Cis-trans photoisomerization of 1,2-diarylethylenes: Effect of charge transfer interactions

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Abstract. This paper describes the results of an extensive study of *trans*→*cis* photoisomerization of various 1,2-diarylethylenes (DAE). The structure effect on the competitive radiative and reactive deactivations and on the isomerization mechanism (singlet/triplet, diabatic/adiabatic) is discussed. The effect of charge-transfer (CT) interactions of DAE with electron donors and acceptors are then presented. Triplet-induced isomerization is generally the common effect in non-polar solvents, and is particularly efficient when a heavy atom is involved. Typical examples of CT-induced triplet photoisomerization of DAE by electron donors and acceptors are illustrated. New results on some fluorescent *cis* compounds are also reported. Prevalent radical ion formation in polar solvents is shown to generally quench isomerization from *trans* to *cis* but to induce isomerization from *cis* to the more stable *trans* radical ion.

Keywords. Photoisomerization; diarylethylenes; charge-transfer; triplet induction; radical ions.

1. Introduction

Stilbene analogues, the 1,2-diarylethylenes (DAE), have been the object of deep investigations during the last decade. Sustained interest in such molecules lies in the fact that they are simple models for the study of *cis-trans* photoisomerization around the ethylenic bond (Saltiel and Charlton 1980; Saltiel and Sun 1990) and of *s-cis*→*s-trans* (photo)isomerization around the quasi-single bond between the aryl and the ethylenic bridge (Mazzucato and Momicchioli 1991) as well as in the inherent importance of these processes for applicative research (photography, photochromism, processes of biological interest such as vision etc.).

Recent studies on photoisomerism of DAE have shown that the excited-state properties depend to a large extent on the size and nature of the aryl groups linked to the ethylenic bridge (Bartocci *et al* 1992; Mazzucato 1982, 1987).

Greater attention has been paid to the *trans* isomers, where fluorescence, isomerization to *cis* in S_1 (singlet mechanism) and intersystem crossing (ISC) (eventually followed by isomerization in T_1 , triplet mechanism) are the competitive deactivation channels of the S_1 state. In the parent molecule, stilbene (S), the avoided crossing between the $S_1(B_u)$ energy curve as a function of the twist angle around the central double bond (with the energy increasing by twisting towards 90° , at the *perp*

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configuration) and the upper (doubly excited?) $S_n(A_g)$ curve (with an "ethylenic" minimum in the *perp* configuration) leads to the well known and widely accepted diabatic isomerization mechanism in S_1 . From the *trans* side, this pathway involves an activated $^1trans^* \rightarrow ^1perp^*$ twisting towards the energy minimum, followed by internal conversion to the ground state configuration, 6perp , and almost 50:50 partitioning to the stable *trans* and *cis* isomers (Saltiel and Charlton 1980; Saltiel and Sun 1990). When a phenyl group (P) of stilbene is replaced by larger polycyclic aryl groups of gradually decreasing S_1 and T_1 energy, such as naphthyl (N), phenanthryl (Ph), chrysenyl (C), pyrenyl (Py) and anthryl (An) groups, the S_1 curve shifts towards lower energies (more in the *trans* and *cis* than in the *perp* geometry) while the S_n curve is less affected by the aryl substitution. Therefore, the $S_1 - S_n$ crossing is no longer possible and a maximum, instead of a minimum, is present at 90° in the S_1 energy curve. The activation energy to twisting in S_1 does gradually increase (Mazzucato 1982, 1987), thus leading to a decrease in the isomerization quantum yield in S_1 , $^1\phi_{t \rightarrow c}$, and can become insuperable at room temperature. The competitive processes of fluorescence (possibly accompanied by some internal conversion) and ISC are then much more favoured, their relative amounts being determined by the nature of the aryl groups (Bartocci *et al* 1992). When ISC is substantial, the triplet mechanism can maintain an overall high isomerization yield, unless high barriers to $^3trans^* \rightarrow ^3perp^*$ twisting completely inhibit the *trans* to *cis* isomerization, as in the case of the anthryl derivatives ("one-way" isomerization, only from *cis* to *trans*) (Sandros and Becker 1987; Arai *et al* 1988; Tokumaru and Arai 1992). A suitable choice of the aryl groups linked to the central ethylenic bridge allows the gradual tuning of the *cis-trans* photoisomerization from a singlet to a triplet pathway and finally the inhibition of the reaction in the *trans* $\rightarrow$ *cis* way.

From the *cis* side, the torsional barriers are always lower compared with those from the *trans* side. Therefore, when a maximum instead of a funnel is present at the $^1perp^*$ configuration, a direct adiabatic mechanism ($^1cis^* \rightarrow ^1trans^*$) can become operative in both the singlet (Spalletti *et al* 1991; Mazzucato *et al* 1993) and triplet (Arai *et al* 1988; Tokumaru and Arai 1992) manifolds.

The fluorescence of *trans*-DAE is quenched by charge transfer (CT) interactions with electron donors (e.g., amines) or acceptors (e.g., cyano-aromatics) and exciplex formation, as evidenced by their typical emission bands, is observed in non-polar solvents (Aloisi *et al* 1980, 1988; Aloisi and Elisei 1990; Elisei *et al* 1992). Singlet-induced CT interactions may result in enhanced formation of DAE triplets in non-polar solvents (Elisei *et al* 1990; Aloisi *et al* 1992; Görner *et al* 1992) and DAE radical ions in polar solvents (Aloisi *et al* 1991, 1992; Görner *et al* 1992). The extent of the quenching, which depends on the nature of the two partners and the solvent, may then affect both the yield and the mechanism of photoisomerization (Aloisi *et al* 1980; Aloisi and Elisei 1990; Aloisi *et al* 1988, 1991; Elisei *et al* 1992).

On the basis of published data obtained from the spectroscopic and photochemical study of a large series of DAE as well as of some new results recently obtained in our laboratory, the main features of the structure effect on photoisomerism of DAE are reported here. The CT interactions of the fluorescent *trans* isomers and some *cis* analogues with electron donors and acceptors will then be discussed to evidence their effects on the excited state behaviour of DAE.

2. Experimental

All compounds were synthesized by standard procedures as per previous work. Fluorimetric, photochemical and flash photolytic measurements were made as described in previous papers (see Bartocci *et al* 1987 and Aloisi *et al* 1992, and papers cited therein). Benzene, *n*-hexane, methylcyclohexane (MCH), chlorobenzene (CB), ethylacetate (EtAc) and acetonitrile (MeCN) from Carlo Erba (RPE grade) were used as solvents, tributylamine (TBA), diethylaniline (DEA), 4-bromo-*N,N*-dimethylaniline (BrDMA) from Fluka AG and potassium iodide from Carlo Erba as electron donors, and chloranil (Chl) from Fluka AG and dicyanobenzene (DCNB) from EGA-Chemie as electron acceptors.

3. Results and discussion

3.1 Photoisomerization

Figure 1 shows a qualitative sketch (a), based on theoretical and experimental data, of the torsional potential energy of the S_1 state of three typical DAE together with a scheme (b) of the energy levels of the lowest singlet excited state of the DAE and of their arene (1L_a , 1L_b) and ethylene (1B_u) chromophores (Bartocci *et al* 1992). Perturbation coupling of the excited state localized on the largest arene chromophore

Figure 1. (a) Sketch of the torsional energy barrier for the S_1 state of stilbene (*S*: singlet mechanism), styrylnaphthalenes (*StN*: prevalent singlet mechanism at room temperature, mixed singlet + triplet mechanism at lower temperatures) and styrylanthracenes (*StAn*: no *trans* $\rightarrow$ *cis* isomerization); (b) sketch of the interactions between the lowest excited states L_a and L_b of the polycyclic aryl chromophore (A) and the B_u state of ethylene (E) to give the resulting S_1 state of the *trans*-DAE (the effect of the relative positions of the energy levels on the fluorescence rate parameter, quantum yield and lifetime and on the photoisomerization quantum yields are also indicated).

(particularly of 1L_a , which has a higher transition moment) with the 1B_u state of ethylene gives rise to lowest excited states of different character for the DAE molecules.

When the energy of the arene 1L_a state is high, not much lower than that of the lowest excited state 1B_u of ethylenic character, the interaction is strong leading to a mixing of local states with a large contribution of the ethylenic π, π^* state to the S_1 state of the DAE. A high $^1\phi_{t \rightarrow c}$ and low ϕ_F is expected in this case, as found for *trans*-S.

When the energy of 1L_a decreases markedly (naphthyl, phenanthryl derivatives), the DAE excitation energy is largely localized in the aryl (prevalent L_a character) and a high torsional barrier in S_1 leads to a small $^1\phi_{t \rightarrow c}$. However, in some cases, particularly when the lowest excited state is the aryl 1L_b state (weak $S_0 \rightarrow S_1$ transition and low extinction coefficients), ISC can become substantial opening the triplet pathway to isomerization.

A limiting situation is reached when 1L_a (lying in such cases below 1L_b) is so far apart from 1B_u that the mixing is very weak (S_1 of aromatic character, as in anthryl derivatives). The barriers to twisting are high in both S_1 and T_1 and no isomerization occurs from *trans* to *cis* but only from *cis* to *trans* ("one-way" isomerization, Arai *et al* 1988, Tokumaru and Arai 1992). The presence of a maximum, instead of a minimum, at the $^1perp^*$ configuration for the pyrene and anthracene derivatives causes the activated twisting of $^1cis^*$ to directly produce $^1trans^*$, thus favouring an adiabatic photoisomerization mechanism, as reported for the triplet state (Arai *et al* 1988; Tokumaru and Arai 1992), particularly in polar solvents where the activation energy in S_1 is lowered because of the stabilization of the zwitterionic twisted configuration (Spalletti *et al* 1991; Mazzucato *et al* 1993).

Figure 2 shows the increase in the fluorescence quantum yield (ϕ_F) and the decrease in the *trans* $\rightarrow$ *cis* photoisomerization quantum yield ($\phi_{t \rightarrow c}$) of some styryl-arenes on increasing the size of the arene and the aromatic character of the S_1 state of the DAE. Table 1 shows how the nature of the largest arene affects the photoisomerization mechanism (singlet/triplet, diabatic/adiabatic). Stilbene isomerizes with high yield *via* a singlet diabatic mechanism (Saltiel and Charlton 1980; Saltiel and Sun 1990). The

Figure 2. Effect of the nature and size of the aryl substituent of styrene on the fluorescence ($\odot$) and *trans* $\rightarrow$ *cis* photoisomerization ($\triangle$) quantum yields of some DAE.

Table 1. Fluorescence, triplet and isomerization quantum yields and prevalent isomerization mechanism for some typical *trans*-DAE in non-polar solvents at room temperature.

Compound	ϕ_F	ϕ_T	$\phi_{t \rightarrow c}$	Prevalent mechanism
S ^a	0.04	< 0.01	0.50	Singlet, diabatic
1-StN ^b	0.72	0.04	0.16	Singlet, diabatic
1-StPh ^c	0.61	0.18	0.14	Triplet, diabatic
2-StPh ^c	0.35	< 0.01	0.24	Upper triplet, diabatic
9-StPh ^c	0.67	0.32	0.13	Mixed, diabatic
1-StPy ^d	0.94	< 0.03	< 0.02	Only <i>cis</i> $\rightarrow$ <i>trans</i> : singlet, adiabatic
9-StAn ^d	0.44	0.32	—	Only <i>cis</i> $\rightarrow$ <i>trans</i> : mixed, adiabatic

References: ^a Saltiel and Charlton (1980); ^b Elisei *et al* (1989); ^c Aloisi and Elisei (1990); Elisei *et al* (1990); ^d Bartocci *et al* (1992).

n-styrylnaphthalenes (*n*-StNs) (Bartocci *et al* 1984; Elisei *et al* 1989) have a prevalent radiative deactivation of S_1 : they isomerize by the same mechanism as *S* above room temperature but follow a prevalent triplet pathway below 270 K (or at slightly lower temperatures in polar solvents). The *n*-styrylphenanthrenes (*n*-StPhs) (Bartocci *et al* 1987) follow a mixed singlet/triplet mechanism already at room temperature due to higher torsional barriers in S_1 and larger triplet yields. In some cases (e.g., in 2-StPh), upper S_n or T_n states of ethylenic character may play a role in the isomerization favouring a fast twisting which by-passes the lowest excited states (Elisei *et al* 1990, Aloisi *et al* 1991a). In fact, 2-StPh has a high torsional barrier in S_1 and a $\phi_{t \rightarrow c}$ value as large as 0.24 which would indicate that at least $\sim 50\%$ of the excited molecules deactivate through a *trans* $\rightarrow$ *perp* twisting in the triplet manifold. However, T_1 cannot be an intermediate since its yield is smaller than 0.01. Therefore, one could think of an isomerizable upper T_n state, almost isoenergetic with S_1 . In fact, at low temperatures, when twisting in T_n is slowed down by the viscosity barrier, the population of T_1 increases substantially by $T_n \rightarrow T_1$ internal conversion and the lowest excited triplet state becomes readily detectable. A similar mechanism was hypothesized for the isomerization of 4-halogenated stilbenes (Görner and Schulte-Frohlinde 1979). In any case, the presence of a shallow minimum in the $^1\text{perp}^*$ configuration of StPhs still seems to favour the diabatic mechanism. Practically, the 1-styrylpyrene (StPy) and *n*-styrylanthracenes (StAns) do not isomerize from *trans* to *cis* because of very high torsional barriers in both S_1 and T_1 . They follow a mixed (singlet/triplet) mechanism from *cis* to *trans* with a prevalent adiabatic character.

In conclusion, the singlet mechanism is favoured at high temperatures and in polar solvents; the adiabatic mechanism is favoured in the presence of a maximum at the $^{1,3}\text{perp}^*$ configurations, particularly in polar solvents where the activation energy is smaller.

3.2 Effect of CT interactions on *trans* $\rightarrow$ *cis* photoisomerization

The *trans* $\rightarrow$ *cis* isomerization quantum yield ($\phi_{t \rightarrow c}$) in the presence of the fluorescence quencher *Q* is the sum of two contributions, by the monomer (non-complexed) molecules (ϕ_{CM}) and by those which react through the exciplex (ϕ_{CE}). When $[Q] \rightarrow \infty$,

the fluorescence and photoisomerization quantum yields of the exciplex reach their limiting values, ϕ_{FE}^{lim} and ϕ_{CE}^{lim} , respectively.

Often, the overall photoisomerization is less quenched than fluorescence or even enhanced by addition of electron donors or acceptors since CT-induced ISC can lead to isomerization in the triplet manifold. In fact, since both S_1 and T_1 are potentially reactive states (the actual reactivity depending on their torsional barriers), the expected effect is generally modest. Since the quenching efficiency of the singlet-excited *trans*-DAE by electron donors or acceptors depends on the redox potential of the two partners, a suitable choice of the additive is required for an efficient CT-induced photoisomerization, based on the following criteria: high quenching rate constant k_Q , low yields of both the radiative decay (ϕ_{FE}) and the internal conversion to the ground state (ϕ_{GE}) and high ISC yield (ϕ_{TE}) of the exciplex so as to induce a substantial population of the reactive triplet state of the olefin.

Figure 3 shows, as an example, the decreasing of fluorescence intensity of 9-StPh together with the parallel increase of the triplet and isomerization yields in the case of the interaction with DEA as donor in *n*-hexane. Table 2 shows some typical cases

Figure 3. Effect of DEA concentration on the quantum yields of fluorescence (squares), photoisomerization (triangles) and triplet (circles) for *trans*-9-StPh/DEA in *n*-hexane.

Table 2. Limiting ($[Q] \rightarrow \infty$) fluorescence and *trans* $\rightarrow$ *cis* photoisomerization quantum yields of some typical DAE in the presence of three amines as donors in *n*-hexane and DCNB as acceptor in benzene.

DAE	ϕ_F	$\phi_{t \rightarrow c}$	ϕ_{FE}^{lim}				ϕ_{CE}^{lim}			
			TBA	DEA	BrDMA	DCNB	TBA	DEA	BrDMA	DCNB
2-StN	0.65 ^a	0.12 ^a	0.17 ^a	0.72 ^b		0.17 ^c	0.10 ^a	0.12 ^b		0.26 ^c
1-StPh ^d	0.61	0.14	0.19	0.36	~ 0.01		0.10	0.20	0.44	
9-StPh	0.67 ^d	0.13 ^d	0.17 ^d	0.57 ^d	$< 0.01^d$	0.37 ^c	0.11 ^d	0.10 ^d	0.28 ^d	0.24 ^c
2,3'-NPE	0.67 ^a	0.15 ^a	0.03 ^a			0.24 ^c	0.09 ^a			0.34 ^c

References: ^a Aloisi *et al* (1980); ^b Aloisi *et al* (1977); ^c Aloisi *et al* (1991b); ^d Aloisi and Elisei (1990).

of the limiting ($[Q] \rightarrow \infty$) quantum yields of radiative and reactive deactivation of the exciplexes with three amine donors and one acceptor in non-polar solvents. Chromatographic control showed that the formation of photoproducts different from the *cis* isomers, as observed for the S/amine systems (Lewis 1979; Lewis and Simpson 1979; Lewis *et al* 1992), is generally negligible in our experimental conditions. Perusal of table 2 shows that substantial isomerization is induced by DCNB in benzene where higher triplet yields were measured even if accompanied by substantial yields of radiative decay of the exciplex. On the other hand, radiative decay is the prevalent deactivation pathway of the exciplex with DEA and internal conversion is the prevalent one with the less efficient TBA quencher. For the exciplex of 9-StPh, quenching rate constants, k_Q , of 9.2 and 3.4 ($10^9 \text{ M}^{-1} \text{ s}^{-1}$) were obtained with DEA and TBA, respectively. As expected, larger induction was obtained with BrDMA. Inclusion of a heavy atom in the solvent or, even better, in one of the two partners increases the isomerization yield because the spin-orbit coupling controlled by the exciplex produces the isomerizable T_1 state. In this case ϕ_{FE} is very low (smaller than 0.01) but enough to demonstrate the existence of the complex and then of a CT-assisted spin-orbit coupling effect.

The data above allow some conclusions to be drawn about the CT effect on the photoisomerization of *trans*-DAE in non-polar solvents. When both the lowest excited states of the olefin can be effectually reactive (as in S and many other DAE) or non-reactive (as in *n*-StAns), the effect of the CT interaction is expected to be zero or very small (both positive and negative), the quenching of S_1 being generally more or less compensated by a recovery of quanta in T_1 . A typical case is offered by DAE with small ϕ_{ISC} and $\phi_{t \rightarrow c}$ and high ϕ_F values (as for *n*-StNs): the quenching can be accompanied here by a gain of reactivity in T_1 , as observed in table 2 for the effect of DCNB on the two DAE bearing a naphthyl group. When, as in the pyrenyl derivative, only T_1 is reactive (because of a high torsional barrier in S_1) but the triplet yield is very small (because of the competitive fluorescence), the addition of Q can again enhance the $\phi_{t \rightarrow c}$ values through induced ISC.

In polar solvents, such as MeCN, non-emitting CT complexes are formed (Aloisi *et al* 1991a, 1992; Görner *et al* 1992). They induce little ISC since the concomitant formation of *trans* radical ions (generally non-isomerizable) prevails. A parallel increase was generally found both in the absorbance change of the radical ion and the conductivity signal (Aloisi *et al* 1991a). The photoreaction yield increases slightly in some cases (e.g. with DCNB as acceptor) probably because the radical recombination can lead, at least in part, to formation of the isomerizable triplet state. In any case, the fluorescence quenching by amines was always accompanied by a decrease in the isomerization yield. For example, in the case of 1-StPh/DEA, the $\phi_{CE_{lum}}$ value was halved (0.07); however, no triplet transient was observed, since T_1 produced by charge recombination is shorter-lived compared with the radical anion. In some experiments, the radical cations of the olefin were sensitized by irradiation of chloranil, a well-known electron acceptor in the triplet state. Figure 4 refers to the system 1-StPy/Chl in MeCN after irradiation of the acceptor at 308 nm. It shows the spectra of the triplet state of the acceptor ($\lambda_{max} = 510 \text{ nm}$) and its radical anion (450 nm) and of the DAE radical cation (590 nm) together with the decay kinetics of the first and last transients. The triplet state of Chl was formed within the laser pulse while the DAE radical reached its maximum ΔA after 0.6 μs and decayed with a lifetime of 2.5 μs .

Figure 4. Time-resolved absorption spectra of the *trans*-1-StPy/Chl system in MeCN recorded 0.2(—) and 1(---) μ s after the laser pulse ($\lambda_{\text{exc}} = 308$ nm). Inset: decay kinetics at 510(—) and 590(---) nm.

An interesting case is presented by azastilbenes, and particularly by 1-(*n*-pyridyl), 2-(*n'*-pyridyl)ethylenes (*n,n'*-DPE), where the photoreaction is inhibited by the high efficiency of the $S_1 \rightarrow S_0$ internal conversion to the ground state induced by the low-lying n, π^* states introduced by the heteroatom. Here, the quenching effect is expected to reduce the internal conversion in favour of reactive deactivation pathways through the complex. However, preliminary experiments indicate that the situation is complicated by formation of by-products. In any case, the S_1 lifetime of DPE is very short, so that high concentrations are needed in order to induce complexation and then isomerization.

An important heavy atom effect was found on using halide anions as quenchers of some DAE and their aza-analogues, the latter in both neutral and protonated forms. Some typical examples showing an important induction of isomerization are reported in table 3. Particularly interesting is the huge increase in reactivity for the two last protonated substrates. Nanosecond laser flash photolysis measurements were carried out to investigate the transients formed by the interaction of iodide anions with some singlet excited *n*-StPhs. No sign of radical anions of the DAE was found but only a substantial production of their T_1 states. Figure 5 shows the $T_1 \rightarrow T_n$ spectrum of 1-StPh ($\lambda_{\text{max}} = 460$ nm) obtained in the presence of KI ~ 0.2 M in MeCN/H₂O (1/1, v/v) together with the enhancement of the triplet population by increasing the KI concentration (inset). The question of the relative importance of the CT and heavy atom effects on the quenching by halide anions has never received a convincing answer (Watkins 1973, 1974). The heavy atom effect probably operates in conjunction with association phenomena, particularly in the case of the charged olefins. In agreement with what was reported for the quaternary salts of DPE (Gutierrez and Whitten 1976), we believe that the actual quenching is controlled by

Table 3. Limiting *trans* $\rightarrow$ *cis* photoisomerization quantum yields of some DAE, their neutral and protonated aza-analogues induced by iodide anions in polar solvents, compared with the intrinsic values in the absence of additives.

Compound	$\phi_{t \rightarrow c}$	ϕ_{CE}^{lim}
2-StN ^a	0.19	0.48
3-StPh ^b	0.13	0.43
9-StPh ^b	0.29	0.40
3-StP ^a	0.44	0.52
2,3'-NPE ^a	0.14	0.38
3-StPH ^{++c}	0.27	0.25
4'-OCH ₃ -3-StPH ^{++c}	0.0006	0.36
3,3'-DPEH ₂ ^{++c}	0.045	0.50 ^d

^a In water–acetonitrile 60:40, (Mazzucato *et al* 1982); ^b in water–acetonitrile 50:50, this work; ^c in water–ethanol 90:10 (Bartocci *et al* 1976/77); ^d quencher: bromine anion.

Figure 5. Triplet–triplet absorption spectrum of *trans*-1-StPh in MeCN/H₂O (1/1, v/v) in the presence of 0.5 M KI recorded 60 ns after the laser pulse ($\lambda_{exc} = 308$ nm). Inset: effect of iodide concentration on the absorbance change at 460 nm.

the electron donor–acceptor interaction while the heavy atom makes the triplet formation of the olefin fast enough to dominate all other paths of exciplex decay.

3.3 Effect of CT interactions on *cis* $\rightarrow$ *trans* photoisomerization

The quenching of the *cis*-DAE by donor–acceptor interactions has been little investigated thus far since these isomers are generally non-fluorescent due to their fast (small barriers) isomerization to *trans* or to polycyclic compounds (dihydrophenan-

threne in the case of *S*) and the consequent very short *S*₁ lifetime. Since photocyclization is a competitive singlet reaction, CT-induced formation of the triplet state can favour the *cis* → *trans* isomerization (particularly for the naphthyl and phenanthryl derivatives which are characterized by substantial cyclization yields). When a maximum is present in ¹*perp**, the ¹*cis** lifetime increases; as mentioned earlier, the twisting becomes more or less activated and leads directly to ¹*trans** by an adiabatic mechanism (Sandros and Becker 1987; Spalletti *et al* 1991; Mazzucato *et al* 1993). In such cases, e.g. for the *cis* isomer of 9-StAn, the CT-induced fluorescence quenching can be measured thus obtaining more quantitative information about the CT interactions. Figure 6 shows the fluorescence spectra of *cis*-9-StAn quenched by DEA with a Stern–Volmer constant ($K_Q = k_Q \tau_F$) of 3.2 and 8 M⁻¹ in MCH (a) and CB (b), respectively. The increase of the fluorescence band of the exciplex is clearly observable in both solvents, particularly in the more polar CB where the emission is weaker but redshifted.

The CT interactions of the *cis*-DAE in polar solvents open a new way to isomerization since their radical ions can thermally convert to the more stable *trans*

Figure 6. Fluorescence spectra of the *cis*-9-StAn/DEA system (a) in MCH without (1) and in the presence of 0.026 (2), 0.13 (3), 0.25 (4) and 0.48 (5) M DEA ($\lambda_{\text{exc}} = 370$ nm) [inset: Stern–Volmer plot obtained from the fluorescence intensities recorded at 420 nm] and (b) in CB without (1) and in the presence of 0.0164 (2), 0.0492 (3), 0.082 (4), 0.13 (5), 0.26 (6) and 0.50 (7) M DEA ($\lambda_{\text{exc}} = 370$ nm) [inset: Stern–Volmer plot obtained from the fluorescence intensities recorded at 470 nm].

Figure 7. Transient absorption spectrum of the *cis*-1-StPy/Chl system in MeCN recorded 0.6 μ s after the laser pulse ($\lambda_{\text{exc}} = 308$ nm). Inset: decay kinetics at 510(—) and 580(---) nm.

radical ions, thus contributing to the overall photoreaction quantum yield. For the *cis* isomers investigated here (1-StPh, 9-StPh and 1-StPy), laser irradiation of *cis*-DAE/Chl produced the radical cation in the *trans* configuration (as indicated by comparison with the transients obtained after direct sensitization of the *trans* isomers and by its mono-exponential decay) due to the fast *cis* $^{\cdot+} \rightarrow$ *trans* $^{\cdot+}$ twisting. Such behaviour is different from that found for *cis*-stilbene in the presence of Chl and reported with different acceptors by other authors (Lewis *et al* 1985; Tokumaru *et al* 1991; Kuriyama *et al* 1992), which showed biexponential decay assigned to the *cis* $^{\cdot+}$ (shorter-lived) and *trans* $^{\cdot+}$ (longer-lived) contributions. This difference can be due to a smaller barrier to twisting for the radical cations of the present compounds. A study of the temperature effect is in progress to confirm such hypothesis. Figure 7 shows an example for the system *cis*-1-StPy/Chl in MeCN. The transient spectrum at room temperature was assigned to the radical cation in the *trans* configuration (see figure 4) formed after $^3\text{Chl}^*$ sensitization of the *cis* cation. The *trans* $^{\cdot+}$ absorption was found to increase by addition of LiClO_4 and by increasing the *cis* concentration (chain mechanism) as reported for *cis*-stilbene (Lewis *et al* 1985). Such effects indicate that the alkali metal cation protects the olefin radical cation from recombination with the acceptor radical anion (back transfer) (Lewis *et al* 1985) or with the superoxide anion (formed by $\text{Chl}^{\cdot-} + \text{O}_2$) (Kuriyama *et al* 1992; Tokumaru *et al* 1991).

Acknowledgement

Financial support by the Italian Consiglio Nazionale delle Ricerche (Progetto Finalizzato Chimica Fine e Secondaria II) and Ministero per l'Università e la Ricerca Scientifica e Tecnologica (Rome) is gratefully acknowledged.

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