Role of Charge-Transfer Interactions in Photoreactions. 6. Photoinduced Electron Transfer and Trans \rightarrow Cis Isomerization for Styrylphenanthrene-Amine Systems in Acetonitrile

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The decay pathways of the lowest excited singlet state (S_1) of *trans-n*-styrylphenanthrenes (*n*-StPh, with the location on phenanthrene n = 1, 2, 3, 4, and 9) were studied in acetonitrile at room temperature. Fluorescence lifetimes (τ_F) , quantum yields of fluorescence (Φ_F) and intersystem crossing (Φ_T^{max}) , some properties of the lowest triplet state (T_1) , and the quantum yield of trans \rightarrow cis photoisomerization (Φ_C) were determined for the five isomers. Evidence is obtained for three different routes in the trans \rightarrow cis photoisomerization: (i) a trans \rightarrow perp rotation via T_1 for 4-StPh, (ii) involvement of both T_1 ($\simeq 20\%$) and mainly S_1 for 9-StPh, and (iii) rotation via an upper triplet state for the others. The formation and decay of the five respective StPh radical cations in the absence of additives were observed by laser flash photolysis. On 353-nm excitation the yield is low (<0.1) but enhanced by fluorescence quenching with 1,4-dicyanobenzene; ionization and decay of the five StPh radical anions are evidenced from optical and transient conductivity results in the presence of amines. They significantly enhance the initial amplitude of the transient conductivity signal and correspondingly quench Φ_F , τ_F , and Φ_C (the latter only to a lesser extent in some cases). The bimolecular interaction between ¹trans^{*} and 4-bromodimethylaniline yields a larger triplet formation and only in some cases an increase of photoisomerization efficiency, with respect to those of the free olefin. Reactions with diethylaniline and tributylamine generate ion pairs. It is concluded that ion-pair recombination is an inefficient pathway to the triplet formation for *trans*-StPh's.

Introduction

The photochemistry and photophysics of *trans-n*-styrylphenanthrenes (*n*-StPh, with the location on phenanthrene n = 1, 2, 3, 4, and 9; trans isomers throughout) and their exciplexes with amines in nonpolar solvents have been widely investigated in the past years.¹⁻⁵ It has been shown that the first excited singlet state (S₁) has a high barrier for the trans \rightarrow perp twisting process. Thus, the trans \rightarrow cis photoisomerization of the five StPh's occurs mainly in the triplet manyfold in nonpolar solvent at room temperature and below.^{1,5}

The charge-transfer interactions between ¹trans^{*} and amines in *n*-hexane and methylcyclohexane, in particular the exciplexes of 9-StPh with diethylaniline (DEA) and tributylamine (TBA), have been extensively investigated; the individual rate constants for the complex formation and decay and the related thermodynamic quantities have been obtained.² Moreover, solvent effects on the exciplex parameters have allowed information on the changes in the electronic structure of the complexes to be collected.³

More recently, the effect of the exciplexes with amines on the quantum yield of trans \rightarrow cis photoisomerization (Φ_C) and on quantum yield of triplet formation (Φ_T , as a measure of intersystem crossing quantum yield, Φ_{ISC}) in *n*-hexane has been studied.^{4,5} The presence of DEA, TBA, and 4-bromodimethylaniline (BrDMA) markedly affects the photoisomerization of StPh's, quenching or enhancing it, depending on the position of the styryl group on phenanthrene, as well as on the quencher and the solvent.⁴ Flash

photolysis experiments have indicated that these quenchers induce the formation of transients having triplet character. However, the transient has been unequivocally ascribed to the isomerizable lowest triplet state of the olefins (T₁) only with BrDMA.⁵ As a general rule, only an electron donor bearing a heavy atom efficiently quenches the fluorescence and is able to enhance Φ_C in nonpolar solvent.⁴

So as to extend and complete this research, it was interesting to study the behavior of these systems in a polar solvent, where the prevailing decay pathway of exciplexes involves radical ions.⁶ The aim of the present paper is the presentation and discussion of the photophysical and photochemical behavior of the five StPh's in acetonitrile both in the absence and in the presence of the three respective amines as electron donors and 1,4-dicyanobenzene (DCNB) as electron acceptor. In particular, the spectral and kinetic properties of the transients produced by nanosecond laser excitation were determined and combined with conductivity changes caused by formation and decay of ion pairs.

It is well-known that organic molecules in acetonitrile undergo photoinduced ionization which can be detected electrically (by a photocurrent or a conductivity) or optically.^{7,8} Since the formation of the radical cations is competitive with the other monomolecular and bimolecular decay pathways, the mechanism

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TABLE I: Fluorescence Lifetimes and Ouantum Yields and Rate Constants for Fluorescence Quenching of StPh's by Amines in Acetonitrile at Room Temperature

			$10^{-10}k_q^c/M^{-1}s^{-1}$		
compd	$\tau_{\rm F}^{a}/{\rm ns}$	Φ _F ^b	TBA	DEA	BrDMA
1-StPh	7.0 (10) ^d	0.74 (0.61) ^d	0.94	2.1	1.9
2-StPh	26.2 (34)	0.54 (0.35)	0.96	2.0	1.8
3-StPh	6.0/15.8 ^e (7.7/18) ^e	0.66 (0.56)	1.1	1.8	1.5
4-StPh	13.6 (18)	0.23 (0.19)	0.6	1.6	1.2
9-StPh	2.0 (5.3)	0.31 (0.67)	0.93	2.1	5.3 ⁷

^aMean deviation of three independent experiments <5%. ^bMean deviation of three independent experiments ca. 5%. 'Estimated error $\pm 10\%$. "Values in parentheses refer to *n*-hexane." Biexponential decay. ^fFor involvement of static quenching, see text.

of StPh photoionization was also investigated.

Experimental Section

The n-StPh isomers were the same as used in previous works.^{1-5,9,10} Solvents were purified by usual methods (water: triply distilled; ethanol, Merck: fractional distilled) or used as received (acetonitrile, Uvasol). Tributylamine and N.N-diethylaniline (Carlo Erba, RPE grade), were distilled and dried before use, 4-bromo-N,N-dimethylaniline (Aldrich) was recrystallized, and 1,4-dicyanobenzene (Aldrich) was used as received. All measurements were carried out at a temperature of 23 ± 2 °C and in deoxygenated solutions (purging with argon or nitrogen) unless indicated otherwise.

Spectra, lifetimes, and quantum yields of fluorescence were measured as described previously.^{1,4,9} The photoisomerization quantum yields (using [StPh's] $\simeq 1 \times 10^{-4}$ M, $\lambda_{exc} = 335$ or 355 nm)⁴ were obtained for $\leq 10\%$ conversion, in order to minimize the back-reaction and the photocyclization of the cis isomer. The photoisomerization quenching was studied spectrophotometrically and chromatographically (HPLC) under the same experimental conditions as the fluorescence. The HPLC measurements were carried out by a Waters apparatus equipped with an Erbasil C_{18} column and a UV detector. The following conditions of analysis were used: water-acetonitrile (20:80, v/v) as eluent, 300 and 335 nm, and diphenylethanedione as internal standard.

Two excitation wavelengths, $\lambda_{exc} = 353$ nm from the third harmonic of a Nd laser and to a lesser extent (where specified) $\lambda_{exc} = 248$ nm from a XeF excimer laser, were used in nanosecond flash photolysis.¹¹ The conductivity quartz cell (path length 5 mm) contained three glassy carbon electrodes which were connected with a pulse generator (200 V) and via an amplifier (10X) with the differential amplifier of a transient digitizer; for data handling and further details see elsewhere.¹² τ_{T} (the time at which the initial signal is reduced to 1/e) and $t_{1/2}$ (the time at which the initial signal is halved) are reported for the transients showing first-order and mixed-order kinetics, respectively.

Results and Discussion

Fluorescence and Photoisomerization of StPh's. The fluorescence and trans \rightarrow cis photoisomerization are the main decay processes of excited StPh's in acetonitrile as in nonpolar solvents.^{1,4} The fluorescence quantum yields and lifetimes of the five isomers are compiled in Table I. All lifetime values in acetonitrile are shorter than those previously measured in nhexane.⁴ This indicates that the increase in solvent polarity causes an increase in one or more of the decay rate parameters of S₁.

TABLE II: Trans → Cis Photoisomerization Quantum Yields of StPh's (Φ_c) in Acetonitrile Together with the Limiting Values ([D] \rightarrow ∞) in the Presence of Amines

		Φ _C ^{lim b}			
compd	$\Phi_{C}{}^{a}$	TBA	DEA	BrDMA	
1-StPh	0.13 (0.14) ^c	0.07	0.07	0.18	
2-StPh	0.24 (0.24)	0.07	0.06	0.20	
3-StPh	0.16 (0.13)	0.06	0.05	0.32	
4-StPh	0.29 (0.30)	0.06 ^d	<0.01*	0.12	
9-StPh	0.33 (0.13)	0.03	<0.01	0.10	

^a Mean deviation of three independent measurements ca. 5%. ^b Estimated error $\pm 10\%$. Values calculated as described in ref 4 unless otherwise indicated. 'Values in parentheses refer to n-hexane." ^d Measured at [TBA] = 0.336 M. ^c Measured at [DEA] = 0.125 M. ^fMeasured at [BrDMA] = 0.012 M.

TABLE III: Spectral and Kinetic Properties of the Radical Cations of the StPh's in Acetonitrile

		$10^{-10}k_{*}/$		
compd	λ_{max}/nm	$t_{1/2}^0 / \mu s$	M ⁻¹ s ⁻¹	₽ _{RC} ^{max}
1-StPh	510, 560 sh (500, 570 sh) ^b	8.1	0.69	0.09
2-StPh	480 sh, 540 (480, 545)	3.6	0.85	0.04
3-StPh	500, 550 sh (500, 560)	5.6	0.71	0.07
4-StPh ^c	490 (500)	7.7	0.23	0.05
9-StPh ^c	510, 560 sh (520, 570)	4.4	0.22	0.03

^a Calculated from the intercept of the equation $(t_{1/2})^{-1} = (t_{1/2}^0)^{-1} + (t_{1/2}^0)^{-1}$ $2^{1/2}k_s$ [n-StPh], and it represents the half-life of the radical cation under conditions of $[n-StPh] \rightarrow 0$ in air-saturated solution. ^b Values in parentheses refer to $EtOH/H_2O(1:1, v/v)$. Cadical characterized in the presence of 0.1 M DCNB.



Figure 1. 1-StPh in acetonitrile (λ_{exc} = 353 nm). Formation and decay of (a) ΔA of trans⁺⁺ at 500 nm and (b) transient conductivity ($\Delta \kappa$) in the absence of additives and (c) ΔA of trans⁻⁻ at 570 nm and (d) $\Delta \kappa$ in the presence of 0.06 M DEA.

For 1-, 2-, 3-, and 4-StPh, Φ_F in acetonitrile is larger than in *n*-hexane (Table I), while the quantum yields of trans \rightarrow cis photoisomerization in the absence of additives $(\Phi_{\rm C})$ in the two solvents are effectively identical (Table II). Thus, the decrease in $\tau_{\rm F}$ is mainly due to an increase in the radiative decay rate constants. These parameters in acetonitrile are, in fact, 1.5-2 times greater than in *n*-hexane.

Laser flash photolysis measurements of 1- and 3-StPh in acetonitrile reveal a substantial reduction of the population of T_1 . This indicates for these two isomers, at least, that the operative mechanism for the isomerization changes on going from nonpolar to polar solvents (see below).

In contrast to the other isomers for 9-StPh, the decrease in $\tau_{\rm F}$ is accompanied by a coupled change of the isomerization and fluorescence quantum yields so that the decrease of Φ_F accounts for the increase of Φ_{C} . This solvent effect can be satisfactorily explained by a decrease of the barrier for trans \rightarrow perp rotation in S_1 on increasing the solvent polarity. The isomerization

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Figure 2. Transient absorption spectra of radical cations of StPh's in acetonitrile, generated at the pulse end in the presence of 0.1 M DCNB ($\lambda_{exc} = 353$ nm).

mechanism of StPh's in acetonitrile is fully discussed later on. Formation of Radical Cations upon 353-nm Excitation. Aromatic compounds are known to undergo photoionization in polar solvents through various mechanisms.⁷ We therefore carried out experiments to check the presence of radical cations after laser excitation of the StPh's in acetonitrile. For anthracene and perylene the quantum yield for the radical cation production in this solvent is 0.06 and 0.02, respectively.⁸ It is not expected to be higher for StPh's since fluorescence and photoisomerization account for almost all the absorbed quanta.

Our laser flash photolysis investigation evidenced the production of a short-lived triplet state (see below) and of a longer lived transient (Tr_{RC}). In fact, for all the five isomers, Tr_{RC} appeared at the pulse end in the absence of additives. It is characterized by a structured absorption spectrum in the 500–600-nm region (Table III), and its decay follows mixed-order kinetics (half-life, $t_{1/2}$ in the microsecond range; see Figure 1a).

The transient Tr_{RC} is assigned to trans^{*+} for the following reasons: (i) Its half-life is not influenced by oxygen. For comparison, the triplet lifetimes (τ_T) are efficiently quenched by oxygen (see below). (ii) Its decay is similar to the short-lived component of the laser-induced conductivity signal at least for 1- and 2-StPh, for which a substantial increase ($\Delta \kappa$) was recorded (see below). (iii) Tr_{RC} is enhanced (without spectral changes) by the addition of DCNB (Figure 2 and Table III), which is a well-known acceptor for excited singlet states of aromatic hydrocarbons⁶ and has been used to produce and to study radical cations.^{13,14} Electron transfer according eq 1 also generates the radical anion of DCNB, which, however, absorbs too weakly to become detectable in our conditions.¹³

$$^{1} \text{trans}^{*} + \text{DCNB} \rightarrow \text{trans}^{*+} + \text{DCNB}^{*-}$$
(1)

The decay of Tr_{RC} is accelerated on increasing the StPh concentration, pointing out that the bimolecular interaction between trans^{•+} and the ground state is an important pathway in the disappearance of the radical cation. The rate constants for this reaction (k_s) , which are very close to the diffusional limit, are listed in Table III. For 4- and 9-StPh, the k_s values were measured in the presence of DCNB in order to enhance the absorption of trans^{•+} because it is otherwise hidden by the $T_1 \rightarrow T_n$ transition (see below).

It should be mentioned that the decay of Tr_{RC} can also be quenched by ferrocene and azulene (results not shown), presum-

ably via electron transfer to trans*+.

The electron ejected from ¹trans^{*} (in the absence of electron acceptors other than the solvent) is rapidly converted into $(CH_3CN)_2^{-,7de}$ which is a short-lived species, generating polymeric radical anion $(CH_3CN)_n^{-,7de}$ Formation of the two charged species is described by eq 2.

$${}^{1} \text{trans}^{*} \xrightarrow{2 \text{CH}_{3} \text{CN}} \text{trans}^{*+} + (\text{CH}_{3} \text{CN})_{2}^{*-}$$
(2)

Time-resolved conductivity measurements in argon-saturated solutions of StPh's reveal the laser-induced formation of ion pairs. A transient conductivity increase ($\Delta \kappa$), although weak, appears within the duration of the laser pulse (≤ 20 ns) for all five isomers. The decay of $\Delta \kappa$ is shown as an example in Figure 1b for 1-StPh.

In order to obtain information about the yield of trans^{*+} formation, the values $\Phi_{\rm RC}^{\rm max} = \Delta A / \Delta A_{\rm DCNB}$ (Table III) have been measured. In this relation ΔA is the optical density of ${\rm Tr}_{\rm RC}$ at $\lambda_{\rm max}$ without additives, and $\Delta A_{\rm DCNB}$ is the same quantity in the presence of high electron acceptor concentration ([DCNB] $\rightarrow \infty$). The reported $\Phi_{\rm RC}^{\rm max}$ values (<0.1) indicate that the ion-pair formation process is less important, in the decay of StPh excited states, than fluorescence and trans \rightarrow perp rotation. On the basis of the $\Phi_{\rm F}$, $\Phi_{\rm C}$, and $\Phi_{\rm RC}^{\rm max}$ values, it cannot be excluded that the recombination of the ion pair leads to the isomerizable triplet, at least for the isomers 1, 2, and 3 for which the sum $\Phi_{\rm F} + \Phi_{\rm C}/\alpha$ $+ \Phi_{\rm RC}^{\rm max}$ slightly exceeds unity ($\alpha \simeq 0.5$ is the fraction of molecules in the perpendicular configuration that goes to the cis form).⁴

Formation of Radical Cations upon 248-nm Excitation. The above assignment of trans^{•+} is also in agreement with the results obtained with excitation of StPh's at 248 nm in ethanol/water (9:1-1:1, v/v). Under these conditions, the StPh's are photoionized, thereby forming the solvated electron (e_{aq}^{-}) and the radical cation:

$$\operatorname{rans} \xrightarrow{n\nu} \operatorname{trans}^{*+} + e_{aq}^{-}$$
(3)

The assignment of the short-lived transient ($\lambda_{max} \simeq 710$ nm), formed within the duration of the laser pulse, to e_{ag}^{-} in all five cases is supported by the result that its lifetime is reduced to less than 10 ns after saturation with N₂O.¹⁵ The involvement of trans^{*+} is evidenced by (i) a further transient at the pulse end and with a much longer half-life than T₁ ($t_{1/2}$ in the microsecond range), (ii) a structured absorption spectrum (λ_{max} in the region 500-600 nm), (iii) the fact that its half-life is not quenched by N₂O and O₂, and (iv) a conductivity increase upon laser excitation (see below).

The spectral and kinetic characteristics of Tr_{RC} under these conditions are practically the same as described above for excitation at 353 nm in acetonitrile once the stronger spectral overlapping of more transients for $\lambda_{exc} = 248$ nm is taken into account. It should also be noted that $S_1 \rightarrow S_n$ in the 500-800-nm range becomes apparent; its ΔA^{max} varies with the type of isomer and the water content in ethanol (generally decreasing with increasing [H₂O]). As examples, the time-resolved transient absorption spectra of 2-, 4-, and 9-StPh in argon-saturated ethanol/water solution are shown in Figure 3. It is possible to separate out the absorption spectrum of each of (i) $S_1 \rightarrow S_n$ transition (recorded at $\lambda > 540$ nm, since the fluorescence overlaps too strongly at shorter wavelength), (ii) the triplet (e.g., $\lambda_{max} = 490$ nm and τ $\simeq 0.8 \,\mu s$ for 9-StPh), (iii) the solvated electron ($\lambda_{max} \simeq 710 \text{ nm}$), and (iv) the longer lived radical cation (e.g., $\lambda_{max} = 520$, 570 nm for 9-StPh). Monophotonic rather than biphotonic photoionization is concluded from the linear dependence of ΔA of the latter two transients on the laser intensity (e.g., for 9-StPh at around 570 and 700 nm, respectively) in all cases. A further transient (e.g., $\lambda_{\text{max}} \leq 400 \text{ nm}$ for 9-StPh) appeared, and its ΔA is higher for 9-StPh than for the other four isomers. This absorption is not quenched by oxygen and N₂O and is virtually constant over 20 μ s. It is tentatively assigned to a side photoproduct.

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Figure 3. Transient absorption spectra of 2-, 4-, and 9-StPh in EtOH:H₂O (1:1, v/v) at 10 ns (\square), 100 ns (O), 500 ns (\triangle), and 2 μ s ($\textcircled{\bullet}$) after the pulse ($\lambda_{exc} = 248$ nm).



Figure 4. Effect of DEA concentration on the relative values of the quantum yields of fluorescence (\bullet) , trans \rightarrow cis photoisomerization (\Box) , and on the radical anion formation (\times) and conductivity increase at the pulse end (Δ) for 1-StPh in acetonitrile.

Fluorescence Quenching by Amines. Addition of TBA, DEA, and BrDMA to StPh's in n-hexane causes a quenching of the olefin fluorescence, the appearance of a new structureless band, and an increase of the triplet population.⁵ In acetonitrile the quenching by these amines, which follows the Stern-Volmer equation, is not accompanied by exciplex emission and leads mainly to the formation of radical ions in the case of TBA and DEA and of StPh triplets with BrDMA (see next section). All the Stern-Volmer plots were linear, even though for 3-StPh a biexponential decay was observed.¹ This point has already been discussed in a previous paper.⁴ The decrease of Φ_F in the presence of increasing concentration of DEA is shown in Figures 4 and 5 for the five isomers. The quenching rate parameters $(k_0, \text{ Table I})$ are calculated from the slopes of the Stern-Volmer plots (least-squares treatment), and their values are close to the diffusional limit (k_{diff}) . It should be noted that, as already found in nonpolar solvents and discussed in previous papers,^{2,4} the quenching by TBA is less efficient than that by the other amines.

A particular quenching mechanism has to be invoked for the 9-StPh-BrDMA system because the k_q value (5.3 × 10¹⁰ M⁻¹ s⁻¹) is larger than k_{diff} (2.7 × 10¹⁰ M⁻¹ s⁻¹),¹⁶ even taking into account



Figure 5. Effect of DEA concentration on the relative values of the quantum yields of fluorescence (\oplus), trans \rightarrow cis photoisomerization (\square), and on the radical anion formation (\times) and conductivity increase at the pulse end (Δ) for StPh's in acetonitrile.

TABLE IV: Spectral and Kinetic Properties of the Triplets of StPh's in Acetonitrile

compd	λ_{max}/nm	$ au_{\mathrm{T}}/\mu\mathrm{s}$	$\frac{10^{-10}k_{ox}a}{M^{-1}s^{-1}}$	Ф _Т ^{тах}
1-StPh ^b	470	0.32	0.75	<0.03 (0.18) ^c
2-StPh ^b	440, 560	0.15	0.83	<0.05 (<0.01)
3-StPh ^b	490	0.35	0.92	<0.06 (0.35)
4-StPh	480	0.34	0.76	0.59 (0.55)
9-StPh	470, 570 sh	1.1	0.51	0.12 (0.32)

^aEstimated error $\pm 10\%$. ^bTriplet characterized in the presence of 0.1 M BrDMA. ^cValues in parentheses refer to *n*-hexane.⁵

the experimental error. Interactions in the ground state leading to static quenching phenomena or electron transfer to the ¹trans^{*} state over distances somewhat larger than the collisional diameter are conceivable and could be invoked to explain this behavior, even though ground-state complexation is not supported by spectroscopic evidence and curved Stern–Volmer plot. However, k_q values larger than k_{diff} were also found in the case of *trans*-stilbene–amine systems and were explained in the same way.^{17,18}

The Triplet State and Its BrDMA-Enhanced Formation. In addition to the transient ascribed to trans⁺⁺ (Tr_{RC}), excitation of 4- and 9-StPh at 353 nm in acetonitrile generates a major transient (Tr_T) with triplet character. The triplet lifetime (τ_T) , in contrast to the half-life of Tr_{RC} , is reduced by oxygen. From the dependence of $k_{obsd} = 1/\tau_T$ on [O₂], the quenching rate constant by oxygen (k_{ox}) was obtained (Table IV). The assignment of Tr_T to the lowest triplet state is evidenced by the comparison of its properties (first-order decay kinetics and $\lambda_{max} \simeq 470-490$ nm) with those of the triplets of StPh's in n-hexane⁵ and by the heavy-atom effect of BrDMA on the population of Tr_T in acetonitrile (see below). Excitation of the other three trans isomers in the absence of additives generates only trans*+. Since both Tr_T and Tr_{RC} are formed within the duration of the laser pulse, singlet excited states should be precursors of these two transients. (T-T absorption spectra of 4- and 9-StPh were also detected by using $\lambda_{\text{exc}} = 248 \text{ nm}; \text{ see Figure 3}).$

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Figure 6. Absorption spectra of the radical anions of StPh's in acetonitrile generated at the pulse end in the presence of 0.1 M DEA ($\lambda_{exc} =$ 353 nm).

In general, when BrDMA is used as quencher, the StPh triplet is the main transient observed. The intersystem-crossing (ISC) catalysis caused by the heavy atom in the amine allows also the triplet properties of 1-, 2-, and 3-StPh to be measured. Spectral and kinetic characteristics (e.g., first-order decay) of the triplets of the five StPh's at room temperature are compiled in Table IV. The absorption maxima and decay lifetimes in acetonitrile are very close to those reported in *n*-hexane.⁵ In particular, the lifetimes, in the 0.1-1- μ s range, are compatible with the presence of a ³trans^{*} \Rightarrow ³perp^{*} equilibrium shifted toward the trans side.^{5,11c,19}

The Φ_T^{max} values (Table IV) are calculated from the enhancement of the triplet population by BrDMA. Φ_T^{max} was equated to the $\Delta A/\Delta A_{BrDMA}$ ratio, where ΔA and ΔA_{BrDMA} are the optical changes of Tr_T at λ_{max} without additives and in the presence of a sufficiently high concentration of BrDMA, respectively. They can be therefore taken as the maximum values for the triplet yield. Only the Φ_T^{max} values of 2- and 4-StPh are practically identical with those in *n*-hexane;⁵ the others are meaningfully smaller. In agreement with the decrease of the twisting barrier in the S₁ state on going to a polar solvent (see above), Φ_T^{max} of 9-StPh is reduced to 1/3 of its value in *n*-hexane, while those of 1- and 3-StPh drop to negligible values in acetronitrile ($\leq 5\%$), probably owing to the population of an isomerizable upper triplet state (see below).

Radical Pair Formation and Enhanced Transient Conductivity in the Presence of Amines. Complexes between excited aromatic compounds and electron donors in acetonitrile (dielectric constant $\epsilon = 37.5$) are generally considered to be nonemitting even though weak fluorescence has been reported for the pyrene-dimethylaniline system.¹⁴ In fact, the formation of solvated ion pairs in polar solvents becomes a very important deactivation pathway of the excited complex. However, electron back-transfer from geminate radical ion pairs leading to the ground state cannot be excluded.²⁰ A tentative model to explain the dynamics of the decay of CT complexes in polar solvents has been proposed by Mataga and co-workers^{14,21} in which the dissociated ions are formed from multiple ion-pair states in equilibrium with multiple exciplex states.

For *trans*-stilbene-amine systems in acetonitrile Lewis and co-workers have suggested that the initial complex leads either to the olefin triplet (able to isomerize) or to the olefin anion.^{17,18}

TABLE V: Spectral and Kinetic Properties of the Radical Anions of StPh's Produced by Interaction with DEA (0.1 M) in Acetonitrile

compd	λ_{max}/nm	$t_{1/2}/\mu s$	$10^{-10}k_{ox}^{a}/M^{-1} s^{-1}$
1-StPh	490 sh, 580	2	2
2-StPh	500 sh, 555	3	2
3-StPh	525	3	1.5
4-StPh	540	1	2
9-StPh	480 sh, 580	1.5	2

"Estimated error $\pm 20\%$.

SCHEME I: Trans \rightarrow Cis Photoisomerization of StPh's in Acetonitrile in the Absence of Additives; Pathways a, b, and c Refer to the Isomerization in S₁, T₁, and an Upper Triplet, Respectively



For the StPh-amine systems in acetonitrile radical anions are expected to be formed via electron transfer from the amine as donor (D):

$$trans^* + D \rightarrow trans^{*-} + D^{*+}$$
 (4)

The absorption spectra of the radical anions of the five StPh's $(\lambda_{exc} = 353 \text{ nm})$ are shown in Figure 6. Their lifetimes are in the 1-3- μ s range under our conditions (see Figure 1c), and the rate constant for quenching by oxygen (Table V) is even larger than that for triplet quenching. Ion-pair formation is supported by the amine-enhanced amplitude of the conductivity signal (compare parts d and b of Figure 1), appearing within the duration of the laser pulse for all the StPh's.

Although the radical anions are diffusionally quenched by oxygen, both the amplitude and half-life of the conductivity signal are not markedly influenced by O_2 concentration (results not shown). This behavior is explained in the following way. The decay kinetics of the ion pair are mainly determined by electron back-transfer from the trans⁻ to amine⁺⁺. The back-reaction in oxygenated acetonitrile involves, however, the O_2^{+} radical anion, formed by the reaction

$$\operatorname{trans}^{\bullet-} + \operatorname{O}_2 \to \operatorname{trans} + \operatorname{O}_2^{\bullet-}$$
 (5)

Thus, trans^{•-} (on optical detection) decays in the presence of oxygen faster than the electron back-transfer (on $\Delta \kappa$ detection) occurs.

When BrDMA is used as fluorescence quencher, the triplet is generally the main transient; its formation occurs at the expense of the radical anion of the given StPh, whose absorption becomes quite low.

The radical cations of the amines have only low extinction coefficients and are mainly overlapped by the absorption of the radical anions of the StPh's. However, the spectra of DEA⁺⁺ ($\lambda_{max} = 460 \text{ nm}, t_{1/2} \simeq 3 \mu s$) and BrDMA⁺⁺ ($\lambda_{max} = 490 \text{ nm}, t_{1/2} \simeq 4 \mu s$) could be detected in air-equilibrated solutions, i.e., after quenching reaction 5. The observed properties of DEA⁺⁺ are in agreement with the literature data.²²

In contrast to trans^{*+} (see k_s in Table III) are the corresponding radical anions not quenched by the ground state. On the other hand, the half-life of the conductivity decreases with increasing StPh concentration. This points to an interaction of the amine^{*+} with the trans ground state, thereby forming more stable charged species.

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Mechanism of Direct Trans \rightarrow Cis Photoisomerization. The trans -> cis photoisomerization of StPh's in nonpolar solvents has been reported to occur in the triplet manifold, 1,5 namely, via T₁ for 1-, 3-, 4-, and 9-StPh and via an upper excited triplet (³trans**) for 2-StPh, where $\Phi_T \leq 0.01^5$ does not explain the high Φ_C . A pathway via S₁ has been excluded owing to the high activation barrier which has to be overcome for the 1 trans* \rightarrow 1 perp* rotation.¹ Among the five isomers the activation energy is smallest for 9-StPh: it is 9.5 kcal/mol in methylcyclohexane and 3.2 kcal/mol smaller in ethanol.¹ It is conceivable that the activation barrier in acetonitrile is even smaller than the latter value. Hence, a pathway via S_1 (a, in Scheme I) may be opened. Indeed, this is suggested for 9-StPh on the basis of the fluorescence, photoisomerization, and intersystem crossing quantum yields (Tables I, II, and IV). The pathway S_1 should reduce the competing fluorescence and intersystem crossing processes which is the case only for 9-StPh: Φ_F in acetonitrile is roughly half the value in *n*-hexane (Table II), and Φ_T is only 0.12 compared to 0.32 (Table IV). This is also in line with a decrease of $\tau_{\rm F}$, taking into account that $k_{\rm F}$ and $k_{\rm ISC}$ are practically unchanged in the two solvents. The Φ_T value in acetonitrile accounts roughly for 20% of Φ_C , indicating a minor contribution of the T1 pathway to the photoisomerization.

Instead of this mixed S_i/T_i mechanism, for 4-StPh in acetonitrile the T_i route (b in Scheme I) as the main pathway is suggested since $\Phi_T^{max} = 0.56$ accounts for $\Phi_C = 0.29$.

For the other three StPh's, Φ_C values (Table II) are practically the same in *n*-hexane and in acetonitrile, while $\Phi_{\rm F}$ and $k_{\rm F}$ increase slightly on increasing polarity. For 1-, 2-, and 3-StPh the involvement of both T_1 and S_1 in the trans \rightarrow perp rotation is unlikely. The singlet route is excluded on energetic reasons as outlined above, and the route via the lowest triplet is ruled out since $\Phi_{\rm T}$ is in any case too low to account for $\Phi_{\rm C} = 0.13 - 0.24$ (Tables IV and II, respectively). Therefore, a contribution via an upper excited triplet (c in Scheme I) has to be considered as a main mechanism for trans \rightarrow cis photoisomerization for these three isomers in acetonitrile at room temperature. The alternative, that the rotation around the double bond to about 90° occurs in a vibrationally excited state of T_1 , is equally possible. This state may be populated from an isoenergetic S_1 or T_n state and may relax favoring a vibrational mode involving torsional coordinates. Trans → cis photoisomerization via upper excited triplet states has already been reported for stilbenes.²³

Concerning the effect of solvent polarity, the most relevant results concern the Φ_T values of 1-, 3-, and 9-StPh which are much lower in acetonitrile (Table IV) than in *n*-hexane. We suggest that for 2- and 4-StPh the mechanism (upper excited and lowest triplet, respectively) remains, while for 1- and 3-StPh the mechanism changes from T_1 to an upper triplet on going from a nonpolar to a polar solvent. For 9-StPh, isomerizing via T_1 in *n*-hexane, the involvement of S_1 (mainly) and T_1 is evidenced in acetonitrile.

Mechanism of the Amine-Induced Trans \rightarrow Cis Photoisomerization. A comparison of the quenching of fluorescence and trans \rightarrow cis photoisomerization for StPh's by amines in *n*-hexane showed that the former is more efficient than the latter. The particular trans isomer for a given amine and also the nature of the amine cause significant changes in the photochemical behavior. In some cases the amine quencher causes an increase of the isomerization quantum yield.⁴ In acetonitrile the characteristics of the complex between ¹trans* and the amine change significantly and, in general, the photoisomerization is reduced (see Figures 4 and 5). The quenching effect is particularly high with DEA and TBA, while an increase of isomerization quantum yield is observed for 1- and 3-StPh with BrDMA. In the presence of amines the experimental $\Phi_C(D)$ values at any [D] can be considered the sum of two contributions: the contribution of the free molecules, which becomes zero at high [D], and that of the quenched molecules isomerizing through the charge-transfer complex (Φ_{CE}). The Φ_{CE} value is related to the concentration of SCHEME II: Trans \rightarrow Cis Photoisomerization of StPh's in Acetonitrile in the Presence of DEA, TBA, and BrDMA (For the Reaction Steps See Text)



quencher by two types of equations; both of them allow the photoisomerization quantum yield of the complex (Φ_C^{\lim}) to be determined by means of linear plots.⁴

The behavior of stilbene-amine systems in acetonitrile¹⁷ is different than that observed for StPh's. In fact, while the Φ_C^{lim} values for the latter systems (Table II) are independent of the quencher concentration (linear plots of $1/\Phi_{CE}$ vs 1/[D] were obtained) in the case of stilbene the quantum yield of complexed molecules decreases with increasing [D]. The authors¹⁷ explain this finding supposing a quenching of an intermediate for the cis isomer formation (probably an ion pair) by the amine in the ground state.

The Φ_c^{lim} values (for $[D] \rightarrow \infty$) for the five StPh's in the presence of TBA, DEA, and BrDMA are reported in Table II. In general, the values are indicative of a low efficiency for the complexed molecules to yield the cis isomer. In particular, the 4-StPh-DEA and 9-StPh-DEA systems, for which the quenching of fluorescence is very similar to that of trans \rightarrow cis photoisomerization, Φ_c^{lim} is zero, and hence they are completely unreactive. Sequence 1, 2, 3t in Scheme II, i.e., complete electron transfer and back-transfer to the starting trans isomer, is suggested to account for the 4- and 9-StPh-DEA systems.

Small Φ_C^{\lim} values have been obtained for StPh's and DEA or TBA systems throughout (Table II). The fluorescence quenching is only slightly more efficient than the quenching of trans \rightarrow cis photoisomerization. The results obtained spectrophotometrically (assuming that the final product is only a cis isomer) were checked by HPLC for DEA and TBA systems. These analysis are in good agreement with the optical results, indicating negligible adduct formation; i.e., bimolecular reactions involving the amine radical cation lead essentially to the trans and to a small extent of the cis isomer. The nonradiative processes that do not lead to isomerization are the prevailing decay pathways of these complexes in acetonitrile.

It is to be noted that this behavior differs from that of the *trans*-stilbene-tertiary amine systems. In polar, aprotic solvents addition and reduction products formed in low yield through an α C-H or N-H homolysis of the tertiary amines, respectively, were found.¹⁷ For styrylnaphthalenes it has been shown that these photoreactions can be neglected because of high Φ_C^{\lim} values and the low amine concentration used.²⁴

The transients identified in the presence of DEA (and TBA) are the radical anions of the StPh's (Table V) and the radical cations of the amines (see above). If we consider the low Φ_C^{lim} values measured, the recombination of the ions does probably not produce the olefin triplet with high efficiency. This is also in contrast with the findings reported for the stilbene-amine system.¹⁷

The results with DEA (except for 4- and 9-StPh, see above) and TBA in Table II indicate that roughly 10% of the excited StPh molecules undergo twisting around the double bond. It is likely that the amount of triplet responsible for the photoisomerization

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to the cis isomer is produced either before the ion-pair formation (pathways 4 plus 5c or 6 plus 7c in Scheme II) or in the recombination process (sequence 1, 2, and 3c). In any case, we found no direct evidence for ISC through such pathways. For TBA, this can be due to the similarity of the triplet lifetime and the radical anion half-life and to the prevalence of the absorption of trans⁻⁻, eventually hiding the T-T absorption. For the 1-, 2-, and 3-StPh-DEA systems, the failure in triplet detection is not surprising since Φ_T^{max} is negligible also in the absence of amines (Table IV). In these systems the involvement of an upper triplet state (pathway 6 plus 7c) is invoked to explain the Φ_{c}^{lim} values.

The complexes of the StPh's with BrDMA in acetonitrile show $\Phi_{\rm C}^{\rm lim}$ values which are smaller (4- and 9-StPh), similar (2-StPh), or even higher (1- and 3-StPh) than those of the unquenched molecules (Table II). The prevailing transient is the triplet (pathway 4 in Scheme II), even though the radical anion (pathway 2) is also observed. For the 1-, 2-, and 3-StPh ISC is substantially enhanced (pathway 4); values of 40–60% are expected from $\Phi_{\rm C}^{\rm lim}$ in Table II. The triplet states of 4- and 9-StPh should be less reactive than those of 1-, 2-, and 3-StPh. A similar although less pronounced behavior has been reported for 4-StPh in n-hexane where the presence of BrDMA leads to an enhanced ISC and to a quenching of photoisomerization.⁴

The Φ_{c}^{lim} values, especially with BrDMA, are in general much higher in n-hexane⁴ than in acetonitrile. The substantial difference of the StPh behavior in the two solvents is explained by comparing their transient features. The only observable transient with BrDMA (and TBA) in *n*-hexane⁵ is the triplet state of the StPh's. The Φ_T^{max} values are close to unity for the brominated amine (and 0.5-1 for the aliphatic one). In acetonitrile the behavior depends more markedly on the presence of the heavy atom in the quencher regarding both the isomerization efficiency and the observable transients. In general, the nonradiative processes that do not lead to the cis isomers are the prevailing decay pathways of these StPh-amine complexes.

Acknowledgment. We thank Profs. U. Mazzucato and D. Schulte-Frohlinde for advice and support and Mr. L. J. Currell and Mr. D. Pannacci for technical assistance. Financial support by the Consiglio Nazionale delle Ricerche and Ministero della Pubblica Istruzione (Rome) is gratefully acknowledged by G.G.A. and F.E.

Oximine Form of the Peptide Bond as a Transient Modification in Enzyme Redox Reactions

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In a study devoted to proton-assisted intramolecular electron transfer (IET) in multiheme cytochromes (an alternative to through-space IET), the possibility that the peptide bond takes up an oximine form at least for a very short time has appeared to be critical. Therefore, a detailed quantum mechanical study of the time-dependent aspects of the tautomerism of the peptide bond has been carried out, using the formamide dimer as a test model. The surprising conclusion is that, due to the rapid decrease of the lifetime of the oximine form when the H bridge length decreases, it is the N-O bridge vibration that determines the return to the stable amine form. Thus, the in situ lifetime of the oximine form is ca. 0.2 ps. An interesting generalization of this result is that proton relay processes (whether assisting IET or not) are time controlled by the slow H bridge vibration.

1. Introduction

Proton and electron tunneling are two important features of biochemical processes.¹⁻³ Certain intramolecular electron-transfer (ET) processes taking place in large enzymes may be realized by a combination of both kinds of tunneling provided some enol-keto tautomerism of the peptide bond is assumed.⁴ This assumption presupposes a satisfactory answer to the following question: are there circumstances under which the enol (oximine) form of the peptide bond is observed, and, if not, on what grounds can it be postulated in the elementary processes under consideration?

This paper contains an analysis of the above question. Its four parts are devoted to (i) explaining in more detail how the general problem has arisen, (ii) showing that the answer hinges on the possibility that the oximine form may be a transient form having a sufficiently long (but not too long) lifetime, (iii) describing the quantum mechanical utilities needed for handling the quantitative aspects of the problem, and (iv) specifying the elementary steps of the isomerization mechanism and reporting lifetime estimates.

2. Proton-Assisted Inner-Shell Electron Transfer

Electron transfer is usually classified into inner-shell and outer-shell ET.⁵ The general theoretical features of outer-shell

ET (i.e., essentially, solvent-mediated ET) have been extensively studied.⁶⁻¹¹ Inner-shell ET takes place within a well-defined structure and may be treated along similar lines, but precise assumptions concerning its mechanistic and structural details are mandatory. This holds especially for intramolecular ET, which is an interesting possibility in biological macromolecules such as multiheme cytochromes, ¹²⁻¹⁴ as well as in recently discovered

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- 0022-3654/91/2095-4231\$02.50/0 © 1991 American Chemical Society

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