creases from chlorine to iodine. Lee et al.¹⁵ give a bond dissociation energy of 0.16 eV for the first excited state of chlorine, as compared to a value of 0.22 eV given in Table I. Kurepa et al.³ and Person²² report purely dissociative curves for bromine and iodine, respectively, while dissociation energies of 0.16 and 0.04 eV for bromine and 0.11 and 0.01 eV for iodine are shown in Table I. The two spin states for iodine cross on different sides of the neutral. Our earlier excited-state curves were purely dissociative, except for bromine.

The second excited state curves are uniquely determined, assuming dissociative curves, except for iodine. For chlorine and bromine the two spin states are apparent. The fit of the data to the two separate peaks is shown in Figures 2, 3, and 5. However, rather than allow the spin orbital states of bromine to cross in the Franck-Condon region, we have chosen to keep the $k_{\rm B}$ values constant and sacrifice the fit of the distribution.

There are four data points for the highest excited states for all the halogens except iodine. The extra data are the dissociative attachment distribution given in Figures 1, 2, 3, and 5. The greatest deviation is for bromine.

Conclusions

The negative ion states of the halogens, including the spin substates, have been characterized by calculating the Morse potential energy curves from experimental data. In order to do this, specific state assignments were made. The Morse potentials of the negative ions were obtained by using three dimensionless parameters to modify the Morse curves of the neutral. Many of the curves are uniquely determined. Where extra data exist, the calculated properties agree well with the experimental values. For the ${}^{2}\Pi_{u,1/2}$ and the ${}^{2}\Sigma_{g}^{+}$ states of iodine, insufficient experimental data exist so that one or two of the parameters were estimated by analogy to the other halogens. These curves are the only complete set of curves in the literature obtained from experimental data and are an improvement over our earlier ones for the first two states.

The values of $k_{\rm B}$ obtained from the experimental data and the values calculated from Badger's rule are consistent, so that in the cases where there are insufficient data this parameter can be estimated from the other two. This parameter for the ground state is an approximate lower limit for the value in the excited states where Badger's rule does not apply.

The dimensionless quantities for a given state are approximately constant for all of the different halogens except for the ground state of fluorine. Based on this observation, limits can be placed on reasonable values of the dimensionless parameters as follows:

> $1.9 \ge k_A \ge 0.0$ $5.0 \ge k_{\rm R} \ge 1.0$ $1.0 \ge k_{\rm B} \ge 0.4$

These limits can be used to test the validity of parameters used for other molecules or can be used to estimate these parameters in the case of limited experimental data.

The ionic radii of the halogen atoms have been determined from the internuclear separation in the ground state to be as follows: $F^- = 1.21 \text{ Å}; CI^- = 1.63 \text{ Å}; Br^- = 1.71 \text{ Å}; I^- = 1.90 \text{ Å}.$ These values are in remarkable agreement (average deviation of 0.06 Å) with ionic radii obtained from X-ray diffraction studies.

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The Role of Triplet States in the Trans \rightarrow Cis Photoisomerization of Quaternary Salts of 4-Nitro-4'-azastilbene and Their Quinolinium Analogues. 6¹

Helmut Görner* and Dietrich Schulte-Frohlinde

Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim a.d. Ruhr, West Germany (Received: January 2, 1985)

The quantum yields of fluorescence (ϕ_f) and of trans \rightarrow cis photoisomerization ($\phi_{t\rightarrow c}$) were measured for four quaternary salts of 4-nitro-4'-azastilbene derivatives ($A_t^+X^-$; $A_t^+ = trans$ -1-alkyl-4-[4-nitrostyryl]pyridinium and -quinolinium; $X^- = trans$ -1-alkyl-4-[4-nitrostyryl]pyridinium; $X^- = trans$ -1-alkyl-4-[4-nitr I⁻, ClO₄⁻, and CH₃SO₄⁻) as a function of solvent polarity, temperature, and concentration of quenchers. Transients (lifetime ≤ 200 ns at 25 °C, $\lambda_{max} \sim 450$ nm) observed by laser flash photolysis were identified as the trans triplet configuration of either the cation (3*A_t⁺) or the ion pair (3*A_t⁺...X⁻) in highly and less polar solvents, respectively. In polar solvents at room temperature ${}^{3*}A_t^+$ is quenched by oxygen, azulene, ferrocene, and I⁻ at rates close to the diffusion-controlled limit. The quenching measurements under pulsed and steady-state conditions suggest that ${}^{3*}A_t^+$ is an intermediate in the trans \rightarrow cis photoisomerization route. In contrast to the pyridinium salts, $\phi_{i\rightarrow c}$ does not follow for the quinolinium salts linear Stern-Volmer dependences on [azulene], [ferrocene], or [I⁻]. It is concluded that for the pyridinium salts trans \rightarrow cis photoisomerization occurs only via the triplet mechanism, whereas a second route, bypassing the lowest triplet state, contributes to a certain extent ($\leq 40\%$) for the quinolinium salts (mixed singlet-triplet mechanism).

Introduction

The cis \Rightarrow trans photoisomerization of neutral azastilbene derivatives has been the subject of several studies.²⁻⁵ Introduction

- (1) Reference 9 is part 5 in the series on cis-trans photoisomerization of stilbazolium salts.
- Whitten, D. G.; Lee, Y. J. J. Am. Chem. Soc. 1972, 94, 9142.
 Bartocci, G.; Mazzucato, U.; Masetti, F.; Galiazzo, G. J. Phys. Chem. 1980, 84, 847
- (4) Bortolus, P.; Cauzzo, G. Trans. Faraday Soc. 1970, 66, 1161.

of a positive charge into the stilbene-like molecule gives rise to new phenomena. $\overline{6}^{-11}$ Quaternary salts of 1-alkyl-4-[4-R-

- Güsten, H.; Schulte-Frohlinde, D. Chem. Ber. 1971, 104, 402.
 Görner, H.; Schulte-Frohlinde, D. Chem. Phys. Lett. 1983, 101, 79.

⁽⁵⁾ For a review see: Mazzucato, U. Pure Appl. Chem. 1982, 54, 1705. (6) Güsten, H.; Schulte-Frohlinde, D. Tetrahedron Lett. 1970, 3567. Schulte-Frohlinde, D.; Güsten, H. Liebigs Ann. Chem. 1971, 749, 49.

⁽⁷⁾ Güsten, H.; Schulte-Frohlinde, D. Z. Naturforsch., B: Anorg. Chem., Org. Chem. 1979, 34B, 1556

styryl]quinolinium (e.g. $R = NO_2$, H, and OCH₃) exhibit thermal cis \rightarrow trans isomerization at room temperature^{6,7} while the noncharged azastilbene does not.^{4,5} For stilbazolium salts the rate constant for thermal cis \rightarrow trans isomerization depends significantly on the polarity of the solvent and to a smaller extent on the substituent in the 4-position of the styrene ring and on the nature of the anion.7 The question arises therefore as to the effects of the solvent polarity, the substituent R, and the anion on the $cis \rightleftharpoons trans photoisomerization of the charged stilbene-like com$ pounds. We have recently shown that a singlet mechanism operates for the trans \rightarrow cis photoisomerization of quaternary iodide of 4-cyano-4'-azastilbene in ethanol solutions while a triplet mechanism operates for the corresponding nitro compound.9 This resembles the case of 4-substituted stilbenes¹² where also a singlet mechanism operates for the cyano compound¹³ and a triplet mechanism for the nitro compound.¹⁴⁻¹⁶

In the present work we have studied the photochemical properties of quaternary salts of 4-nitro-4'-azastilbene derivatives in more detail. The compounds under examination are a pyridinium (P) or a quinolinium (Q) type: 1-methyl-4-[4-nitrostyryl]pyridinium iodide (Pa), 1-ethyl-4-[4-nitrostyryl]quinolinium iodide (Qa), a perchlorate of type P (Pb), and a methosulfate of type Q (Qb). Quenching measurements with azulene, ferrocene, and several anions under steady-state and laser flash excitation conditions confirm the involvement of the observed triplet state in the trans \rightarrow cis photoisomerization. Contribution of an additional minor pathway bypassing the lowest trans triplet state is proposed for the quinolinium salts.

Experimental Section

Apparatus and Procedures. Steady-state irradiation measurements were carried out with a 1000-W mercury-xenon lamp and a monochromator (Schoeffel).9 Trans/cis ratios at various irradiation times and the quantum yield of trans \rightarrow cis photoisomerization $(\phi_{t\rightarrow c})$ were determined by analysis of the absorption spectra using a spectrophotometer (Perkin-Elmer, 554).^{13,15} Application of the potassium ferrioxalate¹⁷ or the aberchrome 540 actinometers¹⁸ gave the same results for $\lambda_{irr} = 366$ nm within 10%. In the presence of ferrocene or azulene $\phi_{t\rightarrow c}$ was corrected for the absorption of these additives at 366 nm. In those cases where only the trans isomer was used, the molar absorption coefficient of the cis isomer (ϵ_c) at λ_{irr} was determined according to the method described by Fischer.¹⁹ $\phi_{c \rightarrow t}$ was obtained from ϵ_t , ϵ_c , photostationary trans/cis ratios, and $\phi_{t \rightarrow c}$ by assuming the validity of eq 1.

$$\phi_{c \to t} = \phi_{t \to c} \frac{\epsilon_t}{\epsilon_c} \left(\frac{[t]}{[c]} \right)_s \tag{1}$$

The quantum yield of fluorescence (ϕ_f) was determined as described in previous work using a spectrofluorometer (Spex-

(15) Schulte-Frohlinde, D.; Görner, H. Pure Appl. Chem. 1979, 51, 279. Görner, H. Ber. Bunsenges. Phys. Chem. 1984, 88, 1199.



Figure 1. Absorption spectra of trans- and cis-Pa (- and ---, respectively; $\epsilon_t = 3.2 \times 10^4$) and trans- and cis-Qa (--- and ..., respectively; $\epsilon_{\rm t} = 3.1 \times 10^4$) in methanol solution at 25 °C.

Fluorolog) and 9,10-diphenylanthracene in ethanol as a standard.²⁰ Fluorescence quenching measurements were carried out on a second fluorometer (Perkin-Elmer, LS 5). For pulsed excitation the third harmonic of a Nd laser ($\lambda_{exc} = 353$ nm) was used.²¹ The laser flash photolysis apparatus has been described elsewhere.^{16,21} Unless otherwise indicated, the trans isomers were freshly dissolved prior to excitation and purged with argon for 10-30 min.

Materials. trans-1-Methyl-4[4-nitrostyryl]pyridinium iodide (trans-Pa) was synthesized according to literature⁷ and recrystallized from methanol-water; trans-Pb was prepared from trans-Pa by treating with AgClO₄. trans-1-Ethyl-4-[4-nitrostyryl]quinolinium iodide (trans-Qa) and trans-1-methyl-4-[4nitrostyryl]quinolinium methosulfate (trans-Qb) were the same as in previous work.⁷ The homogeneity of the stilbazolium salts was checked by TLC. Melting points (in °C) for the trans isomers are as follows: Pa, 234-238; Pb, 217-219; Qa, 232-234; and Qb, 219-220. After reaching the photostationary state ($\lambda_{irr} = 366$ nm), cis-Pa was separated by HPLC on a column (nucleosil, 18/5 mm) using a 2:3 mixture of methanol and triethylammonium acetate in water as eluant (pH 3.5).

The amines are the same as in ref 22, ferrocene (Merck) was recrystallized, azulene (Aldrich), 9,10-diphenylanthracene (EGA), potassium salts (iodide, thiocyanate, and bromide), sodium perchlorate, and several solvents (Merck) were used as supplied, e.g. acetonitrile (Uvasol), or purified on a alumina column: chloroform (p.A.) and dichloromethane (p.A.). Tetrahydrofuran, 2methyltetrahydrofuran, ethanol, and methanol were purified by fractional distillation, and water was triply distilled. For lowtemperature measurements either a 4:1 mixture of ethanol and methanol (E-M) or a 1:1 mixture of 2-methyltetrahydrofuran and dichloromethane (M-D) was used.

Results

Effect of Solvent on the Absorption Spectra and $\phi_{t\rightarrow c}$. Upon irradiation of each of the four trans isomers in polar solvents at room temperature (λ_{irr} = 366 nm), the absorption spectrum changes and shows an isosbestic point (λ_i) , finally reaching a photostationary state. The absorption maximum of the photoproduct is displaced to shorter wavelengths than that of the trans isomer (λ_i) . The photoproduct is assigned to the cis isomer in accordance with previous work.⁷⁻⁹ Absorption spectra of trans and cis isomers in methanol solutions are shown in Figure 1. From UV analysis, formation of up to 88% cis in the photostationary state $((\% \text{ cis})_s)$ with no discernible side reaction was found. The absorption spectrum of trans-P is practically unchanged if the

⁽¹⁰⁾ Steiner, U.; Abdel-Kader, M. H.; Fischer, P.; Kramer, H. E. A. J. Am. Chem. Soc. 1978, 100, 3190. Ikeda, N.; Mataga, N.; Steiner, U.; Ab-del-Kadar, M. H. Chem. Phys. Lett. 1983, 95, 66.

⁽¹¹⁾ Takagi, K.; Ogata, Y. J. Org. Chem. 1982, 47, 1409. Takagi, K.; Aoshima, K.; Sawaki, Y.; Iwamura, H. J. Am. Chem. Soc. 1985, 107, 47. (12) For a review, see: Saltiel, J.; Charlton, J. L. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York,

^{1980;} Vol. 3, p 25

⁽¹³⁾ Görner, H. J. Photochem. 1980, 13, 269.

⁽¹⁴⁾ Bent, D. V.; Schulte-Frohlinde, D. J. Phys. Chem. 1974, 78, 451 Görner, H.; Schulte-Frohlinde, D. Ber. Bunsenges. Phys. Chem. 1977, 81, 713.

⁽¹⁶⁾ Görner, H.; Schulte-Frohlinde, D. J. Phys. Chem. 1978, 82, 2653. Görner, H.; Schulte-Frohlinde, D. Ber. Bunsenges. Phys. Chem. 1984, 88, 1208

⁽¹⁷⁾ Hatchard, C. G.; Parker, C. A. Proc. R. Soc. London, A 1956, 235, 518. Demas, J. N.; Bowman, W. D.; Zalewski, E. F.; Velapoldi, R. A. J. Phys. Chem. 1981, 85, 2766.

⁽¹⁸⁾ Heller, H. G.; Langan, J. R. J. Chem. Soc., Perkin Trans. 2 1981, 341.

⁽¹⁹⁾ Fischer, E. J. Phys. Chem. 1967, 71, 3704.

 ⁽²⁰⁾ Görner, H.; Schulte-Frohlinde, D. J. Phys. Chem. 1979, 83, 3107.
 (21) Görner, H.; Schulte-Frohlinde, D. J. Phys. Chem. 1981, 85, 1835.

⁽²²⁾ Görner, H. J. Phys. Chem., following paper in this issue.

TABLE I: Data Obtained from Trans → Cis Photoisomerization⁴

compd	solvent	λ_i , nm	λ _t , nm	$\phi_{t \rightarrow c}$ °	$\phi_{c \rightarrow t} \circ b$	(% cis) _s
Pa	tetrahydrofuran	303	343	0.02		≲20 ^c
	chloroform	307	344	0.03		≲30 ^c
	dichloromethane	310	345	0.07		≲50¢
	acetonitrile	299	338	0.4	0.4	80
	methanol ^d	299	340	0.6		88
	water	300	340	0.45	0.4	85
Рb	tetrahydrofuran	300	341	0.35		82
	chloroform	<310	344	0.35		82
	dichloromethane	303	345	0.45		85
	water	299	340	0.4	0.4	85
Qa	tetrahydrofuran	313	374	0.005		≲10 ^c
-	chloroform	320	371	0.02		≲25
	dichloromethane	318	375	0.07		≲40
	acetonitrile	314	372	0.4	0.4	85
	methanol ^d	313	373	0.6		88
	water	316	372	0.4	0.4	85
Qb	chioroform	316	371	0.35		78
	dichloromethane	317	374	0.4		80
	methanol	313	372	0.6		88
	water	318	371	04	04	85

^aIn argon-saturated solutions at 25 °C, [trans isomer] = $(2-4) \times 10^{-5}$ M; $\lambda_{irr} = 366$ nm unless otherwise indicated. ^bObtained from irradiation of mixtures containing ~80% cis at 313 nm. ^cAfter reaching a quasi-photostationary state a further photoreaction occurred. ^dThe same values were found in oxygen-saturated solutions.



Figure 2. Semilogarithmic plots of $\phi_{t \to c}$ (O), ϕ_T^{rel} (D), and τ_T^{-1} (Δ) vs. T^{-1} for Qa in E-M.

iodide is replaced by the perchlorate (Pa vs. Pb); the same was found for *trans*-Qa vs. *trans*-Qb in a given solvent (Table I). Solvent polarity has only a small effect on λ_t , which is red-shifted for *trans*-Q as compared to *trans*-P. Variation of the concentration in methanol has virtually no effect on ϵ_t and λ_t (e.g. $[Pa] = 1 \times 10^{-5}-1 \times 10^{-3}$ M). In dichloromethane λ_t is slightly blue-shifted on increasing [Pa]. In addition, a weak shoulder appears at the long-wavelength side of the absorption band which is absent for Pb and also for Pa in polar solvents. This new absorption is tentatively assigned to a charge-transfer (CT) band (cf. ref 23).

The values for $\phi_{t\to c}$ are rather large (0.35–0.6) for the four salts in polar solvents (acetonitrile, methanol, and water) at room temperature and only slightly dependent on the anion and on solvent properties (Table I). However, in solvents of moderate polarity (tetrahydrofuran, chloroform, and dichloromethane) $\phi_{t\to c}$ is markedly smaller for the iodides (Pa and Qa). In these cases only a quasi-photostationary state is reached which is shifted to the trans form. On prolonged irradiation of the iodides a decomposition was observed in contrast to the photochemical behavior of the perchlorate and the methosulfate (Pb and Qb, re-

(23) Briegleb, G.; Jung, W.; Herre, W. Z. Phys. Chem. (Munich) 1963, 38, 253.



Figure 3. Semilogarithmic plots of $\phi_{t \to c}$ (O) and r_T^{-1} (Δ) vs. T^{-1} for Pb in M-D.



Figure 4. Plots of $\phi_{t\to c}/\phi_{t\to c}$ ° (O), I_f/I_f ° (D), and τ_T/τ_T ° (Δ) vs. log [ferrocene] for Qa in methanol solution at 25 °C. The full line is calculated by using $\phi_S = 0.35$, $\phi_T = 0.65$, $\alpha = \beta = 0.5$, $K_S = 30 \text{ M}^{-1}$, and $K_T = 2200 \text{ M}^{-1}$.

TABLE II: Half-Concentrations for Quenching of $\tau_{\rm T}$ and $\phi_{\rm t+c}$ by Azulene and Ferrocene^a

compd	quencher	$10^{-9}s_{q}^{b}, M^{-1} s^{-1}$	$\frac{10^{3} [\text{quencher}]_{\tau/2},^{c}}{\text{M}}$	$\frac{10^{3} [\text{quencher}]_{c/2},^{d}}{\text{M}}$
Pa	azulene	9	2.0	
	ferrocene	10	1.8	1.8
		(12)*	(1.7)	
Qa	azulene	10	0.50	4
Qb	azulene	10	0.45	
Qa	ferrocene	11	0.45	2.5
		(10)	(0.59)	
Qb	ferrocene	9	0.51	1.5
		(12)	(0.42)	

^a In argon-saturated methanol solution at 25 °C unless otherwise indicated. ^b Slope of the linear dependence of τ_T^{-1} vs. [quencher]. ^c Half-concentration for quenching of τ_T ; [quencher]_{$\tau/2} = (<math>\tau_T^{\circ}s_q$)⁻¹. ^d Half-concentration for quenching of $\phi_{t\to c}$; for Qa and Qb no linear dependences of $\phi_{t\to c}^{-1}$ vs. [quencher]. ^e Values in parentheses refer to acetonitrile solution.</sub>

spectively). In the latter cases $\phi_{t \rightarrow c}$ and $(\% \text{ cis})_s$ are similar to the results in polar solvents.

Effect of Temperature on $\phi_{t\rightarrow c}$. The temperature dependence of $\phi_{t\rightarrow c}$ was measured for Pa⁹ and Qa (Figure 2) in a 4:1 mixture of ethanol and methanol (E-M). When the temperature is decreased, $\phi_{t\rightarrow c}$ decreases slightly and falls off rapidly below -150 °C. Below -165 °C trans \rightarrow cis photoisomerization is practically inhibited. In a 1:1 mixture of 2-methyltetrahydrofuran and dichloromethane (M-D), as an example for a solvent of moderate polarity, a similar temperature dependence was found for Pb (Figure 3). $\phi_{t\rightarrow c}$ remains almost constant between 25 and -120 °C and decreases strongly on further cooling. However, in contrast



Figure 5. Plots of $\phi_{t\to c}^{\circ}/\phi_{t\to c}$ (O) and τ_T°/τ_T (Δ) vs. [azulene] for Qa in methanol solution at 25 °C.



Figure 6. Plots of $\phi_{t\to c}/\phi_{t\to c}^{\circ}$ (O), ϕ_f/ϕ_f° (D), and τ_T/τ_T° (Δ) vs. log [I⁻] for Qa in acetonitrile solution. The full line is calculated by using $\phi_S = 0.35$, $\phi_T = 0.65$, $\alpha = \beta = 0.5$, $K_S = 5$ M⁻¹, and $K_T = 2400$ M⁻¹.

to polar solvents, the temperature dependence of $\phi_{t\to c}$ is different for Pa²² and Pb.

Quenching of $\phi_{t\rightarrow c}$ by Additives. Involvement of triplet states in the trans \rightarrow cis photoisomerization was probed by the addition of ferrocene or azulene. In methanol solution at room temperature $\phi_{t \rightarrow c}$ is markedly reduced in the presence of one of these quenchers Values for $[quencher]_{c/2}$, denoting ferrocene or (Figure 4). azulene concentrations at which $\phi_{t\to c}$ is reduced to 1/2 of its maximum value ($\phi_{t\rightarrow c}^{\circ}$), are in the range of (1-4) \times 10⁻³ M (Table II). For Pa essentially a linear (Stern-Volmer) dependence has been found for $\phi_{t\to c}^{-1}$ vs. [ferrocene].⁹ However, for Qa and Qb at high quencher concentrations (≥ 0.1 M) $\phi_{t \rightarrow c}$ does not approach zero but is only reduced to 0.05-0.1. Therefore, no linear Stern-Volmer plots were obtained; $\phi_{t\to c}$ shows a downward curvature on [quencher] (Figure 5). Slope/intercept values of the initial linear part are smaller than those obtained from triplet quenching measurements (see below). For the Q-type salts a second pathway for trans \rightarrow cis photoisomerization, not involving the lowest triplet state, is suggested (see Discussion).

In polar solvents $\phi_{t\to c}$ is also reduced on addition of several anions. Examples for the dependences of $\phi_{t\to c}$ vs. [I⁻] and [SCN⁻] for Pa are shown in the subsequent article²² (Figures 3 and 4, respectively). The half-concentrations of the anion ([X⁻]_{c/2}) increase for Pa and Qa in water in the order I⁻, SCN⁻, Br⁻, and ClO₄⁻. For Pa in acetonitrile and aqueous solutions plots of $\phi_{t\to c}^{-1}$ vs. [I⁻] are linear (within experimental error). However, corresponding plots for Qa show a downward curved dependence; this is illustrated in Figure 6 by a plot of $\phi_{t\to c}$ vs. log [I⁻]. The non-Stern-Volmer behavior for the Q-type salts points again to a second pathway for trans \rightarrow cis photoisomerization (see Discussion).

Fluorescence. Fluorescence emission maxima (λ_f) around 410 and 460 nm were recorded in several solvents at room temperature for the trans isomers of P and Q, respectively (Table III). The

TABLE III: Fluorescence Maximum and ϕ_t^a

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	compd	solvent	<i>T</i> , ⁰C	λ_{f} , nm	$\phi_{\mathrm{f}}^{\circ}$
	Pa	dichloromethane	25	~410	≲0.0001
		acetonitrile	25	414	≲0.0001
		ethanol	25	~410	≲0.0002
			-196	390 , ∼410	≲0.0015
		water	25	410	0.0005
	Pb	dichloromethane	25	406	~0.0001
		ethanol	25	~410	≲0.0002
			-196	390 , ~405	≲0.002
	Qa	dichloromethane	25	462	0.0007
		acetonitrile	25	460	0.0015
		ethanol	25	464	0.0015
			-196	428, 457, 487	0.004
		water	25	465	0.0015
	QЪ	dichloromethane	25	462	0.001
		ethanol	25	464	0.0015
			-196	426, 456, 485	0.004

 a In air-saturated solutions, λ_{exc} = 340 and 366 nm for P and Q, respectively.

TABLE IV: Stern-Volmer Constant of Fluorescence Quenching^a

compd	solvent	quencher ^b	$K_{\rm S}, {\rm M}^{-1}$
Pa	water	I-	≲8
Qb	dichloromethane	DMA	3.0
		DEA	2,3
		TEA	<5
Qa	acetonitrile	I-	2.0
		DABCO	3.3
		DMA	2.6
		TEA	2.4
	methanol	ferrocene	<30
	water	I-	5.0
		SCN ⁻	8
		DABCO	2
		TEA	3
		Br ⁻	<1

^a In air-saturated solutions at 25 °C, $\lambda_{exc} \approx \lambda_t$. ^bAbbreviation of the amines: DABCO, 1,4-diazabicyclo[2.2.2]octane; DMA, N,N-dimethylaniline; DEA, N,N-diethylaniline; and TEA, triethylamine.

anion and the solvent polarity have only a small influence on λ_f . In glassy ethanol at -196 °C the spectrum becomes structured (progression: $\sim 1.5 \times 10^3$ cm⁻¹) for the Q-type salts but it remains essentially unstructured for the P type.

Fluorescence quantum yields of less than 2×10^{-3} were measured for the trans isomers at 25 °C. ϕ_f values are generally smaller for the P-type salts than those of the Q-type salts and show a trend to greater values on going from dichloromethane to polar solvents (Table III). When the temperature is decreased to -196 °C, ϕ_f increases in ethanol solution only slightly to values smaller than 5×10^{-3} , indicating that no activated step competes with fluorescence. This differs from the case of stilbazolium salts not containing a nitro group (R = CN, H, CH₃, and OCH₃). Generally, for the latter compounds, ϕ_f is also low at room temperature but increases strongly to values of almost unity at -196 °C.²⁴

In order to distinguish between the effects of quenching of singlet and triplet states on $\phi_{t\rightarrow c}$, the fluorescence intensity (I_f) was measured in the presence of quenchers. For Qa linear dependences of I_f°/I_f vs. [quencher] were obtained for ferrocene, I⁻, SCN⁻, and several amines at low concentrations. The amines were included in this study in order to estimate the effect of singlet quenching via the electron-transfer process.²² Stern-Volmer constants from fluorescence quenching (K_S) in dichloromethane, acetonitrile, and aqueous solutions are between 2 and 5 M⁻¹ (Table IV). At higher concentrations (e.g. [quencher] > (K_S^{-1}) plots of I_f°/I_f vs. [quencher] show an upward bending dependence in most cases, indicating involvement of a static quenching component. Quenching by azulene is complicated by the absorption in the 400-700-nm region as well as by the S₂ fluorescence of azulene.

⁽²⁴⁾ Görner, H.; Fojtik, A.; Wróblewski, J.; Currell, L. J. Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys. 1985, 40A, 525.



Figure 7. Transient absorption spectra of (a) Qa in E-M (20 ns after the laser pulse) at 25 °C (full line) and at -170 °C (dotted line) and (b) Qb in dichloromethane solution at 25 °C (20 ns (full line) and 200 ns (dashed line) after the laser pulse).



Figure 8. Transient absorption spectra of (a) Pb and (b) Pa in dichloromethane solution at 25 °C (10 ns (full line) and 200 ns (dashed line) after the laser pulse).

Fluorescence quenching of Pa was in most cases impossible under our conditions due to the exceedingly small ϕ_f values (Table III).

Thermal Cis \rightarrow Trans Isomerization. For several substituted stilbazolium salts of type Q thermal cis \rightarrow trans isomerization has been previously studied.^{6,7} For example, an activation energy of 20.5 kcal/mol and a preexponential factor of 8 × 10¹¹ s⁻¹, corresponding to a half-life of 16 min at 25 °C, have been determined for Qa in acetone.⁷ While thermal cis \rightarrow trans isomerization was also found for Pa and Pb in solvents of moderate polarity, virtually no thermal cis \rightarrow trans isomerization could be observed in polar solvents (e.g. acetonitrile and water) at 25 °C.

Properties of the Transient Tr_T . One transient (Tr_T) was observed by laser flash photolysis on direct excitation ($\lambda_{exc} = 353$ nm) of the four salts (at low concentrations, $10^{-4}-10^{-3}$ M) in polar solvents at room temperature. The transient absorption spectra (Figure 7a) range from the trailing edge of the ground-state absorption spectrum to the red with a maximum (λ_{max}) at ~450 nm for P-type compounds and two maxima for Q-type compounds. Similar spectra were observed in several other polar solvents (Table V). On going from 25 to -170 °C the transient absorption spectra of Pa⁹ and Qa (Figure 7a) in E-M remain essentially similar in shape and in λ_{max} .

In solvents of moderate polarity (tetrahydrofuran, chloroform, and dichloromethane) at room temperature virtually the same spectra as in polar solvents were recorded for Pb and Qb as illustrated in Figures 7b and 8a. For the iodides (Pa and Qa) in these solvents, however, a second transient (Tr_R) appears in addition to Tr_T . As an example, time-resolved transient absorption spectra are shown for Pa in dichloromethane (Figure 8b). Since the decay of Tr_T is much faster than the decay of Tr_R (half-life >5 μ s), the absorption after 200 ns is due to Tr_R only. The features

TABLE V: Absorption Maximum and Lifetime of the Triplet and Rate Constant for Triplet Quenching by Oxygen^a

			$\tau_{\rm T}^{\rm o}$,	$10^{-9}s_{ox}$,
compd	solvent	λ_{max} , nm	ns	M ⁻¹ s ⁻¹
Pa	dichloromethane	450	50	6
	acetonitrile	$(\sim 390),^{b} 450$	50	5.6
	methanol	(~390), 450	55	4.0
	E-M	[455]°		
	water	(~390), 450	60	3.5
РЬ	tetrahydrofuran	460	80	
	dichloromethane	(400), 455	65	5.9
	acetonitrile	440	61	5.0
	methanol	(385), 450	70	3.4
	E-M	[455]		
	water	440	57	3.0
Qa	dichloromethane	455	180	
	acetonitrile	450, (510)	170	3.3
	methanol	440, 500	200	3.0
	E-M	[460]		
	water	460	180	4.0
Qb	tetrahydrofuran	460	180	
	dichloromethane	445, (515)	230	2.0
	acetonitrile	445, (545)	200	3.0
	methanol	$440, (\sim 510)$	220	3.0
	EM	[460, 540]		
	water	440, (~520)	200	3.7

^{*a*} In argon-saturated solutions ((0.5–5) × 10⁻⁴ M) at 25 °C unless otherwise indicated. ^{*b*} Values in parentheses indicate a shoulder. ^{*c*} Values in square brackets refer to temperatures below -165 °C; $\tau_{T}^{\circ} \gtrsim 2$ ms throughout.

of Tr_R are described in the subsequent paper.²²

Tr_T decays by first-order kinetics; reciprocal first-order decay rate constants $(k_{obsd}^{-1} = \tau_T)$ in the 100-ns range were obtained in several solvents at room temperature (Table V). In polar solvents similar lifetimes were found when I⁻ was replaced by the perchlorate or the methosulfate while in less polar solvents τ_T is slightly smaller in the presence of I⁻. In the latter cases the absorbance (Δ OD) of Tr_R was subtracted from the total Δ OD.

Effect of Temperature on Tr_T . Plots of k_{obsd} vs. T^{-1} in E-M were obtained for Pa⁹ and for Qa (Figure 2). When the temperature is decreased from +25 to -130 °C, k_{obsd} decreases moderately and falls off significantly between -130 and -156 °C leveling off at lower temperatures and reaching a limiting value, corresponding to $\tau_T \gtrsim 2 \text{ ms at } -196 \text{ °C}$. From linear plots of log k_{obsd} vs. T^{-1} in E-M above -130 °C activation energies (E_τ) of 0.75 and 2.2 kcal/mol and A factors (A_τ) of 0.7 × 10⁸ and 3 × 10⁸ s⁻¹ were calculated for Pa and Qa, respectively. The relative yield of Tr_T (ϕ_T^{rel}) was obtained from ΔOD at λ_{max} by assuming that the absorption coefficient of Tr_T is independent of temperature. ϕ_T^{rel} is practically independent of temperature between 25 and -180 °C (Figure 2).

Also, for Pb in M–D ϕ_T^{rel} remains practically constant between 25 and -180 °C. In this range τ_T^{-1} shows a similar temperature dependence as to the case of Pa in E–M;⁹ i.e., τ_T varies only slightly between 25 and -130 °C, decreases strongly between -138 and -170 °C, and levels off at lower temperatures (Figure 3). From the Arrhenius dependence of k_{obsd} above -130 °C values of $E_\tau = 0.2$ kcal/mol and $A_\tau = 0.3 \times 10^8$ s⁻¹ were obtained ($E \sim 10$ kcal/mol below -138 °C).

Effect of Additives on Tr_T . The quenching of Tr_T by oxygen, ferrocene, and azulene was measured in several solvents at room temperature. Linear dependences of the ratio of lifetimes in the absence and presence of a quencher, (τ_T°/τ_T) vs. [azulene] in methanol solution, are shown in Figure 5. Slopes of these linear plots and of similar dependences of τ_T°/τ_T on [ferrocene] and $[O_2]$ (s_q and s_{ox} , respectively), representing quenching rate constants, are close to the diffusion-controlled limit (Tables II and V). For Pa the half-concentration, [quencher]_{$\tau/2} = K_T^{-1}$, is similar to the value [quencher]_{c/2} obtained from steady-state quenching (Table II). However, for Qa the values of [quencher]_{$\tau/2$} are nearly 1 order of magnitude smaller than the values of [quencher]_{c/2}.</sub></sub>

The decay of Tr_T is also quenched by anions in acetonitrile and aqueous solutions. The slopes of the linear dependences of k_{obsd}



Figure 9. Scheme for trans \rightarrow cis photoisomerization of 4-nitro-4'-stilbazolium salts in polar solvents.

vs. $[X^-]$ show a decreasing trend in the order I⁻, SCN⁻, Br⁻, and ClO₄⁻ (cf. ref 22, Table II). Quenching of Pa and Qa by I⁻ in these solvents is nearly diffusion controlled while for SCN⁻ s_q is lower and decreases on going from acetonitrile to water. In those cases where the quenching of Qa is diffusion controlled (e.g. for I⁻), $[X^-]_{r/2}$ is approximately 1 order of magnitude smaller than $[X^-]_{c/2}$. In the other cases (i.e. for Qa if $s_q < 1 \times 10^9$ M⁻¹ s⁻¹ and for Pa) the half-concentrations from both triplet and steady-state quenching methods are the same (within experimental error).

Discussion

Assignment of Tr_T to the Lowest Trans Triplet State. As recently suggested for Pa in ethanol,⁹ the initial transient (Tr_T) of the salts in polar solvents is assigned to the lowest triplet state of the cation. The reasons are as follows. Firstly, Tr_T is quenched at room temperature by low-energy triplet quenchers (azulene, ferrocene, and oxygen) at rates close to the diffusion-controlled limit (Tables II and V). Secondly, the absorption spectra of Tr_T obtained for Pa under direct and sensitized excitation are practically identical.⁹ Thirdly, the absorption spectrum and the lifetime of Tr_T (Table V) show close similarities to those of the lowest triplet state of 4-nitrostilbenes.¹⁴⁻¹⁶ Finally, the temperature dependence of the reciprocal transient lifetime (Figure 2) exhibits a behavior typical for cases where triplet states are involved in trans \rightarrow cis photoisomerization.^{15,20}

On the basis of temperature-dependent $\phi_{t\to c}$ and laser flash photolysis measurements, Tr_T is further assigned to the trans triplet configuration of the cation (${}^{3*}A_t^+$): $\phi_{t\to c}$ decreases to values smaller than 0.01 on decreasing the temperature below -165 °C (Figure 2); the small $\phi_{t\to c}$ value in the glassy E-M solution implies that trans \rightarrow cis photoisomerization is practically inhibited. In contrast, ϕ_T^{rel} remains constant over the whole temperature range (25 to -180 °C). Furthermore, the T-T absorption spectrum at room temperature is very similar to that in frozen solution (Figure 7a).⁹ Therefore, Tr_T in polar solvents is assigned to ${}^{3*}A_t^+$.

In solvents of moderate polarity the salts are present as ion pairs $(A_t^{+}\cdots X^{-})$ (cf. ref 22). Here, Tr_T is assigned to the trans configuration of the lowest triplet state of the ion pair $({}^{3*}A_t^{+}\cdots X^{-})$. This assignment is based on the features of Tr_T , e.g. absorption spectrum (Figure 8), lifetime (Table V), and the temperature dependences of k_{obsd} and ϕ_T^{rel} (Figure 3); the results are rather similar in highly and less polar solvents. Some additional effects for the iodides are due to photochemical electron transfer.²²

Population of the Triplet. For 4-nitro-4'-stilbazolium salts in polar solvents, where the presence of ion pairs is negligible, the following scheme is proposed (Figure 9): On excitation of the trans ground state (A_t^+) to the first excited singlet $({}^{1*}A_t^+)$, the observed triplet state $({}^{3*}A_t^+)$ is formed by intersystem crossing. This process is fast since the triplet is formed during the laser pulse even at -170 °C. Intersystem crossing at the trans configuration is suggested to be the dominant deactivation step of ${}^{1*}A_t^+$ solutions since ϕ_f is very small in fluid and rigid media (Table III) and ϕ_T^{rel} is substantial and essentially independent of temperature and viscosity (Figure 2). This fast intersystem crossing step is not due to a heavy atom effect produced by I⁻ since the ions are fully dissociated in polar solvents and the perchlorate shows practically the same effects (Tables I, III, and V). In analogy to the features of 4-nitrostilbenes we propose that fast intersystem crossing is the result of the presence of $(n\pi)^*$ states due to the nitro group.¹⁴⁻¹⁶

Intersystem crossing from the excited trans singlet state of the ion pair $({}^{1*}A_{t}^{+}\cdots X^{-})$ is suggested for the population of the triplet in solvents of moderate polarity. Also, in the ion pair Tr_{T} is formed within a few nanoseconds, in line with the assignment of Tr_{T} to $({}^{3*}A_{t}^{+}\cdots X^{-})$. The nature of the anion in the ion pair changes the T-T absorption spectrum only slightly. This is indeed expected since the main band of the ground-state absorption spectrum is also not markedly influenced by formation of an ion pair (see Table I). A dissociation of the ion pair in the excited singlet or triplet state is not probable.

 $Trans \rightarrow Cis Photoisomerization via the Triplet.$ We suggest that the trans \rightarrow cis photoisomerization of Pa and Pb in polar solvents occurs via the triplet route, i.e., the sequence

$$A_{t}^{+} + h\nu \rightarrow {}^{1}*A_{t}^{+} \rightarrow {}^{3}*A_{t}^{+} \rightarrow {}^{3}*A_{p}^{+} \rightarrow A_{p}^{+} \rightarrow (1 - \alpha)A_{c}^{+}$$
(2)

where ${}^{3*}A_p^+$ is the twisted (perpendicular) configuration of the triplet, A_p^+ and A_c^+ are twisted and cis configurations of the ground state, and α is the fraction of ${}^{3*}A_p^+$ decaying to A_t^+ . It seems necessary to also postulate the reverse step ${}^{3*}A_p^+ \rightarrow {}^{3*}A_t^+$ because the same transient with the same relative yield is observed on direct excitation of cis-enriched solutions. Therefore, the triplet state should exist as a configurational equilibrium between the planar and the twisted form $({}^{3*}A_t^+ \rightleftharpoons {}^{3*}A_p^+)$. Establishment of the equilibrium should occur within 10 ns since the observed triplet state is formed within the laser pulse with both A_t^+ and A_c^+ . The existence of a trans \rightleftharpoons perpendicular triplet equilibrium has been established for various phenylethylenes, such as stilbene, ${}^{12.20}$ 4-nitrostilbenes, ${}^{14-16}$ and 1-phenyl-2-naphthylethylenes.

In rigid media it is suggested that ${}^{3*}A_t^+$ decays to A_t^+ without involving a twisting process. This is supported by the long lifetime of ${}^{3*}A_t^+$ (Table V) and by the fact that $\phi_{t\to c}$ is practically zero below -165 °C. When the temperature is increased, (decreasing the viscosity), twisting about the C=C double bond becomes important. This is illustrated by the strong increase of τ_T^{-1} between -160 and -130 °C (Figure 2). Above -130 °C where $\phi_{t\to c}$ has almost reached the maximum value τ_T^{-1} follows an Arrhenius dependence with $E_\tau \leq 2.2$ kcal/mol. Analogous to 4-nitrostilbenes¹⁴⁻¹⁶ E_τ may be interpreted as the enthalpy difference between ${}^{3*}A_p^+$ and ${}^{3*}A_t^+$ by assuming that the intersystem crossing step ${}^{3*}A_p^+ \to A_p^+$ is nonactivated (see Appendix, eq 7).

Triplet Quenching. Quenching measurements of $\phi_{t\rightarrow c}$ and of the observed triplet by azulene and ferrocene essentially support the proposed mechanism for trans \rightarrow cis photoisomerization via the lowest triplet state.⁹ Initial slope/intercept ratios for $\phi_{t\rightarrow c}$, which are larger than 250 M⁻¹ (Table II), are too large to be due to fluorescence quenching (Table IV). From a fluorescence lifetime of smaller than 10 ps (in accordance with the low ϕ_f value and $\epsilon_t \sim 3 \times 10^4$), a much smaller Stern-Volmer constant is expected. Small Stern-Volmer constants (<30 M⁻¹) are also observed for other stilbazolium salts (R = CN, H, CH₃, and OCH₃) which isomerize via excited singlet states.²⁴ Only in the case of Qa and Qb do the quenching measurements (Figures 4 and 5) indicate a second minor route for trans \rightarrow cis photoisomerization bypassing the triplet state (see below).

Since $\phi_{t\rightarrow c}$ is quenched by azulene (ferrocene) via the observed triplet thereby shifting the photostationary state to the trans side, we suggest that only the trans (planar) triplet configuration is quenched to the ground state (eq 3). In analogy to stilbenes we assume also for azastilbenes that the energy of the twisted con-

⁽²⁵⁾ Görner, H.; Eaker, D. W.; Saltiel, J. J. Am. Chem. Soc. 1981, 103, 7164.

⁽²⁶⁾ Lazare, S.; Bonneau, R.; Lapouyade, R. J. Phys. Chem. 1984, 88, 18.

Quaternary Salts of 4-Nitro-4'-azastilbene

$${}^{3*}A_t^+ + \text{quencher} \xrightarrow{\kappa_q} A_t^+ + {}^{3}\text{quencher}^*$$
 (3)

figuration $({}^{3*}A_p^+)$ is too low for quenching by azulene or ferrocene.¹⁴⁻¹⁶ Energy transfer rather than electron transfer is proposed as the quenching mechanism since (i) the process is diffusion controlled (Table II), (ii) no new transient was observed, which could have been attributed to a product of an electron transfer, and (iii) the triplet energy of the quenchers is lower than that of the cation.^{2,12}

The dependences of $\phi_{t\to c}$ and τ_T on X⁻ in polar solvents can be described by a quenching reaction of ${}^{3*}A_t^+$ leading to A_t^+ . However, in addition to physical quenching by I electron transfer is involved²⁷⁻²⁹ as discussed in the subsequent article.²² Triplet quenching is suggested since for Pa the half-concentrations from quenching of $\phi_{t\to c}$ and τ_T are the same within experimental error (cf. ref 22, Table III). For Qa again a second route bypassing the triplet state has to be considered (see below).

Oxygen quenches the triplet state without shifting the photostationary state. A different quenching mechanism of the ${}^{3*}A_t$ \Rightarrow ³*A_p⁺ equilibrium accounts for this result. We assume that oxygen quenches the twisted configuration ³*A_p⁺ by an exchange mechanism similar to that for stilbene (eq 4).³⁰

$${}^{3*}A_{p}^{+} + O_{2} \xrightarrow{\kappa_{\alpha_{x}}} \alpha A_{t}^{+} + (1 - \alpha)A_{c}^{+} + O_{2}$$
(4)

So far the properties of the cation of P and Q are analogous to the case of 4-nitrostilbenes.¹⁴⁻¹⁶ However, there are two main differences between the two classes of compounds. First, photoinduced electron transfer from I- to an excited state of Pa and Qa occurs under suitable conditions.²² Second, a minor contribution from a trans \rightarrow cis photoisomerization pathway not involving the triplet equilibrium operates for nitrostyrylquinolinium salts (see next paragraph) which is absent for 4-nitrostilbenes.^{15,16}

Trans \rightarrow Cis Photoisomerization Not Involving the Triplet State. If trans \rightarrow cis photoisomerization would occur exclusively via the triplet route (eq 2), a linear Stern-Volmer plot would be expected for $\phi_{t\rightarrow c}$.⁹ Furthermore, the half-concentrations from quenching of $\phi_{t \rightarrow c}$ and τ_T should be identical. However, a downard curved dependence was obtained for Qa from a plot of $\phi_{t\to c}^{-1}$ vs. [quencher] (Figure 5). This effect corresponds to larger halfconcentrations obtained from quenching of $\phi_{t\rightarrow c}$ as compared to triplet quenching ([quencher]_{$\tau/2} = K_T^{-1}$; Table II). Therefore,</sub> the existence of a second pathway for trans \rightarrow cis photoisomerization, not involving the lowest triplet, is proposed for Qa and Qb. For Pa the contribution of this pathway is negligible. An alternative possibility is the assumption that the triplet equilibrium is also quenched to A_c^+ in significant quantity. However, when azulene (or ferrocene) is replaced by an electron donor (I⁻, SCN⁻, or amines), similar results were found. The half-concentrations for quenching of $\phi_{t \rightarrow c}$ and τ_T are different for Q on the one hand but similar for P on the other (cf. ref 22, Tables III and IV). For these additives a quenching step leading to the cis form is rather unlikely. This excludes quenching of ${}^{3*}A_p^+$ into A_c^+ and indicates a decay step of ${}^{1*}A_t^+$ bypassing the triplet equilibrium.

From the limiting values of $\phi_{t\rightarrow c}$ for Qa in methanol at [quencher] > 10^{-2} M (Figure 4) it is estimated that 65% of $1*A_t^+$ decays to ${}^{3*}A_t^+$ and that 35% bypasses the ${}^{3*}A_t^+ \rightleftharpoons {}^{3*}A_p$ equilibrium. This minor pathway may be twisting about the C=C double bond in the first excited singlet or in an upper excited triplet state. In the latter case deactivation to ${}^{3*}A_p^+$ would be expected. Since the triplet equilibrium is not populated by the minor pathway, an upper excited triplet pathway is unlikely and a singlet mechanism is assumed (Figure 9).

According to the mixed singlet-triplet mechanism, $\phi_{t \rightarrow c}$ is given by eq 9 (see Appendix). The results for Qa are in agreement with the proposed scheme by assuming $\alpha = \beta = 0.5$, $\phi_T = 0.65$, and

 $\phi_{\rm S} = 0.35$ and using values of $K_{\rm T}$ from Table II. In order to also account for fluorescence quenching, a value of $K_{\rm S} = 30 \ {\rm M}^{-1}$ was used.

Triplet quenching by Br⁻ and ClO₄⁻ plays practically no role since the quenching rate constant is more than 3 orders of magnitude below the diffusion-controlled limit (cf. ref 22, Table II). However, the mixed singlet-triplet mechanism for trans \rightarrow cis photoisomerization of Qa is supported by quenching measurements with I⁻ and SCN⁻. The plot of $\phi_{t\rightarrow c}$ vs. I⁻ cannot be fitted by assuming only a triplet mechanism. Again the proposed mixed mechanism and singlet and triplet quenching to $\overline{A_t}^+$ account for the results. The experimental points in Figure 6 can be fitted by the calculated curve using eq 9, $\phi_{\rm S} = 0.35$, $K_{\rm S} = 5$ M⁻¹, and $K_{\rm T}$ = 2400 M^{-1} . Examples of a mixed singlet-triplet mechanism for trans \rightarrow cis photoisomerization are rare. Evidence for this new mechanism has also been found for 4-nitro-4'-dimethylaminostilbene in nonpolar solvents.³¹

 $Cis \rightarrow Trans Photoisomerization$. For the cis \rightarrow trans photoisomerization pathway the following suggestions can be made. Since the fluorescence intensity decreases on increasing the amount of cis isomer without appearance of a new fluorescence, it is likely that the cis isomer does not fluoresce. This is analogous to the behavior of *cis*-stilbenes.¹²⁻¹⁵ Therefore, ${}^{1*}A_c^+$ should have a lifetime considerably shorter than that of ${}^{1*}A_t^+$ and intersystem crossing or internal conversion to a cis configuration is unlikely. Furthermore, a radiationless decay channel at the cis side $({}^{1*}A_{c})$ \rightarrow A_c⁺) plays no significant role since $\phi_{c \rightarrow t}$ is substantial (Table I). It is therefore proposed that ${}^{1*}A_c^+$ twists rapidly in the excited singlet into ${}^{1*}A_p^+$ which decays to A_t^+ and A_c^+ by internal conversion. Marked involvement of intersystem crossing at the twisted configuration ${}^{1*}A_{p}^{+} \rightarrow {}^{3*}A_{p}^{+}$ is unlikely since in this case the effect of quenching of $\phi_{t \rightarrow c}$ and of photostationary cis/trans ratios should result in different slope/intercept values (or half-concentrations). Evidence for this effect has been reported for 4-nitrostilbenes¹⁵ but was not found for Pa.

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Appendix

Assuming that trans \rightarrow cis photoisomerization occurs via two steps, one involving the observed triplet state and the other bypassing the triplet, $\phi_{t \rightarrow c}$ ° (in the absence of any additives) is given bv

$$\phi_{t \to c}^{\circ} = \phi_{T}(1 - \alpha) + \phi_{S}(1 - \beta)$$
(5)

Here, ϕ_T is the yield of triplet populated from ${}^{1*}A_t^+$, α is the fraction of triplet decaying to A_t^+ , and $\phi_S(1 - \beta)$ is the yield of A_c^+ after excitation of ${}^{1*}A_t^+$ and bypassing the triplet. If Q quenches only the triplet to A_t^+ (e.g. via step 3), $\phi_{t\to c}$ is given by

$$\phi_{t \to c} = \frac{\phi_{T}(1 - \alpha)}{1 + K_{T}[Q]} + \phi_{S}(1 - \beta)$$
(6)

 $K_{\rm T}$ is the product $\tau_{\rm T}^{\circ}s_{\rm q}$. For the equilibrium

$$3*A_t^+ \xrightarrow{k_1} 3*A_p^+$$

 $\tau_{\rm T}^{\circ}$ is given by

$$\tau_{\rm T}^{\,\circ} = (1 + K_1) / (K_1 k_{\rm p}) \tag{7}$$

Here, k_p is the rate constant for the step ${}^{3*}A_p^+ \rightarrow A_p^+$ and K_1 is the equilibrium constant $K_1 = k_1/k_{-1} = [{}^{3*}A_p^+]/[{}^{3*}A_t^+]$. Defining $s_q = k_q/(1 + K_1)$, K_T is given by k_q/K_1k_p , where k_q is the rate constant for quenching of ${}^{3*}A_t^+$ by Q (eq 3).¹⁵ If singlet quenching (eq 8) has to be taken into account

$${}^{1*}A_t^+ + Q \xrightarrow{k_q} A_t^+ + {}^{1}Q^* \text{ (or } Q)$$
(8)

⁽²⁷⁾ Treinin, A.; Hayon, E. J. Am. Chem. Soc. 1976, 98, 3884.

 ⁽²⁸⁾ Watkins, A. R. J. Phys. Chem. 1974, 78, 2555.
 (29) Skizuka, H.; Nakamura, M.; Morita, T. J. Phys. Chem. 1980, 84,

⁹⁸⁹

⁽³⁰⁾ Saltiel, J.; Thomas, B. Chem. Phys. Lett. 1976, 37, 147.

⁽³¹⁾ Görner, H., unpublished results.

$$\phi_{t \to c} = \frac{1}{1 + K_{\rm S}[Q]} \left[\frac{\phi_{\rm T}(1 - \alpha)}{1 + K_{\rm T}[Q]} + \phi_{\rm S}(1 - \beta) \right]$$
(9)

Here, $K_{\rm S} = \tau_{\rm S} k_{\rm q}'$ is the Stern-Volmer constant for fluorescence quenching and $\tau_{\rm S}$ the fluorescence lifetime. The dependence of $\phi_{t\to c}^{\circ}/\phi_{t\to c}$ on [Q] is given by

$$\frac{\phi_{t \to c}^{\circ}}{\phi_{t \to c}} = \frac{[\phi_{T}(1 - \alpha) + \phi_{S}(1 - \beta)](1 + K_{T}[Q])(1 + K_{S}[Q])}{\phi_{T}(1 - \alpha) + \phi_{S}(1 - \beta)(1 + K_{T}[Q])}$$
(10)

If fluorescence quenching may be neglected $(K_S[Q] \le 1)$ and if the triplet mechanism is the only pathway for trans \rightarrow cis photoisomerization (i.e. $\phi_{\rm S} = 0$), a linear Stern-Volmer dependence is predicted from eq 10.

It should be noted that eq 10 is in accordance with the scheme of two trans \rightarrow cis pathways even if no triplet equilibrium between planar and twisted configurations is present (e.g. $k_{-1} \ll k_{p}$). If ${}^{3*}A_t^+$ is quenched by Q to A_t^+ , τ_T° and s_q may be replaced by $1/k_1$ and k_q , respectively. On the other hand, if only ${}^{3*}A_p^+$ is quenched by Q to A_t^+ , τ_T° and s_q may be replaced by $1/k_p$ and k_{a} , respectively.

Registry No. Dabco, 280-57-9; DMA, 121-69-7; DEA, 91-66-7; TEA, 121-44-8; cis-Pa, 97135-70-1; trans-Pa, 25565-20-2; cis-Pb, 97135-72-3; trans-Pb, 93661-87-1; cis-Qa, 97135-73-4; trans-Qa, 38146-54-2; cis-Qb, 97135-75-6; trans-Qb, 97135-69-8; KI, 7681-11-0; KBr, 7758-02-3; KSCN, 333-20-0; O₂, 7782-44-7; ferrocene, 102-54-5; azulene, 275-51-4.

Photoinduced Electron Transfer vs. Trans \rightarrow Cis Photoisomerization for Quaternary Salts of 4-Nitro-4'-azastilbene and Their Quinolinium Analogues. 7

Helmut Görner

Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim a.d. Ruhr, West Germany (Received: January 2, 1985)

Electron transfer from anions and amines to electronically excited quaternary salts of trans-4-nitro-4'-azastilbene and their quinolinium analogues ($A_t^+X_-$) was studied in competition to trans \rightarrow cis photoisomerization. The spectra, yields, and decay kinetics of the triplet state and of an intermediate free radical (A·) were determined by laser flash photolysis. Radical A·, the one-electron-reduction product of A_t^+ , was spectroscopically identified by pulse radiolysis. The quantum yield of trans \rightarrow cis photoisomerization ($\phi_{t\rightarrow c}$) was measured as a function of the concentration of additives, solvent polarity, and temperature. Three processes are distinguished: electron transfer (i) from an amine (e.g. DABCO, triethylamine, or N,N-dimethylaniline) to the trans triplet state of the free cation $({}^{3*}A_t^+)$, (ii) from I⁻ or SCN⁻ to ${}^{3*}A_t^+$, and (iii) from I⁻ to the cation in the excited singlet state of the ion pair. Since A reacts back mainly to the trans form, $\phi_{t \rightarrow c}$ is reduced by electron transfer. In some cases (e.g. (i) with DABCO) the yield of A and $1 - \phi_{t \rightarrow c}$ are correlated, and in others (e.g. (ii)) triplet quenching occurs virtually without formation of A.

Introduction

Quaternary salts of styrylpyridinium and -quinolinium (stilbazolium salts) are suitable examples for the study of the role of a positive charge at the molecule on the cis \Rightarrow trans photoisomerization.¹⁻⁷ In preceding papers it has been shown that in polar solvents the trans \rightarrow cis photoisomerization of the quaternary iodide and perchlorate of 4-nitrostyryl-4'-pyridinium (Pa and Pb, respectively) occurs via a triplet mechanism.^{6,7} For the quaternary iodide and methosulfate of 4-nitrostyryl-4'-quinolinium (Qa and Qb, respectively), a singlet pathway contributes to a minor extent in addition to the main triplet pathway.7 In solvents of moderate polarity, where ion pairs are formed,⁴ the quantum yield of trans cis photoisomerization $(\phi_{t\rightarrow c})$ is efficiently reduced for the iodides (Pa and Qa) and a second transient (Tr_R) is photolytically observed.⁷ This points to a photoinduced electron-transfer process from I⁻ to the excited cation of the ion pair.

Photoinduced electron transfer from a donor (D) to an excited aromatic compound has attracted considerable attention.⁸⁻¹⁵ In

- (1) Güsten, H.; Schulte-Frohlinde, D. Tetrahedron Lett. 1970, 3567. (2) Güsten, H.; Schulte-Frohlinde, D. Chem. Ber. 1971, 104, 402.
- (3) Schulte-Frohlinde, D.; Güsten, H. Liebigs Ann. Chem. 1971, 749, 49.
- (4) Güsten, H.; Schulte-Frohlinde, D. Z. Naturforsch., B: Anorg. Chem., Org. Chem. 1979, 34B, 1556. (5) Takagi, K.; Ogata, Y. J. Org. Chem. 1982, 47, 1409. Takagi, K.; (5) Takagi, K.; Ogata, Y. J. Org. Chem. Soc. 1985, 107, 47
- Aoshima, K.; Sawaki, Y.; Iwamura, H. J. Am. Chem. Soc. 1985, 107, 47.
 (6) Görner, H.; Schulte-Frohlinde, D. Chem. Phys. Lett. 1983, 101, 79.
- (7) Görner, H.; Schulte-Frohlinde, D. J. Phys. Chem., preceding article in this issue.
- (8) Leonhardt, H.; Weller, A. Ber. Bunsenges. Phys. Chem. 1963, 67, 791. Rehm, D.; Weller, A. Ibid. 1969, 73, 834; Isr. J. Chem. 1970, 8, 259.
- (9) Weller, A. Pure Appl. Chem. 1982, 54, 1885; Z. Phys. Chem. (Munich) 1982, 130, 129.

these studies a radical ion pair is produced from neutral molecules. Formation of exciplexes between amines and stilbene-like molecules has been studied by the groups of Lewis and Mazzucato.¹³⁻¹⁵ These and many other studies deal mainly with charge-transfer interactions in excited singlet states.¹³⁻¹⁸ Electron transfer in the triplet state has been investigated for acridine dyes and derivatives.¹⁹⁻²¹ In these studies a radical and D⁺ are produced from a cation and D.

For quinolinium salts Briegleb et al. have reported on a CT absorption and a CT fluorescence.²² For pyridinium iodides Kosower et al. have investigated the effect of solvent polarity on

- (10) Gordon, M.; Ware, W. R. "The Exciplex"; Academic Press: New York, 1975.
- (11) Mataga, N.; Ottolenghi, M. In "Molecular Assocation"; Forster, R., Ed.; Academic Press: London, 1979; Vol. 2, p 1.
- (12) Chibisov, A. K. Russ. Chem. Rev. (Engl. Transl.) 1981, 50, 615. (13) Hub, W.; Schneider, S.; Dörr, F.; Simpson, J. T.; Oxman, J. D.; Lewis, F. D. J. Am. Chem. Soc. 1982, 104, 2044.
- (14) Hub, W.; Schneider, S.; Dörr, F.; Oxman, J. D.; Lewis, F. D. J. Am. Chem. Soc. 1984, 106, 701, 708.
- (15) Aloisi, G. G.; Bartocci, G.; Favaro, G.; Mazzucato, U. J. Phys. Chem. 1980, 84, 2020. Aloisi, G. G.; Mazzucato, U.; Birks, J. B.; Minuti, L. J. Am. Chem. Soc. 1977, 99, 6340.
- (16) Mazzucato, U.; Aloisi, G. G.; Masetti, F. J. Photochem. 1982, 18,
- (17) Mazzucato, O., Mosa, O. G., Massell, F. J. Photochem. 1962, 16, 211. Bartocci, G.; Mazzucato, U.; Bortolus, P. Ibid. 1976/77, 6, 309.
 (17) Mazzucato, U. Pure Appl. Chem. 1982, 54, 1705.
 (18) Iwa, P.; Steiner, U.; Vogelmann, E.; Kramer, H. E. A. J. Phys. Chem. 1982, 86, 1277.
- (19) Steiner, U.; Winter, G.; Kramer, H. E. A. J. Phys. Chem. 1977, 81,
- (20) Steiner, U.; Winter, G. Chem. Phys. Lett. 1978, 55, 364

- (21) Winter, G.; Steiner, U. Ber. Bunsenges. Phys. Chem. 1980, 84, 1203.
 (22) Briegleb, G.; Jung, W.; Herre, W. Z. Phys. Chem. (Munich) 1963, 38, 253. Briegleb, G.; Herre, W.; Jung, W.; Schuster, H. Ibid. 1965, 45, 229.