Singlet Mechanism for Trans → Cis Photoisomerization of Quaternary Salts of 4-Substituted 4′-Azastilbenes ($R = CN$, H, CH_3, and OCH_3) and their Quinolinium Analogues. VIII [1]

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Dedicated to Professor Schulte-Frohlinde on the occasion of his 60th birthday

The trans → cis photoisomerization of a series of substituted stilbazolium salts ($A_t^+X^-$, A_t^+: trans-1-alkyl-4-[4-R-styryl]-pyridinium and -quinolinium, $R = CN$, H, CH_3 and OCH_3, $X^- = I^-$ and ClO_4^-) was studied by laser flash photolysis and steady state irradiation measurements. The quantum yields of cis ⇄ trans photoisomerization ($\phi_{c\to t}$ and $\phi_{t\to c}$) and of fluorescence of the trans isomers (ϕ_f) were determined in several solvents at room temperature and at low temperatures in mixtures of either 2-methyltetrahydrofuran-dichloromethane or ethanol-methanol (E-M). In polar solvents at room temperature $\phi_{t\to c}$ is substantial ($\geqq 0.3$) and ϕ_f is small ($10^{-3} - 10^{-2}$). Competition of fluorescence and an activated step in the trans → cis pathway is indicated by the effects of temperature on ϕ_f and $\phi_{t\to c}$ (activation energy: 2 – 3 kcal/mol). A transient, observed only at low temperatures (lifetime $\tau_T > 0.5$ ms in E-M below $-170\,°C$), is assigned to the lowest triplet state with trans configuration. On the basis of the effects of temperature on ϕ_f, $\phi_{t\to c}$, τ_T, and the triplet yield and those of quenchers on ϕ_f and $\phi_{t\to c}$, involvement of the triplet state in the twisting process at room temperature is excluded. Therefore, a singlet mechanism is suggested for the trans → cis photoisomerization of the stilbazolium salts examined. Significant reduction of $\phi_{t\to c}$ for iodides in solvents of moderate polarity, where ion pairs are present, is accounted for by photoinduced electron transfer in competition to trans → cis photoisomerization.

1. Introduction

Styrylpyridines have attracted considerable interest as simple heterocyclic model compounds showing cis ⇄ trans photoisomerization [2 – 6]. Quaternization may change the photophysical and photochemical features of the azastilbenes due to the introduction of a positive charge into the molecule. Some effects of the positive charge on the properties of the ground state and the excited states of the isomers have been studied for stilbazolium betaines [7 – 9], quaternary salts of bipyridylethylenes [10], and stilbazolium salts [11 – 20]. For quaternary iodides of 4-nitro-4′-azastilbenes and their quinolinium analogues it has recently been suggested that photoinduced electron transfer competes with trans → cis photoisomerization [19]. The electron transfer process occurs either in the triplet state, which is quenched by an amine or an anion (I^- or SCN^-), or in the excited singlet state of the ion pair. Ground state ion pairs ($A_t^+ \ldots I^-$) are present in solvents of moderate polarity as previously shown for 1-ethyl-4-[4-methoxystyryl]quinolinium iodide (**4′a**) [14].

It is well known that pyridinium and quinolinium salts are sensitive to the nature of the solvent [21 – 24]. Kosower et al. have documented that the maximum of the CT absorption band of 1-ethyl-4-carbomethoxypyridinium iodide is a useful measure of the solvent polarity (*Z*-value) [21, 22]. Another frequently used measure for the solvent polarity is a second pyridinium derivative, Dimroth's betaine: 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxid [23]. Whether or not photoinduced electron transfer competes with trans → cis photoisomerization of a stilbazolium salt depends not only on the solvent polarity, but also on the properties of the electron donor and on the lifetimes of the excited states involved. Information therefore is needed about the primary decay processes which are significantly influenced by the substituent of the quaternary salts of azastilbenes; for example, trans → cis photoisomerization changes from a

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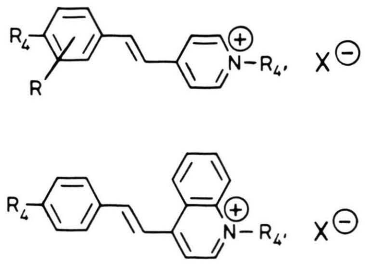
Table 1. Quaternary salts of 4-substituted-4′-azastilbenes and their quinolinium analogues.



No.	Type	R_4	R	R'_4	X^-
1a	P	CN		CH_3	I^-
1b	P	CN		CH_3	ClO_4^-
2a	P	H		CH_3	I^-
2b	P	H		CH_3	ClO_4^-
2c	P	H		C_2H_5	I^-
3a	P	CH_3		C_2H_5	I^-
3b	P	CH_3		C_2H_5	ClO_4^-
4a	P	OCH_3		CH_3	I^-
4b	P	OCH_3		CH_3	ClO_4^-
4c	P	H	2-OCH_3	CH_3	I^-
4d	P	OCH_3	3-OCH_3	CH_3	I^-
1′a	Q	CN		CH_3	I^-
1′b	Q	CN		CH_3	ClO_4^-
2′a	Q	H		C_2H_5	I^-
2′b	Q	H		C_2H_5	ClO_4^-
4′a	Q	OCH_3		C_2H_5	I^-
4′b	Q	OCH_3		C_2H_5	ClO_4^-
4′c	Q	OCH_3		C_2H_5	Br^-

singlet to a triplet mechanism if the cyano group in 4-position is replaced by the nitro group [17].

In this paper, we have studied some photophysical and photochemical properties of a series of quaternary salts of styrylpyridinium and -quinolinium (type P and Q, respectively), which are either unsubstituted or substituted in the 4-position by a cyano, a methyl, or a methoxy group (Table 1; the quinolinium salts are indicated by a prime). The effects of substitution, temperature, additives, and solvent properties on the absorption and emission characteristics of the trans isomers and the quantum yields of fluorescence (ϕ_f) and of trans → cis photoisomerization ($\phi_{t\to c}$) were studied. The effect of temperature on the formation and decay of a triplet was studied by laser flash photolysis. On the basis of the results a singlet mechanism is suggested for the cis ⇄ trans photoisomerization of the stilbazolium salts examined.

2. Experimental

Apparatus and Procedures

Steady state irradiation measurements and the determination of $\phi_{t\to c}$ were performed according to previous work [17–19] using the aberchrome 540 or the ferrioxalate actinometers [25, 26]. Corrected fluorescence emission and excitation spectra at 25 and −196 °C were recorded on a computer controlled Spex-Fluorolog which was equipped with a photon-counting detection system [27]. Temperature-dependent fluorescence spectra were recorded on a spectrofluorimeter (Perkin Elmer, MPF 2A) [28]. 9,10-Diphenylanthracene was used as a fluorescence standard ($\phi_f = 1.0$ in ethanol at −196 °C) [29]. Since trans → cis photoisomerization during the fluorescence measurements influences the determination of ϕ_f, fresh solutions were irradiated for the shortest time periods possible. The samples were handled under red light and the absorption was measured prior to and after irradiation. Generally, less than 5% of the trans isomer was converted to cis during a fluorescence measurement. The spectra were recorded in air-saturated solutions since oxygen has no discernible effect on ϕ_f; this was checked in ethanol solutions at 25 °C for the compounds showing the largest ϕ_f values (e.g. **4d** and **4′a**). The laser flash photolysis set-up has been described in previous work [18, 28, 30]. For excitation at 353 nm the third harmonic of a Nd-laser (J. K. Lasers) was used. Excitation at 308 nm was carried out by using an excimer laser (Lambda Physik). For $\phi_{t\to c}$ and laser measurements the samples were purged with argon.

Materials

Trans isomers of **1a**, **1′a**, **2′a**, and **4′a** were prepared as described elsewhere [14, 31]. The other quaternary stilbazolium iodides are of commercial origin (EGA) and were purified by recrystallization from methanol-water; the perchlorates (index b) were prepared from the corresponding iodides by treating with $AgClO_4$ [14]. Cis isomers of **2a** and **2′a** were prepared from trans-4-azastilbene and 1-methyl-4-styrylquinolinium, respectively, by irradiation, separation on an alumina column and quaternization [14]. Cis isomers of **1a** and **4a** were separated by HPLC on a column nucleosil 18/5 mm using a 2:3 mixture of methanol and triethylammonium acetate in water at pH 3.5 as eluant. Melting points of the trans isomers (in °C): **1a** (282–285), **1b** (260–264), **2a** (222–224), **2b** (196–201), **2c** (190–192), **3a** (230–234), **3b** (188–192), **4a** (219–221), **4b** (253–256), **4c** (186–188), **4d** (264–267), **1′a** (233–236), **1′b** (224–226), **2′a** (262–266), **2′b** (253–254), **4′a** (206–209), **4′b** (171–174), and **4′c** (182–188). Analysis, % calculated (found) for **1a**: $C_{15}H_{13}N_2I$; C 51.7 (50.8), H 3.8 (4.0), N 8.1 (8.1), and I 36.4 (37.1) and for **2a**: $C_{14}H_{14}NI$; C 52.0 (50.0), H 4.4 (4.6), N 4.3 (4.6), and I 39.3 (40.8). 9,10-Diphenylanthracene (EGA) and azulene (Aldrich), were used as received; biacetyl (EGA) was purified by fractional distillation and ferrocene (Merck) was recrystallized. Solvents (Merck) were spectrograde or purified by distillation and checked for absorbing or fluorescing impurities.

3. Results

Trans → cis photoisomerization

The absorption spectra of trans isomers in methanol solutions at room temperature before and after irradiation are shown in Fig. 1 for three typical examples (**2a**, **4a**, and **4′a**). The absorption maximum of the trans isomer (λ_t) is displaced to longer wavelengths by introduction of a methoxy group and, in addition, by replacing the pyridinium ring by the quinolinium ring ($\lambda_t = 345$, 382, and 429 nm for **2a**, **4a**, and **4′a**, respectively). The maxima of the photoproducts, which have smaller molar absorption coefficients (ε_c) than those of the trans isomers (ε_t), are slightly blue-shifted. The absorption spectra show isosbestic points ($\lambda_i = 290$, 300, and 342 nm, respectively) and reach a photostationary state within a few minutes of irradiation. This indicates a clean trans → cis photoisomerization with no discernible side reactions in agreement with previous work [12, 17, 18].

A similar behaviour was also found for the other compounds in polar solvents (Tables 2 and 3). Changing R_4 from CN to H or CH_3 and further to OCH_3 or replacing the pyridinium by the quinolinium ring shifts λ_t to the red. On the other hand, replacing $R_{4'} = CH_3$ by C_2H_5 (**2a** versus **2c**) and the anion I^- by ClO_4^- (**2a** versus **2b** and **4′a** versus **4′b**) has almost no effect on λ_t. Generally, λ_t increases on going from tetrahydrofuran to chloroform and dichloromethane and decreases on increasing the solvent polarity further, as illustrated for **2** and **4′** (Table 2). In polar solvents variation of the concentration (e.g. $[\mathbf{2a}] = 1 \times 10^{-5} - 1 \times 10^{-3}$ M in methanol) has virtually no effect on λ_t and ε_t. However, in dichloromethane λ_t is red-shifted on increasing the concentration (e.g. $\lambda_t = 340$ and 350 nm for $[\mathbf{2a}] = 1 \times 10^{-5}$ and 1×10^{-3} M, respectively).

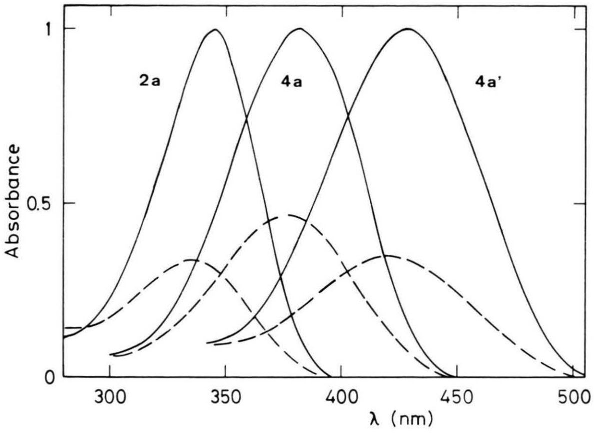


Fig. 1. Absorption spectra of trans-**2a**, trans-**4a**, and trans-**4′a** in methanol solutions at 25 °C before irradiation (full lines, $\varepsilon_t = 4.0 \times 10^4$, 3.5×10^4 and 3.2×10^4, respectively) and in the photostationary state (dashed lines, $\lambda_{irr} = 366$ nm (**2a** and **4a**) and 436 nm (**4′a**)).

Effects of solvent and temperature on $\phi_{t \to c}$

Values for the percentage of cis in the photostationary state ((% (cis)$_s$), $\phi_{t \to c}$, and $\phi_{c \to t}$, using several solvents and irradiation wavelengths (λ_{irr}), are listed in Tables 2 and 3. To varying degrees, depending on the substituents, the anion, λ_{irr}, additives, and solvent properties, the position of the photostationary state lies between ~10 and ~88% cis. The effect of solvent on $\phi_{t \to c}$ is shown for two examples (**2** and **4′**, Table 2). For **2a** $\phi_{t \to c}$ and (% cis)$_s$ increase with increasing the solvent polarity (expressed by the $E_T(30)$ parameter [23]). The effect is similar for **4′a** but absent (or smaller) if the anion iodide is replaced by the perchlorate (**2b** and **4′b**). For iodides, values of $\phi_{t \to c}$ and (% cis)$_s$ are generally smaller in solvents of moderate polarity (e.g. dichloromethane) than in polar solvents (e.g. methanol, Table 3). Introduction of a methoxy group (**4a**–**4c** and **4′**) or of two methoxy groups (**4d**) reduces $\phi_{t \to c}$ slightly. Replacement of the pyri-

Table 2. Effect of solvent on trans → cis photoisomerization[a]

No.	Solvent ($E_T(30)$, kcal/mol)	λ_i[b] (nm)	λ_t[b] (nm)	$\phi_{c \to t}$[c]	$\phi_{t \to c}$	(% cis)$_s$
2a	Tetrahydrofuran[d] (37.4)	~ 310	344		0.03	$\lesssim 15$[e]
	Chloroform[d] (39.1)	319	353		0.08	$\lesssim 40$[e]
	Dichloromethane (41.1)	302	357		0.12	$\lesssim 40$[e]
	Acetonitrile (46.7)	289	343	0.4	0.5	85
	Ethanol (51.9)	285	346		0.5	88
	Methanol (55.5)	290	345		0.55	88
	Water (63.1)	284	338	0.4	0.5	82
2b	Tetrahydrofuran[d]	> 295	344		0.5	80
	Dichloromethane	305	358		0.5	85
	Acetonitrile	289	342	0.4	0.5	85
	Methanol	291	345		0.55	88
	Water	284	336	0.4	0.5	82
4′a	Tetrahydrofuran[d]		427			$\lesssim 10$[e]
	Chloroform[d]	< 380	435		0.05	34[e]
	Dichloromethane	$\lesssim 360$	444		0.10	40
	Acetonitrile		420	0.36	0.40	85, 80[f]
	Methanol	342	429	0.5	0.4	78, 70[f]
	Water		408	0.45	0.4	85, 78[f]
4′b	Tetrahydrofuran[d]		426			> 45
	Chloroform[d]	349	436		0.4	75
	Dichloromethane		445	0.6	0.35	68, 56[f]
	Methanol	342	430	0.4	0.45	85, 81[f]
	Water		410	0.42	0.4	84

[a] In argon-saturated solutions at 25 °C; unless otherwise indicated $\lambda_{irr} = 366$ and 436 nm for **2** and **4′**, respectively.

[b] λ_i and λ_t are the isosbestic point and the absorption maximum of the trans isomer, respectively.

[c] Obtained from irradiation of mixtures containing ~ 80% cis at 313 and 366 nm for **2** and **4′**, respectively.

[d] Thermal cis → trans isomerization at 25 °C.

[e] After reaching a quasi-photostationary state a further photoreaction occurred.

[f] $\lambda_{irr} = 405$ nm.

dinium ring (*P* versus *Q*) has only a small effect on $\phi_{t \to c}$. On prolonged irradiation in solvents with $E_T(30) \sim 37-42$ kcal/mol the perchlorates (**1b**, **2b**, and **4b**) are photostable while the respective iodides (**1a**, **2a**, and **4a**) exhibit a further irreversible photoreaction after reaching a quasi-photostationary state. For **4′a** thermal cis → trans isomerization complicates the measurement of $\phi_{t \to c}$, in contrast to **4′b**.

In order to gain information about the involvement of singlet and/or triplet states in the trans → cis photoisomerization azulene and ferrocene were added. Plots of $\phi^0_{t \to c}/\phi_{t \to c}$ and photostationary trans/cis ratios $(([t]/[c])_s)$ versus [ferrocene] or [azulene] are linear. Slope/intercept values of these plots in methanol solutions at room temperature range from $20-50\ \mathrm{M}^{-1}$ for **1a**, **2a**, **3a**, and **4a** with both, azulene and ferrocene. The effect of oxygen on $\phi_{t \to c}$ and $([t]/[c])_s$ is generally small. For example, changes of less than 10% were found between oxygen- and argon-saturated methanol solutions of **2a** and **4a**.

The temperature dependence of $\phi_{t \to c}$ is shown in Fig. 2 for **2a** and **4′a** in a 4:1 mixture of ethanol and methanol (E-M). On decreasing the temperature $\phi_{t \to c}$ decreases for **2a** only slightly between 25 and −120 °C and drops off below ~ −140 °C while for **4′a** $\phi_{t \to c}$ already decreases below −50 °C. For **4a** $\phi_{t \to c}$ values at a given temperature lie between those for the two former compounds. Similar temperature dependences were obtained for perchlorates in a 1:1 mixture of 2-methyltetrahydrofuran and dichloromethane (M-D), as an example for a solvent of moderate polarity (Figure 3). The plots of $\phi_{t \to c}$ versus T^{-1} were analyzed by using the equation

$$\phi_{t \to c} = \frac{e^{-E_{t \to c}/RT}}{B + e^{-E_{t \to c}/RT}}\,(1 - \beta)\,. \tag{1}$$

Table 3. Effect of solvent and substitution on trans → cis photoisomerization[a].

No.	Solvent	λ_i (nm)	λ_t (nm)	$\phi_{t\to c}$	(% cis)$_s$
1a	Dichloromethane	294	342	0.02	< 30
	Methanol	287	332	0.4	80
1b	Dichloromethane	294	344	0.5	80
	Methanol	291	333	0.5	80
2c	Dichloromethane	304	359	$\leqq 0.1$	$\leqq 20^b$
	Methanol	292	345	0.5	80
3a	Dichloromethane	313	374	$\lesssim 0.1$	$\lesssim 20^b$
	Methanol	290	358	0.4	80
3b	Dichloromethane	310	375	0.4	80
	Methanol	290	359	0.4	80
4a	Dichloromethane	315	401	0.02	$\lesssim 20^b$
	Methanol	~ 300	382	0.5	80, 75^c
4b	Dichloromethane	310	404	0.5	80
	Methanol		382	0.5	80
4c	Dichloromethane	301	380	0.2	^{b}
	Methanol	290	376	0.5	80
4d	Dichloromethane	320	416	0.1	^{b}
	Methanol	292	392	0.3	50, 50^c
1′a	Dichloromethane	< 320	377	$\lesssim 0.1$	$< 50^b$
	Methanol	274	370	0.4	80
1′b	Dichloromethane	276	378	0.4	80
	Methanol	273	372	0.4	80
2′a	Dichloromethane	323	396	0.2	50^b
	Methanol	$\lesssim 320$	386	0.5	75, 85^c
4′b	Dichloromethane^c		432	0.26	69
	Methanol^c		429	0.33	73, 75^d

[a] In argon-saturated solutions at 25 °C; unless otherwise indicated $\lambda_{irr} = 366$ nm.

[b] After reaching a quasi-photostationary state a further photoreaction occurred.

[c] $\lambda_{irr} = 436$ nm. – [d] $\lambda_{irr} = 436$ nm.

We assume that only one thermally activated step is involved ($A_t \exp(-E_{t\to c}/RT)$) on the route from an excited trans to an excited twisted configuration and that the fraction $(1-\beta)$ decaying from the latter state to the cis form is independent of temperature. The activated twisting step competes with the decay in the trans configuration, which is measured by the parameter B. In this analysis nothing is assumed about the nature of the states involved (see Discussion). Values for B and the activation energy ($E_{t\to c}$) are listed in Table 4.

Sensitized trans → cis photoisomerization

In order to avoid direct irradiation into the absorption spectra of the stilbazolium salts, which extend to at least 400 nm, biacetyl was used as sensitizer. Upon sensitized excitation in argon-saturated aceto-

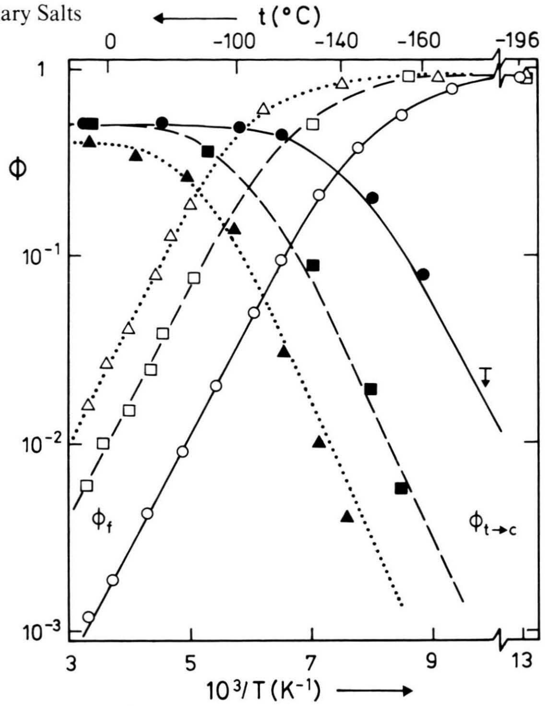


Fig. 2. Semilogarithmic plots of ϕ_f (open symbols) and $\phi_{t\to c}$ (full symbols) versus T^{-1} for **2a** (circles), **4a** (squares), and **4′a** (triangles) in E-M ($\lambda_{exc} = 366$, 405, and 436 nm, respectively).

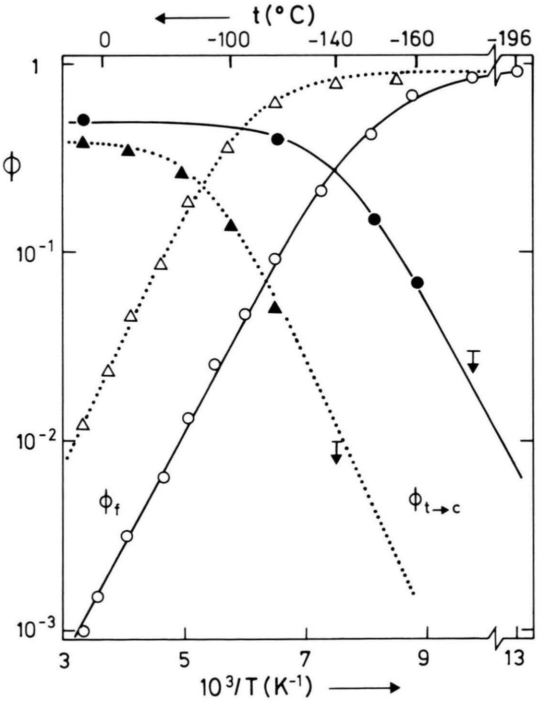


Fig. 3. Semilogarithmic plots of ϕ_f (open symbols) and $\phi_{t\to c}$ (full symbols) versus T^{-1} for **2b** (circles) and **4′b** (triangles) in M-D ($\lambda_{exc} = 366$ and 436 nm, respectively).

Table 4. Activation energies obtained from ϕ_f and $\phi_{t \to c}$ measurements[a].

No.	Solvent	E_v	ϕ_f measurements		$\phi_{t \to c}$ measurements	
			A_v/k_f	k_0/k_f	$E_{t \to c}$	B[b]
		(kcal/mol)	$\times 10^4$		(kcal/mol)	$\times 10^{-4}$
1a	E-M	2	5	0.1		
1b	M-D	2	8			
2a	Dichloromethane	2.0	6			
	Acetonitrile	3.0	12			
	E-M	3.0	14	0.1	3.0	0.10
2b	M-D	2.8	10		3.0	0.1
	E-M	2.9	10	0.1		
4a	Dichloromethane	2.2	1.3			
	Acetonitrile	2.5	1.1			
	E-M	2.9	2.0	0.1	3.2	0.8
4b	M-D	2.8	3.5			
2′a	Dichloromethane	3.0	10			
	Ethanol	2.8	3.5	0.1	3.5	1.0
4′a	Ethanol	3.2	1.3	$\leqq 0.2$	3.4	0.8
4′b	M-D	3.3	2.0			

[a] The ϕ_f and $\phi_{t \to c}$ measurements were carried out in air- and argon-saturated solutions, respectively; $\lambda_{irr} = 366$ nm except for **4′** (436 nm).

[b] For a singlet mechanism $B = k_f/A_v (k_0 \ll k_f)$.

nitrile solutions at room temperature trans → cis photoisomerization was observed. Using [biacetyl] $= 5 \times 10^{-2}$ M, corresponding to an absorbance of 1.0 at $\lambda_{irr} = 436$ nm, and [trans-**2a**] $\sim 2 \times 10^{-4}$ M the photostationary state (~ 70% cis) is reached within 10 min. Control measurements showed a significant reduction of the quantum yield of trans → cis photoisomerization ($\phi_{t \to c}^{sens}$) in the presence of oxygen and formation of less than 5% cis (within 10 min irradiation time) in the absence of biacetyl. Using trans-4-nitrostilbene as a reference [32] $\phi_{t \to c}^{sens} \sim 0.4$ was estimated for **1a**, **1b**, and **2a**. Similar measurements with stilbazolium salts which are substituted by a methoxy group are hampered by the fact that direct and sensitized excitation cannot be fully separated. Therefore, in a second procedure acetone was used as a sensitizer; in a mixture of acetone-acetonitrile (1:5) less than 10% of the incident light ($\lambda_{irr} = 290$ nm) is absorbed by the stilbazolium salt. Also under these conditions sensitized trans → cis photoisomerization in substantial yield was observed (e.g. for **2a**, **3a**, **4a**, and **4′a**).

Fluorescence spectra

The emission spectra of trans isomers are shown in Fig. 4 for **2a** and **4′a** in ethanol solutions at 25 and −196 °C. At room temperature the emission spectra are unstructured and show nearly a mirror image to the absorption spectra, which coincide with the corrected excitation spectra. On irradiation of a trans isomer (e.g. of **1a**–**4a** at $\lambda_{irr} = 366$ nm) the emission intensity decreases corresponding to the reduction of the absorption of the isomer mixture. These findings are in line with the general observation for stilbene-like molecules that only the trans isomers exhibit fluorescence [6, 7, 18, 33]. The emission cannot be attributed to phosphorescence since the intensity is not discernibly quenched by oxygen (e.g. **2a** or **4a** in methanol) and its lifetime is not longer than the pulse width of the laser (~ 10 ns) throughout. We therefore conclude that the emission originates from the first excited singlet states of the trans form. For **2a**, **4a**, **2′a**, and **4′a** in glassy ethanol at −196 °C fluorescence lifetimes (τ_S) of 1.5–2.5 ns were determined with a photon counting apparatus.

The fluorescence maximum (λ_f) exhibits a marked dependence on substitution at the styrene ring. Introduction of a methoxy group in the 4- or 6-position shifts λ_f in ethanol at 25 °C from 421 nm (**2**) to 497–554 nm (**4a** and **4d**) and replacement of the pyridinium ring by the quinolinium ring shifts

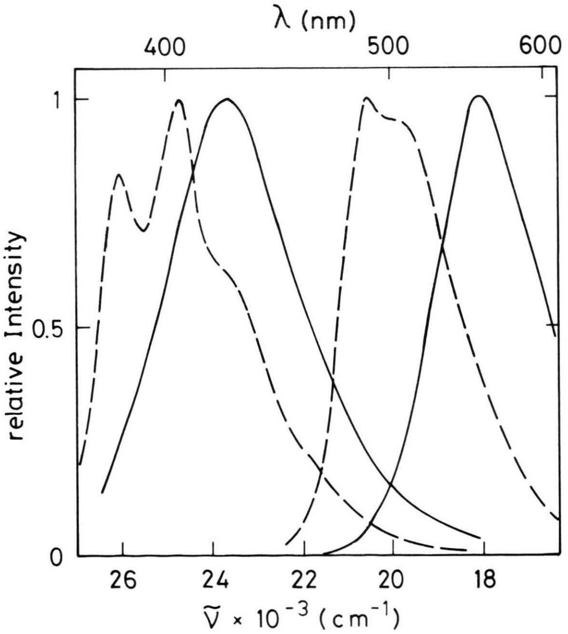


Fig. 4. Fluorescence spectra of trans-**2a** (left side) and trans-**4′a** (right side) in ethanol solutions ($\lambda_{exc} = 366$ nm) at 25 °C (full lines) and at −196 °C (dashed lines).

λ_f further to the red (Tables 5 and 6). Similar to λ_t, λ_f is practically independent of the anion (I^-, Br^-, and ClO_4^-) but in contrast to λ_t (Table 2) the nature of the solvent has only a small effect on λ_f (Table 6). The Stokes shift is therefore influenced by λ_t rather than by λ_f. For **2a** the Stokes shift decreases from $6.3 \times 10^3\ cm^{-1}$ in water to $4.5 \times 10^3\ cm^{-1}$ in dichloromethane. Similar results were found for the other compounds, e.g. for **4′a** $6.5 \times 10^3\ cm^{-3}$ (water) versus $4.4 \times 10^3\ cm^{-1}$ (dichloromethane).

On going to − 196 °C the fluorescence spectra become partly structured and the values for λ_f are blue-shifted throughout (Fig. 4 and Table 5). This blue-shift may be explained by a hindrance of reorientation of the solvent shell around the excited molecule at high viscosities. The effect of viscosity rather than temperature is indicated by the fact that λ_f changes markedly only at low temperatures (e.g. below − 140 °C for **2a**) where the viscosity increases strongly. In glassy media the fluorescence occurs most likely from the non-relaxed Franck-Condon state whereas in fluid media reorientation of the solvent reduces the energy of $^{1*}A_t^+$. Similar observations have been reported for stilbenes and related compounds [20, 34].

Table 5. Quantum yields of fluorescence and emission maxima in fluid and in glassy solutions[a]

No.	Solvent	λ_f (nm)		ϕ_f	
		RT	− 196 °C	*RT*	− 196 °C
1a	Dichloromethane	410		0.0003	
	Ethanol	406	395, 415	0.001	0.9
1b	Dichloromethane	410		0.006	
	Ethanol	403	390, 410	0.001	0.9
2b	Dichloromethane	425		0.0010	
	Ethanol	421	385, 404	0.0012	0.9
2c	Ethanol	422	385, 404	0.0014	0.85
3a	Dichloromethane	450		0.0008	
	Ethanol	443	402, 422	0.0015	0.9
3b	Dichloromethane	450		0.0012	
	Ethanol	444		0.0015	
4b	Dichloromethane	498		0.005	
	Ethanol	496	450	0.006	0.9
4c	Ethanol	509	446	0.01	0.9
4d	Ethanol	554	463, 485	0.09	0.9
1′a	Dichloromethane	472			
	Ethanol	470		0.01	0.9
2′a	Dichloromethane	488		0.0015	
	Ethanol	481	432, 459, 485	0.003	0.9
4′a	Dichloromethane	552		0.012	
	Ethanol[b]	555	485	0.015	0.8
4′b	Ethanol[b]	555	485	0.015	0.7

[a] In air-saturated solutions; $\lambda_{exc} = 366$ nm unless otherwise indicated.

[b] Same λ_f for $\lambda_{exc} = 436$ nm.

Table 6. Effect of solvent on λ_f and ϕ_f[a].

No.	Solvent	λ_f (nm)	ϕ_f
2a	Tetrahydrofuran	424	0.0006
	Dichloromethane	425	0.0005
	Acetonitrile	428	0.0012
	Ethanol	421	0.0012
	Water	429	0.0010
4a	Tetrahydrofuran	503	0.004
	Dichloromethane	498	0.004
	Acetonitrile	507	0.006
	Ethanol	497	0.006
	Water	500	
4′a	Tetrahydrofuran	560	0.009
	Dichloromethane	552	0.007
	Acetonitrile	560	0.020
	Ethanol	560	0.016
	Water	556	0.020

[a] In air-saturated solutions at 25 °C; $\lambda_{exc} = 436$ nm and 366 nm for **4′a** and the other two compounds, respectively.

Effects of solvent and temperature on ϕ_f

In ethanol solutions at room temperature ϕ_f ranges between 1×10^{-3} (**1a**) and 0.09 (**4d**). ϕ_f shows an increasing trend in the order $R_4 = CN$, H, CH_3, OCH_3 (Table 5) and on going from P-type to Q-type compounds. In polar solvents **1–3**, which fluoresce only weakly, exhibit nearly the same ϕ_f values for iodides and perchlorates. However, in solvents of moderate polarity ϕ_f is generally smaller for iodides than for perchlorates. For a given iodide ϕ_f tends to increase on increasing the solvent polarity as shown for **2a**, **4a**, and **4′a** (Table 6). For perchlorates ϕ_f is less solvent dependent as indicated by the comparison between dichloromethane and ethanol. ϕ_f is reduced by addition of ferrocene (but not oxygen); for **4b** and **4′b** in methanol solutions Stern-Volmer constants of about $20\ M^{-1}$ were obtained.

At − 196 °C ϕ_f reaches values close to unity for all stilbazolium salts examined (Table 5). The temperature dependence of ϕ_f is shown for typical examples in E-M (Fig. 2) and M-D (Figure 3). The variation of log ϕ_f versus T^{-1} was analyzed by using the equation

$$\phi_f = \frac{k_f}{k_f + k_0 + A_v\, e^{-E_v/RT}} \,. \qquad (2)$$

Here, k_f and k_0 are the rate constants for radiative and nonactivated radiationless decay of the excited trans singlet state, respectively, and A_v and E_v are the pre-exponential factor and the activation energy, respectively. For example, values of $k_0/k_f = 0.1$, $A_v/k_f = 1.4 \times 10^5$ and $E_v = 3.0$ kcal/mol were obtained for **2a** in E-M. Similar activation energies were found for several other iodides (Table 4). For the perchlorates E_v is only slightly dependent on the solvent polarity (see **2b** in M-D versus E-M). Differences in ϕ_f are mainly determined by A_v rather than by k_f and E_v.

The fluorescence lifetime $\tau_S = \phi_f / k_f$ was estimated from ϕ_f values and data of absorption and fluorescence spectra in ethanol at 25 °C by using the equation [35]

$$k_f = 2.9 \times 10^{-9} \, \tilde{\nu}_m^2 \int \varepsilon_t \, d\tilde{\nu} \, , \qquad (3)$$

where $\tilde{\nu}_m$ is the fluorescence maximum (in cm^{-1}). In a second approach τ_S was estimated from the ratio $\tau_S^0 \times \phi_f / \phi_f^0$ (−196 °C is indicated by 0) thereby assuming that k_f is independent of temperature. From both methods τ_S values of about 3 and 60 ps were calculated for the two extreme cases **2a** and **4′a**, respectively.

Thermal cis → trans isomerization

Stilbazolium salts of Q-type structure exhibit thermal cis → trans isomerization in solution at room temperature [13, 14]. However, cis isomers of P-type structure are thermally stable at room temperature in most cases. This points to a somewhat higher activation barrier and/or a larger pre-exponential factor for the P-type as compared to Q-type compounds. For the former thermal cis → trans isomerization was observed at 25 °C within several hours only in solvents of moderate polarity. Replacement of an iodide by the perchlorate prolongs the half-life ($t_{1/2}$) of the cis isomer [14]. For example, **2a** in chloroform is thermally reversible ($t_{1/2} \sim 10$ h) but the perchlorate (**2b**) exhibits no discernible cis → trans isomerization. In tetrahydrofuran even **2b** shows cis → trans isomerization ($t_{1/2} \sim 20$ h) whereas **2a** shows an irreversible dark-reaction.

Laser flash photolysis

For **2a** at low concentration ($< 10^{-4}$ M) in polar solvents (e.g. acetonitrile and aqueous solutions) at room temperature no transient was observed between 400 and 800 nm immediately after the laser pulse ($\lambda_{exc} = 353$ nm). Under these conditions no transient could be recorded also for the other compounds between the trailing edge of the absorption spectrum and 800 nm, cf. [17]. However, a transient (Tr_T) was observed in E-M solutions at low temperatures. Typical absorption spectra with λ_{max} between 460 and 660 nm are shown in Figure 5. The transient absorbance (ΔOD) at λ_{max} decreases in the sequence **4′a**, **2′a**, and **2a**. ΔOD is generally low, as compared for example with the TT-absorption of benzophenone in benzene solutions at 25 °C ($\lambda_{max} = 530$ nm, $\varepsilon_{TT} = 7.6 \times 10^3$ [36]); ΔOD of **4′a** in E-M solutions at −170 °C is less than 20% of the reference value under similar excitation conditions. In most cases the maximum of ΔOD could be observed only after several 10 − 100 ns because the large fluorescence intensity overlaps the absorption signal, cf. [28].

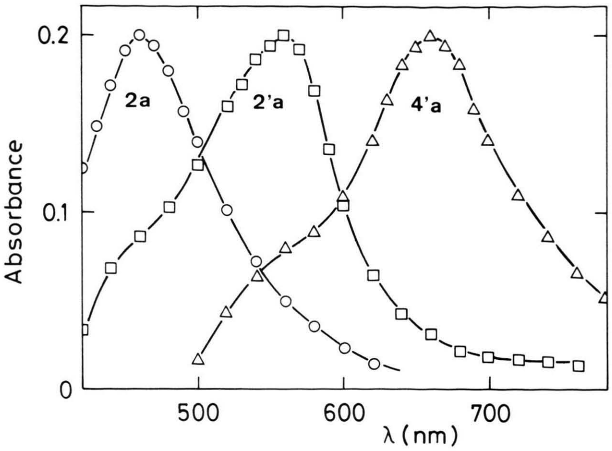


Fig. 5. Transient absorption spectra of **2a** (○○), **2′a** (□□), and **4′a** (△△) in E-M at −170 °C 100 ns after the laser pulse ($\lambda_{exc} = 353$ nm).

ΔOD, which is assumed to be proportional to the relative transient yield (ϕ_T^{rel}), decreases significantly on increasing the temperature (Figure 6). In several cases Tr_T could be detected up to −80 °C with $\phi_T^{rel} \leqq 10\%$ of its maximum value. Decay of Tr_T is generally first-order with the exception of **1a** [17]. On increasing the temperature, the observed constant (k_{obs}) decreases linearly with T^{-1} reaching a limiting value (Figure 6). The corresponding lifetime ($\tau_T = k_{obs}^{-1}$) ranges from $\tau_T^{min} \leqq 1$ µs at the highest temperature observable (t_m) to $\tau_T^{max} \gtrsim 0.5$ ms

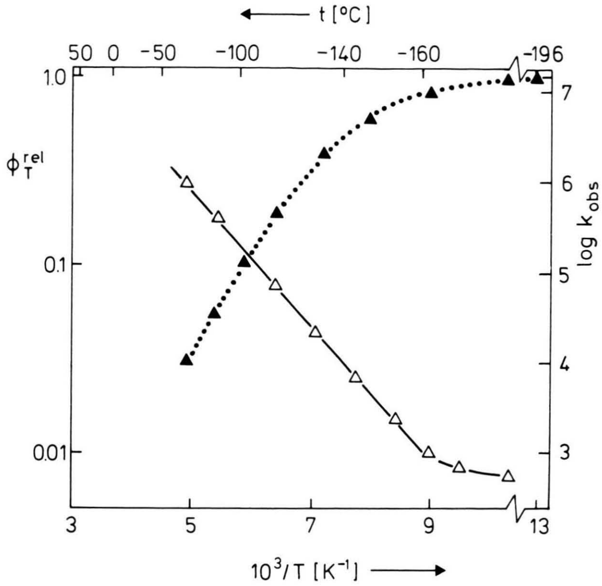


Fig. 6. Plot of log k_{obs} (in S^{-1}, open triangles) and ϕ_T^{rel} (full triangles) versus T^{-1} for **4′a** in argon-saturated E-M ($\lambda_{exc} = 353$ nm).

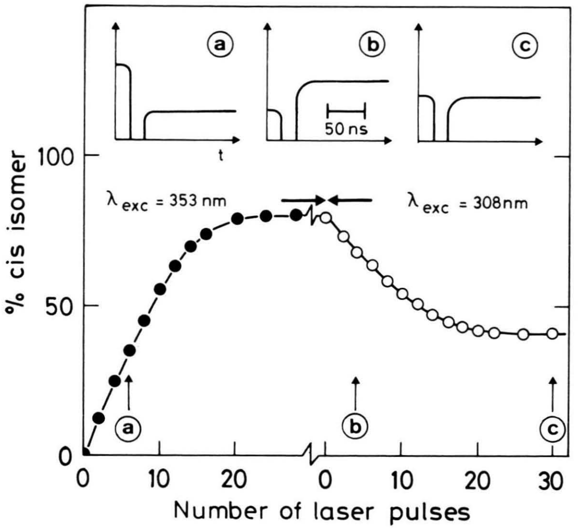


Fig. 7. Cis ⇄ trans photoisomerization of **2b** in acetonitrile solutions at 25 °C on excitation by laser pulses ($\lambda_{exc} = 353$ and 308 nm, full and open circles, respectively); insets (a)–(c): ΔOD at 340 nm as a function of time as indicated.

Table 7. Absorption maximum and first-order decay rate constant for transient Tr_T at low temperatures[a].

No.	t_m (°C)	τ_T^{min} (µs)	λ_{max} (nm)	τ_T^{max} (ms)
1a[b]	− 133	1	415	~ 0.5
2a	− 120	0.1	460	1
3a	− 120	0.1	500	
4a	− 70	0.7	560	≧ 0.7
2′a	− 135	1	560	> 0.5
4′a	− 70	0.5	660	≧ 0.7

[a] In argon-saturated E-M solutions.
[b] Values taken from [17].

at temperatures below $t_0 \approx 160$ °C (Table 7). From the Arrhenius plot between t_m and t_0 an activation energy of 3.8 kcal/mol and a pre-exponential factor of 2×10^{10} s^{-1} was determined for Tr_T of **4′a** in E-M.

The 308 nm line of an excimer laser was used to estimate the upper limit of the time duration of cis → trans photoisomerization at room temperature. For shifting the photostationary state to the trans side a 353 nm pulse is unfavourable for most compounds since (% cis)$_s$ is rather high at $\lambda_{irr} = 366$ nm (see Table 3). On the other hand, an excitation wavelength of $\lesssim 265$ nm should not be used in order to avoid photoionization (e.g. of I$^-$) [19]. Because of the lack of sufficient amounts of pure cis, a cis/trans mixture containing about 80% cis was prepared by excitation of **2b** in acetonitrile at 353 nm. A decrease of ΔOD_{340} immediately after the laser pulse, which is marked by the fluorescence signal (inset (a) of Fig. 7) indicates that trans → cis photoisomerization occurs within 20 ns since in this spectral range ε_c is smaller than ε_t (Figure 1). The photostationary state is reached under our conditions (irradiated volume ~ 0.3 cm^3) after about 20 flashes. Changing λ_{exc} to 308 nm shows an increase of ΔOD_{340} (inset (b)) immediately after the laser pulse, reaching a new photostationary state after repeated flashing, as indicated by no further change in % cis and ΔOD_{340} (inset (c)). This result and those from similar experiments carried out with several other compounds (e.g. **4a**, **1′a**, and **4′a**) at appropriate wavelengths, suggest that cis → trans photomerization is faster than 20 ns.

4. Discussion

Classification of the stilbazolium salts

The compounds examined here (Table 1) are quaternary salts of styrylpyridinium or styrylquinolinium (types P and Q, repectively) which are para-substituted at the styryl ring (by $R_4 = CN$, H, CH_3, or OCH_3) and at the quaternary N-atom (by $R'_4 = CH_3$ or C_2H_5). For several compounds the anion I^- (index a and **2c**, **4c**, and **4d**) is replaced by ClO_4^- (index b) or by Br^- (**4′c**). The properties of cis ⇄ trans photoisomerization depend on the substituents, the anion, solvent properties, and on several other parameters, e.g. temperature, wavelength of irradiation, and additives. In contrast to the thermal cis → trans isomerization (see Results) no evidence was found for a generally different photochemical behaviour when the stilbazolium salts carry either a pyridinium or a quinolinium ring.

The stilbazolium salts may be classified into three groups: One group contains molecules, which are 4-substituted at the styrene ring by CN, H, CH_3, or OCH_3 (this work). As outlined in the following trans → cis photoisomerization in this group occurs via a singlet mechanism thoughout. This justifies a common treatment of these compounds. A second group is constituted by stilbazolium salts, which are 4-substituted by a dialkylamino group [20] and a third group by those which are 4-substituted by a nitro group [17–19]. While molecules of the former group show virtually no trans → cis photoisomerization those of the latter exhibit trans → cis photoisomerization mainly via the triplet state. Within one group the stilbazolium salts show more or less similar photochemical features. The differences between the three groups may be accounted for mainly by different deactivation pathways of the first excited trans singlet state.

Free ions and ion pairs

On the basis of conductivity measurements Güsten and Schulte-Frohlinde have previously shown that the ground state of trans-**4′a** is fully dissociated in alcohols and water and forms an ion pair in solvents of moderate polarity [14]. The absorption spectra of the trans isomers of the perchlorates are very similar, when present either as free ions or as ion pairs. In dichloromethane λ_t depends slightly on the concentration and decreases generally on increasing $E_T(30)$ (Tables 2 and 3). These observations, as well as the small effect of solvent polarity on the fluorescence properties (λ_f and ϕ_f) point to the likelyhood that the ion pair is loosely bound. However, the marked effect of solvent polarity on $\phi_{t \to c}$ for the case of iodides (see below) is in agreement with the assumption that the ions of all compounds examined are fully dissociated in polar solvents at low concentrations ($< 10^{-4}$ M) and form ion pairs in the solvents of moderate polarity ($E_T(30) \leqq 42$ kcal/mol) examined (Fig. 8), cf. [18–20]. Whether the ion pairs are solvent separated or not is an open question.

In polar solvents (protic and non-protic) at room temperature $\phi_{t \to c}$ is substantial throughout (Tables 2 and 3). Variation of the para substituents ($R_4 = CN$, H, CH_3, or OCH_3 and $R'_4 = CH_3$ or C_2H_5) or of the position of the methoxy group (**4a**, **4c**, and **4d**) replacement of the pyridinium ring by the quinolinium ring, and variation of the anion ($X^- = I^-$, Br^-, or ClO_4^-) have only small effects on $\phi_{t \to c}$. This shows that trans → cis photoisomerization is an effective pathway for deactivation of the excited singlet state ($^{1*}A_t^+$) in every compound. In solvents of moderate polarity ($E_T(30) \sim 37-42$ kcal/mol) however, $\phi_{t \to c}$ depends significantly on the nature of the anion. While $\phi_{t \to c}$ is not (or only slightly) reduced in the presence of ClO_4^- (**1b**, **2b**, **4b**, and **4′b**) $\phi_{t \to c}$ decreases markedly on increasing $E_T(30)$ if the anion is I^- (**1a**, **2a**, **4a**, and **4′a**). For $R_4 = NO_2$ (P and Q type) a similar effect has already been explained by an electron transfer step from the iodide to the cation in the excited trans singlet state of the ion pair [19]. A similar mechanism, including a solvent dependent equilibrium between dissociated free ions and the ion pair is also proposed for the stilbazolium salts examined (Figure 8).

The smaller $\phi_{t \to c}$ values for the iodides (as compared to the perchlorates) in solvents of moderate polarity may be accounted for by photoinduced

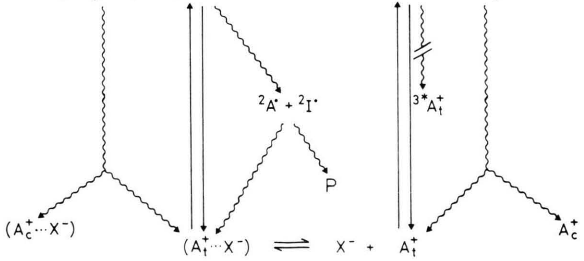


Fig. 8. Scheme for cis ⇄ trans photoisomerization of the cation (in polar solvents) and the ion pair (in solvents of moderate polarity).

electron transfer in competition to trans → cis photoisomerization. Because of the higher oxidation potential of ClO_4^- electron transfer is not expected in this case, cf. [19]. Assuming that the ion pairs are formed to the same degree, the results indicate that electron transfer is more effective for pyridinium than for quinolinium iodides (Tables 2 and 3). Quenching of $\phi_{t\to c}$ by I^- is most pronounced for molecules which are substituted by the electron accepting group (cyano), and the effect is smaller for the donating methoxy group (Tables 2 and 3). This is supported by the observation of a second transient, which is assigned to the radical $A^\bullet$. $A^\bullet$ appears in those cases where $\phi_{t\to c}$ is reduced, e.g. for iodides ($[I^-] \lesssim 10^{-4}$) in solvents of moderate polarity and in polar solvents at high $[I^-]$ ($> 10^{-2}$ M). These phenomena will be discussed elsewhere [37].

Triplet state

The transient Tr_T, which was observed in E-M at low temperatures (Fig. 5 and Table 7), is assigned to the lowest triplet state. For **1a** evidence for the triplet nature of Tr_T has already been presented [17]. For several other compounds the temperature dependences of the lifetime (τ_T) and the relative yield (ϕ_T^{rel}) of the triplet are similar to those of **1a**. On decreasing the temperature (i.e. increasing the viscosity) ϕ_T and τ_T increase (Figure 6). The temperature dependence of τ_T is similar to that of the triplet of 4-nitrostilbazolium salts [17, 18]. However, in contrast to the latter case, ϕ_T is small for the salts examined here. A low ϕ_T value is in agreement with ϕ_f values close to unity at − 196 °C (Table 5). Tr_T is more specifically assigned to the trans configuration ($^{3*}A_t^+$) since $\phi_{t\to c}$ is practically zero below − 170 °C (Figure 2). Twisting about the C=C double bond into the perpendicular triplet configuration ($^{3*}A_p^+$) is therefore unlikely below t_0 and in agreement with a triplet lifetime in the millisecond range.

Involvement of the lowest triplet state in the trans → cis photoisomerization at room temperature is excluded due to the following: First, $^{3*}A_t^+$ is not observed at room temperatures. Extrapolation of ϕ_T^{rel} values (assuming $\phi_T^{max} = 1 - \phi_f^0 \lesssim 0.2$) gives a yield of smaller than 10^{-3} at 25 °C. On the other hand, twisting in the triplet ($^{3*}A_t^+ \rightarrow {}^{3*}A_p^+$) is possible, as indicated by the substantial yield $\phi_{t\to c}^{sens}$ using sensitized excitation (see Results). Secondly, on addition of neutral quenchers, such as azulene or ferrocene, the position of the photostationary state is shifted to the trans side. We suggest that this results from a quenching step of $^{1*}A_t^+$ to the ground state (A_t^+) since from linear plots of $\phi_{t\to c}^0/\phi_{t\to c}$ and ϕ_f^0/ϕ_f versus [ferrocene] similar Stern-Volmer constants were obtained (see Results). However, markedly higher values are expected from the former method if the lowest triplet is involved [15, 16]. Thirdly, the cis isomer is formed within 20 ns whereas a triplet lifetime of 50 − 200 ns has been reported for $R_4 = NO_2$ [17, 18]. We therefore conclude that the lowest triplet is not involved in the trans → cis photoisomerization pathway of the stilbazolium salts examined here.

Trans → cis photoisomerization in polar solvents

For the mechanism of trans → cis photoisomerization in polar solvents two possibilities exist: Twisting about the C=C double bond may occur either in the first excited singlet or in an upper excited triplet state. In the latter case, twisting followed by internal conversion should lead to the lowest twisted triplet state ($^{3*}A_p^+$). A pathway bypassing the lowest triplet is rather unlikely. If, in analogy to 4-nitrostilbazolium salts a $^{3*}A_t^+ \rightleftarrows {}^{3*}A_p^+$ equilibrium with a lifetime of longer than 20 ns is anticipated [17, 18], the upper excited triplet pathway should lead to formation of $^{3*}A_t^+$ in substantial yield. However, $^{3*}A_t^+$ could only be observed at low temperatures (e.g. below $t_m =$ − 133 °C for **1a**) where twisting about the C=C double bond is hindered by the high viscosity. We therefore suggest that the twisting process occurs in the first excited singlet state. The scheme for trans → cis photoisomerization of the stilbazolium depicted in Fig. 8 is analogous to that of a series of 4-R-stilbenes (R = H, OCH_3, CN) [29, 34].

The singlet mechanism is supported by the analysis of the temperature dependences of $\phi_{t\to c}$ and ϕ_f, indicating that trans → cis photoisomerization and fluorescence are competing processes. Since the activation energies, obtained from the former and latter measurements ($E_{t\to c}$ and E_f, respectively), are the same within experimental error, the activated step is assigned to twisting from the planar ($^{1*}A_t^+$) to the twisted ($^{1*}A_p^+$) excited singlet configuration. This is in agreement with an *A*-factor of approximately 10^{13} s^{-1}, as estimated from $A_v/k_f \sim (1-10) \times 10^4$ (Table 4) and $k_f \sim 3 \times 10^8$ s^{-1}. Accordingly, $1 - \beta$ is the ratio of $^{1*}A_p^+$ decaying to the cis form (A_c^+), and the constant B in (1) is given by $(k_f + k_0)/A_v$. Since k_0/k_f is small, B^{-1} should be equal to A_v/k_f, in agreement with the results (Table 4).

Trans → cis photoisomerization in solvents of moderate polarity

As shown in Fig. 8 the singlet mechanism is also proposed for the case of the ion pair ($A_t^+ \ldots X^-$) due to the following: Since $\phi_{t \to c}$ is substantial for perchlorates in solvents of moderate polarity, electron transfer should not markedly compete with trans → cis photoisomerization. On the other hand, flourescence and trans → cis photoisomerization are competing processes, as indicated by the similarity $E_v = E_{t \to c}$ (within experimental error) in M-D (Table 4). Obviously, the perchlorate is only weakly bonded to the cation, since the photophysical features of A_t^+ are only slightly changed (see Tables 2–6). The fluorescence properties even for ($A_t^+ \ldots I^-$) are not much different from those of A_t^+. The maximum changes in ϕ_f (a factor of about 3) for **1a** may be compared with the much greater changes in $\phi_{t \to c}$ (a factor of about 20) (Tables 2, 3, 5, and 6). In a simple approach (assuming that only ${}^{1*}A_t^+$ is quenched) the reduction of ϕ_f and $\phi_{t \to c}$ by I^- in the ion pair should be similar. One possible explanation for the discrepancy is that the electron transfer process occurs not only from the fluorescing (${}^{1*}A_t^+ \ldots I^-$) state. If an additional state in the trans → cis pathway is involved the reduction of $\phi_{t \to c}$ should be larger than that of ϕ_f.

Cis → trans photoisomerization

With our mixtures containing about 80% cis no indication of a new fluorescence, which could be attributed to the cis form, was found (e.g. for **1a** or **4′a** in methanol at room temperature). $\phi_{c \to t}$ is substantial in polar solvents (Table 2) and also for perchlorates in solvents of moderate polarity, since $\phi_{t \to c}$ and $(\%\ \text{cis})_s$ are practically independent of solvent polarity (Tables 2 and 3). This indicates that internal conversion at the cis side is of minor importance and that the excited cis singlet state interconverts rapidly to the perpendicular configuration. Since the trans ground state is formed from cis rich solutions within the duration of the laser pulse (Fig. 7) we suggest that ${}^{1*}A_p^+$ decays rapidly to A_t^+ via the twisted ground state (A_p^+). The proposed pathway is analogous to the case generally accepted for phenylethylenes and their aza analogous [6, 33].

Acknowledgement

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[1] Ref. 19 (20) is No. VII (IX) in the series on cis-trans photoisomerization of stilbazolium salts.

[2] D. G. Whitten and M. T. McCall, J. Amer. Chem. Soc. **91,** 5097 (1969); D. G. Whitten and Y. J. Lee, ibid. **94,** 9142 (1972).

[3] P. Bortolus and G. Cauzzo, Trans. Faraday Soc. **66,** 1161 (1970).

[4] P. Bortolus, G. Favaro, and U. Mazzucato, Mol. Photochem. **2,** 311 (1970); G. Bartocci, U. Mazzucato, F. Masetti, and G. Galiazzo, J. Phys. Chem. **84,** 847 (1980).

[5] G. Bartocci, U. Mazzucato, and P. Bortolus, J. Photochem. **6,** 309 (1976/77); U. Mazzucato, G. G. Aloisi, and F. Masetti, ibid. **18,** 211 (1982).

[6] For a review see: U. Mazzucato, Pure Appl. Chem. **54,** 1705 (1982).

[7] U. Steiner, M. H. Abdel-Kader, P. Fischer, and H. E. A. Kramer, J. Amer. Chem. Soc. **100,** 3190 (1978).

[8] K. A. Al-Hassan and M. A. El-Bayoumi, Chem. Phys. Lett. **76,** 121 (1980).

[9] N. Ikeda, N. Mataga, U. Steiner, and M. H. Abdel-Kader, Chem. Phys. Lett. **95,** 66 (1983).

[10] A. R. Gutierrez and D. G. Whitten, J. Amer. Chem. Soc. **98,** 6233 (1976).

[11] H. Güsten, KFK 244 (Kernforschungszentrum Karlsruhe) 1964.

[12] H. Güsten and D. Schulte-Frohlinde, Chem. Ber. **104,** 402 (1971).

[13] H. Güsten and D. Schulte-Frohlinde, Tetrahedron Lett. **1970,** 3567; D. Schulte-Frohlinde and H. Güsten, Liebigs Ann. Chem. **749,** 49 (1971).

[14] H. Güsten and D. Schulte-Frohlinde, Z. Naturforsch. **34 b,** 1556 (1979).

[15] K. Takagi and Ogata, J. Org. Chem. **47,** 1409 (1982).

[16] M. S. A. Abdel-Mottaleb, Laser Chem. **4,** 305 (1984).

[17] H. Görner and D. Schulte-Frohlinde, Chem. Phys. Lett. **101,** 79 (1983).

[18] H. Görner and D. Schulte-Frohlinde, J. Phys. Chem. **89** (1985), in press.

[19] H. Görner, J. Phys. Chem. **89** (1985), in press.

[20] H. Görner and H. Gruen, J. Photochem. **28** (1985), in press.

[21] E. M. Kosower and J. C. Burbach, J. Amer. Chem. Soc. **78,** 3493 (1956); E. M. Kosower and P. E. Klinedienst, Jr., ibid. **78,** 5838 (1956); E. M. Kosower, ibid. **80,** 3253 (1958).

[22] E. M. Kosower, Progr. Phys. Org. Chem. **3,** 81 (1965).

[23] C. Reichardt and K. Dimroth, Fortschr. Chem. Forsch. **11,** 1 (1968); C. Reichardt, Angew. Chem. **91,**

119 (1979); C. Reichardt, Solvent Effects in Organic Chemistry, Verlag Chemie, Weinheim 1979.

[24] G. Briegleb, W. Jung, and W. Herre, Z. Phys. Chem. N.F. **38,** 253 (1963); G. Briegleb, W. Herre, W. Jung, and H. Schuster, Z. Phys. Chem. N.F. **45,** 229 (1965).

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

[26] H. G. Heller and J. R. Langan, J. Chem. Soc. Perkin II, **1981,** 341.

[27] A. R. Holzwarth, H. Lehner, S. E. Braslavsky, and K. Schaffner, Liebigs Ann. Chem. **1978,** 2002.

[28] H. Görner and D. Schulte-Frohlinde, J. Phys. Chem. **83,** 3107 (1979).

[29] G. Heinrich, S. Schoof, and H. Güsten, J. Photochem. **3,** 315 (1974/75).

[30] H. Görner and D. Schulte-Frohlinde, J. Phys. Chem. **85,** 1835 (1981).

[31] A. P. Phillips, J. Org. Chem. **14,** 302 (1949), L. Horwitz, J. Amer. Chem Soc. **77,** 1687 (1955); J. L. R. Williams, R. E. Adel, J. M. Carlson, G. A. Reynolds, D. G. Borden, and J. A. Ford, Jr., J. Org. Chem. **28,** 387 (1963).

[32] H. Görner and D. Schulte-Frohlinde, J. Photochem. **8,** 91 (1978).

[33] For a review see: J. Saltiel and J. L. Charlton, in: Rearrangements in Ground and Excited States (P. De Mayo, ed.) Academic Press, New York 1980, Vol. 3, p. 25.

[34] H. Stegemeyer, Ber. Bunsenges. Phys. Chem. **72,** 335 (1968); Ch. Geodicke, H. Stegemeyer, G. Fischer, and E. Fischer, Z. Phys. Chem. N.F. **101,** 181 (1976).

[35] S. J. Strickler and R. A. Berg, J. Chem. Phys. **37,** 814 (1962).

[36] R. Bensasson and E. J. Land, Trans. Faraday Soc. **67,** 1904 (1971).

[37] H. Görner, in preparation.