

PHOTOPHYSICAL PROPERTIES OF QUATERNARY SALTS OF 4-DIALKYLAMINO-4'-AZASTILBENES AND THEIR QUINOLINIUM ANALOGUES IN SOLUTION: IX[†] ‡

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Summary

The decay processes of excited quaternary salts of *trans*-1-alkyl-4-[4-dialkylaminostyryl]-pyridinium and *trans*-1-alkyl-4-[4-dialkylaminostyryl]-quinolinium ($A_t^+X^-$; $X^- \equiv \Gamma^-$ or ClO_4^-) were studied by pulse and steady state methods as a function of temperature, quenchers (ferrocene and azulene) and solvent polarity. Introduction of the dialkylamino group markedly reduces the quantum yield $\phi_{t \rightarrow c}$ of *trans* \rightarrow *cis* photoisomerization and slightly enhances the quantum yield ϕ_f of fluorescence. In polar solvents deactivation of the first excited singlet $^1A_t^+$ predominantly by internal conversion via an activated step is suggested by the temperature dependence of ϕ_f and a low yield for intersystem crossing. In solvents of moderate polarity (e.g. dichloromethane) a major short-lived transient (Tr_T) ($\lambda_{max} \approx 400$ nm, ≥ 700 nm; $\tau_T \approx 1 - 10 \mu s$) and a minor long-lived transient (Tr_R) ($\lambda_{max} \approx 400$ nm; $t_{1/2} > 10 \mu s$) were observed for the iodides by laser flash photolysis. Pulse radiolysis studies permit the assignment of Tr_R to a radical A^\cdot . Tr_T , which was also observed for iodides and perchlorates in polar solvents either on addition of excess Γ^- or on sensitized excitation, is assigned to the lowest triplet state $^3A_t^+$ of the *trans* configuration. On the basis of results from energy transfer experiments with a range of sensitizers, the energy of $^3A_t^+$ is estimated to be 180 kJ mol^{-1} and 165 kJ mol^{-1} for the pyridinium and quinolinium salts respectively. In solvents of moderate polarity Tr_T is assigned to the triplet state ($^3A_t^+ \dots \Gamma^-$) of the ion pair, the population of which is enhanced by the heavy atom effect.

1. Introduction

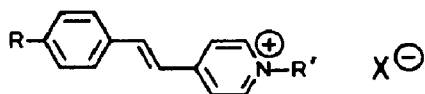
Quaternization of styrylpyridines or styrylquinolines introduces a positive charge into a stilbene-like molecule. The thermal *cis* \rightarrow *trans* and

[†]Dedicated to Professor Dr. Dietrich Schulte-Frohlinde on the occasion of his 60th birthday.

[‡]Papers V-VIII of this series on *cis-trans* isomerization of stilbazolium salts are published as refs. 1 - 4.

the photochemical *trans* → *cis* isomerization of some stilbazolium salts have been investigated in previous work [1 - 10]. The pathway of *trans* → *cis* photoisomerization changes from a singlet mechanism to a triplet mechanism when the substituent in the 4-position of the styrene ring ($R \equiv H, CH_3, OCH_3$ or CN) is replaced by the nitro group [1, 4]. In both cases the quantum yield $\phi_{t \rightarrow c}$ of *trans* → *cis* photoisomerization is substantial in polar solvents at ambient temperature. However, introduction of a dialkylamino group in the 4-position reduces $\phi_{t \rightarrow c}$ significantly [5]. An analogous effect has been reported for 4-nitrostilbenes [11 - 15]. Solvent polarity has a marked influence on the photophysical and photochemical properties of *trans*-4-nitro-4'-dialkylaminostilbenes [11 - 18]. For 4-nitro-4'-dimethylaminostilbene in polar solvents it has been suggested that the reduction of $\phi_{t \rightarrow c}$ is due to internal conversion at the *trans* configuration [13 - 15].

In the present work the primary photophysical relaxation steps of quaternary salts of 4-styrylpyridinium (P) and 4-styrylquinolinium (Q) substituted at the 4-position of the styrene ring by a dimethylamino or diethylamino group were studied. The following compounds were selected:

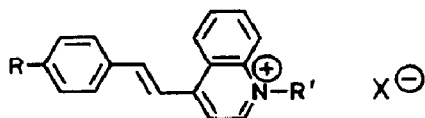


Pa: $R \equiv N(CH_3)_2, R' \equiv CH_3, X^- \equiv I^-$

Pb: $R \equiv N(CH_3)_2, R' \equiv CH_3, X^- \equiv ClO_4^-$

Pc: $R \equiv N(CH_3)_2, R' \equiv C_2H_5, X^- \equiv I^-$

Pd: $R \equiv N(CH_3)_2, R' \equiv C_2H_5, X^- \equiv I^-$



Qa: $R \equiv N(CH_3)_2, R' \equiv CH_3, X^- \equiv I^-$

Qb: $R \equiv N(CH_3)_2, R' \equiv CH_3, X^- \equiv ClO_4^-$

In order to obtain a better understanding of the decay mechanism of the excited states the fluorescence and *trans* → *cis* photoisomerization processes were analysed. Transients observed by laser flash photolysis and pulse radiolysis are assigned to a triplet state and a radical; their involvement in the decay mechanism is discussed. In contrast with analogous compounds substituted by an electron-accepting group ($R \equiv CN$ or NO_2) [2 - 4], the presence of I^- in the ion pair leads mainly to heavy-atom-enhanced inter-system crossing rather than to photoinduced electron transfer for $R \equiv N(CH_3)_2$.

2. Experimental details

2.1. Apparatus and procedure

Steady state irradiation measurements and the determination of $\phi_{t \rightarrow c}$ were carried out as described previously [2, 4]. The absorption spectra were recorded on a spectrophotometer (Perkin-Elmer 554). Corrected fluorescence spectra at 25 and -196 °C were recorded on a computer-controlled Spex-Fluorolog spectrofluorometer with photon-counting detection. Temperature-dependent spectra were recorded on another fluorometer (Perkin-Elmer MPF 2A) [4, 19]. 9,10-Diphenylanthracene (EGA) and rhodamine 101 (Lambda Physik) were used as fluorescence standards [20]. Sensitized irradiation at $\lambda_{\text{irr}} \leq 400$ nm unavoidably excited the salts to a certain extent (10% or less) at the same time since the absorption spectra of the salts extend into the visible range ($\lambda_t = 470 - 530$ nm in acetonitrile). In a typical experiment the concentrations of sensitizer and acceptor were adjusted such that the total absorbance (1 cm cell) was 10 at 366 nm and 1 at λ_t .

The second and third harmonics (530 nm and 353 nm respectively) of a neodymium laser (J. K. Lasers) were used in conjunction with an appropriate transient detection system [1 - 4, 21]. The conventional flash photolysis [22] and pulse radiolysis (3 MeV Van de Graaff accelerator) [23] systems were essentially the same as described. The coefficient for triplet-triplet (T-T) absorption was obtained from the ratio of the absorbances of the sensitizers (at 20 ns) to those of the salts (after 100 ns) using known ϵ_{TT} values for the sensitizers. Unless indicated otherwise (*e.g.* temperature-dependent fluorescence measurements and quenching of the short-lived transient by oxygen), the samples were purged with argon. Data analysis and treatment of the samples was as described in previous papers [1 - 4].

2.2. Materials

Trans isomers of 1-methyl-4-[4-dimethylaminostyryl]-pyridinium (Pa), 1-ethyl-4-[4-dimethylaminostyryl]-pyridinium (Pc), 1-ethyl-4-[4-diethylaminostyryl]-pyridinium (Pd) iodides and 1-methyl-[4-dimethylaminostyryl]-quinolinium iodide (Qa) were purchased commercially (EGA) and recrystallized from methanol-water. The perchlorates (Pb and Qb) were prepared from the iodides by treatment with AgClO_4 . The melting points were as follows: Pa, 260 - 263 °C; Pb, 226 - 230 °C; Pc, 244 - 246 °C; Pd, 227 - 230 °C; Qa, 286 - 288 °C; Qb, 207 - 212 °C. Most sensitizers were used as in previous studies [21]; xanthone (EGA), benzophenone (EGA), 2-acetonaphthone (Eastman), 2-nitronaphthalene (K and K Lab), 9-fluorenone (Fluka), acridine (Fluka), anthracene (EGA) and 9,10-dibromoanthracene (EGA). The additives and solvents were essentially the same as those used in recent work [2 - 4].

3. Results

3.1. Absorption spectra and steady state irradiation

Substitution of quaternary salts of 4-R-4'-azastilbene ($R \equiv H$) by the dimethylamino group shifts the absorption maximum λ_t of the *trans* isomer from the UV (about 350 nm) [4] to the red (about 450 - 510 nm (Table 1)). Replacement of the pyridinium ring by the quinolinium ring shifts λ_t to longer wavelengths (about 500 - 580 nm). The iodides and the corresponding perchlorates exhibit essentially the same absorption spectra in a given solvent. On increasing the solvent polarity λ_t generally tends to be

TABLE 1

Absorption and fluorescence maxima $\phi_{t \rightarrow c}$ and ϕ_f ^a

Compound	Solvent	λ_t (nm)	$\phi_{t \rightarrow c}$ ^b	(<i>cis</i>) _s content ^b (%)	λ_f (nm)	ϕ_f ^b
Pa	Tetrahydrofuran	≈ 486		< 5		0.02
	Dichloromethane	512	≤ 0.01 ^c	8 ^c	611	0.02
	Dimethylformamide	466	< 0.005	≤ 2	614	0.003
	Sulpholane	474	< 0.002	≤ 1		
	Acetonitrile	469	< 0.005	3	614	0.001
	Ethanol	475			612	0.006
	Methanol	473	< 0.002	3		
	Water	445	< 0.001	< 2	615	≤ 0.001
Pb	Dichloromethane	512	< 0.01 ^c	8 ^c	611	0.02
	Ethanol	474	< 0.005	3	609	0.006
Pc	Dichloromethane	510			613	0.02
	Ethanol	475			612	0.005
Pd	Dichloromethane	528	< 0.01	5	615	0.015
	Ethanol	486	< 0.002	2	614	0.005
	Water	466			620	≤ 0.002
Qa	Tetrahydrofuran	≈ 542			≈ 670	
	Dichloromethane	582	≤ 0.005	6	688	0.03
	Dimethylformamide	536	≤ 0.005	< 2	680	0.005
	Sulpholane	540	≤ 0.002			
	Acetonitrile	533	≤ 0.002	< 2	682	0.002
	Ethanol	544	< 0.002	< 2	682	0.01
	Water	506	< 0.001	< 2	670	0.002
Qb	Dichloromethane	582	< 0.01	8	680	0.03
	Ethanol	542	< 0.005	≤ 3	≈ 680	0.02

^a*trans*-Isomers in argon- and air-saturated solutions for measurements of $\phi_{t \rightarrow c}$ ($(2.5) \times 10^{-5}$ M) and ϕ_f ($< 2 \times 10^{-5}$ M) at 25 °C; errors in λ_t and λ_f are ± 1 nm and about 3 nm respectively; water at pH 7.

^bUnless otherwise indicated λ_{irr} is 436 nm for P and 546 nm for Q.

^cUsing $\lambda_{irr} = 546$ nm; (*cis*)_s is smaller for λ_{irr} values of 366 nm and/or 436 nm.

blue shifted, *e.g.* for Pa from about 512 nm in dichloromethane to 445 nm in water (Table 1). Whereas λ_t is independent of concentration in polar solvents (*e.g.* a change of less than 2 nm for Pa or Qa in methanol for a concentration range of $(0.2 - 50) \times 10^{-5}$ M), λ_t is blue shifted on increasing the concentration in solvents of moderate polarity. For example, for Pa in dichloromethane λ_t ranges from 500 nm (5×10^{-4} M) to 520 nm (2×10^{-6} M), and for Qa in the same solvent λ_t ranges from 565 nm (2×10^{-6} M) to 587 nm (5×10^{-4} M). Virtually the same effect was found for the corresponding perchlorates.

Substitution by a dialkylamino group in the 4-position markedly reduces $\phi_{t \rightarrow c}$ and leads to a shift of the photostationary state at room temperature to a (*cis*)_s content of less than 8% (Table 1) compared with at least 70% for R \equiv H [4]. Variation of the solvent and replacement of I⁻ by ClO₄⁻ as the anion (Pa *versus* Pb) has no significant effect on the (*cis*)_s content. This pattern was found for all compounds examined (Table 1). In dimethylformamide at higher temperatures (*e.g.* above about 70 °C) $\phi_{t \rightarrow c}$ and the (*cis*)_s content increase markedly. Formation of the *cis* isomer is confirmed by observation of the reversible back reaction (thermal *cis* \rightarrow *trans* isomerization). For Pa and Qa an isosbestic point was observed at λ_i values of about 415 nm and about 480 nm respectively. However, no photostationary state is reached since on prolonged irradiation the compounds decompose. A much smaller change in the absorption spectrum (less than 5% at λ_t) and no decomposition was found for Pa in sulpholane at 80 - 100 °C.

3.2. Fluorescence spectra and yield

In all solvents used the compounds exhibit emission in the red spectral region. Owing to its short lifetime, the emission (observed within the laser pulse, *i.e.* lifetime less than 20 ns) is attributed to fluorescence rather than phosphorescence (*cf.* refs. 2 and 4). At room temperature the fluorescence maximum λ_f is almost independent of the nature of the anion and the excitation wavelength, and is only slightly dependent on the solvent polarity. The λ_f value for the quinolinium salts is red shifted compared with λ_f for the pyridinium salts (Table 1). For example, Stokes shifts $\bar{\nu}_t - \bar{\nu}_f$ of 3.0×10^3 cm⁻¹ and 6.2×10^3 cm⁻¹ were obtained for Pa in dichloromethane and aqueous solutions respectively. The Stokes shift is believed to reflect the effect of the solvent on the ground state energy rather than on the energy of the fluorescing state (*cf.* values in Table 1).

For Pa and Qa in ethanol solutions the fluorescence maximum undergoes a blue shift on going from 25 to -196 °C (Fig. 1). This effect is attributed to the hindrance of reorientation in frozen solutions and has also been observed for other stilbazolium salts (R \equiv H, CN and NO₂) [2, 4]. The maxima of the fluorescence excitation and absorption spectra, which almost coincide, show a small red shift on going from 25 to -196 °C. Temperature-dependent λ_f values indicate the similarity of the effect of temperature (viscosity) for perchlorates and iodides (Table 2). Whereas in ethanol $\bar{\nu}_f$ increases monotonically on decreasing the temperature (Fig. 2), in a 1:1 mix-

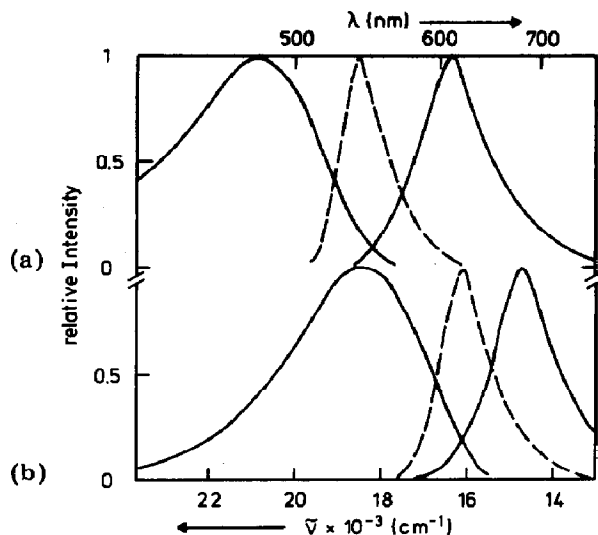


Fig. 1. Fluorescence emission and excitation spectra in ethanol solutions at 25 °C (—) and -196 °C (---) for (a) Pa and (b) Qa.

TABLE 2

Activation energy, λ_f and ϕ_f ^a

Compound	Solvent	E_v (kJ mol ⁻¹)	λ_f (nm)		ϕ_f ^b	
			25 °C	-196 °C	25 °C	-196 °C
Pa	M-D	8	614	540	0.02	0.8
	Dichloromethane	14	611		0.02	
	Ethanol	13	612	540	0.006	0.8
Pb	M-D	8	612	542	0.02	0.8
	Ethanol	17	609	540	0.006	0.8
Pd	Ethanol	14	614	546	0.005	0.8
Qa	M-D	8	685	622	0.03	0.8
	Dichloromethane	15	688		0.03	
	Ethanol	13	682	620	0.01	0.8
Qb	M-D	9	680	621	0.03	0.9

^aIn air-saturated solutions ($\lambda_{exc} \approx \lambda_f$).

^bExperimental error, $\pm 30\%$.

ture of 2-methyltetrahydrofuran and dichloromethane (M-D) $\tilde{\nu}_f$ decreases slightly between 25 and -130 °C and increases rapidly on further cooling (Fig. 3). Different temperature dependences of $\tilde{\nu}_f$ in *n*-butyl alcohol and 2-methyltetrahydrofuran have also been reported for *trans*-4-cyano-4'-dimethylaminostilbene [19].

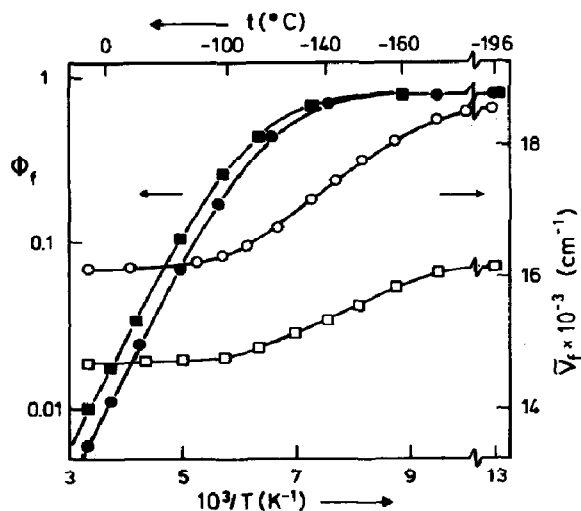


Fig. 2. Semilogarithmic plots of ϕ_f (\bullet , \blacksquare) and $\tilde{\nu}_f$ (\circ , \square) vs. T^{-1} for Pa (\bullet , \circ) and Qa (\blacksquare , \square) in ethanol solutions.

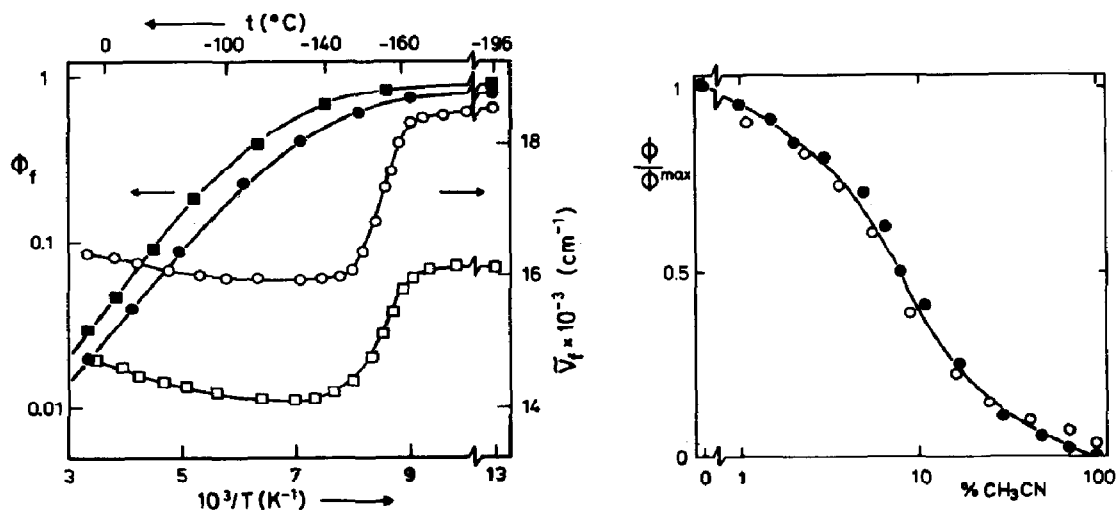


Fig. 3. Semilogarithmic plots of ϕ_f (\bullet , \blacksquare) and $\tilde{\nu}_f$ (\circ , \square) vs. T^{-1} for Pb (\bullet , \circ) and Qb (\blacksquare , \square) in M-D.

Fig. 4. Plots of ϕ_f (\circ) and ϕ_T (\bullet) as functions of the percentage of acetonitrile in dichloromethane solutions for Pa at 25 °C.

In solution at room temperature the quantum yield ϕ_f of fluorescence lies between about 1×10^{-3} and 3×10^{-2} . For both iodides and perchlorates ϕ_f values show a decreasing trend on increasing the solvent polarity (Table 1). This is illustrated in Fig. 4 for Pa in solvent mixtures of dichloromethane and acetonitrile. This effect contrasts with the results obtained for other stilbazolium salts where it was found that ϕ_f for iodides in solvents of moderate polarity is generally smaller than that for iodides in polar solvents [2, 4]. Formation of ion pairs may account for this effect (see Section 4).

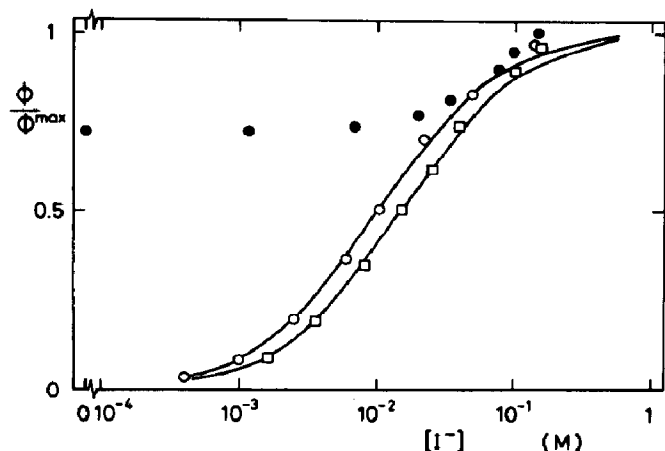


Fig. 5. Plots of ϕ_f (●) and ϕ_T (○, □) as functions of $\log [I^-]$ for Pa (●, ○) and Qa (□) in acetonitrile solutions at 25 °C.

Changing the substituent at the phenyl or pyridinium ring (Pa, Pc and Pd), changing the anion (Pa versus Pb) or replacing the pyridinium by the quino-
linium ring (P versus Q) has only a minor effect on ϕ_f (Table 1).

Temperature-dependent ϕ_f measurements were carried out for Pa in ethanol and M-D (Figs. 2 and 3 respectively). On decreasing the temperature ϕ_f increases from 0.03 or less and approaches values close to unity at -196 °C (Table 2). The temperature dependence of ϕ_f was evaluated according to the following equation by introducing an activated step competing with fluorescence (rate, k_f) and a second non-activated step (rate, k_0):

$$\phi_f = \frac{k_f}{k_f + k_0 + A_\nu \exp(-E_\nu/RT)} \quad (1)$$

Activation energies E_ν between 8 and 17 kJ mol⁻¹ (Table 2) were obtained from linear plots of $\log(\phi_f^{-1} - 1)$ versus T^{-1} (at higher temperatures). A similar analysis yielding comparable E_ν values has been carried out for other substituted stilbazolium salts (e.g. R ≡ H, OCH₃ and CN) [4]. The ratio A_ν/k_f is 1.2×10^3 for Pb in M-D and 3×10^4 for Pa in ethanol. Pre-exponential factors of the order of 10^{12} s⁻¹ are obtained by using estimated k_f values from absorption and emission spectra [4].

On increasing the iodide concentration ϕ_f increases slightly for Pa and Qa in acetonitrile solutions at room temperature (Fig. 5). This is surprising since for analogous compounds with R ≡ CN and NO₂ fluorescence quenching has been found on addition of a variety of electron donors [2 - 4]. When I⁻ is replaced by ClO₄⁻ the increase in ϕ_f is larger. For an explanation, the role of ion pairs at high concentrations of X⁻ has to be considered (see Section 4).

3.3. Sensitized steady state irradiation

It was found that irradiation of a number of sensitizers (e.g. xanthone, benzophenone and anthracene) in the presence of Pa, Pb or Qb resulted in

decomposition of the salts rather than *trans* → *cis* photoisomerization. For example, in argon-saturated acetonitrile solutions of benzophenone and Pb the absorption of the cation was bleached (more than 50%) within 10 min of irradiation at 366 nm. The decomposition was not observed for stilbazolium salts which were not substituted by a dialkylamino group [4]. For some sensitizers (e.g. 2-nitronaphthalene and 2-acetonaphthone) an isosbestic point was clearly observable and the bleaching was only found after prolonged irradiation (more than 30 min). Examination of the spectra gave λ_t values of about 415 nm and 480 nm for Pb and Qb respectively; the maximum of the photoproduct is blue shifted by more than 5 nm and the molar absorption coefficient is less than $0.6\epsilon_t$, as expected for *trans* → *cis* photoisomerization. The yield for the 2-nitronaphthalene–Pb system is less than 10% of that observed for the corresponding stilbazolium salt with $R \equiv OCH_3$ [4].

3.4. Transients

The following methods of pulsed excitation were used in view of recent studies of quaternary salts of *trans*-4-R-4'-azastilbene ($R \equiv NO_2$ and CN) [2, 4]: direct laser excitation ($\lambda_{exc} = 353$ and/or 530 nm) in (i) solvents of moderate polarity and (ii) polar solvents in the presence of high concentrations of SCN^- or I^- ; (iii) sensitized laser excitation ($\lambda_{exc} = 353$ nm) in polar solvents; (iv) pulse radiolysis.

3.4.1. Transients in solvents of moderate polarity

The transient absorption spectra of Pa in dichloromethane solutions at room temperature taken 20 ns and 1 μs after the laser pulse ($\lambda_{exc} = 530$ nm) show two absorption bands, one on each side of the ground state absorption spectrum, and bleaching (maximum, λ_b) around λ_t (Fig. 6(a)). Each absorption band consists of a short-lived transient (Tr_T) and a long-lived transient

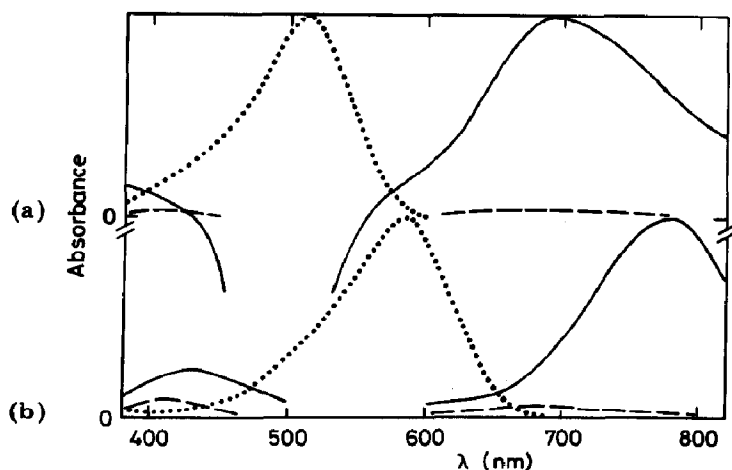


Fig. 6. Transient absorption spectra of (a) Pa and (b) Qa in dichloromethane solutions at 25 °C plotted 20 ns (—) and 2 μs (---) after the laser pulse ($\lambda_{exc} = 530$ nm); the ground state absorption spectra (.....) are also shown.

TABLE 3

Absorption maximum and lifetime of Tr_T ^a

Compound	Solvent	Additive	Method	λ_{max} (nm)	τ_T (μs)
Pa	Tetrahydrofuran	None	(i)	< 400, 700	
	Dichloromethane	None	(i)	360, 690	0.8(50) ^b
	Acetonitrile	Γ^- (0.05 M)	(ii)	370, 680	4
	Water	Γ^- (0.01 M)	(ii)	400, 710	10
Pb	Dichloromethane	None	(i)	— ^c	
Pc	Dichloromethane	None	(i)	380, 700	1
	Acetonitrile	Γ^- (0.02 M)	(ii)	690	5
Pd	Dichloromethane	None	(i)	390, \approx 740	2
	Acetonitrile	Γ^- (0.02 M)	(ii)	720	5
Qa	Chloroform	None	(i)	430, 780	4
	Dichloromethane	None	(i)	430, 780	0.2(20)
	Acetonitrile	Γ^- (0.02 M)	(ii)	410, 760	1
Qb	Dichloromethane	None	(i)	— ^c	

^a In argon-saturated solutions ($(0.5 - 5) \times 10^{-4}$ M) at 25 °C with $\lambda_{\text{exc}} = 530$ nm unless indicated otherwise.

^b Values in parentheses were obtained by conventional flash photolysis (concentrations $< 3 \times 10^{-5}$ M).

^c $\Delta A < 0.01$.

(Tr_R); the latter has a much smaller absorbance ΔA . When the ΔA of Tr_R (observed after more than about 5 μs) is subtracted from the total ΔA (if necessary), the decay of Tr_T is found to be first order. First-order rate constants ($k_{\text{obsd}} = \tau_T^{-1}$) for the decay of Tr_T (monitored at $\lambda_{\text{max}} = 370$ and 680 nm) and the recovery (monitored at $\lambda_b \approx 500$ nm) were found to be identical within experimental error. When concentrations of typically $(1 - 10) \times 10^{-4}$ M were used in laser experiments lifetimes shorter than 5 μs were found, whereas longer lifetimes ($\tau_T \geq 20$ μs) were obtained with conventional flash photolysis using lower concentrations (Table 3). The two concentration ranges can be compared since no second-order reaction was found for Tr_T even at the highest concentrations used.

The spectra and lifetimes for Tr_T of the other pyridinium iodides (Pa, Pc and Pd) are quite similar (Table 3). For Qa, λ_{max} is red shifted (Fig. 6(b)). Similar results were found for the iodides in chloroform and tetrahydrofuran (if the compound was sufficiently soluble). However, for Pb and Qb almost no transient was found. At high concentrations and laser intensities an absorption spectrum similar to Tr_T but with a much lower ΔA was detected; the presence of trace amounts of iodide in the perchlorates could account for the appearance of Tr_T . Owing to the low ΔA for Tr_R the half-life $t_{1/2}$ could only be estimated (Table 4).

TABLE 4
Absorption maxima of Tr_R and Tr'_R ^a

Compound	Solvent	Method ^b	λ_{max} ^c (nm)	λ_b ^c (nm)	$t_{1/2}$ (μs)
Pa	Tetrahydrofuran ^d	(iv)	340, 410, > 600	495	> 20
	Dichloromethane	(i)	400, 640		> 10
	Acetonitrile	(iv)	430, \approx 600	490	> 10
	Water	(iv)	420, 640	480	> 20
Pb	Water	(iv)	420, 630	480	> 10
Pd	Tetrahydrofuran ^d	(iv)	430, > 650	500	> 100
	Water	(iv)	430, \geq 630	480	> 100
Qa	Tetrahydrofuran ^d	(iv)	400, 490, \approx 700	550	> 500
	Dichloromethane	(i)	410, 680		> 5
	Water	(iv)	400, 500, 700	540	> 500
Qb	Tetrahydrofuran ^d	(iv)	410, 480, \approx 700	560	> 50

^aAt 25 °C in argon-saturated solutions unless indicated otherwise.

^bMethods (i) and (iv) using laser flash photolysis ($\lambda_{\text{exc}} = 530 \text{ nm}$; $(0.5 - 5) \times 10^{-4} \text{ M}$) and pulse radiolysis ($\leq 3 \times 10^{-5} \text{ M}$) respectively.

^cExperimental error, $\pm 5 \text{ nm}$.

^dIn air-saturated solutions.

Whereas the formation and decay of Tr_R are not discernibly affected by oxygen, τ_T is reduced. For example, lifetimes of 300 ns and 60 ns were observed for Pa in air- and oxygen-saturated dichloromethane solutions respectively at 25 °C. From a linear plot of k_{obsd} versus $[\text{O}_2]$ a slope of $k_{\text{ox}} = 2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was determined using $[\text{O}_2] = 1.6 \times 10^{-3} \text{ M}$ for air-saturated solutions. The decay of Tr_T is also quenched by ferrocene and azulene. From linear plots of k_{obsd} versus [ferrocene] or [azulene] slopes of $k_{\text{fe}} = 6 \times 10^9$ and $k_{\text{az}} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ were determined for Pa, i.e. the quenching rate constants are close to the diffusion-controlled limit. Similar results were also found for other iodides in dichloromethane (Table 5). For Qa, however, k_q is significantly smaller for azulene than for ferrocene.

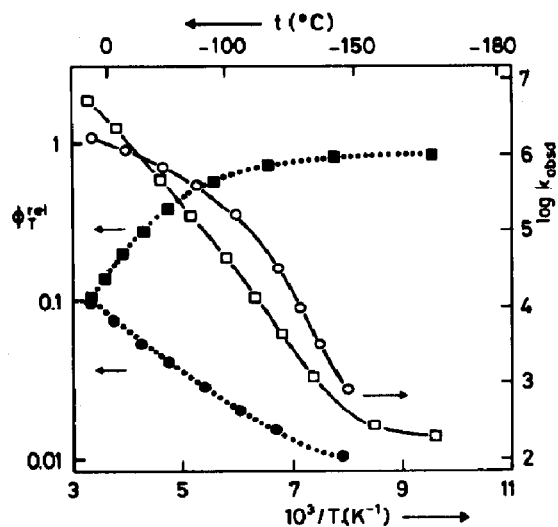
The temperature dependence of the formation and decay of Tr_T was measured in M-D (Fig. 7). On decreasing the temperature k_{obsd} decreases; from the linear parts of the plots of $\log k_{\text{obsd}}$ versus T^{-1} activation energies E_T of 15 kJ mol^{-1} and 13 kJ mol^{-1} were obtained for Pa and Qa respectively. When it is assumed that ΔA (at λ_{max} in the red) is proportional to the relative yield ϕ_T , i.e. the absorption coefficient of Tr_T is independent of temperature, the behaviour of ϕ_T for Pa is different from that for Qa. ϕ_T for Pa decreases by a factor of about 10 on cooling from 25 to -130 °C. In contrast, ϕ_T for Qa increases monotonically on cooling (Fig. 7).

TABLE 5

Rate constants for quenching of Tr_T by oxygen, ferrocene and azulene^a

Compound	Solvent	Additive	Method	k_{ox} ($\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)	$k_{\text{te}} (k_{\text{az}})$ ($\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)
Pa	Dichloromethane	None	(i)	2.5	6(5) ^b
Pc	Dichloromethane	None	(i)		
Pd	Dichloromethane	None	(i)	2	4(3)
Qa	Dichloromethane	None	(i)	1.5	6(< 0.02)
	Chloroform	None	(i)		
Pa	Acetonitrile ^b	Γ^- (0.05 M)	(ii)	4	9(9)
Pd	Acetonitrile ^b	Γ^- (0.05 M)	(ii)	5	6
Qa	Acetonitrile ^b	Γ^- (0.05 M)	(ii)	2	6(< 0.1)
Pa	Water	Γ^- (0.1 M)	(ii)	1	

Values in parentheses are for azulene.

^aAt 25 °C; $\lambda_{\text{exc}} = 530 \text{ nm}$ unless otherwise indicated.^b $\lambda_{\text{exc}} = 353 \text{ nm}$.Fig. 7. Semilogarithmic plots of ϕ_T (\bullet , \blacksquare) and k_{obsd} (s^{-1}) (\circ , \square) vs. T^{-1} for Pa (\bullet , \circ) and Qa (\blacksquare , \square) in M-D.

3.4.2. Transients in polar solvents

On addition of acetonitrile to dichloromethane solutions of Pa ϕ_T decreases if it is assumed that the absorption coefficient of Tr_T does not depend strongly on the solvent properties. For example, ϕ_T decreases to half its maximum value on addition of 8% acetonitrile (Fig. 4). In contrast with the appearance of Tr_T in solvents of moderate polarity only a small ΔA or no transient was observed in the red spectral region in polar solvents (aceto-

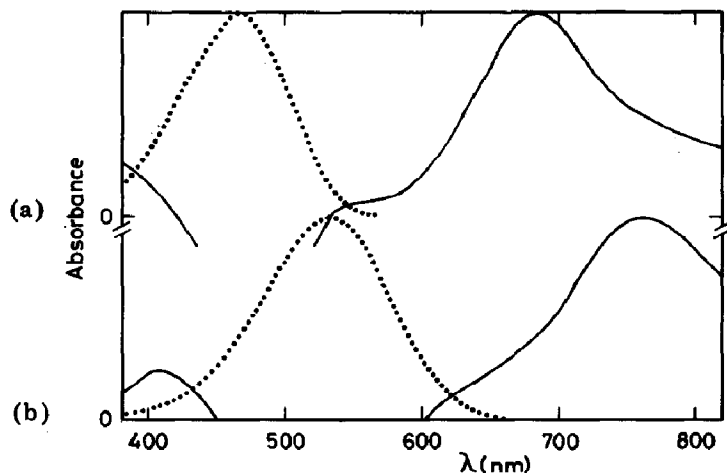


Fig. 8. Transient absorption spectra of (a) Pa and (b) Qa in acetonitrile solutions at 25 °C in the presence of 5×10^{-2} M Γ 20 ns (—) after the laser pulse ($\lambda_{\text{exc}} = 530$ nm); the ground state absorption spectra (.....) are also shown.

nitrile and water) at low concentrations (e.g. $[A_t^+] = [\Gamma] \leq 10^{-4}$ M). Even in 4:1 ethanol-methanol mixtures (E-M) at low temperatures (down to -160 °C) almost no transient absorption was observed for Pa. However, if iodide is added in excess ($[\Gamma] > 10^{-3}$ M) to Pa in acetonitrile at room temperature (method (ii)), a transient develops (Fig. 8). The absorption spectrum is very similar to that of Tr_T in solvents of moderate polarity (Fig. 6). The similarity of the spectra obtained in two types of solvents (Table 3) and the effect of quenchers (Table 5 and see below) suggest that the nature of the short-lived transient is the same.

ϕ_T increases on increasing $[\Gamma]$ (Fig. 5). From a plot of ϕ_T versus $[\Gamma]$ for Pa in acetonitrile the concentration $[\Gamma]_{1/2}$ of Γ at which ϕ_T had reached half its maximum value was estimated to be 1.2×10^{-2} M. A similar plot with $[\Gamma]_{1/2} = 5 \times 10^{-2}$ M $^{-1}$ was obtained in water; however, $[\Gamma]$ is limited because precipitation was observed at higher concentrations (above about 0.1 M). The addition of 0.1 M SCN^- to Pa in acetonitrile leads to Tr_T with a smaller yield and analogous experiments with Br^- and ClO_4^- give no transient.

From the first-order decay of Tr_T in acetonitrile and aqueous solutions lifetimes of 1 - 10 μs were found (Table 3). Although Γ is necessary for the formation of Tr_T , τ_T is also reduced by Γ ; for Pa in acetonitrile a quenching rate constant k_q of about 1×10^7 M $^{-1}$ s $^{-1}$ was estimated. Therefore the lifetimes (methods (i) and (ii)) depend on $[\Gamma]$. The addition of 0.1 M ClO_4^- has no marked effect ($k_q < 10^6$ M $^{-1}$ s $^{-1}$). The lifetime of Tr_T is reduced by oxygen, ferrocene and azulene (as also found in method (i)) at rates close to the diffusion-controlled limit (Table 5).

Tr_R was also observed with method (ii) to different degrees and generally with a small ΔA . On addition of high concentrations (1 M or more) of *N,N*-diethylaniline or triethylamine Tr_R was observed (e.g. $\lambda_{\text{max}} \approx 410$ nm

for **Qa** in acetonitrile solutions) but there was almost no evidence of Tr_T . The ground state absorption spectrum is only slightly changed in the presence of the amines.

3.4.3. Sensitized laser excitation

On generation of the triplet state of xanthone or benzophenone in acetonitrile (λ_{max} values of 630 nm and 530 nm respectively) in the presence of **Pa** or **Qa**, a new transient appears (Fig. 9). The absorption spectrum is similar to that of Tr_T obtained in methods (i) and (ii). The nature of the transient is also confirmed to be the same since quenching constants with oxygen and ferrocene are almost diffusion controlled. However, since decay of the donor triplet is also quenched by these additives ϕ_T is also reduced. In method (iii) τ_T decreases on addition of Γ^- as found for method (ii). Tr_T is also formed from the perchlorates (**Pb** and **Qb**) on sensitized excitation (Table 6) different from that of method (i). In these cases τ_T is significantly larger than its value for the iodides in agreement with the effect of quenching of Tr_T by Γ^- but not by ClO_4^- . The smaller τ_T values obtained by laser excitation compared with those from conventional flash photolysis also indicate quenching by Γ^- .

In order to obtain information about a possible energy transfer process the energy E_T of the donor triplet was varied (Table 6). Acridine ($E_T = 190 \text{ kJ mol}^{-1}$) and several other compounds with higher E_T values are able to transfer energy from the triplet state to Tr_T at a diffusion-controlled rate, whereas 9,10-dibromoanthracene ($E_T = 168 \text{ kJ mol}^{-1}$) is not. The rate constant k_{en} for decay of the donor triplet is almost the same as that for the formation of Tr_T within experimental error. With anthracene k_{en} is smaller for **Pa** than for **Qa**.

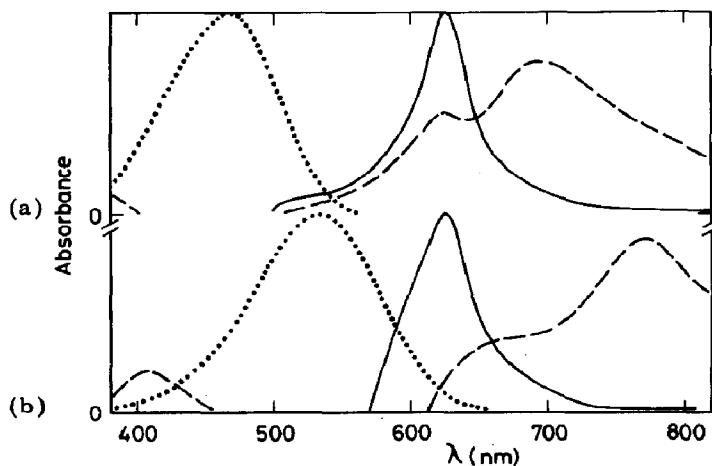


Fig. 9. Transient absorption spectra of (a) **Pa** and (b) **Qa** in acetonitrile solutions at 25 °C on xanthone-sensitized excitation plotted 20 ns (—), and 200 ns (---) after the laser pulse ($\lambda_{\text{exc}} = 353 \text{ nm}$); the ground state absorption spectra (.....) are also shown.

TABLE 6

Rate constants for energy transfer from triplet donors and values for λ_{\max} and τ_T of Tr_T^a

Compound	Sensitizer	E_T (kJ mol ⁻¹)	k_{en} ($\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)	λ_{\max} (nm)	τ_T^b (μs)
Pa	Xanthone	310	20	< 400, 690	5
	Benzophenone	287	15	670	> 2
	2-Acetonaphthone	249	18	680	5
	2-Nitronaphthalene	234	18	680	3
	Fluorenone	223	10	680	3
	Benzanthrone	197	16	660	3
	Acridine	190	15		3
	Anthracene	178	< 0.5		
9,10-Dibromoanthracene	168	≤ 0.01			
Pb	Xanthone	310	≥ 10	670	10
	2-Nitronaphthalene	234		660	20
Qa	Xanthone	310	15	410, 770	10
	Benzophenone	287	20	410, 770	5
	2-Acetonaphthone	249	10	760	8
	2-Nitronaphthalene	234	15	770	6
	Acridine	190	18	760	5
	Anthracene	178	< 5		
	9,10-Dibromoanthracene	168	< 3		
Qb	Xanthone	310	> 10	410, 750	10
	2-Nitronaphthalene	234		770	12

^aIn argon-saturated acetonitrile solutions at 25 °C; $\lambda_{\text{exc}} = 353 \text{ nm}$ (method (iii)).^bLifetime for Pa and Qa limited by quenching with I^- (typically $[\text{A}_T^+] = [\text{I}^-] \approx 1 \times 10^{-4} \text{ M}$).

3.4.4. Pulse radiolysis

Two transients were observed by pulse radiolysis of Pa in argon-saturated aqueous solutions (pH 7) in the presence of *tert*-butanol (0.1 M). The short-lived transient (lifetime, less than 5 μs ; $\lambda_{\max} = 700 \text{ nm}$) is assigned to the solvated electron (e_{solv}^-) on the basis of its absorption spectrum and the fact that it is quenched by N_2O . The long-lived transient (Tr'_R) exhibits absorption maxima at 420 and 640 nm, a shoulder at 340 nm and bleaching around 480 nm (Fig. 10). Maxima around 400 - 500 nm and a weak band in the red spectral region and bleaching around λ_f were also found for the other compounds (Table 4). By variation of $[\text{Pa}]$ it was found that the decay of e_{solv}^- and the formation of Tr'_R coincide (minimum rate, $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). The decay of Tr'_R , which is essentially second order ($t_{1/2} \geq 100 \mu\text{s}$), was not studied further here. Oxygen reduces the ΔA value of Tr'_R but does not change the decay discernibly ($k_{\text{ox}} < 10^6 \text{ M}^{-1} \text{ s}^{-1}$). Tr'_R was also observed in acetonitrile solutions but, owing to the shorter lifetime of e_{solv}^- , ΔA is significantly smaller than in aqueous solutions [3].

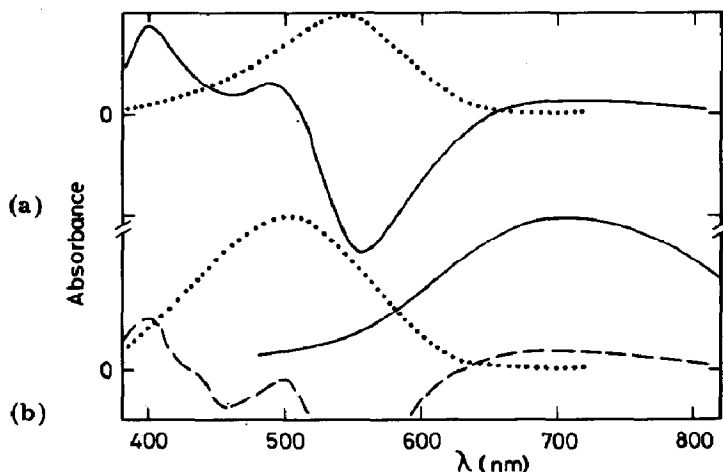


Fig. 10. Transient absorption spectra of Qa in (a) air-saturated tetrahydrofuran and (b) argon-saturated aqueous solutions (0.1 M *tert*-butanol) 0.5 μ s (—) and 50 μ s (---) after the electron pulse.

As shown by the absorption spectra, Tr'_{R} is clearly different from Tr_{T} (Fig. 10 compared with Figs. 6, 8 and 9). Therefore the question arises as to whether Tr'_{R} (method (iv)) has the same nature as Tr_{R} (method (i)). Pulse radiolysis measurements were also carried out in tetrahydrofuran as a solvent of moderate polarity; absorption spectra similar to those in aqueous solutions were recorded in air-saturated solutions (Table 4). Despite the low ΔA values of Tr_{R} in most cases, the spectra of Tr_{R} and Tr'_{R} are considered to be the same.

4. Discussion

4.1. The lowest *trans* triplet state

On excitation of the quaternary salts of *trans*-4-dialkylamino-4'-aza-stilbene and their quinolinium analogues the main transient Tr_{T} was observed under the following conditions. First, Tr_{T} is formed in solvents of moderate polarity (*e.g.* tetrahydrofuran and dichloromethane) on direct excitation of the iodides (Pa, Pc, Pd and Qa (Fig. 6 and Table 3)) but not of the perchlorates (Pb and Qb). By analogy with other stilbazolium salts not containing a dialkylamino group [3, 10] we assume that the compounds under examination are present as ion pairs in these solvents. This implies that one prerequisite for the formation of Tr_{T} is the close proximity of I^- to A_t^+ after excitation. Secondly, Tr_{T} is also formed on addition of I^- in excess in polar solvents (*e.g.* acetonitrile and water) in which A_t^+ and X^- are assumed to be fully dissociated (Fig. 8). The fact that almost no transient was observed at low concentrations (less than 10^{-4} M) in the absence of additives also points to the interaction of I^- with the excited cation since ϕ_{T} is small on addition of other anions (SCN^- , Br^- or ClO_4^-). Thirdly, Tr_{T} is formed on excitation

of various high energy triplet donors in the presence of the iodides as well as the perchlorates (Fig. 9 and Table 6). The latter finding strongly suggests the assignment of Tr_T to a triplet state. The triplet nature of Tr_T is supported by the results that the decay of the triplet donor and the formation of Tr_T follow the same kinetics and that τ_T is quenched by oxygen, azulene (for the P type only) and ferrocene at rates close to the diffusion-controlled limit (Table 5). Since $\phi_{t \rightarrow c}$ is small in all solvents, twisting about the C=C double bond is strongly reduced compared with the cases $R \equiv \text{OCH}_3$, H, CN and NO_2 . Thus the triplet is further attributed to the *trans* configuration.

When sensitizers with $E_T \geq 190 \text{ kJ mol}^{-1}$ are used the lowest *trans* triplet state $^3\text{A}_t^+$ of the cation is formed after energy transfer from the triplet donor (method (iii)) according to



In acetonitrile the formation of $^3\text{A}_t^+$ is independent of the kind of anion (Table 6). The rate constant for energy transfer is in the diffusion-controlled limit ($k_{\text{en}} = (1 - 2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) and decreases strongly for $E_T \leq 178 \text{ kJ mol}^{-1}$. From these results and the rate constants for quenching of $^3\text{A}_t^+$ by ferrocene and azulene with E_T values of 165 kJ mol^{-1} and 163 kJ mol^{-1} respectively [24] (Table 5), triplet energies of about 180 kJ mol^{-1} and 165 kJ mol^{-1} are estimated for Pa and Qa respectively.

Since $^3\text{A}_t^+$ can be quenched by Γ its observed lifetime can be regarded as a lower limit; values of up to $50 \mu\text{s}$ were obtained in dichloromethane by conventional flash photolysis using smaller concentrations (Table 3). For rotation about the C=C double bond a smaller triplet lifetime is generally expected [14, 21]. A long lifetime points to an intersystem crossing step at the *trans* configuration in agreement with inefficient *trans* \rightarrow *cis* isomerization under sensitized conditions (see Section 3). An analogous case has been reported for α, ω -diphenylpolyenes [25]. Since the observed *trans* triplet state decays mainly into the *trans* form the activation energy E_τ should be ascribed to an activated step for quenching by Γ [24]. This is supported by the finding at room temperature that k_q is of the order of $10^7 \text{ M}^{-1} \text{ s}^{-1}$.

For quaternary salts of 4-R-4'-azastilbenes and their quinolinium analogues ($R \equiv \text{CN}, \text{H}, \text{CH}_3, \text{OCH}_3$) $^3\text{A}_t^+$ was observed in E-M only at low temperatures where configurational changes are strongly reduced [1, 4]. The small ΔA value observed for Pa in E-M at low temperatures indicates that for the dissociated salt ($[\text{A}_t^+] = [\text{X}^-] < 10^{-4} \text{ M}$) the intersystem crossing yield ϕ_{isc} is very low. The possibility that the absorption coefficient ϵ_{TT} for T-T absorption is small is unlikely in view of the estimate of $\epsilon_{\text{TT}} \approx 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ from method (iii) (Fig. 9).

The question arises as to whether Tr_T can also be assigned to $^3\text{A}_t^+$ in solvents of moderate polarity. By analogy with other stilbazolium salts ($R \equiv \text{OCH}_3, \text{H}, \text{CN}$ and NO_2) [3, 4, 10] we assume that the salts are fully dissociated in polar solvents (the Dimroth parameter $E_T(30)$ is larger than 45 [26]) and form ion pairs in solvents of moderate polarity ($E_T(30) \leq 42$):



This is also the case for $R \equiv$ dialkylamino. In the light of the results for $R \equiv \text{NO}_2$ it is probable that the salt remains as an ion pair after generation of the triplet state rather than dissociating to ${}^3A_t^+$ and X^- [2, 3]. We therefore propose that ${}^3A_t^+$ and $({}^3A_t^+ \dots \Gamma^-)$ have very similar spectral and kinetic properties and that Tr_T be assigned to one of these depending on the polarity of the solvent.

4.2. The radical A^\cdot

When pulse radiolysis (method (iv)) is used in acetonitrile or aqueous solutions the initial reactive species is identified as the solvated electron. The second long-lived transient Tr'_R observed in the presence of a stilbazolium salt (Fig. 9) is assigned to a radical A^\cdot since the rate constants for decay of e_{solv}^- and formation of Tr'_R are identical. In polar solvents A^\cdot is formed via a one-electron reduction step



independent of the presence of Γ^- or ClO_4^- (Table 4). The similarity of the absorption spectra of Tr'_R in tetrahydrofuran solutions and the two polar solvents suggests that A^\cdot is also formed in a solvent in which the salts are present as ion pairs (see below). Comparable results have been obtained for other stilbazolium salts ($R \equiv \text{NO}_2$ and CN) [3, 27].

When laser flash photolysis is used in solvents of moderate polarity (method (i)) the second minor transient Tr_R has an absorption spectrum similar to that of Tr'_R . The similarity is also supported by the results that the lifetime of Tr_R is longer than $10 \mu\text{s}$ and is not discernibly affected by oxygen or ferrocene. We therefore suggest that the radical A^\cdot is formed by electron transfer in an excited state of the ion pair. In polar solvents the radical A^\cdot is either not observed (method (iii)) or is formed only with low yield (method (ii)) in contrast with the case of stilbazolium salts carrying an electron-accepting group ($R \equiv \text{NO}_2$ and CN) [3, 27].

4.3. Deactivation of the excited cation

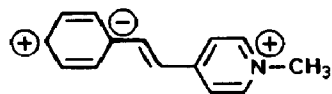
Substitution of the stilbazolium salts by a dialkylamino group (in the 4-position of the styrene ring) leads to strong red shifts of the absorption and fluorescence maxima and shifts the position of the photostationary state to the *trans* side in all solvents used. Two questions arise: which deactivation channels of the cation after excitation into the first excited *trans* singlet state ${}^1A_t^+$ play an important role, and why is $\phi_{t \rightarrow c}$ strongly reduced by a dialkylamino group? The simplest case that ϕ_f and $\phi_{t \rightarrow c}$ are correlated is excluded since ϕ_f values, although larger than those for corresponding stilbazolium salts ($R \equiv \text{NO}_2$, CN , H , CH_3 and OCH_3) [2, 4], are much too small to account for the decrease in $\phi_{t \rightarrow c}$ at room temperature (Table 1). ${}^1A_t^+$ can be deactivated via the following steps: fluorescence, internal conversion and intersystem crossing at the *trans* configuration, by twisting in an

excited state and by a reaction with the anion. Rotation about the C=C double bond to a twisted configuration seems to be inefficient since at ambient temperature the (*cis*)_s content is less than 8% (Table 1). An activated step leading to the *cis* form is indicated by irradiation measurements in dimethylformamide at higher temperatures. Measurements of ϕ_f in ethanol at lower temperatures show the existence of an activated radiationless process in competition with fluorescence. This activated step ($A_v \exp\{-(E_v/RT)\}$) does not lead to a marked increase in the *cis* form since a much higher $\phi_{t \rightarrow c}$ value at room temperature is expected on the basis of ϕ_f values at 25 and -196°C (Table 1). Also, for dimethylformamide no corresponding shift of the photostationary state to the *cis* form was found on varying the temperature. Therefore, and since ϕ_{isc} is very low, we propose that the activation step is the population of a higher excited *trans* singlet state ${}^1A_t^+$ which decays to A_t^+ but not to A_c^+ . Owing to the indirect measurement the nature of ${}^1A_t^+$ cannot be specified further.

Preliminary results of a modified neglect of differential overlap calculation for the *trans*-4-methyl-4'-dialkylaminoazastilbene cation provide support for an enhanced double-bond character of the central ethylenic bond in the "first" excited singlet state compared with the ground state, whereas the reverse was found for the unsubstituted *trans*-4-methylazastilbene cation [28]. This is in accord with a higher barrier to twisting in the excited singlet state leading to the *cis* form (more than 100 kJ mol^{-1} for $R \equiv \text{dimethylamino}$ (see high temperature measurements in dimethylformamide) compared with $10-15 \text{ kJ mol}^{-1}$ for $R \equiv \text{H}$ [10]). In a description of the first excited state and specifically of the double-bond character of the ethylenic bond the resonance structure



for the dimethylamino compound should have greater weight than the comparable structure



for the unsubstituted compound. This view is supported by the numerical values of the linear combination of atomic orbitals coefficients of the highest occupied molecular orbital and the lowest unoccupied molecular orbital characterizing the strength of the ethylenic bond in the first excited singlet state.

4.4. Deactivation of the excited ion pair

A scheme describing the deactivation channels of the ion pair after excitation is presented in Fig. 11. In solvents of moderate polarity fluorescence also competes with an activated step; the activation barrier is of the

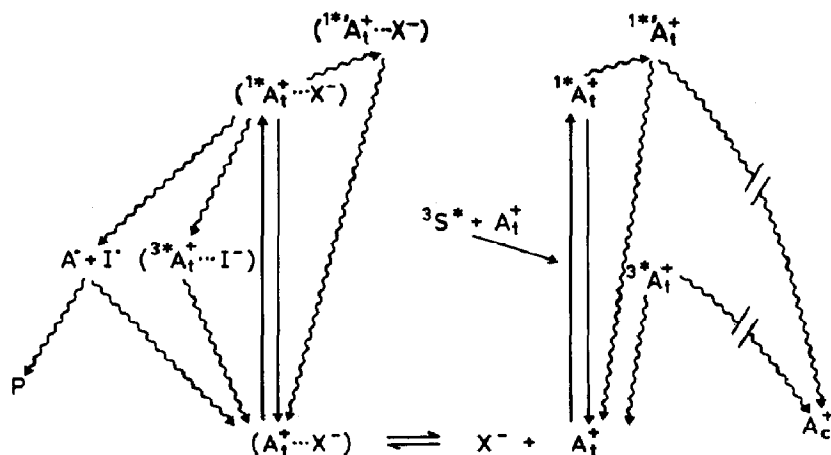
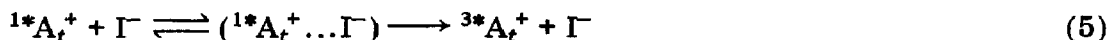


Fig. 11. Scheme for the decay of the cation and the ion pair after excitation.

same magnitude as that for the cation (Fig. 3 and Table 2). Again, this activated step does not lead to a measurable yield of the *cis* form (Table 1). A second deactivation step is the formation of ($^3A_t^+ \dots X^-$) if I^- is the anion (Fig. 6). The temperature dependence of ϕ_T shows that triplet formation is activated for Pa but not for Qa (Fig. 7). In the former case a further excited *transoid* configuration (e.g. an upper excited triplet state) may be involved. A third deactivation step is the formation of A^\cdot which occurs with low yield (Table 4). Electron transfer may occur in the excited singlet or the lowest triplet state [9, 27]. For $R \equiv$ dialkylamino the latter case is unlikely since triplet quenching by oxygen does not reduce the yield of A^\cdot . Therefore electron transfer in the excited singlet state is proposed in agreement with the result that almost no A^\cdot is formed from $^3A_t^+$ even at high $[I^-]$ (method (iii)). For stilbazolium salts carrying an electron-accepting group ($R \equiv$ CN and NO_2) it has been suggested that A^\cdot is formed from ($^1A_t^+ \dots I^-$) [3, 27]. Compared with the latter salts the yield of A^\cdot is probably much smaller for $R \equiv$ dialkylamino. These observations are in agreement with the expectation that electron transfer is less favourable as a result of substitution of the styrene ring by an electron-donating group.

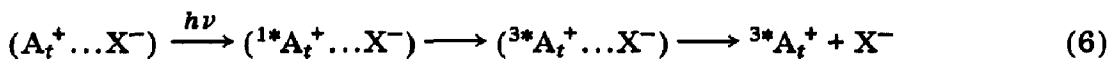
For the perchlorates, where ($^3A_t^+ \dots ClO_4^-$) and A^\cdot are not formed, no enhancement of $\phi_{f \rightarrow c}$ was found. This suggests that the main deactivation pathway of ($^1A_t^+ \dots X^-$) is activated internal conversion at a *transoid* geometry. Compared with the excited cation, the internal conversion seems to be slightly reduced for the excited ion pair since ϕ_f values show a trend to decrease on increasing the solvent polarity (Table 1 and Fig. 4). It appears surprising that the formation of ion pairs enhances both ϕ_f and ϕ_{isc} . In the simplest case enhancement of ϕ_{isc} should reduce ϕ_f . However, fluorescence and intersystem crossing are suggested to be the minor deactivation steps of $^1A_t^+$ at ambient temperature. A reduction of the rate of the activated excited singlet state internal conversion step ($^1A_t^+ \dots X^-$) \rightarrow ($^1A_t^+ \dots X^-$) may well lead to an increase in both ϕ_f and ϕ_{isc} .

At high $[\Gamma]$ and in the absence of a sensitizer Tr_T is also formed (method (ii)). One possibility would be enhancement of intersystem crossing by the heavy atom after formation of an encounter complex:



In this case ϕ_f should decrease on increasing $[\Gamma]$. However, the opposite effect was found (Fig. 5). Therefore eqn. (5) cannot account for the formation of ${}^3\text{A}_t^+$. Furthermore, since the lifetime of ${}^1\text{A}_t^+$ is probably shorter than 0.2 ns, fluorescence quenching by Γ should play only a minor role [2 - 4].

A second possibility is that the addition of X^- shifts the equilibrium in the ground state (eqn. (3)) to the side of the ion pair. For the excited ion pair ($\text{X}^- \equiv \Gamma, \text{SCN}^-$) we propose the following heavy-atom-enhanced intersystem crossing step in competition with fluorescence and internal conversion:



This may explain why ϕ_T is smaller for SCN^- than for Γ and why Tr_T was not observed in the presence of Br^- or ClO_4^- even at the highest concentrations possible. Dissociation into ${}^3\text{A}_t^+$ and Γ (eqn. (6)) in polar solvents could not be checked experimentally since the characteristics of ${}^3\text{A}_t^+$ and ${}^3(\text{A}_t^+ \dots \text{X}^-)$ are believed to be very similar. The increase of ϕ_f on increasing $[\text{ClO}_4^-]$ may be due to a higher ϕ_f value of the ion pair compared with the cation. The reduction of this effect for Γ can be explained by the higher ϕ_{isc} value which reduces ϕ_f of the ion pair.

Acknowledgments

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References

- 1 H. Görner and D. Schulte-Frohlinde, *Chem. Phys. Lett.*, **101** (1983) 79.
- 2 H. Görner and D. Schulte-Frohlinde, *J. Phys. Chem.*, **89** (1985), in the press.
- 3 H. Güsten, *Rep. KFK 244*, 1964 (Kernforschungszentrum Karlsruhe).
- 4 H. Güsten and D. Schulte-Frohlinde, *Tetrahedron Lett.*, (1970) 3567; *Chem. Ber.*, **104** (1971) 402.
D. Schulte-Frohlinde and H. Güsten, *Justus Liebigs Ann. Chem.*, **749** (1971) 49.
- 5 J. L. R. Williams, J. M. Carlson, R. E. Adel and G. A. Reynolds, *Can. J. Chem.*, **43** (1965) 1345.
- 6 K. Takagi and Y. Ogata, *J. Org. Chem.*, **47** (1982) 1409.
- 7 M. S. A. Abdel-Mottaleb, *Laser Chem.*, **4** (1984) 305.
- 8 H. Güsten and D. Schulte-Frohlinde, *Z. Naturforsch.*, **34b** (1979) 1556.
- 9 H. Görner, *J. Phys. Chem.*, **89** (1985), in the press.
- 10 H. Görner, A. Fojtik, J. Wróblewski and L. J. Currell, *Z. Naturforsch.*, **40a** (1985), in the press.

- 11 D. Schulte-Frohlinde, H. Blume and H. Güsten, *J. Phys. Chem.*, **66** (1962) 2486.
- 12 D. Gegiou, K. A. Muszkat and E. Fischer, *J. Am. Chem. Soc.*, **90** (1968) 3907.
- 13 H. Görner and D. Schulte-Frohlinde, *J. Photochem.*, **8** (1978) 91.
- 14 D. Schulte-Frohlinde and H. Görner, *Pure Appl. Chem.*, **51** (1979) 279.
- 15 H. Görner and D. Schulte-Frohlinde, *J. Mol. Struct.*, **84** (1982) 227.
- 16 E. Lippert, W. Lüder, F. Moll, W. Nägele, H. Boos, H. Prigge and I. Seibold-Blankenstein, *Angew. Chem.*, **73** (1961) 695, and references cited therein.
- 17 J. M. Warman, M. P. De Haas, A. Hummel, C. A. G. O. Varma and P. H. M. Van Zeyl, *Chem. Phys. Lett.*, **87** (1982) 83.
- 18 M. P. De Haas and J. M. Warman, *Chem. Phys.*, **73** (1982) 35.
- 19 H. Gruen and H. Görner, *Z. Naturforsch.*, **38a** (1983) 928.
- 20 G. Heinrich, S. Schoof and H. Güsten, *J. Photochem.*, **3** (1974/1975) 315.
T. Karstens and K. Kobs, *J. Phys. Chem.*, **84** (1980) 1871.
- 21 H. Görner, *J. Photochem.*, **13** (1980) 269; *J. Phys. Chem.*, **86** (1982) 2028.
- 22 H. Hermann, G. Koltzenburg and D. Schulte-Frohlinde, *Ber. Bunsenges. Phys. Chem.*, **77** (1973) 677.
- 23 N. Getoff and F. Schwörer, *Radiat. Res.*, **41** (1970) 1.
S. Solar, W. Solar and N. Getoff, *Radiat. Phys. Chem.*, **23** (1984) 371.
- 24 W. G. Herkstroeter, *J. Am. Chem. Soc.*, **97** (1975) 4167.
- 25 H. Görner, *J. Photochem.*, **19** (1982) 343.
- 26 C. Reichardt and K. Dimroth, *Fortschr. Chem. Forsch.*, **11** (1968/1969) 1.
- 27 H. Görner, to be published.
- 28 J. Ciosłowski and H. Gruen, unpublished.