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Dynamics of the Singlet Excited States of Diarylethenes in the Presence of Charge-Transfer Interactions. A Picosecond Laser Flash Photolysis Study

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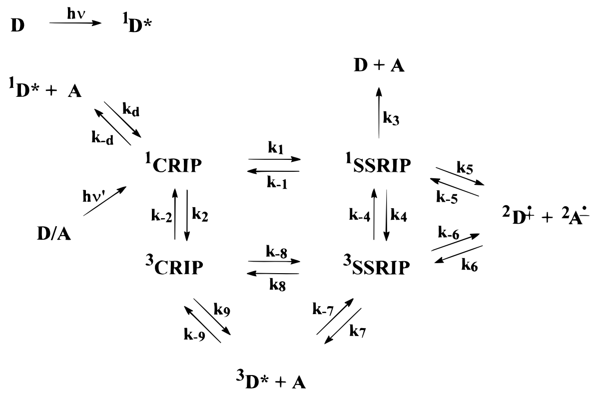
Charge-transfer interactions of singlet excited trans isomers of *n*-styrylnaphthalene (*n*-StN, with $n = 1$ and 2), 9-styrylanthracene (9-StAn), and *n*-styrylphenanthrene (*n*-StPh, with $n = 1$, 2, and 9) with electron donors (*N*,*N*-diethylaniline, DEA, and 4-bromo-*N*,*N*-dimethylaniline, BrDMA) and acceptors (*p*-dicyanobenzene, DCNB) were studied in polar and nonpolar solvent at room temperature by absorption picosecond laser flash photolysis. The transient absorption formed within the laser pulse, already attributed to $S_1 \rightarrow S_n$ and $S_2 \rightarrow S_n$ transitions, were replaced, in the presence of amine quenchers, by the absorption of the exciplex (nonpolar solvent) or of contact radical ion pairs (CRIP, polar solvent). The time evolution of these transients showed the formation of the solvent-separated radical ion pair (SSRIP) and then of the longer-lived absorption of triplet state and/or radical anions. In the presence of DCNB in polar solvent the evolution of the first excited singlet showed the formation of CRIP, SSRIP, and radical cations. The criteria of the transient attribution and the spectral and kinetic characteristics of the transients are reported.

Introduction

Charge-transfer interactions of the excited states of *trans*-diarylethenes with electron donors and acceptors have been widely studied during the past two decades.[1−10] Formation and decay of the exciplexes in nonpolar solvents and the complete photoinduced electron transfer in acetonitrile in the presence of aromatic and aliphatic amines and different electron acceptors have been investigated for stilbene and styryl derivatives of naphthalene, phenanthrene, and anthracene. In particular, the radical anions and cations were characterized in terms of absorption spectra, extinction coefficients, lifetimes, and formation quantum yields.[2a,b,4−11] The quenching of singlet excited diarylethenes by amines (especially those bearing a heavy atom, e.g., bromo-*N*,*N*-dimethylaniline, BrDMA) or by electron acceptors in polar and nonpolar solvents was shown to produce an increase of the triplet population and of the photoisomerization quantum yield.[2c,d,4−9] In acetonitrile, the quenching of diarylethene fluorescence by BrDMA produces the triplet state of the olefin for styrylphenanthrenes and -anthracenes[4,5,10,11] or, as the case of styrylnaphthalenes and their aza derivatives,[12] mainly the radical ions. Fluorescence quenching by BrDMA, due to the enhancement of ISC process, was used in several cases to determine the efficiency of ISC of diarylethenes with low triplet quantum yield.[5,l0−12]

The results of a recent study of fluorescence and transient absorption of some diarylethenes in the picosecond region[15−17] have shown that the lowest excited singlets (S_1 and S_2) can absorb and fluoresce, populate the lowest triplet, and, in the presence of electron donors and acceptors, be quenched at close to the diffusional limit.[15−17] The spectral and kinetic behavior of 2-StN in the picosecond time scale[15,16] was complicated by the presence of two conformers at room temperature. In fact, two transients assigned to the $S_1 \rightarrow S_n$ transitions of the two rotamers have been detected.[15,16]

SCHEME 1:



The charge-transfer processes and the related ionic transient species formed in the bimolecular quenching of excited states have been widely investigated by several authors.[l3−23] The commonly accepted scheme for photoinduced electron transfer shows three main intermediates which differ in their energies, center-to-center distance, and degree of solvation. In polar solvents, excitation of CT complexes is generally believed to produce contact radical ion pairs (CRIP) which can either undergo charge recombination or evolve along the solvent coordinate to become solvent-separated radical ion pairs (SSRIP) and ultimately free ions (FI).[18−28] The formation and decay of these transients generated in the photoexcitation of donor (D)/acceptor (A) systems or in the diffusive quenching of D* by A is described in Scheme 1, redesigned on the basis of that by Peters and Lee concerning stilbene−fumaronitrile complexes.[25] In nonpolar, solvent fluorescent exciplex (^{1}E*) replaces CRIP.

According to this scheme, the triplet state ^{3}D is formed by CRIP, by SSRIP, and by the recombination of the free ions. Moreover, a long-range back electron transfer in SSRIP takes place and generates D and A in the ground state. In the case of stilbene−fumaronitrile complexes, lifetimes of ca. 100 and 1000 ps were measured for CRIP and SSRIP, respectively, with a rate constant of 0.6×10^9 s^{-1} for the formation of FI from SSRIP.[25] For other systems (intermolecular complexes of

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aromatics with pyridinium-analogue acceptors in zeolites), the free ions were formed within the laser pulse duration (25 ps).[29]

The possibility of a long-range electron transfer in the diffusional bimolecular quenching process of an excited state A* by an electron donor D (or vice versa, of an excited state D* by an electron acceptor A) was introduced by Gould et al.[31] on the grounds of the measurements of fluorescence quantum yields and lifetimes of exciplexes (E) in solvents of different polarity. They defined an encounter excited pair having a dynamic structure where A* and D are separated by the solvent (S). The encounter complex, A*/S/D (or A/S/D*), can form E or CRIP or SSRIP directly through a long-range electron transfer. In this scheme, SSRIP can be formed in two ways, but the final outcome is the same fate.[31]

It seemed of interest, in this context, to extend the flash photolysis investigation to diarylethenes[15−17] in the presence of DEA, BrDMA, and DCNB in order to follow the dynamics of the CT interactions in the picosecond−nanosecond region and to observe the evolution of the first formed CT intermediate (E or CRIP) until the formation of FI. It was also of interest to try to understand whether the triplet state was produced in a pathway parallel to that of the ion formation or in the process of ion recombination. A picosecond laser flash photolysis investigation concerning the kinetic and spectroscopic properties of the transient species originated in the diffusive quenching of the DAE fluorescence by different quenchers is reported in this paper. Time-resolved spectra of styryl derivatives of naphthalene, phenanthrene, and anthracene in the presence of DEA, BrDMA, and DCNB in polar and nonpolar solvent are presented, and the assignments of the transients to the singlet states, CT, and/or ion pair states are discussed.

Experimental Section

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 the same as used for previous work.[32]

N,N′-Diethylaniline (DEA, Carlo Erba, RPE grade), 4-bromo-*N,N′*-dimethylaniline, (BrDMA, Aldrich Chemie), and 1,4-dicyanobenzene (DCNB, Aldrich Chemie) were used as quenchers. DEA was distilled under vacuum before use; BrDMA and DCNB were used as received. The solvents (Fluka, ACS grade) were distilled and dried (acetonitrile, MeCN; ethanol, EtOH) or used as received (cyclohexane, CH; *n*-hexane, *n*-H; 1,2-dichloroethane, DCE; ethyl acetate, EtAc).

Picosecond laser flash photolysis studies were carried out with the third harmonic ($\lambda_{\mathrm{exc}} = 355$ nm, pulse width 30 ps, and energy <5 mJ) 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 already been described.[33] The “zero time” was taken as the time at which 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 to give a 7 ns pulse at 355 nm (energy < 10 mJ/pulse).

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

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

Results and Discussion

Criteria of the Transient Assignment. Laser flash photolysis measurements on diarylethenes (DAEs) in the presence of electron donors or acceptors showed that both singlet states S_l and S_2 are quenched with rate constants (k_q) close to the diffusional limit.[15−17] The fluorescence quenching followed the Stern−Volmer equation at least for quencher concentrations below 0.01 M; at higher concentrations, evidence of static quenching was observed. For all the DAEs, the nature and evolution of the transients were dependent on the characteristics of the quencher and the polarity of the solvent. The transients with charge-transfer character (E or CRIP, SSRIP, and FI) and the triplet states were assigned on the basis of the following arguments and experimental observations: (i) in a nonpolar solvent the transient absorption decaying with a lifetime close to that of exciplex fluorescence was attributed to the exciplex; (ii) in a polar solvent (where the complexes do not emit) the absorption spectrum similar to that assigned to the exciplex in a nonpolar solvent was attributed to the contact radical ion pair (CRIP); (iii) the transient absorption having features close to those of the radical ions,[10−12] but with a shorter decay lifetime, was attributed to solvent-separated radical ion pair SSRIP (this species decays in the nanosecond time scale, while the free ions generally in the microsecond time scale); (iv) the transient species having an absorption similar to that of T_1 but decaying faster was identified as the triplet complex; and (v) the radical ions and triplet states of the olefins were identified through the comparison of their transient absorption characteristics with those already recorded in the microsecond time scale.[10−12] The absorption of the quencher-derived radical ions was too weak to be detected.[10−12]

In the presence of amines, the lifetimes of the two rotamers of 2-StN became close to each other, and the transients produced by CT interactions did not show spectral and kinetic changes attributable to the presence of two rotamers.

Interactions with *N,N*-Diethylaniline. Addition of DEA at concentrations below 10^{-2} M to solutions of DAE in a nonpolar solvent quenched the fluorescence with concomitant formation of emitting exciplexes (with fluorescence lifetime τ_E of tens of nanoseconds for StPhs)[3,13] but did not markedly affect the shape of the transient spectra obtained just after the laser pulse, with respect to those in the absence of additives. At delay times longer than 3 ns, a longer-lived absorption was observable in the spectral region where the singlet states absorbed. The decay lifetimes recorded at the wavelength of the absorption maximum showed that S_l decayed faster than in the absence of the amine (due to the quenching process)[3,12,13] and that a longer-lived species (with lifetime longer than the unquenched S_l) was formed. This transient absorption was assigned to the singlet−singlet transitions of the exciplex because (i) its lifetime matched that of the exciplex determined by fluorimetric techniques,[3,13] (ii) its lifetime value depended on the DEA concentration, and (iii) it disappeared in the absence of DEA or DAE. The exciplex absorption evolved toward a spectral form similar to that of the triplet state but decayed faster and was assigned to the triplet exciplex. The formation of the triplet exciplex was more easily observed at DEA concentrations greater than 10^{-2} M where the static interactions became important and the quenching of singlets was more efficient. For 1-StN, the lifetimes of S_1 and S_2 became kinetically indistinguishable, since the former was shortened more than the latter. In these experimental conditions, spectral changes were observed for all the *n*-StPh isomers even at delay times longer than 0.5 ns. These changes are probably due to differences in the absorption spectra of the singlets and of the exciplexes. The transient absorption spectra

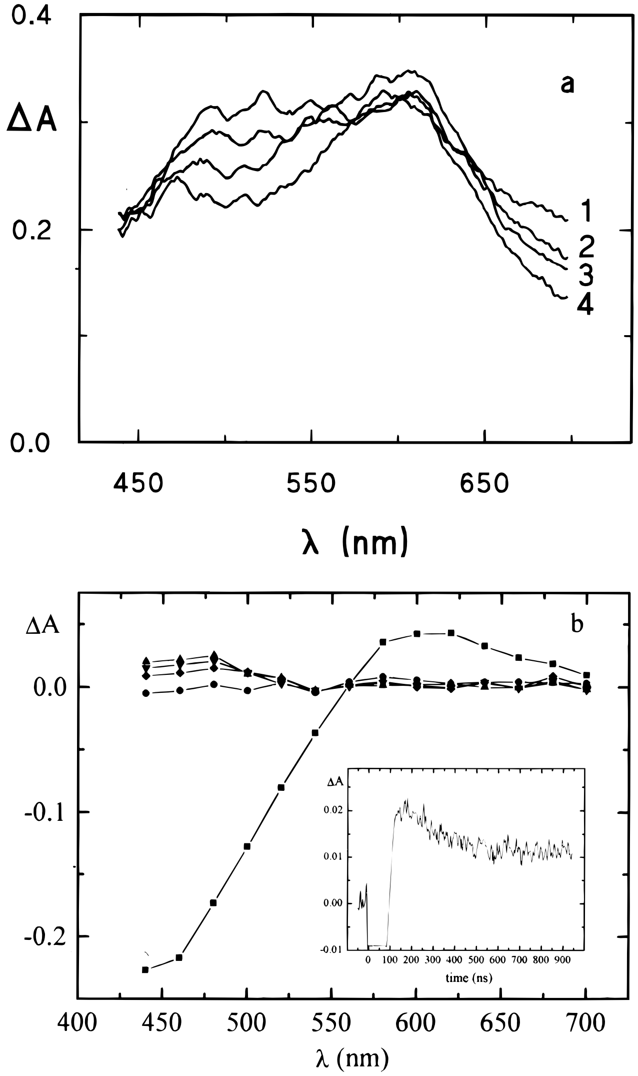

Figure 1. Time-resolved absorption spectra of 1-StPh in CH in the presence of 0.06 M DEA (a) recorded at "zero time" (1) and at 0.6 (2), 1.3 (3) and 1.9 ns (4) after the laser pulse and of 1-StPh in *n*-H in the presence of 0.003 M DEA (b) recorded at 35 (□), 95 (○), 200 (△), 290 (▽), and 390 ns (◇). Inset: decay kinetics at 480 nm.

TABLE 1: Spectral Properties of the Transients Formed by Laser Excitation of DAE in Cyclohexane in the Presence of DEA and Their Assignment

compd	[DEA] (10^{-2} M)	λ_{max} (nm)	delay (ns)	transient
1-StN	4	515, 595	0	S_1, S_2
		480, 600	2.9	$^1E^*$
1-StPh	6	490, 550, 620	0	S_1, S_2
		470, 600	1.9	$^1E^*$, $^3E^*$
2-StPh	10	570, 620	0	S_1, S_2
		565	2.9	$^1E^*$, $^3E^*$

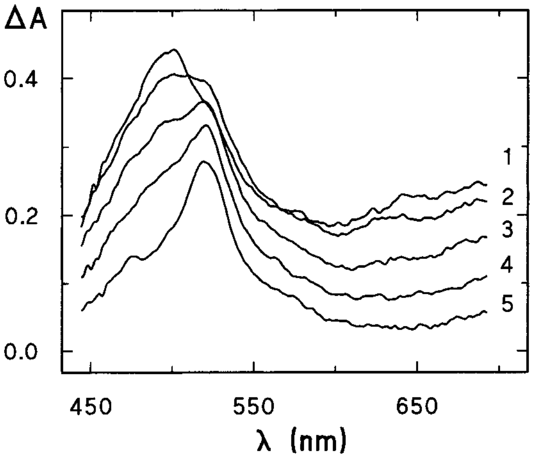

Figure 2. 2-StN in MeCN: time-resolved absorption spectra in the presence of 0.02 M DEA recorded at "zero time" (1) and at 0.3 (2), 0.9 (3), 1.9 (4), and 4.6 ns (5) after the laser pulse.

of 1-StPh in CH in the presence of 0.06 M DEA are reported in Figure 1a as an example. The absorption of the singlet states were replaced at ~600 nm by that of the exciplex which has a lifetime τ_E of ~25 ns, (in good agreement with that obtained from fluorescence measurements.[13] The absorption located around 460 nm is in the region of that of the triplet but decays faster and is therefore assigned to the triplet exciplex ($^3E^*$). Its decay is shown in Figure 1b for the 1-StPh/DEA system in the nonpolar solvent *n*-hexane; in particular, the kinetics recorded at 480 nm is reported.

The residual absorption at longer times is attributed to the triplet of 1-StPh. Unfortunately, it was not possible to record the formation of $^3E^*$ by emission techniques ($^3E^*$ does not emit) or by absorption (the growth of the triplet exciplex is hidden by the exciplex fluorescence). However, clear evidence for the formation of the triplet exciplex for StPhs/DEA systems in *n*-hexane was reported in a previous paper where the equilibrium constant for the formation of the exciplex between ^{3}StPh and DEA was also measured ($\approx 10^4$ M^{-1}).[5] All the StPhs, except 2-StPh, have efficient ISC.[5] However, in the presence of DEA concentrations such as those in Figure 1, the direct ISC seems to be completely quenched, and the triplet state is mainly formed via exciplex ($^1E^* \rightarrow {}^3E^*$). In fact, for 1-, 2-, 3-, and 9-StPh in *n*-H, the enhancement factor for the triplet induction by DEA changes from 1.7 to 11, depending on the StPh. $^3E^*$ decays in hundreds of nanoseconds (see Figure 1b), giving rise to a species whose kinetic and spectral properties correspond to those of the triplet state of the previously described DAE($^3E^* \rightarrow {}^3DAE^*$).[5] The absorption characteristics of 1-StN, 1-StPh, and 2-StPh in the presence of DEA in cyclohexane are reported in Table 1.

In a polar solvent such as acetonitrile, a longer-lived absorption was observed after the decay of the singlet state. Since experiments carried out under the same conditions excluded the presence of exciplex emission, it was assigned to a nonfluorescent CT transient characterized by a complete charge separation: a nonfluorescent CRIP. In this solvent, the transient absorption spectra also show changes at low DEA concentrations (probably because the quenching is more efficient than in a nonpolar solvent). In fact, for the 2-StN/DEA system, at amine concentrations around 10^{-2} M, the singlets decayed completely in a few hundred picoseconds and gave rise to a new species ($\lambda_{max} \cong 530$ nm) that was attributed to the nonfluorescent CRIP (Figure 2).

At higher DEA concentrations, the spectral shapes were also modified at "zero time" due to the static interactions between the DAE and the amine.[16] The decay lifetime of CRIP (curves 3−5 of Figure 2) increased with the DEA concentration and reached a limiting value (~10^{-8}s) which was different for each compound. The decay of CRIP caused the appearance of a broad absorption in the region where the anions of DAEs were shown to absorb.[10−12] This absorption was assigned to the solvent-separated ion pair (SSRIP, curve 5, Figure 2), a species with larger charge separation than the CRIP and formed from the latter through relaxation along the solvation coordinates or directly by a long-distance electron transfer as described in ref 31. At longer delay times the SSRIP absorption decayed (lifetime 10^{-8}−10^{-7} s) and/or became structured and assumed the shape of the spectrum of the DAE radical anion, well characterized in previous works and having lifetimes in the

TABLE 2: Spectral Properties of the Transients Formed by Laser Excitation of DAE in Acetonitrile in the Presence of DEA and Their Assignment

compd	[DEA] (10^{-2} M)	λ_{max} (nm)	delay (ns)	transient
9-StAn	0.6	<450, 570, 730	0	S_1, S_2
		460, 570, 690	3.3	CRIP
	10	<450, 575, 700	0	S_1, S_2, CRIP
		450, 620 sh, 690	2.6	CRIP, SSRIP
1-StN	5	510, 570, >700	0	S_1, S_2
		485, 580	1.9	CRIP
2-StN	2	495, >700	0	S_1, S_2
		475 sh, 545	4.6	SSRIP
1-StPh	10	515, 580	0	S_1, S_2, CRIP
		520, 575	1.8	CRIP, SSRIP
2-StPh	2	555, 615	0	S_1, S_2
		500 sh, 560, 615 sh	1.8	CRIP, SSRIP
	6	555, 615	0	S_1, S_2
		510 sh, 560	1.8	SSRIP
9-StPh	10	500, 585, 700	0	S_1, S_2, CRIP
		480, 540, 585	1.8	CRIP, SSRIP

microsecond range.[10−12] In some cases, e.g., 2-StN[16] and 2-StPh, the kinetics of the radical anion was recorded, and it was possible to verify that it was coupled with the decay, in the pico−nanosecond time domain of the singlets and of their successors. The spectral properties of the transients observed in acetonitrile for some DAEs in the presence of DEA are summarized in Table 2.

In solvents of medium polarity such as ethyl acetate (EtAc) and dichloroethane (DCE), the interactions of the DAEs with DEA gave rise to exciplex formation. Previous fluorimetric measurements showed that in these solvents the emission is still an efficient decay pathway for the CT complex.[13] The picosecond laser flash photolysis on these systems gave time-resolved absorption spectra such as those of 9-StPh in DCE in the presence of different DEA concentrations which are shown in Figure 3.

In the top panel a, without DEA, the decay of the singlet state in the first 3 ns is shown. The presence of DEA (panel b) causes differences between 450 and 650 nm which can be attributed (up to a delay time of 500 ps) to different extinction coefficients of the singlets and exciplex. At longer delays small but clear-cut absorption bands appeared at 480 and 570 nm. These two transients absorb in the region of the triplet and the radical anion,[10] respectively, even though they decay faster (curves 4 and 5 of Figure 3b and more clearly curves 3, 4, and 5 of Figure 3c). For these reasons they were attributed to the $^3E^*$ and SSRIP, respectively.

The SSRIP lifetime and formation efficiency depend on the quencher concentration. In particular, the time-resolved spectra of the 1-StPh/DEA system in DCE (Figure 4) clearly showed that an increased amine concentration caused a greater SSRIP absorption ($\lambda_{max} = 580$ nm) and longer lifetime. In Figure 4b (DEA concentration = 0.003 M), in fact, at $\lambda > 500$ nm (beyond the region hidden by the DAE fluorescence, 400−500 nm) there is only the absorption of the singlet.

With increasing DEA concentration, a peak at 580 nm appeared at the end of the laser pulse. In Figure 4d, this absorption is very pronounced even at "zero time", and since it changes in the nanosecond time scale, it was attributed to SSRIP. Figure 4d also shows also a pronounced absorption in the region of the triplet ($\lambda_{max} = 460$ nm) which is hidden in panels a−c by the fluorescence of DAE and exciplex fluorescence. The interference of the fluorescence decay prevents the kinetic analysis of the transient at 460 nm to be recorded. The spectral properties of the transients observed for 2- and 9-StPh in solvents of medium polarity in the presence of DEA upon picosecond laser excitation are summarized in Table 3.

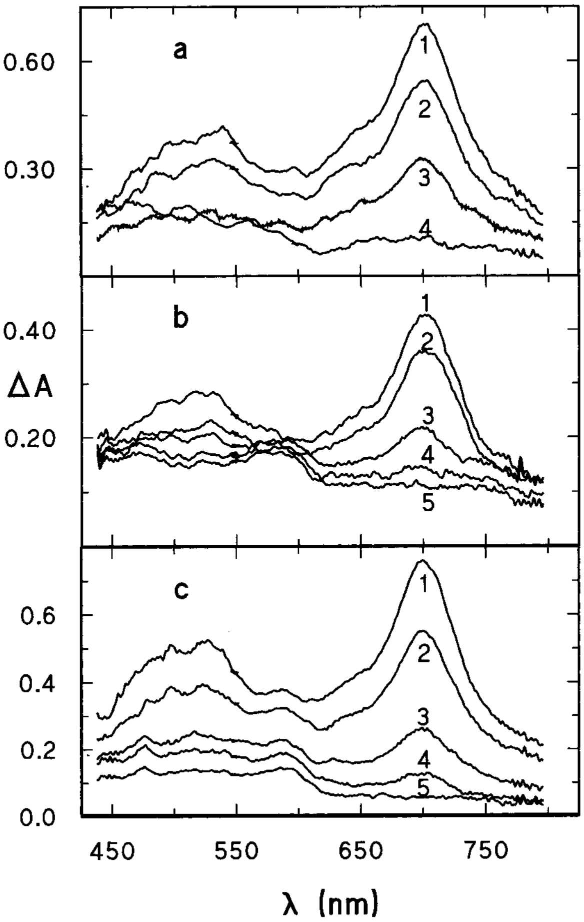

Figure 3. 9-StPh in 1,2-dichloroethane: time-resolved absorption spectra in the absence of additives (a) recorded at "zero time" (1) and at 0.25 (2), 0.6 (3), and 2.3 ns (4) after the laser pulse and in the presence of 0.02 M DEA (b) recorded at "zero time" (1) and at 0.25 (2), 1.3 (3), 2.3 (4), and 3.6 ns (5) after the laser pulse and in the presence of 0.4 M DEA (c) recorded at "zero time" (1) and at 0.25 (2), 0.6 (3), 1.3 (4), and 2.3 ns (5) after the laser pulse.

Interaction with BrDMA. The time evolution of the transients formed upon excitation of DAEs in the presence of BrDMA shows, with respect to DEA, a pronounced enhancement of triplet formation due to the effect of heavy atom on the spin−orbit coupling. In a nonpolar solvent, BrDMA quenches the fluorescence lifetime of DAEs with a rate constant close to the diffusional limit, with k_q values larger than 10^{10} M^{-1} s^{-1} for 1- and 2-StN[12] and $(0.8-2) \times 10^{10}$ M^{-1} s^{-1} for StPh isomers.[4] After the decay of the singlet state (∼3 ns) a transient absorption was observable (curve 5, Figure 5) in the spectral region where the olefin triplets absorb (∼480 nm). However, the observed spectrum had a broad shape and decayed with a lifetime much shorter than the triplet. (Characteristics of the triplet state of DAEs were reported in refs 5 and 10−12.) This absorption was assigned to a CT intermediate with triplet character because of its short lifetime. In fact, the heavy atom effect could induce a rapid process of ISC inside the exciplex[34] giving rise to a triplet complex ($^3E^*$), as already mentioned for the 1-StN/BrDMA system in cyclohexane,[16] which, in tens of nanoseconds, gave the longer-lived DAE triplet. Spectral properties of transients of some DAEs in CH in the presence of BrDMA are reported in Table 4.

In acetonitrile, BrDMA quenched the fluorescent state, giving rise to the formation of CRIP. In this solvent, the CRIP could

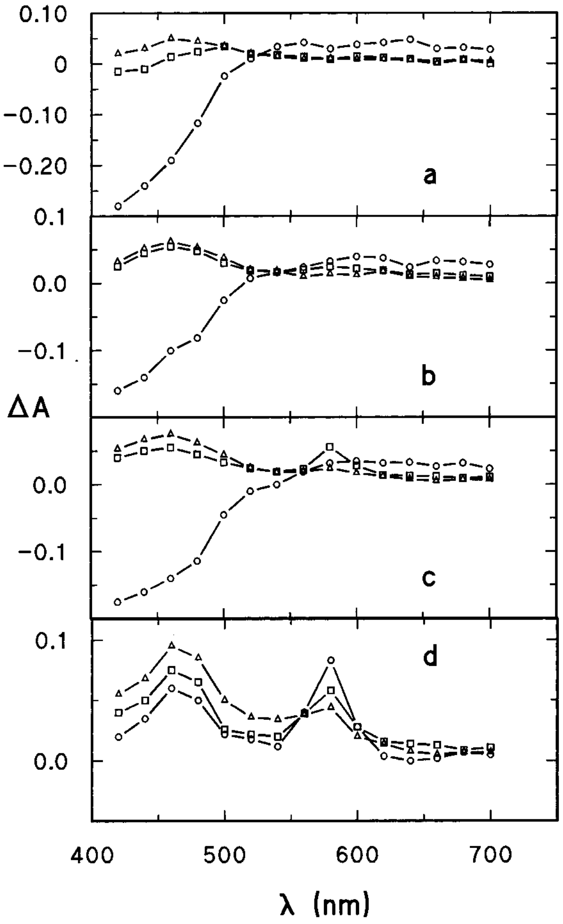

Figure 4. 1-StPh in 1,2-dichloroethane: time-resolved absorption spectra in the absence of additives (a) and in the presence of 0.003 (b), 0.006 (c), and 0.012 M (d) DEA recorded 7 (○), 20 (□), and 50 ns (Δ) after the laser pulse.

TABLE 3: Spectral Properties of the Transients Formed by Laser Excitation of DAE in 1,2-Dichloroethane and Ethyl Acetate in the Presence of DEA and Their Assignment

compd	solvent	[DEA] (10^{-2} M)	λ_{max} (nm)	delay (ns)	transient
2-StPh	ethyl acetate	2	570, 615	0	S_1, S_2
			565, 620	3.0	CRIP, SSRIP
9-StPh	ethyl acetate	2	500, 795	0	S_1, S_2
			535, 590, 702 sh	3.0	CRIP, SSRIP
	dichloroethane	4	520, 695	0	S_1, S_2
			470, 585	3.6	CRIP, SSRIP

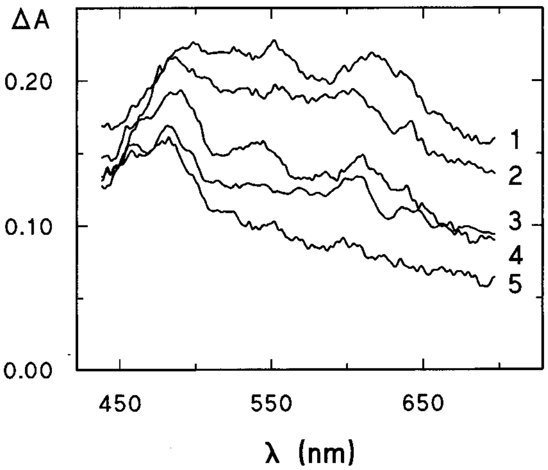

Figure 5. 1-StPh in CH in the presence of 0.05 M BrDMA: time-resolved absorption spectra recorded at "zero time" (1) and at 0.35 (2), 0.9 (3), 1.3 (4), and 2.6 ns (5) after the laser pulse.

TABLE 4: Spectral Properties of the Transients Formed by Laser Excitation of DAE in Cyclohexane in the Presence of BrDMA and Their Assignment

compd	[BrDMA] (10^{-2} M)	λ_{max} (nm)	delay (ns)	transient
1-StN	1	515, 590, >700	0	S_1, S_2
		480, 520 sh, 620 br	2.9	$^3E^*$
1-StPh	2	500, 550, 620	0	S_1, S_2
		460, 480	2.6	$^3E^*$
2-StPh	3	550, 620	0	S_1, S_2
		500, 560	3.0	$^3E^*$

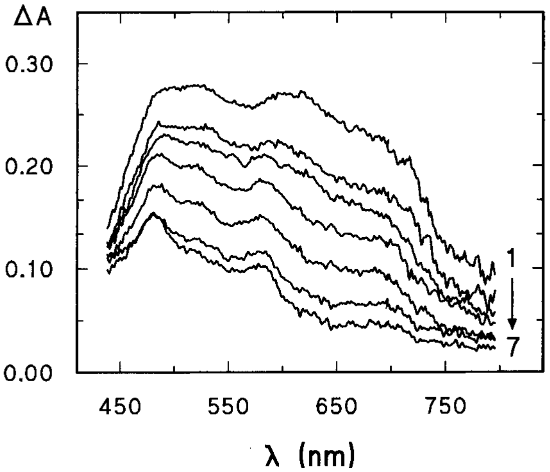

Figure 6. 1-StPh in MeCN in the presence of 0.06 M BrDMA: time-resolved absorption spectra recorded at "zero time" (1) and at 0.35 (2), 0.6 (3), 0.9 (4), 1.3 (5), 2.3 (6), and 3.6 ns (7) after the laser pulse.

decay through two different competitive pathways: (i) formation of a triplet complex and, successively, of the T_1 state of the olefin or (ii) formation of SSRIP and then free ions. The final products of these two pathways (triplet state and FI) have already been well-characterized by laser flash photolysis experiments in the nanosecond time scale[10,12] and by the observation of trans → cis isomerization of StPhs.[10] Examples of time-resolved absorption spectra obtained by picosecond laser flash photolysis in acetonitrile are shown in Figures 6 and 7 for the 1-StPh/BrDMA and 9-StPh/BrDMA systems, respectively.

At rather low concentration of BrDMA, the spectrum recorded at "zero time" was identical with that obtained in the absence of quenchers and previously assigned to the $S_1 \rightarrow S_n$ and $S_2 \rightarrow S_n$ transitions.[15,16] At longer delay time, when the absorption of the singlets had disappeared, the remaining absorptions presented three maxima centered at about 470, 580, and 700 nm (Figures 6 and 7). The kinetic analysis at different wavelengths showed that the three absorptions decayed with three different lifetimes. The band at 700 nm which decayed in a few nanoseconds was assigned to the CRIP (see above). For instance, the lifetime of the S_1 state of 9-StPh quanched by BrDMA in the experimental conditions of Figure 7a−c was about 1, 0.3, and 0.2 ns, while the CRIP (λ_{max} = 700 nm) decayed slower than the singlets, with $\tau \leq 4$ ns. The time-resolved absorption spectra clearly show that CRIP is a precursor of the transients absorbing at 470 and 580 nm (formed within 3 ns). These transients, also present at low quencher concentrations, become much more evident when high BrDMA concentrations (for instance, 0.1 M, Figure 7c) produce static quenching. The spectra of Figure 7c differ from the others in the 480−600 nm region. Here, at high [Q], an absorption appeared at "zero time" which was probably due to the direct excitation of

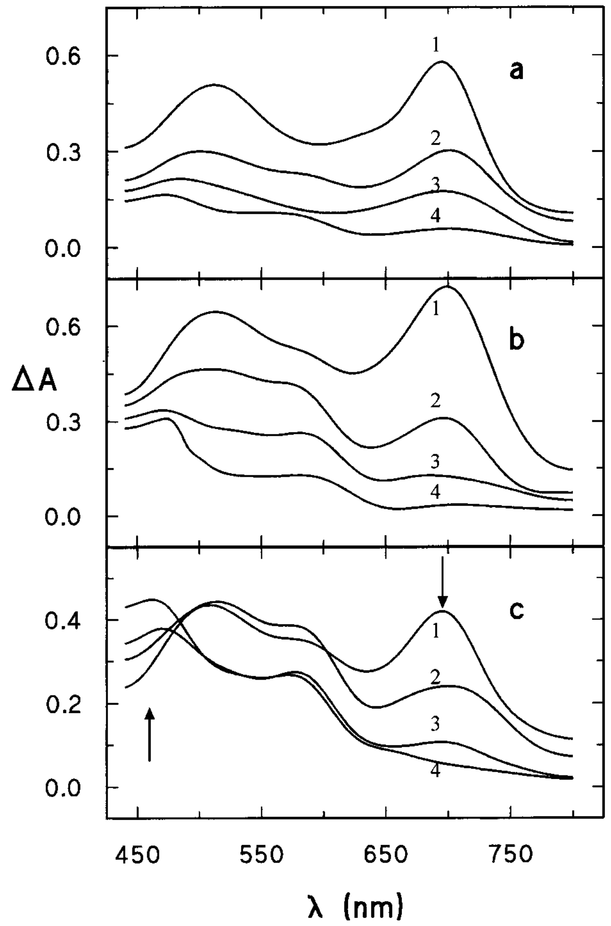

Figure 7. 9-StPh in MeCN: time-resolved absorption spectra in the presence of 0.01 (a), 0.05 (b), and 0.1 M (c) BrDMA recorded at "zero time" (1) and at 0.6 (2), 1.8 (3), and 3.0 ns (4) after the laser pulse.

TABLE 5: Spectral Properties of the Transients Formed by Laser Excitation of DAE in Acetonitrile in the Presence of BrDMA and Their Assignment

compd	[BrDMA] (10^{-2} M)	λ_{max} (nm)	delay (ns)	transient
9-StAn	0.6	<450, 570, 730	0	S_1, S_2
		460, 575, 700	3.3	CRIP
	10	<450, 575, 700	0	S_1, S_2, CRIP
		460, 700	3.0	CRIP, SSRIP
1-StN	1	510, 570, >700	0	S_1, S_2
		460, 560	1.9	CRIP
2-StN	5	490, 620 br	0	S_1, S_2, CRIP
		520	3.3	SSRIP
1-StPh	6	510, 610	0	S_1, S_2, CRIP
		460, 580, 690 sh	3.6	CRIP, SSRIP
2-StPh	1	560, 615	0	S_1, S_2
		500 sh, 550	3.0	CRIP, SSRIP
9-StPh	1	510, 690	0	S_1, S_2, CRIP
		470, 580 sh, 690	2.6	CRIP, SSRIP
	10	520, 580, 690	0	S_1, S_2, CRIP
		470, 580	1.9	CRIP, SSRIP

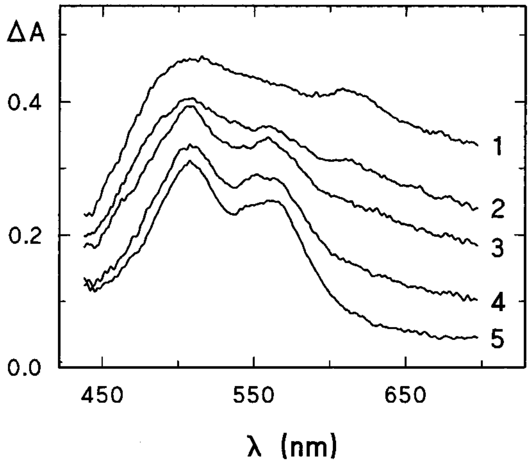

Figure 8. 1-StPh in MeCN in the presence of 0.01 M DCNB: time-resolved absorption spectra recorded at "zero time" (1) and at 0.15 (2), 0.6 (3), 1.3 (4), and 2.9 ns (5) after the laser pulse.

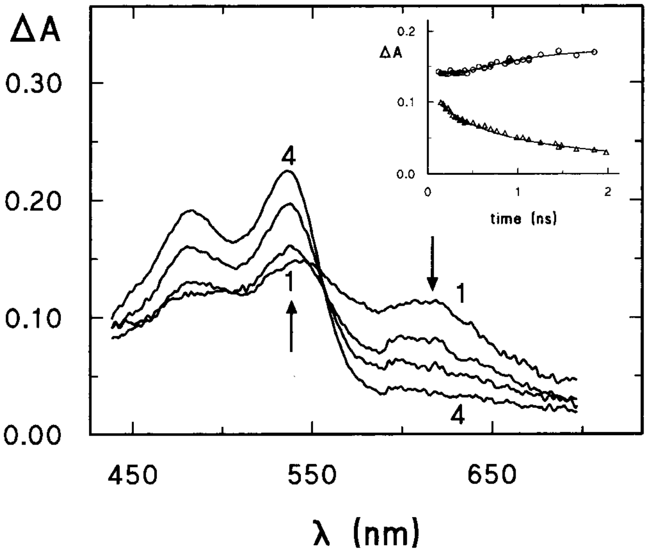

Figure 9. 2-StPh in MeCN in the presence of 0.03 M DCNB: time-resolved absorption spectra recorded at "zero time" (1) and at 0.6 (2), 1.2 (3), and 4.2 ns (4) after the laser pulse. Inset: kinetics recorded at 540 (○) and 613 nm (△).

the DAE/BrDMA ground-state complex, which in turn gave a charge-separated species.

The two new transients absorbing at 470 and 580 nm were assigned to the triplet complex and SSRIP, respectively. These assignments were suggested by the analogy of the spectra of the two transients with those of the triplet and DAE radical anion, respectively, and by the fact that the DAE radical anions have much longer lifetimes. The growth of the triplet species, combined with the decay at 680 nm, could indicate the formation of the triplet in the back-electron-transfer process. The time evolution of the transients at 580 and 470 nm produced the radical anion and the triplet as shown by the spectra recorded at longer times. The spectral characteristics of the transient formed by the quenching of DAE fluorescence by BrDMA in acetonitrile are reported in Table 5.

Interactions with DCNB. Upon ps irradiation of DAEs in acetonitrile in the presence of an electron acceptor such as DCNB, transients of a different nature with respect to the amines are produced. In all cases, the absorption spectra recorded at the end of the laser pulse correspond to the $S_1 \rightarrow S_n$ and $S_2 \rightarrow S_n$ transitions.[15,16] The time-resolved spectra of 1-StPh/DCNB system in acetonitrile are reported in Figure 8.

After 600 ps, two typical peaks of the radical cations appeared and at ~ 3 ns (curve 5) the singlet absorption bands were replaced by absorptions with a shape and position similar to those of DAE radical cations.[10] The kinetic analysis of the signal showed that DCNB shortened the fluorescence lifetime with bimolecular rate constants close to the diffusional limit. The quenching process induced the formation of an intermediate which decayed at a slower rate (10^8 s^{-1}) and then evolved toward a shape that resembled the spectrum already assigned to $DAE^{\bullet +}$(lifetimes ~ 10^{-6}–10^{-5} s). Only when the extinction coefficients of $DAE^{\bullet +}$ (or the intermediate SSRIP) were larger

TABLE 6: Spectral Properties of the Transients Formed by Laser Excitation of DAE in Acetonitrile in the Presence of DCNB and Their Assignment.

compd	[DCNB] (10^{-2} M)	$\lambda_{\max}$ (nm)	delay (ns)	transient
9-StAn	3	<450, 580, 660, 730	0	S_1, S_2
		<450, 580, 655	3.3	SSRIP, $\mathrm{DAE}^{\bullet+}$
1-StPh	1	510, 610	0	S_1, S_2
		510, 570	2.9	SSRIP, $\mathrm{DAE}^{\bullet+}$
2-StPh	3	480, 545, 620	0	S_1, S_2, CRIP
		480, 535	4.0	SSRIP, $\mathrm{DAE}^{\bullet+}$

than those of the singlets, was the growth of $\mathrm{DAE}^{\bullet+}$ observed as in the case of 2-StPh/DCNB whose time-resolved spectra in acetonitrile are reported in Figure 9. In these cases, both the singlet decay and radical cation growth were recorded. The kinetics indicated that the two processes are coupled. The spectral properties of the transient formed in MeCN in the presence of DCNB are reported in Table 6.

Conclusions

Absorption measurements by picosecond laser flash photolysis on the DAEs/donor/acceptor systems showed that fluorescent state is quenched by DEA, BrDMA and DCNB with close to almost diffusional rate constants. The static and dynamic quenching led to the formation of longer-lived fluorescent exciplex in nonpolar solvents or CRIP in polar solvents. Experiments performed in a nonpolar solvent showed that the singlet exciplex is precursor of a triplet complex (^{3}E*) that subsequently decays, yielding the triplet state of the DAEs. On the other hand, the evolution of CRIP in polar solvent gave rise to the SSRIP and finally to either the radical anion (when the quencher was an amine) or to the cation (when the quencher was DCNB). In solvent of medium polarity, transient absorptions assigned to both the triplet complex and to the CRIP were observed. In general, the results obtained allowed a spectroscopic and kinetic characterization of the transient generated in the CT interactions to be performed. In the presence of BrDMA, evidence was obtained of a transient at "zero time" formed in the static quenching of ^{1}DAE* and of triplet formation through ion recombination.

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