\chi^{2\ c}$
9-StAn	CH	330	3.5 ± 0.12	1.9	0.68 ± 0.3	3.48 ± 0.03	≤0.0001	1.2
		370	3.56 ± 0.04	1.3	0.43 ± 0.20	3.59 ± 0.06	0.0044	0.98
	MeCN	330	3.88 ± 0.12	1.6	0.69 ± 0.30	4.05 ± 0.07	0.032	0.7
		370	4.00 ± 0.09	2.6	0.35 ± 0.20	4.10 ± 0.05	0.015	0.82
1-StN	CH	302	1.67 ± 0.04	8.4	0.62 ± 0.16	1.82 ± 0.05	0.097	1.7
		360	1.64 ± 0.01	3.7	0.41 ± 0.15	1.75 ± 0.03	0.041	1.05
	MeCN	302	0.68 ± 0.02	1.8	0.32 ± 0.05	0.76 ± 0.02	0.14	1.2
		355	0.62 ± 0.01	2.7	0.62 ± 1.2	0.62 ± 1.2	0.06	2.9
2-StN	CH	320	15.0 ± 2.8	20.0	4.8 ± 1.0	24.0 ± 3.0	0.27	6.6
		350	5.6 ± 0.9	122	3.76 ± 0.05	22.3 ± 0.7	0.70	0.8
	MeCN	320	10.2 ± 1.9	7.9	3.1 ± 0.4	16.3 ± 2.0	0.15	2.9
		350	5.7 ± 1.1	104	3.1 ± 0.08	18.1 ± 0.8	0.58	2.7
1-StPh	CH	320	8.45 ± 0.06	2.6	0.30 ± 0.6	8.5 ± 0.05	0.001	1.1
		360	8.38 ± 0.43	13.3	0.21 ± 0.09	8.5 ± 0.08	0.016	1.18
	MeCN	320	6.9 ± 0.18	7.3	0.83 ± 0.22	7.0 ± 0.3	0.02	6.0
		360	6.85 ± 0.14	4.3	0.78 ± 0.15	7.0 ± 0.05	0.02	0.67
2-StPh	CH	320	33.7 ± 0.54	1.9	0.30 ± 0.15	33.7 ± 0.4	0.001	1.3
		360	32.6 ± 1.2	25.4	0.23 ± 0.18	32.9 ± 0.4	0.005	1.3
	MeCN	325	29.2 ± 0.57	10	0.49 ± 0.20	30.0 ± 0.2	0.006	1.2
		360	29.0 ± 0.9	7.3	0.45 ± 0.14	29.2 ± 0.2	0.006	1.0
9-StPh	CH	300	4.08 ± 0.05	2.2	0.40 ± 0.30	4.09 ± 0.03	0.0006	0.25
		350	3.95 ± 0.03	1.8	3.6 ± 3.4	4.3 ± 4.3	0.47	1.8
	MeCN	325	1.77 ± 0.06	5.7	0.31 ± 0.09	1.89 ± 0.03	0.04	1.2
		370	1.63 ± 0.03	4.2	0.33 ± 0.16	1.69 ± 0.02	0.04	1.8

[a] Broad band emission. [b] Obtained from monoexponential analysis. [c] Obtained from biexponential analysis. [d] Amplitude of the component with decay time τ_1 determined by a nonlinear least-squares fitting.
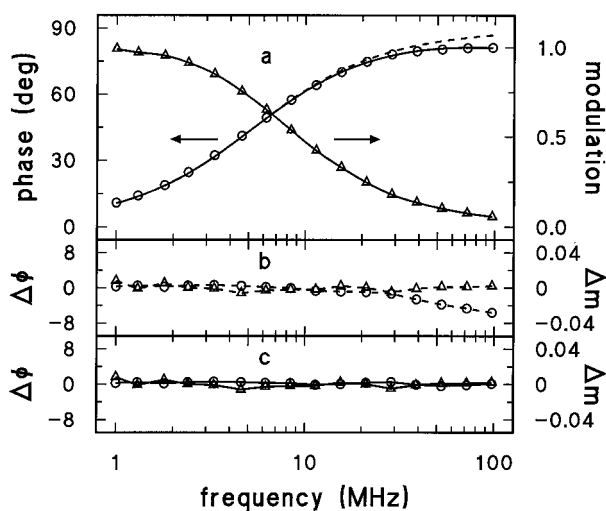

Figure 4. Frequency response of 2-StPh in MeCN fitted by monoexponential (- -) and biexponential (—) functions (a) together with the residual distribution for monoexponential (b) and biexponential (c) fittings (λ_{exc} = 355 nm, broad band emission).
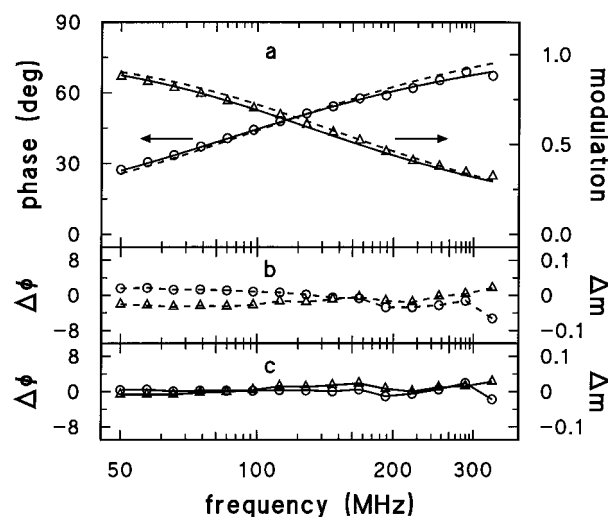

Figure 5. Frequency response of 9-StPh in MeCN fitted by monoexponential (- -) and biexponential (—) functions (a) together with the residual distributions for monoexponential (b) and biexponential (c) fittings (λ_{exc} = 355 nm, broad band emission).

contribution of the short-lived component decreased with the increase of λ_{exc}.

Absorption picosecond laser experiments on 2-StPh in MeCN were carried out to check the effect of λ_{exc} on the transients produced. In fact, both the short- and longer-lived components of the decay were detected upon excitation at 266 and 355 nm. Similar τ_S values were obtained in the two experiments.

The presence of the short-lived component was also checked at different laser intensities for some DAEs. The ΔA values recorded at 550 nm (maximum of the singlet−singlet absorption) obtained by irradiating an oxygen-free solution of 9-StPh in *n*-H (λ_{exc} = 355 nm) are plotted in Figure 6 versus the laser dose. The linear trend, over a wide range of laser intensities, which passes through zero, is typical of transients produced monophotonically upon light absorption.

The effect of λ_{exc} was also investigated by steady-state experiments. Fluorescence quantum yields (ϕ_F) of four DAEs in *n*-H were measured in a wide range of λ_{exc}. The results,

compiled in Table 4, show that for 9-StAn and 9-StPh the ϕ_F values were practically constant (within the experimental error), while a marked effect was found for the other two compounds. In fact, for 1-StN and 2-StPh, ϕ_F increased with λ_{exc}, the highest values (ϕ_F = 0.85 and 0.50 for 1-StN and 2-StPh, respectively) being obtained using an excitation energy close to the 0−0 transition. The same investigation was not performed with 1-StPh and 2-StN, because the conformational equilibrium at room temperature between two different rotamers[23] could have hidden such an effect.

The effect of λ_{exc} on $\phi_{t\rightarrow c}$ of 1-StN and 2-StPh was also investigated (Table 4). The yield of 1-StN decreased markedly when λ_{exc} increased from 320 ($\phi_{t\rightarrow c}$ = 0.16) to 365 nm ($\phi_{t\rightarrow c}$ = 0.07). A similar, but less evident, effect was found for 2-StPh, for which $\phi_{t\rightarrow c}$ values between 0.30 and 0.25 were measured in the 280−370 nm range.

In previous papers, it has been reported that, contrary to the case of 2-StN, the fluorescence quantum yield of 1-StN did not
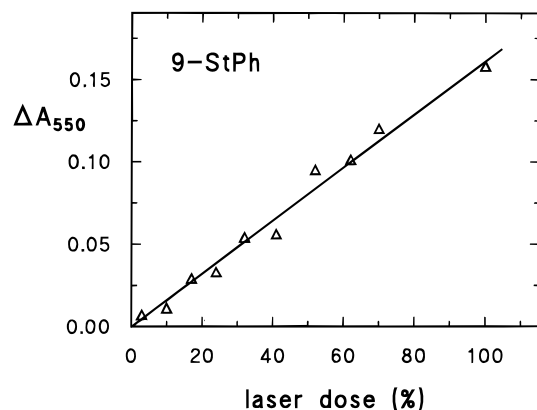
Figure 6. Effect of laser dose on the absorbance change at 550 nm of 9-StPh in *n*-hexane at "zero" time (λ_{exc} = 355 nm, Ar-saturated solution).

Table 4. Effect of the Excitation Wavelength (λ_{exc}, nm) on the Fluorescence Quantum Yield (ϕ_F) and on the *Trans → Cis* Photoisomerization Quantum Yield ($\phi_{t\to c}$) of DAEs in *n*-H

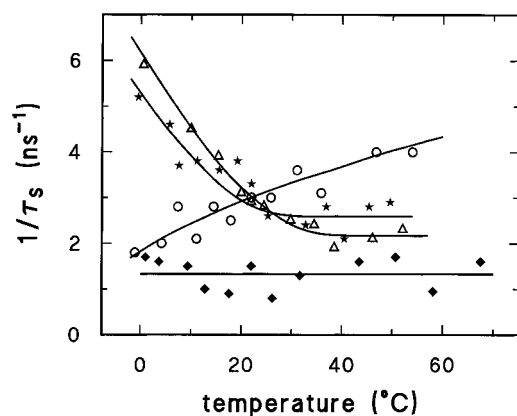| 9-StAn		1-StN			2-StPh			9-StPh	
λ_{exc}	ϕ_F	λ_{exc}	ϕ_F	$\phi_{t\to c}$	λ_{exc}	ϕ_F	$\phi_{t\to c}$	λ_{exc}	ϕ_F
370	0.49	300	0.70		280	0.32	0.30	293	0.62
384	0.49	310	0.70		290	0.37		300	0.65
400	0.49	320	0.69	0.16	300	0.39		310	0.65
420	0.48	340	0.70	0.15	310	0.42		320	0.64
430	0.48	350	0.77	0.10	325		0.27	340	0.64
		360	0.80	0.08	330	0.42		350	0.65
		365	0.83	0.07	340		0.28	360	0.70
		370	0.85		355	0.45	0.24	370	0.67
					372	0.50	0.25		

Figure 7. Temperature effect on the lifetime (τ_S) of the short-lived component of the singlet-singlet absorptions of 1-StN (○), 9-StAn (◆), 2-StPh (△), and 9-StPh (★) in Ar-saturated MeCN.

vary with the frequency of the exciting light.[6,23,28] This was taken as a demonstration of a shift of the ground state conformational equilibrium toward the more stable rotamer of 1-StN. As a matter of fact, the λ_{exc} effect had been explored in our laboratory in the 270−340 nm range. Therefore, our measurements failed to show the increase of ϕ_F now observed in the 340−370 nm range, a trend which is not consistent with the presence of rotamers.

3.4. Temperature Effect. To check the presence of activated decay processes in the singlet manifold, τ_S of four DAEs (9-StAn, 1-StN, 2-StPh, and 9-StPh) was measured in MeCN in the 0−70 °C temperature range; the results obtained are summarized in Figure 7 where the plots of the decay rate constants (τ_S^{-1}) *vs* temperature are shown. Three different
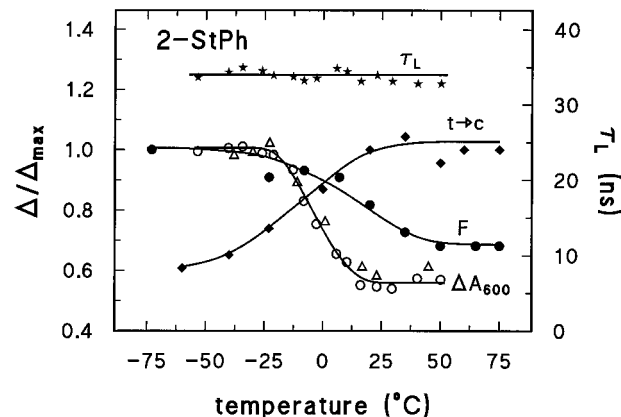
(28) Fischer, E. *J. Phys. Chem.* **1981**, *85*, 1770.

Figure 8. Temperature effect on the relative change of absorbance ($\Delta A/\Delta A_{max}$) at 600 nm (extrapolated at "zero" time) of 2-StPh in *n*-hexane (○) and MeCN (△), on the longer lifetime τ_L (★) in *n*-hexane, and on the relative ϕ_F (●) $\phi_{t\to c}$ (◆) values in methylcyclohexane (taken from ref 8).

behaviors were recorded: (*i*) τ_S of 9-StAn was practically constant over the temperature range investigated, (*ii*) for 1-StN there was an increase of τ_S^{-1} with the temperature (typical behavior expected in the presence of an activated decay process), and (*iii*) for the two StPh isomers, a decrease of the decay rate constant was obtained on increasing the temperature between zero and 25 °C, while above room temperature, τ_S remained practically constant. This atypical behavior could not be followed below 273 K owing to the limits of the picosecond setup.

For 2-StPh, whose fluorescence lifetime is rather long (tenths of nanoseconds), nanosecond flash photolysis experiments allowed the relative population of the longer-lived transient (measured as relative ΔA_L at 600 nm) to be followed at different temperatures (over a −75 ÷ 50 °C range). Figure 8 shows the relative absorbance change (ΔA_L) obtained in the nonpolar *n*-H and in the polar MeCN. The two, practically identical, trends look like titration curves with a plateau below −25 °C (maximum concentration of the transient), an inflection point at about 0 °C, and another plateau above 25 °C (minimum concentration of the transient). This behavior can be compared with those of fluorescence and *trans → cis* photoisomerization quantum yields of 2-StPh in methylcyclohexane[8] shown in the same figure. The effect of temperature on ϕ_F is reminiscent of that on ΔA_L, while $\phi_{t\to c}$ increases with temperature over −60 ÷ 25 °C and remains practically constant at higher values of temperature.[8] Figure 8 also shows the τ_L values obtained over the same temperature range; since they are constant within the experimental error, no activated decay processes are expected for this longer-lived transient.

4. Discussion

4.1. Transient Assignment. All the DAEs investigated displayed a biexponential decay of both the singlet−singlet absorption transients produced by short-pulse laser excitation (lifetimes τ_S and τ_L) and the fluorescence emission (lifetimes τ_1 and τ_2).

The lifetimes, measured by the two techniques, coincide within the experimental error indicating that they originate from the same electronic states. Only in the case of 2-StN, the fast component was not detected by fluorimetry, the two long-lived components being assigned to the known s-trans and s-cis rotamers of this molecule.[6,23]

While the similarity of the longer-lived components, τ_L and τ_2, to the known lifetimes measured by nanosecond fluorimetry

(τ_F in Table 1) clearly indicates that they refer to the $S_1 \rightarrow S_n$ and $S_1 \rightarrow S_0$ transitions, respectively, the assignment of the shorter ones, τ_S and τ_1, is less straightforward and not discussed in the literature for these stilbene-like molecules.

The two decay components cannot be due (with the exception of the fluorimetric measurements on 2-StN) to the presence of s-trans−s-cis rotamers since for some compounds (9-StPh, 9-StAn) no rotamerism is expected and for others (1-StN, 1-StPh) the rotamer equilibrium is expected to be almost completely shifted toward the more stable species.[23] Moreover, previous studies of the conformational equilibria of DAEs, carried out in our and other laboratories, have shown that the S_1 lifetimes of the existing rotamers are generally in the nanosecond time scale and relatively close one to each other.[23] This does not exclude that conformations more or less deviating from planarity (due to small angles of twisting about the ethenic bridge or the 1-α bond between the ethenic carbons and the aryl groups) may play a role in the relaxation processes of the lowest excited singlet states, mainly affecting the internal conversion (IC) rate (see below).

The fast decay component is more reasonably assigned to an upper excited state which lives long enough to relax through decay channels competitive with IC to S_1.

Indications of a role of upper states in the photoisomerization of *trans*-stilbene itself had been reported in the past by K. Fuke *et al.* on the basis of the results obtained by using two-photon fluorescence excitation and thermal lensing methods.[29] Another indication was previously reported by some of us for a similar flexible molecule, *trans*-2-StAn.[30] In addition to the dual slow fluorescence, assigned to two equilibrated conformers, a third emission component was detected for this anthryl derivative above 200 K at $\lambda_{exc} < 410$ nm and assigned to an anti-Kasha emission from a thermally populated S_2 state.

Theoretical calculations[6,8,9] have shown that these flexible DAEs generally have the S_2 state closely located to the lowest fluorescent state S_1, and, in fact, the fast transient was not detected in the absence of the flexible styryl substituent (see sections 3.1 and 3.2 for phenanthrene and anthracene).

Discussing first the absorption results, the fast transient detected in the present work was assigned to a transition from an upper excited state, probably implying the second excited singlet ($S_2 \rightarrow S_n$), based on the following: (*i*) it was produced, monophotonically, within the laser pulse; (*ii*) it decayed by a first order decay kinetics; (*iii*) it was observed for all the DAEs investigated at different λ_{exc} and in a number of solvents; (*iv*) its lifetime is practically equal to the short-lived component of the fluorescence decay; and (*v*) like S_1, it interacted efficiently with concentrated additives such as heavy-atom-containing compounds (e.g., using BP as solvent) or electron donors or acceptors, thus inducing the formation of triplet states or radical ions, respectively.[27,31]

This assignment could appear not consistent with the small changes observed for the singlet−singlet absorption spectra with the delay time; anyway, it seems to us reasonable considering the probable strong mixing between the two states (see below). It is to be noted that, as already observed for *n*-StN,[27] the transient spectrum (a pure electronic property) depends linearly on the oscillator strength of the transitions from the composite states to S_n, while the dynamic properties depend exponentially on the vibronic rearrangement of the two states during their relaxations.

Other possible explanations for the short decay component were considered.[27] One could think, e.g., of τ_S reflecting the rate of equilibration of the upper state toward S_1. However, this hypothesis seems to be ruled out by the largely different ratios of the pre-exponential factors of the absorption (*ca.* 1) and emission (generally, < 0.05) decays. In case of an equilibration, one would expect to observe only one state and then expect a ratio depending only on the equilibrium rate and independent of the detection technique. In fact, the large difference in the measured ratios should reflect the difference in the extinction coefficients (absorption) and fluorescence yields (emission) of the two states. A similar explanation could be offered by the relaxation of the Franck−Condon (transoid) S_1 state towards more stable twisted conformations. However, the fact that the shape of the fluorescence spectra is independent of λ_{exc} and temperature seems to rule out such hypothesis too. Other possible assignments, such as transitions from the $^1perp^*$ configuration, must be ruled out since the precursor twisting from S_1 ($^1trans^* \rightarrow {}^1perp^*$) would be too slow to be operative during the laser pulse. Moreover, it would not be expected for 9-StAn, because it does not isomerize at room temperature. On the other hand, the occurrence of some kind of solvent rearrangement is expected to be faster than the lifetime of the observed transient.

An important support for the assignment of the short-lived component (τ_S) observed by absorption measurements to the S_2 state came from the decay component (with an amplitude, A_1, generally smaller than 4%) measured in emission with practically the same lifetime (τ_1). Another evidence for all the DAEs investigated is the general increase of A_1 on increasing the excitation energy (see Table 3).

The reliability of the present assignment of the short-lived component seems to receive further support by theoretical calculations in progress.[32] In fact, a perturbative treatment, based on vibronic coupling, shows that the two lowest excited states of 1-StN and other related molecules are mixed and that they have noncommunicating decay pathways, characterized by different rates. The fast component could remain hidden in the emission spectrum being the minor one, as indicated by the small amplitudes measured in the fluorescence decay.

The unexpected long lifetime assigned to S_2 deserves some comments. It has to be noted that the rate constant of the $S_2 \rightarrow S_1$ internal conversion (k_{IC}) depends on several factors including the energy gap, the vibronic coupling, the vibrational density of the destination state and the Franck−Condon factor. When the energy gap (ΔE) is high (e.g., 20 000−30 000 cm^{-1}), k_{IC} depends mainly on the energetic factor and increases when ΔE decreases. However, when the two states are close ($\Delta E < 3000$ cm^{-1}), k_{IC} depends strongly on the vibronic coupling also. If the nature of the two states is rather different, the adiabatic coupling between S_2 and S_1 decreases. In the meantime, the vibrational density of the destination state decreases by many orders of magnitude. In the literature, there are several examples of upper excited states, with lifetimes up to hundreds of picoseconds, having rather slow IC when the two states are very close.[33] Quantum-mechanical (semiempirical) calculations on our compounds have shown that the nature of S_2 and S_1 is rather different (one state is more ethenic and the other more arylic, depending on the compound[5,6,32]), and, consequently, the k_{IC} value predicted is in agreement with the long lifetime measured for S_2 in the present work.

4.2. Decay Channels from S_2 and S_1. The competition of

(29) Fuke, K.; Sakamoto, S.; Ueda, M.; Itoh, M. *Chem. Phys. Lett.* **1980**, *74*, 546.

(30) Bartocci, G.; Mazzucato, U.; Spalletti, A.; Elisei, F. *Spectrochimica Acta* **1990**, *46A*, 413.

(31) Latterini, L. *et al.* Unpublished results.

(32) Marconi, G. Private communication.

(33) See, e.g.: Ferrante, C.; Kensy, U.; Dick, B. *J. Phys. Chem.* **1993**, *97*, 13457. Sahyun, M. R. V.; Sharma, D. K. *Chem. Phys. Lett.* **1992**, *189*, 571.

the relaxation processes from the S_1 state of DAEs (fluorescence, ISC, isomerization) has been described in previous papers from our and other laboratories.[1-9] In this discussion more attention will be paid to the decay from the upper excited singlet state. The dominant relaxation process seems to be very dependent on the nature of the DAE.

Intersystem crossing to the triplet manifold, starting from S_2, was evidenced for the anthryl derivative, 9-StAn. This is shown in Figure 1, where the biexponential decay kinetics of S_1 and S_2 (precursors) correspond to the rise of the band at 460 nm, assigned to the $T_1 \rightarrow T_n$ absorption.[10,21,26] The absence of isomerization of 9-StAn, ascribed to high torsional barriers in both the singlet and triplet manifolds,[9] was here confirmed by the constancy of the fluorescence quantum yield with λ_{exc} (Table 4) and of the lifetime τ_S with the temperature (Figure 7), which indicates the absence of activated relaxation channels.

For the naphthyl derivatives, which have a substantial yield of isomerization to *cis* but a negligible triplet yield,[1-3,6,7] the decay of S_2 is generally faster than for 9-StAn (Tables 1 and 3), indicating a possible intervention of twisting already in the upper state. Moreover, for these derivatives, which have been reported to exist in two ground-state isomeric conformations,[23] some interesting information was obtained from the longer-lived transient. In the case of 1-StN, for which the equilibrium between the two rotamers is markedly shifted toward the more stable rotamer,[6,23,28,34] only one slow decay component, independent of the monitoring wavelength, was observed. This is in agreement with the results of the fluorimetric measurements which indicated only one rotamer in fluid solutions over a large temperature range. On the other hand, two different, longer-lived decay components, in addition to the fast one, were observed in the transient absorption of 2-StN when monitoring at 450 nm or at longer wavelengths. These transients were assigned to the two rotational isomers, already described in several papers.[6,23,27,28,34,35] For 1-StN, the short lifetime τ_S decreased with the increase of temperature, as reported for the longer τ_F value,[6,28,34] indicating activated twisting leading to the *cis* isomer in both S_2 and S_1 states.

For 1-StN and 2-StPh, an increase of ϕ_F with λ_{exc} was observed, the maximum yield being obtained when the excitation approached the 0−0 transition (Table 4). A parallel decrease of $\phi_{t \rightarrow c}$ with λ_{exc} was found for both compounds, particularly evident for the naphthyl derivative. In the singlet manifold, the diabatic isomerization mechanism accepted for these DAEs[1-9] consists in the $^1trans^* \rightarrow {}^1perp^*$ twisting followed by IC to the ground state ^1perp and then partitioning (*ca.* 50:50) to the ground state *trans* and *cis* isomers. On this basis, one can get information on the nonradiative and nonreactive deactivations by the difference $[1 - (\phi_F + 2 \times \phi_{t \rightarrow c})]$. For the compounds listed in Table 4, this difference was never found to be higher than 0.08, which indicates, taking into account the experimental uncertainty, that the IC to the ground state is generally negligible. The radiative quanta lost on exciting at an energy level higher than that corresponding to the 0-0 transition are then recovered at the upper level through the reactive pathway. One can conclude that excitation to upper excited singlet states of molecules whose twisting in S_1 is highly activated can increase the isomerization yields through a faster, less-activated, twisting in S_2.

(34) Haas, E.; Fischer, G.; Fischer, E. *J. Phys. Chem.* **1978**, *82*, 1638. Fischer, E. *J. Photochem.* **1981**, *17*, 331.

(35) Alfimov, M. V.; Shenck, Yu. B.; Kovalenko, N. P. *Chem. Phys. Lett.* **1976**, *43*, 154 and references therein. Matthews, A. C.; Sakurovs, R.; Ghiggino, K. P. *J. Photochem.* **1982**, *19*, 235 and references therein. Bartocci, G.; Mazzucato, U.; Masetti, F.; Aloisi, G. G. *Chem. Phys.* **1986**, *101*, 461 and references therein. Saltiel, J.; Sears, D. F., Jr.; Choi, J.-O.; Sun, Y.-P.; Eaker, D. W. *J. Phys.Chem.* **1994**, *98*, 35.

The transients of the three phenanthryl derivatives investigated absorb in the same spectral region but display different behavior. The solvent effect, particularly investigated for 9-StPh (Table 2), showed no clear trend with polarity and viscosity. The shortest lifetimes for both transients were measured in BrP (as expected, due to the favored spin-orbit coupling induced by the heavy atom, which favors ISC in both excited singlet states), in alcoholic solvents (probable implication of H-bonded structures which favor planar or quasi-planar conformations and their radiationless deactivation by IC), and in EtG (possibly due to fast IC from specific conformations favored in the viscous solvent, see below).

It is not easy to explain the unusual temperature effect found on 2-StPh and 9-StPh in MeCN (Figure 7), whose lifetime τ_S increased with temperature from 0 to 25 °C remaining practically constant at higher temperatures. It seems that at least a second distinct decay process, probably IC, is influenced by temperature in addition to the activated *trans* → perp** rotation. In fact, one cannot exclude that temperature modifies the conformational distribution of these flexible molecules with a subsequent change of the k_{IC} value. Therefore, the increase in the short lifetime with temperature can be considered the result of two opposite effects, namely a slower IC process, dominant for both compounds, and a faster twisting in S_2, which is evident only in the case of 2-StPh since the isomer 9 is known to isomerize in the lowest S_1 and T_1 states.[8,11,12] This tentative explanation of the role of twisted geometries is speculative but reasonable considering that such conformations can strongly affect the vibronic coupling between S_1 and S_2 and then the rate of internal conversion. A similar explanation could apply to the effect of the viscous solvent cited above. It is to be noted that these two phenanthrene derivatives are expected to isomerize at a low rate from S_1 due to the high torsional barrier measured by fluorimetry.[8] Moreover, isomer 2 has the lowest state of L_b character,[8] weakly coupled with the ethenic B_u state, and is therefore expected to display an even lower reactivity.

Figure 8, which refers to 2-StPh, offers further indications on the behavior of this DAE. First of all, it shows that τ_L remains constant indicating that no activated channels are operative in S_1, which can therefore be considered as a nonisomerizable state. In the same temperature range, the trend of the optical density of the longer-lived transient in *n*-H and MeCN, practically the same in both solvents, can be compared with the trends of the fluorescence and photoisomerization quantum yields in methylcyclohexane. These trends of the quantum yields and transient absorptions are in very close agreement each other, considering the different solvent and techniques involved. They show that from room temperature upward the minimum population of S_1 corresponds to the minimum emission yield and maximum reactivity, while the opposite situation is observed from −25 °C downward; the two limiting situations are connected by an inflection of the various parameters in the −25 to +25 °C range. Taken together, these observations indicate that S_2 is the state that is mainly responsible for isomerization of 2-StPh, either by direct twisting to the $^1perp^*$ configurations in the singlet manifold or through ISC followed by twisting in the triplet manifold. Both decay processes of S_2 are probably operative. In fact, a contribution of an upper triplet has been indicated by previous flash photolytic measurements mentioned in the Introduction.[11,12,24] However, considering that the $T_1 \rightarrow T_n$ spectrum was readily observable in fluid solution in the presence of perturbers (triplet donor sensitizers or heavy-atom containing compounds), but was not detectable by direct excitation, a contribution, at least partial,

of twisting in S_2 itself can now be considered as a more convincing explanation.

For 9-StPh in *n*-H, the negligible effect of λ_{exc} shown in Table 4 is in agreement with a *trans** → *perp** rotation in the T_1 state, as pointed out from previous works.[8,11,12]

5. Conclusions

The results of the absorption and emission measurements in the picosecond region allowed the decay kinetics of the upper excited singlet state of the DAEs investigated to be spectroscopically detected. The role played by this upper state in the reactive and radiationless relaxations was demonstrated for some compounds, on the basis of temperature and λ_{exc} effects. Depending on the nature of the polycyclic aryl group of the DAE, a fast radiative relaxation of the upper singlet to the ground state (2-StAn, previously reported[30]) or its fast nonradiative relaxation toward the triplet manifold (9-StAn) or toward the isomerization channel (1-StN and 2-StPh) can compete with the IC pathways to S_1 and S_0.

This phenomenon appears to be more common than imagined so far. It falls also into line with the results of the two-photon fluorescence-excitation experiments on stilbene[29] mentioned in section 4.1, which showed the existence of a λ_{exc}-dependence of ϕ_F assigned to the presence of a fast decay channel from an upper singlet state, namely a barrierless twisting to the nonfluorescent $^1perp*$ state. Unlike the case of the twisting in the S_1 state, this process in the upper state could be fast enough to compete with the vertical internal conversion to S_1.

JA961859C