Photoinduced Electron Transfer between Styrylanthracenes and Electron Donors and Acceptors in Acetonitrile

Helmut Görner

Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim an der Ruhr, Germany Fausto Elisei and Gian Gaetano Aloisi* Dipartimento di Chimica, Università di Perugia, I-06100 Perugia, Italy

The decay pathways of the lowest singlet and triplet excited states (${}^{1}trans^{*}$ and ${}^{3}trans^{*}$) of trans-n-styrylanthracenes (*n*-StA, where n = 1, 2 or 9 on the anthracene) have been studied in acetonitrile at room temperature. Fluorescence lifetimes ($\tau_{\rm F}$) and quantum yields ($\phi_{\rm F}$), as well as the yield and spectral and kinetic properties of the lowest triplet state of the three StAs, were determined by steady-state and transient techniques. The formation and the decay of the respective StA radical cations ($trans^{*+}$) were observed by laser flash photolysis; the yield of photoionization is *ca*. 0.07 on 353 nm excitation and is enhanced by fluorescence quenching with 1,4-dicyanobenzene. The formation and decay of the StA radical anions ($trans^{*-}$) in the presence of diethylaniline (DEA) is concluded from transient conductivity ($\Delta \kappa$) and optical results. DEA significantly enhances the yield of $trans^{*-}$ and the initial amplitude of $\Delta \kappa$ and correspondingly quenches $\phi_{\rm F}$. The bimolecular interaction between ${}^{1}trans^{*}$ and 4-bromodimethylaniline enhances the triplet population.

The charge-transfer (CT) interactions in electronic excited states between 1,2-diarylethylenes and amines have been extensively investigated over several years in one of our laboratories.¹⁻⁶ Previously, the exciplexes of trans-n-styrylphenanthrenes (n-StPh; n = 1, 2, 3, 4 and 9) with amines have been studied in methylcyclohexane;² their spectral and kinetic properties and the influence of solvent polarity on their photophysical parameters has been obtained.^{2,3} Moreover, the effect of exciplexes with amines on the quantum yields of trans \rightarrow cis photoisomerization (ϕ_c) and triplet formation ($\phi_{\rm T}$, as a measure for that of intersystem crossing, $\phi_{\rm ISC}$) in *n*-hexane has been studied.^{4,5} The presence of diethylaniline (DEA) or 4-bromodimethylaniline (BrDMA) markedly affects $\phi_{\rm C}$, quenching or enhancing, depending on the solvent and the position of styrene substitution in phenanthrene.4,5

The study of StPhs has been complemented by photophysical and photochemical experiments in acetonitrile; three pathways, depending on the styrene substitution in phenanthrene, have been suggested for *trans* \rightarrow *cis* photoisomerization.⁶ The addition of an amine generally quenches both fluorescence and *trans* \rightarrow *cis* photoisomerization; in the presence of an amine other than BrDMA, ion pairs are generated in acetonitrile, while for the amine bearing the heavy atom, the main effect is the $\phi_{\rm T}$ enhancement.⁶

For the purpose of investigating the effect of the aryl chromophore nature on the photophysical and photochemical decay pathways of exciplexes, we have extended the study of the three *trans-n*-styrylanthracenes (*n*-StA, where n = 1, 2 and 9). These compounds show a peculiar behaviour since they do not undergo *trans* \rightarrow *cis* photoisomerization in any environment,⁷⁻¹⁴ even though some of their derivatives are known to isomerize.^{8,12} For the 2- and 9-StA/ dimethylaniline systems, CT interaction and enhanced $\phi_{\rm T}$ have been reported.^{15,16}

The present paper deals with the photophysical and photochemical behaviour of the three StA isomers in acetonitrile and their complexes with electron donors or acceptors. In particular, the features (ϕ_F , τ_F) of the ¹trans* decay processes and the characteristics of the related triplets and radical cations (trans⁺⁺) in the absence of additives were examined. In addition, the spectral and kinetic properties of radical anions (trans⁻⁺) and trans⁺⁺, produced by electron transfer in the presence of DEA and 1,4-dicyanobenzene (DCNB), respectively, were studied.

Experimental

The trans-n-StA isomers were the same as in ref. 13 and 14. N,N-Diethylaniline (Carlo Erba, RPE grade) was distilled and dried before use, 4-bromo-N,N-dimethylaniline (Aldrich), and chloranil (2,3,5,6-tetrachloro-p-benzoquinone, Fluka) were recrystallized before use, and 1,4-dicyanobenzene (Aldrich/EGA) was used as received. Solvents were purified (ethanol, Merck, by fractional distillation; water, by using a millipore, Milli-Q system) or used as received (acetonitrile: Carlo Erba RPE-ACS or Uvasol quality). All measurements were carried out at 24 ± 2 °C; the samples were deoxygenated (by purging with argon or nitrogen) unless indicated otherwise.

The fluorescence lifetimes, quantum yields and rate constants for quenching (using [StA] $\leq 1 \times 10^{-4}$ mol dm⁻³, $\lambda_{irr} = 335$ or 355 nm) were measured as described previously.^{4,6,17,18} Excitation wavelengths of 248, 308, 347 and 353 nm from one of two excimer lasers (Lambda Physik, EMG 200 and EMG 50E), a ruby laser (J. K., second harmonic) and a Nd-laser (J. K., third harmonic), respectively, were used in ns flash photolysis experiments (pulse width ≤20 ns and energy 5-30 mJ per pulse); unless specified otherwise, $\lambda_{exc} = 353$ nm.¹⁹ The optical signals with $\lambda_{exc} =$ 308 and 347 nm (Perugia) were fed into a transient digitizer (Tektronix DSA 602) and analysed by a computer (Tektronix PEP 301). Conductivity measurements were carried out in a 'flow-through' quartz cell, containing three glassy carbon electrodes and using a DC bridge, giving a overall time resolution of 20 ns.6,20

Results and Discussion

Triplet State

In previous studies it has been shown that the dominant transient of StAs in solvents of low polarity is the triplet state $({}^{3}trans^{*}).{}^{12,13,15,16}$ This holds also for the three StAs in acetonitrile using laser flash photolysis ($\lambda_{exc} = 248$ or 353 nm). The major transient with triplet character [Fig. 1(*a*), 2(*a*), 3(*a*)





Fig. 1 Transient absorption spectra for 1-StA in acetonitrile (in the absence of additives): (a) argon-saturated at 0.5 (\bigcirc) and 50 (\triangle) µs after the pulse, (b) air-saturated at 0.2 (\bigcirc) and 1 (\square) µs after the pulse; $\lambda_{\rm exc} = 353$ nm

and Table 1] shows two (or three) bands, one around 330 nm and a second with λ_{max} between 450 nm (9-StA) and 555 nm (1-StA). The triplet appeared within the pulse duration (or after the strong fluorescence signal) and its decay in the absence of oxygen follows first-order kinetics at low laser pulse intensities. T-T annihilation generally limits the decay kinetics.

The triplet lifetime (τ_T) in the absence of oxygen is in the 40-50 µs range (Table 1). From the dependence of τ_T^{-1} on $[O_2]$, the quenching rate constant by oxygen (k_{ox}) was obtained. The values are similar to those of comparable cases and somewhat larger than for anthracene (Table 1). The tran-



Fig. 2 Transient absorption spectra for 2-StA in acetonitrile (in the absence of additives): (a) argon-saturated at 1 (\bigcirc) and 40 (\triangle) µs after the pulse, (b) air-saturated at 0.02 (\bigcirc), 0.05 (\bigcirc), 0.2 (\triangle) and 1 (\square) µs after the pulse; $\lambda_{\rm exc} = 353$ nm



Fig. 3 Transient absorption spectra for 9-StA in acetonitrile (in the absence of additives): (a) argon-saturated at 0.5 (\bigcirc) and 40 (\triangle) µs after the pulse, (b) air-saturated at 0.1 (\bigcirc) and 0.5 (\square) µs after the pulse; $\lambda_{\rm exc} = 353$ nm

sient absorption spectra in air-saturated acetonitrile [Fig. 1(b), 2(b), 3(b)] at the accessible wavelengths are more complicated than under argon. In addition to the triplet absorption a short-lived component at $\lambda > 600$ nm, *e.g.* for 2-StA [Fig. 2(b)], which can be assigned to an $S_1 \rightarrow S_n$ transition, and a long-lived transient assigned to the radical cation (see below) were observed.

BrDMA; Enhanced Intersystem Crossing

Quenching of the StPh fluorescence by amines has been shown to increase ϕ_T strongly; the enhancement with BrDMA is particularly high due to the heavy-atom effect. This effect has been used to determine absolute ϕ_T values from the ratio of the triplet absorbances in the absence and presence of BrDMA.⁶ Also for StAs the ISC is efficiently induced by BrDMA. Evidence for the triplet character of the induced transient comes from absorption spectra and/or O₂ effect on decay kinetics. In fact, for the three isomers the quenching rate constants by oxygen are in agreement with those in Table 1.

For StAs in benzene, ϕ_T was recently measured by energy transfer from the benzophenone triplet.¹³ In order to determine this yield independently in acetonitrile, we used another method.²¹ The ratio of fluorescence quantum yields in the absence and presence of BrDMA (ϕ_F/ϕ'_F), which is equated to that of the intensities, is related to the ratio of the absorbances of the triplet in the absence and at different concentrations of BrDMA ($\Delta A_T/\Delta A'_T$). In particular, assuming that fluorescence quenching by BrDMA does not lead to the *trans* ground state (which is also the case of StPhs⁶) the following relationship is valid;²¹

$$\phi_{\rm F}/\phi_{\rm F}' - 1 = \phi_{\rm T}(\phi_{\rm F} \Delta A_{\rm T}'/\phi_{\rm F}' \Delta A_{\rm T} - 1) \tag{1}$$

Table 1 Spectral and kinetic properties of the triplets of StAs^a

| compound | λ _{max} /nm | $\tau_T/\mu s$ | ϕ_{T} | $k_{\rm ox}^{\ b}/10^9 \ {\rm dm}^3 \ {\rm mol}^{-1} \ {\rm s}^{-1}$ |
|--------------------|----------------------|--------------------------|---------------------|--|
| anthracene | 425 | ≥5 | 0.66 | 2.2 |
| 1-StA | 340, 555 | ca. 45 (85) ^c | $0.09 \ (0.20)^d$ | 4.6 |
| 2-StA | 325, 430, 600 | ca. 45 (115) | 0.10 (0.10) | 3.6 |
| 9-StA | 325, 450 | ca. 45 (45) | 0.22 (0.32) | 6.9 |
| 9-StA ^e | 325, 450 | | 0.25 | 4 |

^{*a*} In acetonitrile, argon-saturated except for k_{ox} . ^{*b*} Taking $[O_2] = 1.6 \times 10^{-3}$ mol dm⁻³ in air-saturated acetonitrile. ^{*c*} Values in parentheses refer to benzene. ^{13 *d*} Values in parentheses refer to benzene and have been re-determined using relation (1). ^{*c*} Taken from ref. 12.

30



Fig. 4 Relative changes (Δ/Δ_{max}) for 1-StA in argon-saturated acetonitrile as a function of the DEA concentration: ΔA_{445} (radical anion, \blacktriangle), conductivity amplitude (\square) at 0.2 µs ($\lambda_{exc} = 353$ nm) and fluorescence intensity ($\textcircled{\bullet}$); insets: change in voltage (proportional to $\Delta\kappa$) vs. time for: (a) [DEA] = 0 and (b) in the presence of 0.1 mol dm⁻³ DEA

The dependence of $\phi_F/\phi'_F - 1$ on the parameter ($\phi_F \Delta A'_T/\phi'_F \Delta A_T - 1$) should be linear and the slope represents ϕ_T .

In fact, using $\lambda_{\text{exc}} = 347$ nm for the ΔA measurements and keeping in mind that addition of BrDMA does not change the spectral and kinetic properties of the StA transients, we found for the three cases that these plots (not shown) are linear. In order to substantiate the previous results, we reexamined the three $\phi_{\rm T}$ values in benzene. The agreement between the new (Table 1, in parentheses) and previous¹³ values is within the experimental error of $\pm 10\%$. The $\phi_{\rm T}$ values in acetonitrile (Table 1) show that ISC is largest for 9-StA (a similar value of $\phi_{\rm T} = 0.25$ has been reported)¹² where $\phi_{\rm F}$ is smallest.

Radical Cation Formation

Close inspection of the spectra ($\lambda_{exc} = 353$ nm) in the absence of additives but in presence of oxygen shows at least two species, ³trans^{*} and a second transient: trans^{*+}. The two spectra can be separated kinetically, even when they are similar since the rate constant for quenching by oxygen of ³trans^{*} is larger than that of trans^{*+}. Examples in airsaturated acetonitrile are shown in Fig. 1(b), 2(b) and 3(b) for 1-, 2- and 9-StA, respectively.

It is well known that for aromatic molecules in acetonitrile in the absence of an (added) electron acceptor, the electron can be ejected from an excited state and rapidly converted into $(CH_3CN)_2^{-..6,2-25}$ This is a short-lived species, generating the polymeric radical anions $(CH_3CN)_n^{-..23b,c}$ For 9-StA the second transient ($\lambda_{max} = 640$ nm) has tentatively been assigned to the radical cation.¹² For StAs, generation of the two charged species is described by eqn. (2).

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

Time-resolved conductivity measurements for StAs in argonsaturated acetonitrile support this. They reveal a conductivity increase ($\Delta \kappa \propto \Delta U$) within the duration of the laser pulse (≤ 20 ns) and a decay by mixed first- and second-order [inset (a) of Fig. 4]. These changes in ion mobility indicate formation of ion pairs.

Many organic molecules in polar solvents undergo photoinduced ionization in the singlet excited state.23-25 For example, the quantum yield (ϕ_{PI} , PI stands for photoionization) for radical cation production of anthracene, perylene and StPhs in acetonitrile is 0.065,²⁴ 0.024,²⁵ and 0.03-0.09,⁶ respectively. The $\phi_{\rm PI}$ values for StAs were determined by calibrating the flash photolysis system with benzophenone triplet, using optically matched solutions and the molar absorption coefficient of trans⁺⁺ [ϵ (trans⁺⁺) measured in the presence of chloranil, see below]. For benzophenone triplet in acetonitrile $\varepsilon_{520} = 6.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} 26$ and $\phi_{ISC} = 1$ were taken. ϕ_{PI} was measured in air-equilibrated acetonitrile in order to quench the StA triplet by oxygen; the values (Table 2) are somewhat larger than those for the abovementioned cases. Moreover, in the absence of oxygen, $\phi_{\rm PI}$ should be somewhat higher, particularly for 2-StA, if photoionization takes place in the relaxed singlet, since the fluorescence is quenched by oxygen. This latter effect is expressed by the $\phi_{\rm F}/\phi_{\rm F}^{\rm air}$ ratio (Table 3).

Formation of Radical Cations in the Presence of Electron Acceptors

DCNB is a well known electron acceptor for excited singlet states of aromatic hydrocarbons and has often been used to study radical cations.^{6.27} For StAs in the presence of oxygen (to separate against T–T absorption) formation of *trans*^{*+} is enhanced by the addition of DCNB. The absorption spectra for StAs (plus 0.02 mol dm⁻³ DCNB) in aerated acetonitrile reveal characteristic structures [Fig. 5(*a*), 6(*a*), 7(*a*)] and maxima in the 310–335, 430–450 and 600–690 nm regions (Table 2). Their decay follows mixed-order kinetics with $t_{1/2}$ in the range 2.5–5 µs and is essentially independent of [StA]. Electron transfer according to eqn. (3)

$${}^{1}trans^{*} + DCNB \rightarrow trans^{*+} + DCNB^{*-}$$
(3)

also generates the radical anion of DCNB which, however, absorbs too weakly to be detected (cf. ref. 6). Since the halflife decreases with increasing [DCNB] the back-electron transfer cannot be neglected, unlike the case of StPhs, thus making a proper determination of $\phi_{\rm PI}$ by the DCNB enhancement method impossible.⁶

In order to measure $\epsilon(trans^{+})$ for the StAs (and hence to obtain ϕ_{PI}), chloranil (CA) was used ($\lambda_{exc} = 308$ nm). CA is a

Table 2 Formation quantum yields (ϕ_{Pl}) and spectral and kinetic properties of the radical cations of StAs^a

| compound | λ _{max} /nm | t _{1/2} ^b /μs | $\phi_{\mathrm{Pl}}{}^{c}$ | $\epsilon(trans^{+})[\lambda/nm]/10^{3} \text{ dm}^{3} \text{ mol}^{-1} \text{ cm}^{-1}$ |
|--------------------|-------------------------|--------------------------------------|----------------------------|--|
| anthracene | 320, 360, 430, 730 | 2.5 | 0.065 ^d | |
| 1-StA | 335, 430, 690 | 2.5 | 0.07 | 16 [690] |
| 2-StA | 310, 430, 600 | 3.6 | 0.07 | 10 16001 |
| 2-StA ^e | 320, 430, 600 | | | |
| 9-StA | 330, 450, 640 | 5.0 | 0.08 | 13 [640] |

^a In aerated acetonitrile. ^b In the presence of 0.02 mol dm⁻³ DCNB. ^c Values measured with laser intensity ca. 1×10^6 W cm⁻². ^d Taken from ref. 24. ^e Using $\lambda_{exc} = 248$ nm.

| | | | k _q | | |
|--------------------|--------------------|-------------------|----------------|---------------------------------------|------------------------------------|
| compound | $	au_{\mathbf{F}}$ | ϕ_{F} | DEA | BrDMA | $\phi_{ m F}/\phi_{ m F}^{ m air}$ |
| anthracene | 4.8 | 0.26 | | · · · · · · · · · · · · · · · · · · · | |
| 1-StA | 6.1 $(5)^{b}$ | $0.75 (0.64)^{b}$ | 1.46 | 1.65 | 1.3 |
| 2-StA ^c | 14/26 (8.9/28) | 0.75 (0.82) | 1.52 | 1.65 | 2.3 |
| 9-StA | 4.2 (3.6) | 0.46 (0.44) | 1.70 | 1.54 | 1.2 |

Table 3 Fluorescence lifetimes ($\tau_{\rm F}/\rm{ns}$) and quantum yields ($\phi_{\rm F}$) of StAs together with rate parameters ($k_{\rm q}/10^{10}$ dm³ mol⁻¹ s⁻¹) for fluorescence quenching by DEA and BrDMA^a

^a In argon-saturated acetonitrile; experimental error is $\pm 5\%$ for ϕ_F and τ_F and $\pm 10\%$ for k_q . ^b Values in parentheses refer to benzene.¹⁴ ^c Biexponential decay.

strong electron acceptor and has been successfully used to produce radical cations of aromatics *via* its triplet state (${}^{3}CA^{*}$, $\phi_{ISC} \approx 1^{28}$). Taking into account that the free energy change for the electron-transfer process in the ${}^{3}CA^{*}/9$ -StA system is -1.3 eV [as obtained from eqn. (2) of ref. 28(*b*) using $E_{1/2}^{\infty} = 0.95$ V as measured by cyclic voltammetry], reaction (4) is thermodynamically allowed.

$$^{3}CA^{*} + trans \rightarrow CA^{*-} + trans^{*+}$$
 (4)



Fig. 5 Transient absorption spectra for 1-StA in acetonitrile under the conditions: (a) air-saturated, in the presence of 0.02 mol dm⁻³ DCNB, at 0.1 (\bigcirc) and 0.5 (\triangle) µs after the pulse and (b) argonsaturated, in the presence of 0.02 mol dm⁻³ DEA, at 0.1 µs (\bigcirc) after the pulse; $\lambda_{exc} = 353$ nm



Fig. 6 Transient absorption spectra for 2-StA in acetonitrile under the conditions: (a) air-saturated, in the presence of 0.02 mol dm⁻³ DCNB, at 0.1 (\bigcirc) and 1 (\triangle) µs after the pulse and (b) argonsaturated, in the presence of 0.02 mol dm⁻³ DEA, at 0.05 (\bigcirc) and 0.5 (\triangle) µs after the pulse; $\lambda_{exc} = 353$ nm

Indeed, on addition of a StA the lifetime of ${}^{3}CA^{*}$ ($\lambda = 490$ nm) is strongly reduced; *e.g.* by a factor of *ca.* 10 in the presence of *ca.* 1×10^{-4} mol dm⁻³ StA, corresponding to *ca.* 0.35 µs. For the StA isomers the $\varepsilon(trans^{\cdot+})$ values were obtained using $\varepsilon_{450}(CA^{\cdot-}) = 9.7 \times 10^{3}$ dm³ mol⁻¹ cm⁻¹,²⁹ and assuming plausibly $[CA^{\cdot-}] = [trans^{\cdot+}]$, after correction for the absorption of *trans*^{\cdot+} at 450 nm. This was possible because *trans*^{\cdot+} is the only absorbing species in the 600–690 nm region and the ratio of $\varepsilon(trans^{\cdot+})$ at the two wavelengths is known.

The spectra obtained in air-saturated acetonitrile [Fig. 1(*b*), 2(*b*), 3(*b*)] are in agreement with $\phi_{\rm T}$ and $\phi_{\rm PI}$ values of 0.09–0.22 and 0.07–0.08, respectively, on one hand and $\epsilon(^3trans^*)$ and $\epsilon(trans^{*+})$ values of *ca*. 2×10^4 dm³ mol⁻¹ cm⁻¹ ^{13.16} and $(1.0-1.6) \times 10^4$ dm³ mol⁻¹ cm⁻¹ on the other, taking into account that a significant fraction of the triplet is quenched by oxygen at 0.1–0.2 µs after the pulse. Internal conversion appears to be significant only for 9-StA, while for 1- and 2-StA the sum $\phi_{\rm F} + \phi_{\rm T} + \phi_{\rm PI}$ accounts for virtually all absorbed photons.

Formation of Radical Cations upon Excitation at 248 nm

The above assignment of $trans^{++}$ is in agreement with results obtained on excitation at 248 nm in argon-saturated ethanolwater (8 : 2, v : v). Under these conditions the StAs are photoionized, thereby forming $trans^{++}$ and the solvated electron (e_s⁻). The assignment to a short-lived transient ($\lambda_{max} \approx 680$ nm), formed within the duration of the laser pulse, to e_s⁻ is supported by the result that the spectrum is changed on saturation with N₂O. The spectral and kinetic characteristics of $trans^{++}$ under these conditions (not shown) are practically the



Fig. 7 Transient absorption spectra for 9-StA in acetonitrile under the conditions: (a) air-saturated, in the presence of 0.02 mol dm⁻³ DCNB, at 0.1 (\bigcirc) and 1 (\triangle) µs after the pulse and (b) argonsaturated, in the presence of 0.02 mol dm⁻³ DEA, at 0.1 µs (\bigcirc) after the pulse; $\lambda_{exc} = 353$ nm

same as described above for excitation at 353 nm in acetonitrile. However, it was not possible to separate the absorption spectra of the solvated electron from those of the other species. The suggested reason is that e_s^- reacts efficiently with a non-excited substrate, thereby forming the radical anion. For 9-StA, besides for the triplet, spectroscopic indication was found for (i) the solvated electron, (ii) the radical cation and (iii) the radical anion. Biphotonic rather than monophotonic photoionization is concluded from the nearly linear dependences of ΔA of the latter two transients on the square of the laser intensity (results not shown).

For comparison we also recorded the transient absorption spectra of the StAs in acetonitrile with $\lambda_{exc} = 248$ nm. The main species is ³*trans*^{*}, and *trans*^{*+} became observable in the presence of air, while *trans*^{*-} and e_s^- did not appear; the absence of the latter two species is expected from the fast reaction (<20 ns) of e_s^- with CH₃CN.

Fluorescence Quenching by Amines

The fluorescence quenching of StAs^{15,16} and several other styrylaromatics^{2,30} by amines is accompanied by exciplex fluorescence in non-polar solvents. The decay processes, yields and kinetics of excited StAs in media of low polarity are well known.^{9,10,12,14} A special case is 2-StA, for which two conformers have been established.^{9,10,14} Here the sum of the quantum yields $\phi_{\rm F}$ and $\phi_{\rm T}$ is virtually unity, whereas for 1- and 9-StA internal conversion is not negligible since $\phi_{\rm F}$ + $\phi_{\rm T}$ account for only 80% of the absorbed photons.^{13,14} Fluorescence and intersystem crossing are also the main decay processes for all the isomers in acetonitrile, although, owing to the electron accepting ability of the medium, photoionization contributes (see Table 2).

Values for τ_F , ϕ_F and the quenching rate constants (k_q) by DEA and BrDMA are compiled in Table 3 for anthracene and its styryl derivatives. The k_q values, calculated from the slopes of Stern–Volmer plots for fluorescence (least-squares treatment), are close to the diffusional limit $(k_{diff} \approx 2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in acetonitrile) throughout. Linear Stern–Volmer plots were obtained for all the isomers even though for 2-StA a biexponential fluorescence decay, due to the presence of two conformers, has been reported.^{9,14} A comparison of the ϕ_F and τ_F values in acetonitrile with those in toluene indicates that the solvent polarity does not cause a relevant change in these parameters, contrasting to other parameters, *e.g.* ϕ_T for 9-StA.¹²

Radical-pair Formation in the Presence of DEA

For electron donors showing no heavy-atom effect, the formation of solvated ion pairs is generally the unique channel for decay of the excited complex in polar solvents.³¹ Recently Mataga and co-workers have proposed a tentative model to describe the dynamics of formation and decay for encounter complexes.³² For the *trans*-stilbene/amine systems in acetonitrile Lewis and co-workers have suggested that both the isomerizable triplet and the alkene radical anion originate from the initial CT complex.³³

For the StA/DEA system in acetonitrile, radical anions of the *trans* form are expected to be produced via electron transfer from the amine:

$$^{1}trans^{*} + \text{DEA} \rightarrow trans^{*-} + \text{DEA}^{*+}$$
(5)

The structured transient absorption spectra shown in Fig. 5(b), 6(b) and 7(b) are ascribed to *trans*⁻⁷. The radical cation of DEA has only a low absorption coefficient and its contribution can be neglected in comparison to the absorption of the radical anions of the StAs. Their half-lives are in the 10 μ s

Table 4 Spectral and kinetic properties of the radical anions of $StAs^{a}$

| compound | λ _{max} /nm | t _{1/2} /μs | k_{ox} /10 ¹⁰ dm ³ mol ⁻¹ s ⁻¹ |
|------------|-------------------------|-------------------------|---|
| anthracene | 700 ^b | > 0.1 | ≥1.6 |
| 1-StA | 320, 550 | ≥10 | 1.3 |
| 2-StA | 310, 435, 610 | ≥10 | > 1 |
| 9-StA | 310, 450, 690 | ≥5 | 2 |

^{*a*} Produced in argon-saturated acetonitrile in the presence of 0.1 mol dm^{-3} DEA. ^{*b*} The region below 380 nm is hidden by ground-state absorption.

range under our conditions. The spectrum of *trans*^{•-} for the 2-StA/dimethylaniline system, $\lambda_{max} = 445 \text{ nm}$,¹⁵ is in agreement with the result for the related system used here [Fig. 6(*b*)].

The decay of the radical anions is strongly influenced by oxygen. The rate constants for quenching, obtained from linear plots of $1/t_{1/2}$ vs. $[O_2]$, are close to the diffusion-controlled limit (Table 4), *i.e.* they are larger than those for triplet quenching (Table 1). Reaction (6), leading to the O_2^{-7} radical anion is suggested as quenching process.

$$trans^{\bullet-} + O_2 \rightarrow trans + O_2^{\bullet-} \tag{6}$$

Ion-pair formation is supported by the DEA-enhanced amplitude of the conductivity signal (besides the increase in ΔA as a measure of the yield of *trans*^{•-}). This amplitude increases with increasing [DEA] [inset (b) of Fig. 4], as one would expect from the high mobility of the two ions, and is in rough agreement with the results for $\phi_{\rm F}$ and $\Delta A(trans^{-})$. An example is shown in Fig. 4 for 1-StA. The decay kinetics of the ion-pair are determined mainly by electron back transfer from trans^{*-} to DEA^{*+}. The decay kinetics of the radical anions are not influenced by variation of StA concentration ([StA] $\leq 2 \times 10^{-4}$ mol dm⁻³). The half-life of the conductivity decay, however, decreases with increasing [StA]. An interaction of DEA⁺⁺ with the trans ground state, thereby forming a more stable charged species may account for this, as already suggested for the StPhs.6 The back-reaction in oxygenated acetonitrile is suggested to involve the longerlived O_2^{*-} radical anion in reaction (6). Thus, in the presence of oxygen, trans^{•-} (with optical detection) decays faster than the back-electron transfer to DEA⁺⁺ (with $\Delta \kappa$ detection) occur.

Conclusion

We emphasize that StAs constitute a class of diarylethylenes, showing (i) no $trans \rightarrow cis$ photoisomerization, either via singlet or triplet states, (ii) that eventually all processes lead back ($\geq 99\%$) to the trans ground state and (iii) enhancement of the $S_1 \rightarrow T_1$ transition by BrDMA, (iv) photoionization and ion-pair formation in acetonitrile: the amount is moderate in the absence of additives and is enhanced in the presence of an electron donor (DEA) or acceptor (DCNB).

The authors are grateful to Professors D. Schulte-Frohlinde and U. Mazzucato for their support and advice, thank Mr L. J. Currell for technical assistance and thank Professor C. Rol for cyclic voltammetric measurements. Financial support by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Rome) is gratefully acknowledged by G.G.A. and F.E.

References

1 U. Mazzucato, G. G. Aloisi and F. Masetti, J. Photochem., 1982, 18, 211.

- 2 G. G. Aloisi, F. Masetti, F. Elisei and U. Mazzucato, J. Phys. Chem., 1988, 92, 3394, and references therein.
- 3 F. Elisei, G. G. Aloisi and F. Masetti, J. Chem. Soc., Faraday Trans. 2, 1989, 85, 789.
- 4 G. G. Aloisi and F. Elisei, J. Phys. Chem., 1990, 94, 5813.
- 5 F. Elisei, G. G. Aloisi and U. Mazzucato, J. Phys. Chem., 1990, 94, 5818.
- 6 G. G. Aloisi, F. Elisei and H. Görner, J. Phys. Chem., 1991, 95, 4225
- 7 (a) H.-D. Becker and K. Andersson, J. Org. Chem., 1983, 48, 4542; (b) H.-D. Becker, K. Andersson and K. Sandros, J. Org. Chem., 1985, 50, 3913.
- 8 K. Sandros and H.-D. Becker, J. Photochem., 1987, 39, 301.
- 9 (a) G. Fischer and E. Fischer, J. Phys. Chem., 1981, 85, 2611; (b)
 T. Wismontski-Knittel, P. K. Das and E. Fischer, J. Phys. Chem., 1984, 88, 1163; (c) K. P. Ghiggino, P. F. Skilton and E. Fischer, J. Am. Chem. Soc., 1986, 108, 1146; (d) V. Krongauz, N. Castell and E. Fischer, J. Photochem., 1987, 39, 285.
- (a) U. Mazzucato, Gazz. Chim. Ital., 1989, 117, 661; (b) G. Bartocci, F. Masetti, U. Mazzucato, I. Baraldi and E. Fischer, J. Mol. Struct., 1989, 193, 173.
- 11 (a) T. Karatsu, T. Arai, H. Sakuragi and K. Tokumaru, Chem. Phys. Lett., 1985, 115, 9; (b) H. Hamaguchi, M. Tasumi, T. Karatsu, T. Arai and K. Tokumaru, J. Am. Chem. Soc., 1986, 108, 1698; (c) T. Arai, T. Karatsu, H. Misawa, Y. Kuriyama, H. Okamoto, T. Hiresaki, H. Furuuchi, H. Zeng, H. Sakuragi and K. Tokumaru, Pure Appl. Chem., 1988, 60, 989.
- 12 H. Görner, J. Photochem. Photobiol., A: Chem., 1987, 43, 263.
- 13 G. Galiazzo, A. Spalletti, F. Elisei and G. Gennari, Gazz. Chim. Ital., 1989, 119, 277.
- 14 G. Bartocci, F. Masetti, U. Mazzucato, A. Spalletti, G. Orlandi and G. Poggi, J. Chem. Soc., Faraday Trans. 2, 1988, 84, 385.
- 15 T. Wismontski-Knittel and P. K. Das, J. Phys. Chem., 1984, 88, 1168.
- 16 K. Bhattacharyya, S. K. Chattopadhyay, S. Baral-Tosh and P. K. Das, J. Phys. Chem., 1986, 90, 2646.
- 17 G. Bartocci, F. Masetti, U. Mazzucato, A. Spalletti, I. Baraldi and F. Momicchioli, J. Phys. Chem., 1987, 91, 4733.
- 18 (a) G. Bartocci, F. Masetti, U. Mazzucato and G. Marconi, J. Chem. Soc., Faraday Trans. 2, 1984, 80, 1093; (b) F. Barigelletti, S. Dellonte, G. Orlandi, G. Bartocci, F. Masetti and U. Mazzucato, J. Chem. Soc., Faraday Trans. 1, 1984, 80, 1123.
- 19 (a) F. Elisei, U. Mazzucato and H. Görner, J. Chem. Soc., Faraday Trans. 1, 1989, 85, 1469; (b) F. Elisei, U. Mazzucato, H.

Görner and D. Schulte-Frohlinde, J. Photochem. Photobiol., A: Chem., 1989, 50, 209.

- 20 F. Elisei, G. Favaro and H. Görner, J. Photochem. Photobiol., A: Chem., 1991, 59, 243.
- 21 T. Medinger and F. Wilkinson, Trans. Faraday Soc., 1965, 61, 620.
- 22 S. Nakamura, N. Kanamaru, S. Nohara, H. Nakamura, Y. Saito, J. Tanaka, M. Sumitani, N. Nakashima and K. Yoshihara, Bull. Chem. Soc. Jpn., 1984, 57, 145.
- 23 (a) M. Ottolenghi, Chem. Phys. Lett., 1971, 12, 339; (b) Y. Hirata and N. Mataga, J. Phys. Chem., 1983, 87, 1680; (c) T. Saito, K. Haida, M. Sano, Y. Hirata and N. Mataga, J. Phys. Chem., 1986, 90, 4017 and references therein.
- 24 E. Vauthey, E. Haselbach and P. Suppan, Helv. Chim. Acta, 1987, 70, 347.
- 25 E. Vauthey, P. Suppan, E. Haselbach and R. S. Davidson, Helv. Chim. Acta, 1986, 69, 430.
- 26 I. Carmichael and G. L. Hug, J. Phys. Chem. Ref. Data, 1986, 15, 1.
- 27 K. H. Grellmann, A. R. Watkinson and A. Weller, J. Phys. Chem., 1972, 76, 469.
- 28 (a) M. O. Delcourt and M. J. Rossi, J. Phys. Chem., 1982, 86, 3233; (b) R. Gschwind and E. Haselbach, Helv. Chim. Acta, 1979, 62, 941 and references therein.
- 29 J. J. Andrè and G. Weill, Mol. Phys., 1968, 15, 97.
- 30 G. G. Aloisi, G. Bartocci, G. Favaro and U. Mazzucato, J. Phys. Chem., 1980, 84, 2020.
- 31 (a) N. Mataga and T. Kubota, in Molecular Interactions and Electronic Spectra, Marcel Dekker, New York, 1970; (b) H. Beens and A. Weller, in Organic Molecular Photophysics, ed. J. B. Birks, John Wiley, London, 1975, vol. 2, p. 159; (c) N. Mataga and M. Ottolenghi, in Molecular Association, ed. R. Foster, Academic Press, London, 1979, vol. 2, p. 1; (d) N. Mataga, Pure Appl. Chem., 1984, 56, 1255, and references therein.
- 32 (a) Y. Hiata, Y. Kanda and N. Mataga, J. Phys. Chem., 1983, 87, 1659; (b) Y. Hiata, T. Saito and N. Mataga, J. Phys. Chem., 1987, 91, 3119.
- 33 (a) W. Hub, S. Schneider, F. Dörr, J. D. Oxman and F. D. Lewis, J. Am. Chem. Soc., 1984, 106, 701; (b) 1984, 106, 708; (c) F. D. Lewis, Adv. Photochem., 1986, 13, 165.

Paper 1/04845G; Received 19th September, 1991

Published on 01 January 1992. Downloaded by Brown University on 29/10/2014 23:27:50

34