# Excited-State Properties of *trans*-1-(9-Anthryl)-2-(4-R-phenyl)ethylenes with Electron-Donating and -Accepting Substituents ( $R = N(CH_3)_2$ , OCH<sub>3</sub>, CH<sub>3</sub>, Br, CN, and NO<sub>2</sub>)

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The decay pathways of the lowest excited singlet state (1t\*) of trans-1-(9-anthryl)-2-(4-R-phenyl)ethylenes  $(trans-R-StAs, where R = N(CH_3)_2, OCH_3, CH_3, Br, CN, and NO_2 on the 4-position of the styryl) were studied$ in solution at room and low temperatures. Fluorescence lifetime  $(\tau_f)$  and quantum yield  $(\Phi_f)$  as well as the yield  $(\Phi_T)$  and spectral and kinetic properties of the lowest triplet state were determined by steady-state and transient techniques. The solvent polarity has a large effect on the Stokes shift for (H<sub>3</sub>C)<sub>2</sub>N- and O<sub>2</sub>N-StA, the two derivatives with the strongest electron-donating and -accepting substituents. The smallest changes in  $\Phi_f$  and  $\Phi_T$ , in comparison with the case of parent 9-StA, are caused by the Br or CH<sub>3</sub> groups. For O<sub>2</sub>N- and  $(H_1C)_2N$ -StA, and to a lesser degree for NC- and H<sub>3</sub>CO-StA,  $\Phi_f$  and  $\tau_f$  become significantly smaller with increasing solvent polarity. Efficient deactivation by charge transfer via an excited singlet state with essentially trans configuration (A<sup>\*</sup>) is proposed for these derivatives. The  ${}^{1}t^{*} \rightarrow A^{*}$  relaxation pathway in polar solvents is activated and competes with fluorescence and intersystem crossing. For NC-, H<sub>3</sub>CO-, and (H<sub>3</sub>C)<sub>2</sub>N-StA at room temperature trans  $\rightarrow$  cis photoisomerization occurs with substantial quantum yield ( $\Phi_{t\rightarrow c}$ ) in those solvents in which the presence of the postulated A\*-state efficiency reduces fluorescence and intersystem crossing. A contribution of a triplet mechanism to trans  $\rightarrow$  cis photoisomerization can be excluded throughout. A special case is O<sub>2</sub>N-StA, which exhibits virtually no photochemistry in both nonpolar and polar solvents, but  $\Phi_{t-c}$  is up to 0.2 in slightly polar solvents, e.g., toluene.

#### Introduction

The properties of excited states of unsubstituted *trans-n*styrylanthracenes (*trans-n*-StAs, n = 1, 2, and 9) have been extensively studied by several groups.<sup>1-24</sup> The three StAs are characterized by efficient fluorescence and triplet formation at ambient and low temperatures; their spectral and kinetic properties and the influence of solvent polarity on the photophysical parameters have been investigated.<sup>1,9,13,19-21</sup> Most of the investigations are related to *trans*-2-StA,<sup>1-14</sup> where rotational conformers (rotamers) could be identified by fluorescence spectra and decay kinetics at low temperatures.<sup>1,2,8-13</sup> No nonequivalent rotamers are possible for *trans*-9-StA.<sup>13</sup>

Another interesting effect with trans-n-StAs is electron transfer from additives, such as amines.<sup>3,14,22</sup> In the presence of amines, the formation of exciplexes in nonpolar solvents has been reported.<sup>2</sup> Corresponding studies have been performed with trans-nstyrylphenanthrenes (trans-n-StPhs, n = 1, 2, 3, 4, and 9).<sup>25</sup> The three StAs, in contrast to the five StPhs, exhibit virtually no trans  $\rightarrow$  cis photoisomerization.<sup>5,9</sup> Bartocci et al. have discussed several possible reasons for this.<sup>10</sup> On the other hand, Sandros and Becker have shown that introduction of certain substituents into 9-StA to give 1-(9-anthryl)-2-(4-R-phenyl)ethylenes (henceforth abbreviated as R-StAs), where R is formyl or phenylsulphonyl, opens the pathway of trans  $\rightarrow$  cis photoisomerization in acetonitrile.<sup>18</sup> For the latter two 9-StA derivatives, a triplet route has been excluded on the basis of the quantum yields of trans  $\rightarrow$ cis photoisomerization ( $\Phi_{t\rightarrow c}$ ) and triplet formation ( $\Phi_{T}$ , as a measure for that of intersystem crossing,  $\Phi_{isc}$ ) in various solvents.<sup>23</sup>

The present paper aims to further reveal the relaxation processes of the excited singlet state (<sup>1</sup>t\*) of *trans*-9-StA. It deals with the photophysical and photochemical behavior of several *trans*-R-StAs, where  $R = N(CH_3)_2$ , OCH<sub>3</sub>, CH<sub>3</sub>, Br, CN, and NO<sub>2</sub> and which were synthesized for this purpose.  $\Phi_f$ ,  $\Phi_{t\to c}$ , and  $\Phi_{c\to t}$  values have recently been reported for five of these derivatives in cyclohexane and acetonitrile at room temperature.<sup>19-21</sup> Here, the features of the 't\* decay processes and the characteristics of the related triplet state were studied with respect to solvent polarity and temperature, and the influence of substituents and solvent polarity on  $\Phi_{t\rightarrow c}$  was examined. Interestingly, both electrondonating and -accepting groups affect the excited-state properties of *trans*-9-StA such that the otherwise closed pathway of *trans*  $\rightarrow cis$  photoisomerization is opened. The  $\Phi_{t\rightarrow c}$  values depend on R and on environmental conditions in a complex fashion.



#### **Experimental Section**

Materials. Diethyl(9-anthrylmethyl)phosphonate  $(I)^{26}$  was prepared as the basis compound for synthesis of the *trans*-R-StA isomers. 9-(Chloromethyl)anthracene (2 g, 8.8 mmol) was dissolved in 5 mL of toluene, containing triethyl phosphite (6 g, 35 mmol). The mixture was refluxed at 140 °C for 2 h and cooled to room temperature after removing excess solvent by distillation. *n*-Pentane was added to the reaction mixture, precipitating a yellow solid. After recrystallization from *n*-hexane, yellow-green crystals of I were obtained (yield 78%, mp 103.5– 104.0 °C).

The trans-R-StAs were prepared from I and the corresponding 4-R-benzaldehydes.<sup>27</sup> For example, I (0.5 g, 1.5 mmol) and 4-cyanobenzaldehyde (0.21 g, 1.5 mmol) were dissolved in 2 mL of dimethylformamide (DMF). This solution was added, under vigorous stirring at 60 °C, dropwise to a DMF suspension (1.8 mL), containing potassium tert-butylate (0.34 g, 3.0 mmol). After continued stirring at room temperature for 3 h, the mixture was neutralized with acetic acid and diluted with methanol/water (1:1 v/v). The yellow solid was filtered, washed with water, and

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| TADLE I. ENCLUT Solvent on the Photoscence Maximum of K-St | TABLE | I: | Effect | of Solvent | on the | Fluorescence | Maximum | of ] | R–StA |
|--|-------|----|--------|------------|--------|--------------|---------|------|-------|
|--|-------|----|--------|------------|--------|--------------|---------|------|-------|

|                          |                            | $\lambda_{f}$ , for given R, nm  |           |             |           |           |                 |  |
|--------------------------|----------------------------|----------------------------------|-----------|-------------|-----------|-----------|-----------------|--|
| solvent                  | $E_{\rm T}(30)$ , kcal/mol | N(CH <sub>3</sub> ) <sub>2</sub> | OCH3      | H           | Br        | CN        | NO <sub>2</sub> |  |
| MCH                      | ≈31.2                      | 515                              | 485       | 468         | 482       | 490       | 508             |  |
| cyclohexane <sup>c</sup> | 31.2                       | 514                              | 490       | 469         |           | 488       | 505             |  |
| ČCl₄                     | 32.5                       |                                  |           |             |           |           | 525             |  |
| toluene                  | 33.9                       | 535                              | 492       | 478         | 483       | 500       | 550             |  |
| benzene                  | 34.5                       |                                  |           |             |           |           | 560             |  |
| MTHF                     | 36.5                       | 560                              | 492       | 474         | 482       | 502       | 582             |  |
| chloroform               | 39.1                       |                                  | 494       |             |           | 505       | 635             |  |
| acetone                  | 42.2                       | 590                              | 494       |             |           | 510       | 670             |  |
| DMF                      | 43.8                       | 608                              | 496       | <b>48</b> 1 |           | 520       | >700            |  |
| acetonitrile             | 46.0                       | 608                              | 494       | 476         | 482       | 512       | >700            |  |
| acetonitrilec            |                            | 608                              | 490       | 469         |           | 509       |                 |  |
| ethanol                  | 51.9                       | 570                              | 485       | 474         | 482       | 510       | >700            |  |
| MCH                      |                            | (474,501)                        | (445,467) | (438,460)   | (440,463) | (460)     | (520)           |  |
| MTHF                     |                            | (505)                            | (447,475) | (439,462)   | (442,465) | (452,480) | (528)           |  |
| ethanol                  |                            | (445,467)                        | (446,468) | (434,460)   | (440,463) | (455,476) | (533)           |  |

<sup>a</sup> In solution at 24 °C,  $\lambda_{exc}$  = 390 nm. Values in parentheses refer to -196 °C. <sup>b</sup> Values taken from ref 23. <sup>c</sup> Values taken from ref 20.

dried. After recrystallization  $(3\times)$  from ethanol, yellow needlelike crystals of *trans*-NC-StA were obtained.

The samples were recrystallized two to four times from ethanol except for  $H_3C$ -StA (acetic acid) and  $(H_3C)_2N$ -StA (*n*-butanol). The structures of the trans-R-StAs were identified by melting point, IR (KBr), and MS (EI), the data being given in this order: O<sub>2</sub>N-, NC-, Br-, H<sub>3</sub>C-, H<sub>3</sub>CO-, and (H<sub>3</sub>C)<sub>2</sub>N-StA: 231-232 °C, 985.2 and 1341.5 cm<sup>-1</sup>, 325 (calculated 325); 176.5–177 °C, 977.0 and 2221.7 cm<sup>-1</sup>, 305 (305); 166-166.5 °C, 971.6 and 496.5 cm<sup>-1</sup>, 358 and 360 (359); 165-166 °C, 971.9 cm<sup>-1</sup>, 294 (294); 203-204 °C, 967.6 and 1252.7 cm<sup>-1</sup>, 310 (310); 181.5-182.5 °C, 965.7 and 1352.7 cm<sup>-1</sup>, 323 (323). (Unless otherwise indicated StAs refers henceforth to trans isomers.) Solvents (Merck unless otherwise indicated) were distilled (acetone, ethanol, methylcyclohexane (MCH), 2-methyltetrahydrofuran (MTHF), toluene) or used as received (acetonitrile, Uvasol quality; cyclohexane; benzene; DMF, Aldrich, gold label; chloroform, Fluka).

Apparatus and Procedure. The absorption spectra were recorded on a spectrophotometer (Perkin-Elmer, Model 554); for the fluorescence spectra either a Spex Fluorolog or a Perkin-Elmer LS-5 fluorimeter was used. The fluorescence quantum yield and lifetime were measured as described previously;<sup>23,28-31</sup> the experimental error for  $\Phi_f$  and  $\tau_f$  measurements at room temperature (unless the values are below 0.01 and 0.2 ns, respectively) is typically  $\pm 20$  and  $\pm 15\%$ , respectively. For  $\Phi_f$ measurements (in aerated solutions) the absorbances at  $\lambda_{exc} =$ 390 nm were kept at a value of 0.25, corresponding to concentrations of (2-3)  $\times 10^{-5}$  M; the quenching effect on  $\Phi_f$  by oxygen was determined separately and the values in Table II were correspondingly corrected; no correction for the refractive index in different solvents was performed. 9-StA in acetonitrile ( $\Phi_f =$ 0.45)<sup>14,23</sup> was used as reference for  $\Phi_f$  measurements.

For continuous irradiation, either a 200-W Hg lamp combined with filters (water, 390-nm cutoff plus 405-nm interference) or a 1000-W Xe–Hg lamp combined with a monochromator<sup>23</sup> was used for  $\lambda_{irr} = 405$  nm or other wavelengths, respectively. OHC– StA in acetonitrile at  $24 \pm 2$  °C with  $\Phi_{t\rightarrow c} = 0.38^{18,23}$  was used as reference; the error in  $\Phi_{t\rightarrow c}$  (unless the values are <0.01) is  $\pm 20\%$ . The concentrations of the *trans* isomers were typically (0.8–1.2) × 10<sup>-4</sup> M. The samples (2 or 3 mL) were deoxygenated by vigorous bubbling with argon during the whole procedure. The amounts of formation of *cis*-R–StAs and photobleaching (absorbance loss) were typically determined from the absorption spectra for different irradiation times and checked by GC analysis (column, PS-428; length, 40 m; temperature range, 100–280 °C; gradient, 8 °C/min) for an appropriate conversion.

Excitation wavelengths of 248 and 353 nm from an excimer laser (Lambda Physik, EMG 201MSC) and an Nd laser (J. K., third harmonic), respectively, were used in nanosecond flash photolysis experiments (pulse width  $\leq 20$  ns, energy  $\leq 100$  mJ/pulse),<sup>14,28-30</sup> unless specified  $\lambda_{exc} = 353$  nm. For  $\Phi_{T}$  measurements the absorbances of the *trans* isomers were adjusted to a value of  $A_{353} = 0.50$ ; the parent 9-StA in toluene and acetonitrile was used as reference ( $\Phi_{T} = 0.25$  and 0.22, respectively).<sup>14,23</sup> The yields were obtained from the relative  $\Delta A$  values at the maximum ( $\lambda_{T}$ ) in the visible and by extrapolation to t = 0. The assumption was made that  $\epsilon(\lambda_{T})$  is the same in all cases. This is supported by the result from xanthone-sensitized triplet formation and the known values of  $\epsilon(\lambda_{T}) = (2.0-2.3) \times 10^4 \, \text{M}^{-1} \, \text{cm}^{-1}$  for OHC–StA and the three StA.<sup>12,20,21</sup> The relative error in  $\Phi_{T}$  is  $\pm 20\%$ . Details concerning sensitized measurements are given in previous publications.<sup>23,30</sup> Unless indicated otherwise, the *trans* isomers were deoxygenated (by purging with argon) and measured at  $24 \pm 2 \, ^{\circ}$ C.

### **Results and Discussion**

Excited Singlet State of trans-R-StAs at Room Temperature. The fluorescence properties, such as the emission maximum ( $\lambda_f$ ),  $\Phi_f$ , and  $\tau_f$ , of the parent *trans*-9-StA at ambient temperature reveal virtually no dependence on the nature of solvent.<sup>10,18,23</sup> One exception is *m*-dibromobenzene, in which a smaller  $\Phi_f$  and a shorter  $\tau_f$  value result from a larger  $\Phi_{isc}$  due to the external heavy-atom effect.<sup>23,32</sup> When substituents were introduced (R = CHO and SO<sub>2</sub>-C<sub>6</sub>H<sub>5</sub><sup>23</sup> or N(CH<sub>3</sub>)<sub>2</sub>, OCH<sub>3</sub>, CH<sub>3</sub>, Br, CN, and NO<sub>2</sub>), the following results were obtained from fluorescence measurements.

First, for  $(H_3C)_2N$ -StA (and even more pronounced for  $O_2N$ -StA)  $\lambda_f$  shows a red-shift on increasing the polarity of the solvent. As a measure of the solvent polarity, Dimroth's empirical  $E_T(30)$  parameter is taken (Table I). Examples for the fluorescence spectra of  $(H_3C)_2N$ -, NC-, and  $O_2N$ -StA are shown in Figure 1. The fluorescence excitation spectra are very similar (or identical) to the absorption spectra throughout, i.e., fluorescence originating from a different source (e.g., trace impurities) was not observable. A similar steady increase of  $\lambda_f$  vs  $E_T(30)$  has previously been reported for OCH-StA.<sup>23</sup> The Stokes shift ( $\tilde{\nu}_a - \tilde{\nu}_f$ ) is almost linear as a function of  $E_T(30)$ , the slopes increasing in the order OHC-,  $(H_3C)_2N$ -, and  $O_2N$ -StA (Figure 2).

Secondly, in a nonpolar solvent such as MCH,  $\Phi_f = 0.4-0.5$ for most cases, i.e., for R = OCH<sub>3</sub>, CH<sub>3</sub>, H, Br, CHO, and CN.  $\Phi_f$  is moderately reduced for O<sub>2</sub>N–StA and still further reduced for (H<sub>3</sub>C)<sub>2</sub>N–StA (Table II). For R = SO<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>, CHO,<sup>18,23</sup> CN, OCH<sub>3</sub>, and N(CH<sub>3</sub>)<sub>2</sub>,  $\Phi_f$  decreases significantly on increasing the polarity parameter E<sub>T</sub>(30). A typical effect is a tenfold change between nonpolar (cyclohexane, MCH) and strongly polar solvents (DMF, acetonitrile, ethanol), and this effect is even larger for O<sub>2</sub>N–StA.

Thirdly, the fluorescence decay, measured typically around 500 nm, is monoexponential in most cases. The  $\tau_f$  values compiled



Figure 1. Fluorescence emission and excitation spectra for (a)  $(H_3C)_2N$ -StA in MCH and acetontrile at 24 °C and in ethanol at -196 °C (solid, dashed, and dot-dashed lines, respectively;  $\lambda_{exc} = 390 \text{ nm}$ ,  $\lambda_f = 500 \text{ nm}$ ), (b) NC-StA in ethanol at 24 and -196 °C (solid and dot-dashed lines, respectively), and (c) O<sub>2</sub>N-StA in MCH, toluene, and acetone at 24 °C (solid, dot-dashed, and dashed lines, respectively).



Figure 2. Stokes shift  $(\bar{\nu}_a - \bar{\nu}_f)$  as a function of the solvent polarity parameter  $E_T(30)$  for  $(H_3C)_2N$ -, OHC-, and  $O_2N$ -StA  $(\Box, \Delta, \text{ and } O, \text{ respectively; arrows indicate values larger than <math>1 \times 10^4 \text{ cm}^{-1}$ ).

in Table III reflect generally the changes in  $\Phi_f$ , for example,  $\tau_f$  is about 3 ns for those cases where  $\Phi_f$  is 0.4–0.5.

Effects of Temperature. The fluorescence excitation and emission spectra in glassy media (Figure 1) are similar in shape to those at room temperature, but  $\lambda_f$  at -196 °C is blue-shifted (Table I). This is most pronounced in those cases where  $\lambda_f$  at room temperature is red-shifted in polar solvents, compared to nonpolar solvents. For example, for O<sub>2</sub>N-StA in MTHF and ethanol the shift in  $\lambda_f$  between 24 and -196 °C is  $1.7 \times 10^3$  and > $3.2 \times 10^3$  cm<sup>-1</sup>, respectively. The respective Stokes shift at room temperature is even stronger,  $7.8 \times 10^3$  and > $9.4 \times 10^3$ cm<sup>-1</sup>. For comparison, the Stokes shift of the parent 9-StA is 4.0  $\times 10^3$  cm<sup>-1</sup> both in cyclohexane and acetonitrile.<sup>18</sup>

 $\Phi_f$  shows little dependence on temperature for the parent 9-StA in solvents of widely varying polarity.<sup>18,23</sup> Similarly, only small changes in  $\Phi_f$  between 24 and -196 °C were found for H<sub>3</sub>CO-, Br-, NC-, and O<sub>2</sub>N-StA in MCH. For all derivatives examined (including (H<sub>3</sub>C)<sub>2</sub>N-StA but with the exception of Br-StA) in moderately (MTHF) and strongly polar solvents (ethanol), however,  $\Phi_f$  at -196 °C is significantly larger than that at 24 °C

TABLE II: Effect of Solvent on the Quantum Yield of Fluorescence for R-StAs<sup>4</sup>

|                           | $\Phi_{\rm f}$ for given R       |       |       |                |        |        |                 |  |  |  |
|---------------------------|----------------------------------|-------|-------|----------------|--------|--------|-----------------|--|--|--|
| solvent                   | N(CH <sub>3</sub> ) <sub>2</sub> | OCH3  | CH3   | H <sup>b</sup> | Br     | CN     | NO <sub>2</sub> |  |  |  |
| мсн                       | 0.08                             | 0.46  | 0.44  | 0.46           | 0.35   | 0.48   | 0.28            |  |  |  |
| cyclohexane <sup>c</sup>  | 0.28                             | 0.49  | 0.46  |                |        | 0.48   | 0.27            |  |  |  |
| toluene                   | 0.022                            | 0.38  | 0.36  | 0.45           | 0.28   | 0.25   | 0.19            |  |  |  |
| MTHF                      | 0.012                            | 0.22  |       | 0.42           | 0.22   | 0.12   | 0.17            |  |  |  |
| chloroform                |                                  | 0.15  | 0.38  |                |        | 0.10   | 0.038           |  |  |  |
| DMF                       | 0.01                             | 0.04  | 0.26  | 0.40           |        | 0.05   | < 0.003         |  |  |  |
| acetonitrile              | 0.009                            | 0.028 | 0.20  | 0.45           | 0.16   | 0.03   | < 0.002         |  |  |  |
| acetonitrile <sup>c</sup> | 0.008                            | 0.004 | 0.38  |                |        | 0.024  |                 |  |  |  |
| ethanol                   | 0.011                            | 0.07  | 0.28  | 0.44           | 0.22   | 0.040  | 0.002           |  |  |  |
| мсн                       | (0.5)                            | (0.5) | (0.4) | (0.48)         | (0.3)  | (0.55) | (0.32)          |  |  |  |
| MTHF                      | (0.4)                            | (0.5) | • •   | (0.50)         | (0.3)  | (0.5)  | (0.3)           |  |  |  |
| ethanol                   | (0.35)                           | (0.5) | (0.5) | (0.56)         | (0.35) | (0.55) | (0.4)           |  |  |  |
|                           |                                  |       |       |                |        |        |                 |  |  |  |

<sup>a</sup> Measured in aerated solution at 24 °C and corrected for quenching by oxygen,  $\lambda_{exc} = 390$  nm. Values in parentheses refer to -196 °C. <sup>b</sup> Values taken from ref 23. <sup>c</sup> Values taken from refs 19 and 20.

 TABLE III:
 Effect of Solvent on the Fluorescence Lifetime of R-StAs<sup>a</sup>

|              | $	au_{\rm f}$ , for given R, ns  |       |                 |       |       |       |                 |  |  |  |
|--------------|----------------------------------|-------|-----------------|-------|-------|-------|-----------------|--|--|--|
| solvent      | N(CH <sub>3</sub> ) <sub>2</sub> | OCH3  | CH <sub>3</sub> | H۵    | Br    | CN    | NO <sub>2</sub> |  |  |  |
| МСН          | ≤0.7                             | 3.0   | 3.0             | 3.6   | 1.7   | 3.1   | 1.7             |  |  |  |
| toluene      | ≤0.5                             | 2.5   | 2.6             | 3.5   | 1.7   | 2.1   | 2.2             |  |  |  |
| acetonitrile | <0.5                             | ≤0.5  | 2.7             | 4.2   | 1.9   | <0.4  |                 |  |  |  |
| ethanol      |                                  | <0.5  | 2.8             |       | 1.7   | ≤0.4  |                 |  |  |  |
| MCH          | (2.6)                            | (2.6) | (2.7)           | (2.8) |       | (2.6) | (2.9)           |  |  |  |
| ethanol      | (2.5)                            | (2.5) | (2.8)           | . ,   | (1.3) | (2.7) | (3.1)           |  |  |  |

<sup>a</sup> Measured in aerated solution at 24 °C and noncorrected for quenching by oxygen  $\lambda_{exc} = 353$  nm. Values in parentheses refer to -196 °C. <sup>b</sup> Values in deoxygenated solution taken from ref 23.



Figure 3. Semilogarithmic plots of  $\Phi_f$  vs  $T^{-1}$  for  $(H_3C)_2N-(\blacksquare)$ ,  $Br-(\blacklozenge)$ ,  $NC-(\blacktriangle)$ , and  $O_2N$ -StA ( $\bullet$ ) in ethanol and  $(H_3C)_2N$ -StA in MCH ( $\Box$ ).

(Table II). This is correlated to a similar increase in  $\tau_{\rm fr}$  e.g., when  $\tau_{\rm f}$  is smaller than 0.5 ns at 24 °C, it becomes around 3 ns in the frozen glass (Table III).

Plots of log  $\Phi_f$  vs  $T^{-1}$  are shown in Figure 3 for several R-StAs. Generally,  $\Phi_f$  increases steadily with  $T^{-1}$ , the increase being small for Br-StA in MCH, MTHF, and ethanol but significant for the other R-StAs in polar media. The maximum change in the relevant cases occurs in the temperature range above ca. -120 °C. From plots of ln  $\{\Phi_f^{-1} - (\Phi_f^{\max})^{-1}\}$  vs  $T^{-1}$ , i.e., essentially from the linear sections of the Arrhenius plots in Figure 3, activation energies of  $E_f = 1.3$ , 1.1, and 2.4 kcal/mol were obtained for  $(H_3C)_2N-$ , NC-, and O<sub>2</sub>N-StA in ethanol, respectively. For



Figure 4. Transient absorption spectra of  $Br-(\diamondsuit)$ ,  $NC-(\bigtriangleup)$ , and  $O_2N-StA(\textcircled{O})$  in argon-saturated cyclohexane (in the absence of additives) upon direct excitation at 0.5  $\mu$ s after the pulse (353 nm).

 TABLE IV:
 Effect of Solvent on the Maxima and Lifetimes

 of the Triplet State for R-StAs<sup>a</sup>

| R                                | solvent              | sensitizer                           | λ <sub>T</sub> , nm | $	au_{\mathrm{T}}, \mu \mathrm{s}$ |
|----------------------------------|----------------------|--------------------------------------|---------------------|------------------------------------|
| N(CH <sub>3</sub> ) <sub>2</sub> | cyclohexane          |                                      | 540                 | 50                                 |
|                                  | MCH                  |                                      | (580)               | (600) <sup>b</sup>                 |
|                                  | acetonitrile         |                                      | ≈550                | 45                                 |
|                                  | acetonitrile         | xanthone                             | 570                 | >10                                |
|                                  | acetonitrile         | acetophenone                         | 570                 | >10                                |
|                                  | acetonitrile         | 9,10-Br <sub>2</sub> -A <sup>d</sup> | 580                 | >10                                |
|                                  | ethanol <sup>b</sup> |                                      | (620)               | (700)                              |
| OCH <sub>3</sub>                 | cyclohexane          |                                      | 330,480             | 30                                 |
| CH3                              | MCH                  |                                      | 325,465             | 40                                 |
| H                                | cyclohexane          |                                      | 325,445             | 40                                 |
| Br                               | cyclohexane          |                                      | 330,475             | 12                                 |
|                                  | MCH                  |                                      | (490)               | (100)                              |
|                                  | toluene (100 °C)     |                                      | 480                 | 11                                 |
|                                  | toluene              |                                      | 335,480             | 15                                 |
|                                  | acetonitrile         |                                      | 325,470             | 13                                 |
|                                  | acetonitrile         | xanthone                             | 470                 | ≈10                                |
|                                  | ethanol              |                                      | 335,470             | 14                                 |
|                                  | ethanol              |                                      | (500)               | (200)                              |
| CN                               | MCH (100 °C)         |                                      |                     | 30                                 |
|                                  | cyclohexane          |                                      | 335,485             | 35                                 |
|                                  | МСН                  |                                      | (520)               | (800)                              |
|                                  | toluene (100 °C)     |                                      | 490                 | 30                                 |
|                                  | toluene              |                                      | 340,490             | 40                                 |
|                                  | MTHF                 |                                      | (530)               | (800)                              |
|                                  | acetonitrile         |                                      | 330,480             | 35                                 |
|                                  | acetonitrile         | xanthone                             | 485                 | >10                                |
|                                  | ethanol              |                                      | (520)               | (800)                              |
| NO <sub>2</sub>                  | cyclohexane          |                                      | 350,530             | 35                                 |
| -                                | ŃСН                  |                                      | (590)               | (500)                              |
|                                  | MTHF                 |                                      | (620)               | (500)                              |
|                                  | acetonitrile         |                                      | 350,560             | 35                                 |
|                                  | acetonitrile         | xanthone                             | 570                 | >10                                |
|                                  | ethanol              |                                      | ≤400,560            | 40                                 |
|                                  | ethanol              |                                      | (580)               | (500)                              |
|                                  |                      |                                      |                     | • •                                |

<sup>*a*</sup> In argon-saturated solution,  $\lambda_{exc} = 353$  nm, and 24 °C unless indicated otherwise. <sup>*b*</sup> Values in parentheses refer to -196 °C. <sup>*c*</sup>  $\lambda_{exc} = 248$  nm. <sup>*d*</sup> 9,10-Dibromoanthracene. <sup>*e*</sup> Values for  $\lambda_T$  were taken from ref 23.

 $(H_3C)_2N$ -StA in MCH,  $E_f$  is approximately 1 kcal/mol, i.e., the barrier for the activated process competing with fluorescence is significantly smaller in a nonpolar than a polar solvent. For Br-,  $H_3CO$ -, and NC-StA in MCH and toluene, it was found that increasing the temperature to 100 °C reduces  $\Phi_f$  only slightly ( $\leq 30\%$ ). It follows that in solvents of low polarity no accessible activated process competes with fluorescence.

Triplet State of trans-R-StAs at Room Temperature. From laser flash photolysis studies it is known that the dominant transient of trans-9-StA in fluid or glassy media is the triplet state with essentially trans character  $({}^{3}t^{*}).{}^{12,14,22,23}$  This triplet and that of the derivatives shows generally two bands, one around 330 nm (R = OCH<sub>3</sub>, CH<sub>3</sub>, H, Br, CN) and a second with  $\lambda_T$ between 445 and 500 nm; the second maximum is red-shifted for (H<sub>3</sub>C)<sub>2</sub>N- and O<sub>2</sub>N-StA (Figure 4 and Table IV). The triplet appears within the pulse duration (or after the strong fluorescence signal); the decay follows first-order kinetics at low laser pulse

TABLE V: Effect of Solvent on the Quantum Yield of Intersystem Crossing for R-StAs<sup>4</sup>

|   | $\Phi_{\rm T}$ for given R       |                              |                              |                              |                              |                              |                              |  |  |  |
|---|----------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|--|--|--|
| solvent   | N(CH <sub>3</sub> ) <sub>2</sub> | OCH3                         | CH3                          | Hø                           | Br                           | CN                           | NO <sub>2</sub>              |  |  |  |
| cyclohexane<br>toluene<br>acetonitrile<br>ethanol | 0.06<br>0.02<br>0.005<br>0.01    | 0.20<br>0.15<br>0.02<br>0.01 | 0.30<br>0.25<br>0.18<br>0.16 | 0.32<br>0.25<br>0.22<br>0.15 | 0.45<br>0.40<br>0.38<br>0.36 | 0.30<br>0.20<br>0.02<br>0.03 | 0.38<br>0.22<br>0.02<br>0.04 |  |  |  |

<sup>a</sup> In argon-saturated solution at 24 °C,  $\lambda_{exc} = 353$  nm. <sup>b</sup>  $\Phi_T$  taken from ref 23.



Figure 5. Transient absorption spectra for (a)  $(H_3C)_2N$ -StA and (b)  $O_2N$ -StA upon xanthone-sensitized excitation in argon-saturated acetontrile at 0.2 and 1  $\mu$ s after the pulse (full and open symbols, respectively);  $\lambda_{exc} = 353$  nm.

intensities. T-T annihilation and self-quenching, which generally limit the decay kinetics of triplet states in the absence of oxygen, were found to be of minor importance. The triplet lifetime  $(\tau_T)$ is in the 30-50- $\mu$ s range for various cases but characteristically shorter for Br-StA (Table IV). The latter indicates an internal heavy-atom effect for the <sup>3</sup>t<sup>\*</sup>  $\rightarrow$  <sup>1</sup>t transition.

Several methods have been applied for determination of  $\Phi_{iac}$ of *trans*-StAs; for 9-StAs in benzene,  $\Phi_T = 0.32$  has recently been measured by energy transfer from the benzophenone triplet.<sup>12,14</sup> This is consistent with  $\Phi_T = 0.32^{22}$  or  $0.25^{23}$  in toluene.  $\Phi_T$  values, using direct excitation at 353 nm, are listed in Table V.  $\Phi_T =$ 0.15-0.5 for most derivatives, except for (H<sub>3</sub>C)<sub>2</sub>N-StA, in either nonpolar (cyclohexane) or slighly polar solvents (toluene). However, for H<sub>3</sub>CO-, NC-, and O<sub>2</sub>N-StA in strongly polar solvents,  $\Phi_T$  is 10-30-fold reduced (Table V).

To generate the triplet state in those cases where  $\Phi_T$  is too small, sensitizers were used. Examples from xanthone-sensitized excitation are shown in Figure 5 for  $(H_3C)_2N$ - and  $O_2N$ -StA in acetonitrile. The maximum in the visible range is almost the same as that in nonpolar solvents in the absence of a sensitizer (Table IV). An estimate of the energy for the  $(H_3C)_2N$ -StA triplet of  $\leq 40$  kcal/mol can be made from the result that energy is efficiently transferred from triplet 9,10-dibromoanthracene (Table IV). For *trans*-9-StA in toluene, a triplet energy of about 38-40 kcal/mol was estimated on the basis of (i) energy transfer from triplet anthracene<sup>23</sup> and (ii) quenching of triplet 9-StA by ferrocene with a rate constant of  $5.7 \times 10^7$  M<sup>-1</sup> s<sup>-1,22</sup>

Effects of Temperature. At temperatures below -150 °C, the T-T absorption spectra of *trans*-R-StAs are similar in shape to those at room temperature but  $\lambda_T$  is slightly displaced toward longer wavelengths (Table IV). This further supports the assignment of <sup>3</sup>t<sup>\*</sup>, the *trans* triplet configuration, since obviously geometrical changes are inhibited by the high viscosity of the



Figure 6. Semilogarithmic plots of  $\Phi_{\rm T}$  (open symbols) and  $\tau_{\rm T}^{-1}$  (full symbols) vs  $T^{-1}$  for (H<sub>3</sub>C)<sub>2</sub>N-(squares), Br-(diamonds), NC-(triangles), and O<sub>2</sub>N-StA (circles) in ethanol;  $\lambda_{\rm exc} = 353$  nm.

glassy media. Moreover, the red-shift of  $\lambda_T$  on going from 24 to -196 °C indicates that the energy for the  $T_1 \rightarrow T_n$  transition is smaller when the geometry is fixed at the *trans* configuration by the high viscosity. Consequently, the relaxed geometry of the observed triplet state at room temperature should involve some twisting (e.g., <40°) about the C=C bond.

The major effects of cooling are (i) generally a 20–50 time increase of the triplet lifetime on going from 24 to -196 °C and (ii) an increase in  $\Delta A$  in some cases, e.g., for  $(H_3C)_2N$ -,  $H_3CO$ -, OHC-, NC-, and  $O_2N$ -StA in ethanol. This is illustrated by the plots of log  $\tau_T^{-1}$  and log  $\Phi_T$  vs  $T^{-1}$  (Figure 6). Virtually no effect of temperature on  $\Phi_T$  occurs for Br-StA and the parent 9-StA in ethanol, which are the two cases that reveal the smallest change in  $\Phi_T$  on variation of the solvent polarity at room temperature (Table V). The increase of  $\Phi_T$  on cooling in the other cases reflects a corresponding effect of  $\Phi_f$  (Figure 3). This can be explained by a radiationless, activated step bypassing the triplet state.

For Br-, H<sub>3</sub>CO-, and NC-StA in MCH or toluene,  $\Phi_T$  is only slightly reduced when the temperature is increased to 100 °C. This supports the above conclusion that in solvents of low polarity no accessible activated process competes with deactivation of <sup>1</sup>t\*. Likewise,  $\tau_T$  is only moderately ( $\leq 30\%$ ) reduced at 100 °C, which should be ascribed to a better diffusion at higher temperatures rather than to an activated decay process originating from <sup>3</sup>t\*. It is thus concluded (second paragraph above) that the potential energy curve has a minimum between the <sup>3</sup>t\* and the perpendicular (<sup>3</sup>p\*) conformation and that a too high activation barrier between this minimum and <sup>3</sup>p\* completely hinders a pathway from <sup>3</sup>t\* to <sup>1</sup>c, i.e., 90° rotation about the double bond in the triplet manifold (Schemes I and II).

**Photochemical Reactions.** In contrast to the parent 9-StA, several derivatives, e.g., NC-, H<sub>3</sub>CO-, and (H<sub>3</sub>C)<sub>2</sub>N-StA, show efficient *trans*  $\rightarrow$  *cis* photoisomerization at room temperature (Table VI). This has also been reported for H<sub>5</sub>C<sub>6</sub>-O<sub>2</sub>S- and OHC-StA.<sup>18,23</sup> While the absorption spectra of the *trans* isomers show no structure, those containing *cis*-R-StAs exhibit three maxima in the 330-390-nm range;<sup>19-21,24</sup> *trans*  $\rightarrow$  *cis* photo-isomerization is supported by GC analysis. Upon irradiation of NC-StA in acetonitrile at 405 nm, for example, the conversion reaches a photostationary state which, with shorter  $\lambda_{irr}$  (e.g., 254 nm), is displaced more to the *trans* side. In addition, other photochemical processes are present for certain cases which are taken together here (without further analysis) by measuring the

SCHEME I: Photophysical and -chemical Relaxation Processes of Excited *trans*-R-StAs under Conditions Where  $\Phi_{t\rightarrow c}$  Is Small



SCHEME II: Photophysical and -chemical Relaxation Processes of Excited *trans*-R-StAs under Conditions Where  $\Phi_{t\rightarrow c}$  Is Large



TABLE VI: Effect of Solvent on the Quantum Yields of  $trans \rightarrow cis$  Photoisomerization and Absorbance Loss for R-StAs<sup>4</sup>

|              | $\Phi_{t \rightarrow c}$ for given R |         |               |         |         |        |                 |  |  |
|--------------|--------------------------------------|---------|---------------|---------|---------|--------|-----------------|--|--|
| solvent      | N(CH <sub>3</sub> ) <sub>2</sub>     | OCH3    | CH3           | H٥      | Br      | CN     | NO <sub>2</sub> |  |  |
| cyclohexane  | 0.29                                 |         | < 0.004       |         |         |        | <0.001          |  |  |
| cyclohexane  | 0.24                                 | 0.02    | <0.01         | <0.01   |         | <0.01  | 0.13            |  |  |
| MCH          | 0.30                                 | < 0.001 | < 0.004       | <0.01   | < 0.002 | ≤0.001 | <0.001          |  |  |
| toluene      | 0.32                                 | 0.10    | < 0.002       | <0.02   | < 0.001 | 0.28   | 0.20            |  |  |
| benzene      |                                      |         |               |         |         |        | 0.15            |  |  |
| acetonitrile | 0.30                                 | 0.28    | 0.12          | < 0.002 | < 0.002 | 0.36   | <0.001          |  |  |
| acetonitrile | 0.22                                 | 0.33    | 0.18<br>0.07ª | 0.003   |         | 0.41   | 0.02            |  |  |
| ethanol      | 0.25                                 | 0.17    | 0.02          |         | <0.001  | 0.38   | <0.001          |  |  |
|              |                                      |         | $\Phi_{al}$   |         |         |        |                 |  |  |
| MCH          | ne                                   | 0.001   | 0.004         | 0.001   | 0.002   | 0.0015 | 0.0006          |  |  |
| toluene      | n                                    | n       | 0.002         | 0.001   | 0.001   | n      | <0.01           |  |  |
| acetonitrile | n                                    | n       | n             | 0.002   | 0.002   | n      | ≤0.0004         |  |  |

<sup>a</sup> In argon-saturated solution at 24 °C,  $\lambda_{irr} = 405$  nm. <sup>b</sup> Taken from ref 23 or remeasured for  $\Phi_{al}$ . <sup>c</sup> Values taken from refs 19 and 21. <sup>d</sup> Values taken from ref 20. <sup>e</sup> n: absorbance loss (photobleaching) is not significant, due to  $\Phi_{al} \ll \Phi_{t \rightarrow c}$ .

bleaching of the absorption in the 330-450-nm range. To minimize the effect of absorbance loss,  $\lambda_{irr} = 405$  nm was used. Examples for *trans*  $\rightarrow$  *cis* photoisomerization and the percentage of absorbance loss (% al) as a function of irradiation time are shown in Figure 7.

For  $O_2N-$ , NC-, OHC-, H<sub>3</sub>CO-, and (H<sub>3</sub>C)<sub>2</sub>N-StA in toluene  $\Phi_{t\rightarrow c}$  is 0.1-0.2, being much larger than the quantum yield for absorbance loss ( $\Phi_{al}$ ). This is not so for the parent 9-StA and Br-StA where, although  $\Phi_{al}$  is small, absorbance loss is still too effective to allow determination of  $\Phi_{t\rightarrow c}$  (Table VI). The relationship  $\Phi_{t\rightarrow c} \gg \Phi_{al}$  was also found for NC-, OHC-, H<sub>3</sub>CO-, and (H<sub>3</sub>C)<sub>2</sub>N-StA in acetonitrile or ethanol, while for O<sub>2</sub>N-StA in polar solvents *trans*  $\rightarrow cis$  photoisomerization is virtually inhibited. On the other hand, for the above five R-StAs showing



Figure 7. Percentage of bleaching (inset: % al) and *cis* as a function of irradiation time ( $\lambda_{irr} = 405 \text{ nm}$ ) for *trans* isomers of (H<sub>3</sub>C)<sub>2</sub>N-StA in MCH ( $\square$ ), NC-StA in acetontrile ( $\Delta$ ), and O<sub>2</sub>N-StA in toluene (O) (inset: Br-StA in toluene ( $\nabla$ ), NC-StA in MCH ( $\Delta$ ), and O<sub>2</sub>N-StA in MCH ( $\bullet$ )).

 $\Phi_{t\rightarrow c} > 0.1$  in toluene or in more polar solvents,  $\Phi_{t\rightarrow c}$  is drastically reduced (by a factor of 10 or even more) in cyclohexane or MCH (Table VI).

For cases with  $\Phi_{t\to c} \ll \Phi_{sl}$  it could be that a possible *trans*  $\rightarrow$  *cis* photoisomerization escaped observation due to thermal *cis*  $\rightarrow$  *trans* back-conversion, as reported in other cases, e.g., azomethines.<sup>30</sup> This possibility was experimentally checked for NCand O<sub>2</sub>N-StA in MCH. However, no bleaching around 400 nm was found after triplet decay, in contrast to other cases where  $\Phi_{t\to c}$  is substantial (e.g., NC-StA in polar solvents).

The temperature dependence of  $\Phi_{t\rightarrow c}$  was measured for several cases in the range 24 to -100 °C. Generally,  $\Phi_{t\rightarrow c}$  is decreased with decreasing temperature, as already reported for OHC-StA.<sup>23</sup> Results for  $(H_3C)_2N$ -StA in MCH or toluene and  $H_3CO$ - or NC-StA in ethanol indicate that the activation barrier  $(E_{t\rightarrow c})$ , obtained from the linear part (at lower temperatures) of the plot of log  $\Phi_{t\rightarrow c}$  vs  $T^{-1}$  (not shown), is larger than that activation barrier  $(E_t)$  obtained from the corresponding plot of log  $\Phi_f$  vs  $T^{-1}$  (at higher temperatures).

Effects of Substituents on the Relaxation Pathways of Excited trans-R-StAs. The influence of substitution on  $\Phi_{t\to c}$  could seem to be somewhat of a puzzle, if other important parameters, influenced by the environment, are not carefully taken into account. In the following, characteristics of each compound are first compiled and then the common mechanistic models are discussed.

*Br-StA*. This derivative is more or less similar to the parent 9-StA with respect to the effects of solvent polarity and temperature on the photophysical properties of the excited singlet and triplet states and the quasi-nonoccurrence of *trans*  $\rightarrow$  *cis* photoisomerization ( $\Phi_{t\rightarrow c} \leq \Phi_{al}$ ). The main differences are internal heavy-atom effects on the <sup>1</sup>t<sup>\*</sup>  $\rightarrow$  <sup>3</sup>t<sup>\*</sup> and <sup>3</sup>t<sup>\*</sup>  $\rightarrow$  <sup>1</sup>t transitions. The former is reflected by smaller  $\Phi_{f}$  and larger  $\Phi_{T}$  values of Br-StA vs 9-StA (Tables II and V), and the latter follows from significantly smaller  $\tau_{T}$  values in the whole temperature range studied (Figure 6 and Table IV).

Fluorescence and intersystem crossing account for 63-78% of the photons absorbed by 9-StA in several solvents at room temperature; for Br-StA the amount (56-80%) is comparable but depends more on the solvent properties (Table VII). The influence of the bromo group on the yields is modest. A much stronger enhancement of intersystem crossing was found, for example, for the azomethine analogue of Br-StA.<sup>30</sup> For *trans*-1-(1-naphthyl)-2-(4-R-phenyl)ethylenes (1-(4-R-styryl)naphthalenes: R-StNs) it has been shown that substitution by R = Br enhances  $\Phi_T$  at the expense of  $\Phi_f$  and opens, besides the singlet pathway for *trans*  $\rightarrow$  *cis* photoisomerization, the lowest triplet pathway.<sup>28</sup>

 $O_2N-StA$ . For this derivative the effects of solvent polarity on the fluorescence properties ( $\lambda_f$ ,  $\Phi_f$ ,  $\tau_f$ ) are the largest among the R-StAs (Tables I-III). Also the influence of temperature on  $\Phi_f$  (Figure 3) and  $\Phi_T$  (Figure 6) is remarkably large for  $O_2N-$ 

TABLE VII: Percentage of R-StAs Relaxing from the <sup>1</sup>t\*-State to the *trans* Ground State without Twisting (% tr) or by Converting to the <sup>1</sup>p\*-State (% perp)<sup>4</sup>

|                                  | noi<br>sc | npolar<br>lvent | sli<br>polar | ghtly<br>solvent <sup>b</sup> | strongly<br>polar solvent <sup>c</sup> |          |  |
|----------------------------------|-----------|-----------------|--------------|-------------------------------|--|----------|--|
| R                                | (% tr)    | (% perp)        | (% tr)       | (% perp)                      | (% tr)                                 | (% perp) |  |
| N(CH <sub>3</sub> ) <sub>2</sub> | 14        | 60              | 4            | 64                            | 2                                      | 55       |  |
| OCH <sub>3</sub>                 | 66        | <1              | 53           | 20                            | 7                                      | 48       |  |
| CH <sub>3</sub>                  | 74        | <1              | 61           | <1                            | 41                                     | 14       |  |
| н                                | 78        | <2              | 70           | <4                            | 63                                     | <1       |  |
| Br                               | 80        | <1              | 68           | <1                            | 56                                     | <1       |  |
| SO2-C6H5d                        | 76        | 12              | 55           | 40                            | 8                                      | 74       |  |
| CHO4                             | 70        | 4               | 62           | 40                            | 8                                      | 58       |  |
| CN                               | 78        | <1              | 45           | 56                            | 6                                      | 74       |  |
| NO <sub>2</sub>                  | 66        | <1              | 41           | 35                            | 3                                      | <1       |  |

<sup>a</sup>% tr =  $100\{\Phi_{f} + \Phi_{T}\}$  (Tables II and V), i.e., neglecting internal conversion at the *trans* side; % perp =  $200\Phi_{t \rightarrow c}$  (Table VI), i.e., assuming conversion of the twisted <sup>1</sup>p state to the stable *trans* and *cis* ground states at 50% each. <sup>b</sup> Typically toluene (and benzene). <sup>c</sup> Acetonitrile and ethanol. <sup>d</sup> Taken from ref 23.



Figure 8. Semilogarithmic plots of  $\Phi_f + \Phi_T$  as a function of the solvent polarity parameter  $E_T(30)$  for 9-StA ( $\Phi$ ) and (H<sub>3</sub>C)<sub>2</sub>N-, H<sub>3</sub>CO-, Br-, OHC-, NC-, and O<sub>2</sub>N-StA ( $\Box$ ,  $\nabla$ ,  $\blacktriangle$ ,  $\Delta$ ,  $\diamond$ , and O, respectively).

StA in polar solvents. To account for this, a charge separation after excitation of the *trans* isomer is postulated which efficiently leads to a nonemitting excited state (A\*) as intermediate in the deactivation of <sup>1</sup>t\* (Scheme II). Intramolecular charge transfer (CT) phenomena are well-known in 9-substituted anthracenes.<sup>33,34</sup> However, in several cases it has been found that smaller  $\Phi_f$  values are due to enhanced, activated intersystem crossing.<sup>35</sup> Obviously, this is not the case for R–StAs, since for all derivatives (except for Br–StA) a lower  $\Phi_f$  goes along with a smaller  $\Phi_T$  (compare Tables II and V). Moreover, 9-nitroanthracene is quite different from other anthracene derivatives; photochemical reactions, arising from triplet 9-nitroanthracene, are known.<sup>36</sup>

When  $\approx 66\%$  of the photons absorbed by O<sub>2</sub>N-StA lead to fluorescence and intersystem crossing in nonpolar solvents, this amount is already reduced to  $\approx 40\%$  in slightly polar solvents, toluene or benzene, and negligible in acetonitrile or ethanol (Table VII). Population of the postulated A\*-state probably hinders an otherwise possible enhancement of intersystem crossing. The decrease of the sum  $\Phi_f + \Phi_T$  with increasing solvent polarity is illustrated in Figure 8 for several cases. For O<sub>2</sub>N-StA in polar solvents, e.g., with E<sub>T</sub>(30) > 40 kcal/mol, 90\% or more of the molecules in the <sup>1</sup>t\* state are in principle available for deactivation via the <sup>1</sup>t\*  $\rightarrow$  A\* CT transition.

Enhanced intersystem crossing is commonly observed for nitroaromatics and caused by the  $n,\pi^*$  states which are provided by the nitro group. Introduction of a nitro group into 1-StN

changes the relaxation properties of <sup>1</sup>t<sup>\*</sup> drastically; the singlet pathway for *trans*  $\rightarrow$  *cis* photoisomerization is completely replaced by the triplet pathway.<sup>29</sup> For the azomethine analogue of O<sub>2</sub>N– StA, a related process has been reported.<sup>30</sup> In contrast,  $\Phi_{t\rightarrow c}$  is very small for O<sub>2</sub>N–StA both in nonpolar and polar solvents (Table VI; the case of a slightly polar medium is discussed below). While low-lying n, $\pi^*$  states, induced by the nitro group, could play a role in the relaxation process for O<sub>2</sub>N–StA, this is unlikely for the other derivatives. Therefore, the nature of the A\*-state could be different in these two classes of CT interaction.

NC-StA. The results for NC-StA are similar to those of  $H_5C_6-O_2S-$  and OHC-StA,<sup>23</sup> in particular the opening of a pathway for *trans*  $\rightarrow$  *cis* photoisomerization on increasing the solvent polarity at the expense of fluorescence and intersystem crossing (Tables II, V, and VI). For NC-StA in a polar solvent  $\Phi_T$  is enhanced by decreasing the temperature (Figure 6) in roughly the same manner as  $\Phi_f$  (Figure 3). A triplet route for *trans*  $\rightarrow$ *cis* photoisomerization is excluded, since there is no correlation between  $\Phi_T$  and  $\Phi_{t\rightarrow c}$  in solvents of different polarity at ambient temperatures. On the contrary, a *trans*  $\rightarrow$  *cis* pathway in competition with intersystem crossing is likely, since  $\Phi_{t\rightarrow c}$  is largest in polar solvents where  $\Phi_T$  is smallest (Tables V and VI).

 $(H_3C)_2N$ -StA. The fluorescence data of  $(H_3C)_2N$ -StA point to a large dipole moment of <sup>1</sup>t<sup>\*</sup>, the effect of solvent polarity on  $\lambda_f$  being smaller than that for O<sub>2</sub>N-StA but larger than that for OHC-StA (Figure 2). It should be mentioned that for *trans*-4-nitro-4'-(dimethylamino)stilbene (*trans*-NDS), a stilbene with "pull and push" groups, where the dipole moment is extremely large ( $\approx$ 32 D), comparable effects on the Stokes shift are known.<sup>31</sup>

Interestingly, either strong electron donating (dimethylamino) or strong electron accepting (nitro) groups at R-StAs lead to similar trends in the fluorescence data. The reason for small  $\Phi_{\rm f}$ ,  $\tau_{\rm f}$ , and  $\Phi_{\rm T}$  values in the case of (H<sub>3</sub>C)<sub>2</sub>N-StA in slightly and strongly polar solvents is again proposed to be a nonemitting A\*-state as intermediate in the deactivation route, caused by charge separation after excitation. The smallness of the sum  $\Phi_{\rm f}$ +  $\Phi_{\rm T}$  and the decrease with increasing solvent polarity (Figure 8) are strong evidence for the <sup>1</sup>t\*  $\rightarrow$  A\* CT transition. For 9-anthracene-(CH<sub>2</sub>)<sub>3</sub>-dimethylaniline, exciplex formation in nonpolar solvents is well-known.<sup>34</sup>

 $H_3CO-StA$ . A comparatively smaller dipole moment of <sup>1</sup>t<sup>\*</sup> is expected for  $H_3CO-StA$  on the basis of the dependence of  $\lambda_f$  on  $E_T(30)$  (Table I). Nevertheless, the decrease in  $\Phi_f$  on increasing the solvent polarity (Table II) indicates involvement of the A<sup>\*</sup>state in the relaxation process of <sup>1</sup>t<sup>\*</sup>.

 $CH_3$ -StA. The methyl group causes only small changes in the photophysical parameters, but in polar solvents a pathway for *trans*  $\rightarrow$  *cis* photoisomerization is opened (Table VI). Some photochemical features of the latter two derivatives were reported recently.<sup>24</sup> It should be noted that intramolecular CT interaction has also been studied for analogues of H<sub>3</sub>C-, H<sub>3</sub>CO-, and (H<sub>3</sub>C)<sub>2</sub>N-StA, where 9-anthryl is replaced by 1-pyrenyl.<sup>37</sup>

Conditions for Efficient trans  $\rightarrow$  cis Photoisomerization. The conditions for the photochemical reactivity of the StA derivatives under examination may be classified as follows: High  $\Phi_f$  and  $\Phi_{isc}$  values are indicative of inefficient trans  $\rightarrow$  cis photoisomerization (Tables II, V, and VII). This "nonreactive" case is exemplified by the parent 9-StA and Br–StA in all solvents and by virtually all derivatives in nonpolar media, with the exception of  $(H_3C)_2N$ –StA. The other extreme "reactive" case is exemplified by derivatives with electron-donating or -accepting groups on the styrene moiety in polar solvents.

The reason for  $\Phi_{t\to c} < 0.02$  ("nonreactive" case) can be (i) too high a barrier against twisting to the <sup>1</sup>p\* conformation in the excited singlet manifold (S<sub>1</sub>), (ii) a minimum in the potential energy profile of S<sub>1</sub>, displaced transoid with respect to the maximum in S<sub>0</sub> (<sup>1</sup>p), e.g., at an angle between 40° and 80°, or (iii) thermally activated internal conversion at the *trans* configuration. One alternative, that a possible trans  $\rightarrow$  cis photoisomerization escaped observation due to thermal back-conversion, was already excluded (see above). Possibility i predicts an enhancement in  $\Phi_{t\rightarrow c}$  upon heating, but for OHC-StA, where this question was previously raised, no indication for such a process was found.<sup>21</sup> Possibility iii is unlikely on the basis of  $\Phi_f$  and  $\tau_f$ values in MCH. Once 't\* is populated from 't\*' (the Franck-Condon state),  $\Phi_f$  should be significantly smaller in fluid (24 °C) compared to rigid (-196 °C) media; under the latter conditions only the nonactivated transitions,  ${}^{1}t^{*} \rightarrow {}^{1}t$  and  ${}^{1}t^{*} \rightarrow {}^{3}t^{*}$  are expected to occur. The data in MCH (Tables II and III) rule out a thermally activated relaxation to <sup>1</sup>t at room temperature. Therefore, and in view of the effect of solvent polarity on  $\Phi_{t\rightarrow c}$ , possibility ii (Scheme I) is the most conceivable. Accordingly, 100% - % tr - % perp values in Table VII reflect the relative amount of 1t\* deactivating by internal conversion at a geometry which is transoid with respect to the maximum in  $S_0$ .

The reason for  $\Phi_{t\rightarrow c} > 0.1$  ("reactive" case) for  $O_2N$ -, NC-, and  $(H_3C)_2N$ -StA in the relevant media cannot be twisting from <sup>1</sup>t\* to <sup>1</sup>p\*, following the same potential energy profile of S<sub>1</sub> as for other 1,2-diarylethylenes.<sup>8,9,15,28</sup> Twisting in the triplet manifold was already excluded (see above and ref 21). The drastic changes in deactivation of <sup>1</sup>t\* by variation of the solvent polarity are suggested to be due to charge delocalization. This pathway via A\* is illustrated in Scheme II. Accordingly,  $\Phi_{t\rightarrow c}$  is large when the step A\*  $\rightarrow$  <sup>1</sup>p\* is efficient and reduced when the radiationless transition A\*  $\rightarrow$  <sup>1</sup>t competes successfully. This branching and an activation barrier for the twisting step (with  $E_{t\rightarrow c} \geq E_t$ ) is indicated in several cases.

In addition to the two main reaction pathways, two special cases may be considered: (i)  $(H_3C)_2N$ -StA in nonpolar media and (ii) O<sub>2</sub>N-StA in solvents of medium polarity, such as benzene and toluene. To account for case i it seems that the A\*-state is already populated in nonpolar solvents (Scheme II). Thus  $\Phi_{\rm f}$ and  $\Phi_{\rm T}$  are small and  $\Phi_{\rm t \rightarrow c}$  is large with  $\approx 60\%$  twisting (Table VII). The reason for the substantial  $\Phi_{t\rightarrow c}$  in case ii is probably a continuous shift in two excited trans states with increasing solvent polarity such that the optimum conditions for trans  $\rightarrow$ cis photoisomerization are given only in certain environments. For trans-NDS it has been proposed that a polar state with trans geometry (A\*<sub>NDS</sub>) and originating from CT is more polar than <sup>1</sup>t<sup>\*</sup>.<sup>31</sup> A consequece is a strong increase in  $\Phi_f$  on going from a nonpolar to a slightly polar solvent and a strong decrease in  $\Phi_{t\rightarrow c}$ on increasing the polarity further.  $A_{NDS}^*$  is suggested to lie above and below the fluorescing 1t\*-state in nonpolar and polar solvents, respectively.<sup>31</sup> Such a strong polarity-induced shift could also account for the opening of the pathway to 1p\* in the case of  $O_2N$ -StA in slightly polar solvents. Involvement of a polar transoid A\*-state has also been suggested for 4-cyano-4'-(dimethylamino)stilbene.38

Conclusions. Br-StA and the parent 9-StA are suggested to exhibit virtually no trans  $\rightarrow$  cis photoisomerization because of inefficient twisting (less than 80°) about the double bond in the excited singlet state followed by internal conversion to <sup>1</sup>t. Introduction of an electron-accepting group or a weakly electrondonating group does not change this deactivation mechanism in a nonpolar solvent. In slightly and strongly polar media, however, CT between 4-R-styrene, containing electron-donating or -accepting groups, and anthracene is suggested to overcome this restriction against rotation in the excited singlet state. Thereby, the fluorescent <sup>1</sup>t\*-state is thermally deactivated via a transoid <sup>1</sup>A\*-state with strong CT character. Twisting to the related perpendicular conformation, internal conversion, and further twisting leads eventually to 1c. For (H<sub>3</sub>C)<sub>2</sub>N-StA the CT interaction occurs already in nonpolar solvents, whereas for O2N-StA in polar solvents the energy of <sup>1</sup>A\* is probably lowered by so much that the  ${}^{1}A^{*} \rightarrow {}^{1}p^{*}$  step can no longer compete with the  ${}^{1}A^{*} \rightarrow {}^{1}t$  transition.

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