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Triplet Pathways in the *cis* ⇄ *trans* Photoisomerization of 4-Acetyl- and 4-Benzoyl-stilbene

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The photochemical properties of 4-acetylstilbene (AS) and 4-benzoylstilbene (BS) have been studied in various solvents using steady-state irradiation and ns laser flash photolysis. The quantum yields of *trans* ⇄ *cis* photoisomerization ($\Phi_{t\to c}$, $\Phi_{c\to t}$) are substantial ($\geqslant 0.3$) over a wide temperature range, while the quantum yield of fluorescence is small even at −196 °C (*e.g.* $\Phi_f \leqslant 0.04$). Similar transient absorption spectra, showing maxima at *ca.* 380 and *ca.* 415 nm in fluid and frozen media, respectively, were recorded for *trans*-AS and also for *cis*-AS. The transient is assigned to the triplet state in either case; its lifetime between 25 and −196 °C varies by a factor of *ca.* 10^5. These two virtually identical T–T absorption spectra are suggested to originate from the *trans* ($^3t^*$) and the *cis* ($^3c^*$) triplet state, respectively, since at −196 °C intersystem crossing occurs without significant configurational changes. Apart from small spectral differences BS behaves similarly. Quenching measurements by ferrocene of $\Phi_{t\to c}$, in comparison with those of the triplet decay, support that the triplet state is intermediate in the *trans* → *cis* photoisomerization pathway. The spectral and kinetic features of the triplet state are interpreted on the basis of the intermediacy of the twisting step from $^3c^*$ to the perpendicular conformation ($^3p^*$) in the *cis* → *trans* photoisomerization pathway, the $^3t^* \rightleftarrows {}^3p^*$ equilibrium and decay to the ground states *via* the $^3p^* \to {}^1p$ intersystem-crossing step.

The *cis* ⇄ *trans* photoisomerization of stilbene occurs *via* the singlet mechanism,[1–8] a triplet pathway can be induced only by application of sensitizers.[1–6,9–13] There is general agreement that the *trans* triplet state ($^3t^*$) can be quenched by azulene, whereas oxygen reacts preferentially with the perpendicular triplet conformation ($^3p^*$) leading *via* the ^1p conformation into ^1t and ^1c, the two ground states.[1–7,11] The establishment of a fast triplet equilibrium

$$^3t^* \rightleftarrows {}^3p^* \qquad (1)$$

for stilbene has long since been proposed. The potential-energy surface of the lowest triplet as a function of the angle of twist around the C=C double bond, however, is still under debate.[4,5] The concept of a rapidly established $^3t^* \rightleftarrows {}^3p^*$ equilibrium has also been widely accepted for various 1,2-diarylethylenes, such as naphthyl- or anthryl-styrenes.[14–28]

On direct excitation of *trans*-stilbene, the $^3t^*$ state can be populated in rigid glasses,[29,30] but the quantum yield of intersystem crossing (Φ_{isc}) is quite low, as concluded from the quantum yield of phosphorescence.[31] Since Φ_{isc} is virtually zero for stilbene and many stilbene derivatives at room temperature,[3,10,13,30,31] studies of the triplet properties are hampered by the necessary presence of a sensitizer. Time-resolved spectroscopic observation of the triplet states requires a high stilbene concentration, $(1–70) \times 10^{-3}$ mol dm^{-3}, which may lead to complications because the triplet lifetime at ambient temperatures, $\tau_T \approx 60$ ns,[9–13] is rather short.

4-Nitrostilbenes have been chosen as attractive alternatives to probe for the triplet pathway since their Φ_{isc} values are sufficiently large and the *trans* → *cis* photoisomerization occurs only or mainly *via* the triplet pathways.[20–28] From the similarity of the T–T absorption spectra of a given *trans*-4-nitro-4′-R-stilbene (R: NO_2, H, OCH_3 and NH_2) in either fluid or frozen media it has been concluded that the triplet state at room temperature has mainly *trans* configuration.[20–26] For stilbene the T–T absorption spectra at 25 and −196 °C are quite different, they show a marked blue shift of the maximum as compared to glassy media and no structure in fluid solution.[10,29]

The introduction of a carbonyl group in a *trans*- or *cis*-stilbene adds n,π* states to the π,π* states and this should greatly enhance Φ_{isc} without significantly changing the photochemical properties and the energies of the states involved. However, only a few properties of 'keto'-stilbenes[31,32] and no data concerning transients are known, as yet. This study with 4-acetylstilbene (AS) and 4-benzoylstilbene (BS) was therefore undertaken to characterize and understand better the photophysical and photochemical properties of stilbenes exhibiting efficient intersystem crossing.

The results show that the features of the excited states of both 4-ketostilbenes are very similar in the temperature range from 25 to −196 °C and, interestingly, the spectral and kinetic triplet data of a *trans* and a *cis* isomer are more or less identical. In particular, a *cis* triplet state ($^3c^*$), which often escapes observation,[9,17,29] could be detected. The spectral changes, at least, are not as large as those which would be due to substitution by a nitro group. This made it possible to study the triplet state of stilbenes which have greater similarity to the parent compound than 4-nitrostilbene and its 4′-substituted derivatives.

Experimental

trans-AS and *trans*-BS were the same as used before;[31,32] *trans*-AS was kindly donated by Prof. Ernst Fischer. The *cis* isomers were prepared by irradiation at 313 nm and separation on a column using standard techniques.[20,23] Ketones as trace impurities (<0.1%) in the four samples were indicated on the basis of phosphorescence at −196 °C. The samples were freshly dissolved prior to use, handled under red light and purged with argon unless indicated otherwise.

For steady-state irradiation measurements a 1000 W mercury–xenon lamp and a monochromator were used. The quantum yields Φ_f, $\Phi_{t\to c}$ and $\Phi_{c\to t}$ were determined as described in preceding papers.[21–26] The fluorescence spectra (wavelength of irradiation, $\lambda_{irr} = 313$ nm) were recorded on a Spex-Fluorolog or a Perkin-Elmer spectrofluorometer (LS-5).[31] The concentrations (in 1 cm cells) were typically 1×10^{-5}, 3×10^{-5} and 6×10^{-5} mol dm^{-3} for emission, *trans* → *cis* photoisomerization and *cis* → *trans* photoisomerization measurements, respectively, except for quenching measurements of $\Phi_{t\to c}$ by ferrocene, where they were 10 times larger (here the pathlength was 1 mm). Ferrocene (Merck) was recrystallized twice from ethanol. The solvents (Merck) were checked for impurities and purified where necessary, *e.g.* MCH, 2-methyltetrahydrofuran (MTHF), using standard methods.

For excitation at 248 and 353 nm an excimer laser (Lambda Physik, EMG 201MSC; pulse width 20 ns, energy 5–50 mJ) and a neodymium laser (JK Lasers; pulse width 15 ns, energy 5–20 mJ) were employed, respectively.[14,16] The concentrations were adjusted such that the absorbances (A_{353} or A_{248}) were about 0.2 per mm. The incident laser power was limited to the range of a linear dependence of ΔA_{380} *vs.* intensity, corresponding to ΔA_{380} values of $\leqslant 0.3$. In the cases of quenching measurements by oxygen it was checked that k_{obs} (using the wavelength of excitation, $\lambda_{exc} = 353$ nm) in O_2-saturated solution was equal to the limit of observation (*ca.* 7×10^7 s^{-1}). The signals were recorded on a transient digitizer (Tektronix 7912AD) and analysed on an Archimedes 440 computer.

Results and Discussion

Quantum Yields of *cis* ⇄ *trans* Photoisomerization

The quantum yields of *trans* → *cis* and *cis* → *trans* photoisomerization ($\Phi_{t \to c}$, $\Phi_{c \to t}$) are substantial for both ketostilbenes in non-polar, moderately polar (2-methyltetrahydrofuran, MTHF) and strongly polar (ethanol, acetonitrile) solvents at room temperature (Table 1). For $\lambda_{irr} = 313$ nm the photostationary state lies on the *cis* side owing to the much larger molar absorption coefficient (ε) of the *trans vs. cis* isomer. The *cis* content is smaller on going to $\lambda_{irr} = 254$ nm owing to the smaller $\varepsilon_t/\varepsilon_c$ ratio.[32]

$\Phi_{t \to c}$ is significantly reduced when ferrocene is added to BS (Fig. 1). Moreover, the $1/\Phi_{t \to c}$ values increase linearly with the ferrocene concentration (inset of Fig. 1). The ferrocene concentration at which $\Phi_{t \to c}$ is 50% is taken as the reciprocal Stern–Volmer constant, being 4.8×10^{-3} and 4.4×10^{-3} mol dm^{-3} for AS and BS in acetonitrile, respectively.

$\Phi_{c \to t}$ is small (*ca.* 10^{-3}) for both ketostilbenes in MTHF or ethanol at −196 °C but not zero, whereas $\Phi_{t \to c}$ is at least a hundred times smaller. Fischer and co-workers have reported that the $\Phi_{c \to t}$ values are almost constant for AS and BS in a 1 : 1 mixture of methylcyclohexane (MCH) and isohexane (IH) over a large temperature range.[32] For AS in ethanol the largest drop in $\Phi_{t \to c}$ occurs on decreasing the temperature between −130 and −150 °C (Fig. 2), just where the viscosity increases by many orders of magnitude. In comparison to this viscosity effect, the thermal activation in the +30 to −120 °C range is small in both cases (Fig. 2 and 3).

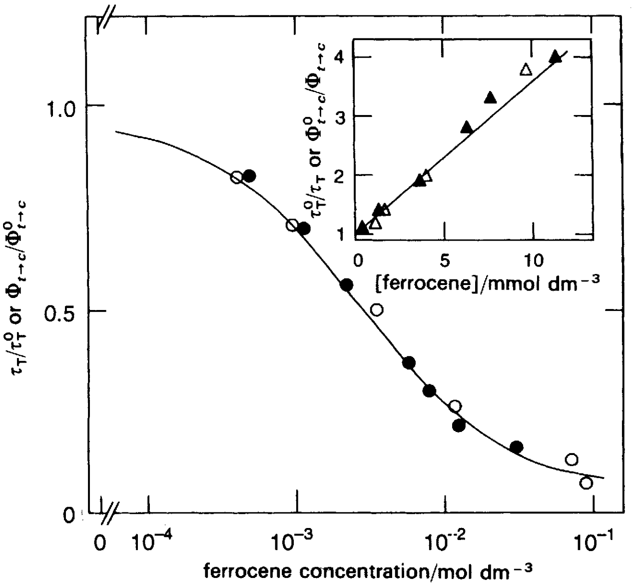


Fig. 1 Plots of τ_T (●, ▲, $\lambda_{exc} = 343$ nm) and $\Phi_{t \to c}$ (○, △, $\lambda_{irr} = 366$ nm) as a function of ferrocene concentration (log scale; inset, linear scale) for *trans*-BS in acetonitrile at 25 °C

Emission

The emission of *trans*-AS and *trans*-BS in fluid solution, showing a maximum (λ_f) around 400 nm, is ascribed to fluorescence for reasons of energy. The phosphorescence at −196 °C has a maximum at 580 nm,[31] and was not further examined here. The fluorescence spectra of the two *trans* isomers at −196 °C are slightly structured (*e.g.* $\lambda_f = 405$ and 425 nm) and the excitation spectra almost match the absorption spectra. The quantum yield of fluorescence is small in glassy media, the largest value is $\Phi_f = 0.04$ for *trans*-AS in ethanol at −196 °C, and Φ_f is negligible ($< 10^{-3}$) at room temperature. Accurate registration of data for the *cis* isomers is generally hampered (i) by the result of an even smaller quantum yield of fluorescence ($< 10^{-2}$ at −196 °C) and (ii) by the observation of a phosphorescence originating from trace impurities in glassy media. The latter is determined

Table 1 Quantum yields of *trans* → *cis* and *cis* → *trans* photoisomerization and percentage of *cis* in the photostationary state[a]

compound	solvent	temperature/°C	$\Phi_{t \to c}$	$\Phi_{c \to t}$	(% *cis*)$_s$
AS	cyclohexane	25	0.5	0.3	82
	MCH-IH[b]	25	0.5	0.3	
		−150	0.5	0.3	
	acetonitrile	25	0.5	0.3	80
	ethanol	25	0.48	0.31	79
		−150	0.03	0.3	22
		−160	0.0013	0.2	2
BS	cyclohexane	25	0.5	0.3	79
	MCH-IH[b]	25	0.54	0.27	
		−150	0.52	0.27	
		−160	0.31	0.21	
		−180	0.02	0.11	
	MTHF	25	0.52	0.32	80
		−150	0.1	0.25	45
	ethanol	25	0.47	0.32	78
		−150	0.16	0.3	52
		−160	0.04	0.3	20
	acetonitrile	25	0.4	0.3	77

[a] In argon-saturated solutions, $\lambda_{irr} = 313$ nm. [b] Taken from ref. 32.

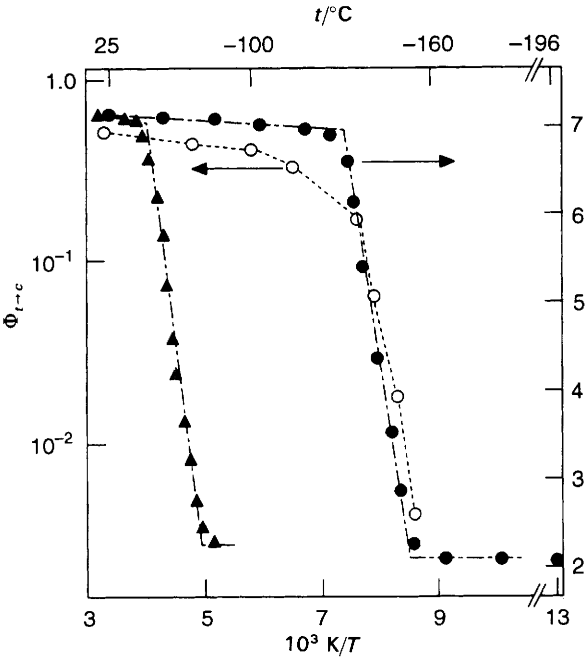


Fig. 2 Semilogarithmic plots of τ_T^{-1} (full symbols, $\lambda_{exc} = 353$ nm) and $\Phi_{t\to c}$ (open symbols, $\lambda_{irr} = 313$ nm) *vs.* T^{-1} for *trans*-AS in GT (triangles) and ethanol (circles)

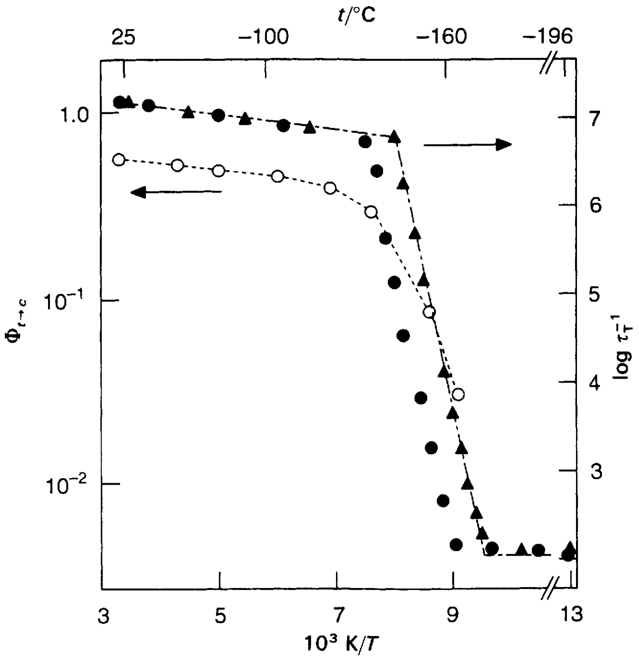


Fig. 3 Semilogarithmic plots of τ_T^{-1} (full symbols, $\lambda_{exc} = 248$ nm) and $\Phi_{t\to c}$ (open symbols, $\lambda_{irr} = 313$ nm) *vs.* T^{-1} for *trans*-BS in MTHF (triangles) and ethanol (circles)

from the differences between excitation and absorption spectra.

Properties of the Triplet State at Room Temperature

The transient absorption spectra of *trans*-AS in several solvents at room temperature are similar, showing a broad band with a single absorption maximum (λ_T) around 380 nm (Table 2), extending to *ca.* 600 nm and overlapping with the ground-state absorption below 360 nm [Fig. 4(*a*)]. The transient is assigned to a triplet state due to the following: It is formed within the laser pulse width and decays by first-order kinetics. The lifetime ($1/k_{obs} = \tau_T$) shows no marked dependence on the properties of the solvent (Table 2) and is reduced in the presence of ferrocene and oxygen. Rate constants for quenching by oxygen in the range $5 \leqslant k_{ox}/10^9$ dm^3 mol^{-1} s^{-1} $\leqslant 8$ (Table 2) were obtained from k_{obs} in argon- and air-saturated solutions. From the linear dependence of k_{obs} *vs.* ferrocene concentration, a rate constant of $k_q = 2.5 \times 10^9$ dm^3 mol^{-1} s^{-1} was found in acetonitrile.

The properties (λ_T, τ_T, k_{ox}, k_q) of the triplet of *trans*-BS at room temperature, in particular the kinetic data, are similar

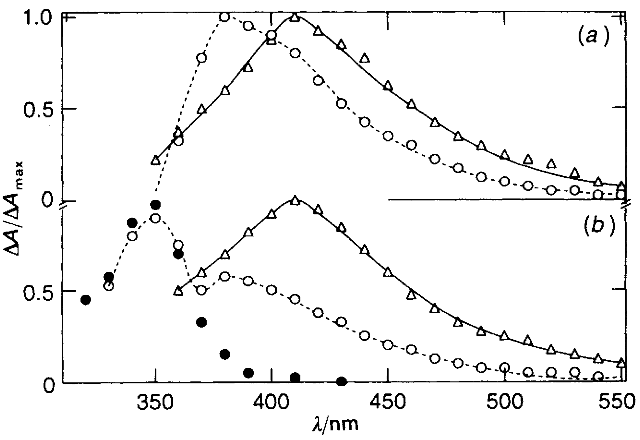


Fig. 4 T–T absorption spectra of (*a*) *trans*-AS and (*b*) *cis*-AS in cyclohexane solution at room temperature at the pulse end (○) and after 0.5 μs (●), and in MCH at −196 °C (△), 1 μs after the pulse, $\lambda_{exc} = 248$ nm

Table 2 T–T absorption maximum, triplet lifetime and rate constants for quenching by oxygen (k_{ox}) and ferrocene (k_q)[a]

compound	solvent	λ_T/nm	τ_T/ns	$k_{ox}/10^9$ dm^3 mol^{-1} s^{-1}	$k_q/10^9$ dm^3 mol^{-1} s^{-1}
trans-AS	cyclohexane[b]	380	60	6	
	benzene	380	70	5	
	GT	385	90		
	acetonitrile	<300, 390	75	5	2.5
	ethanol	<300, 375	70	7	
trans-BS	cyclohexane	380	70	8	
	benzene	380	75	8	2
	MTHF	380	85		
	acetonitrile	390	75	8	3
	ethanol[b]	390	70		
cis-AS	cyclohexane[b]	380	65		
cis-BS	ethanol[b]	400	70		

[a] In argon-saturated solution at room temperature, $\lambda_{exc} = 353$ nm, unless otherwise indicated. [b] $\lambda_{exc} = 248$ nm.

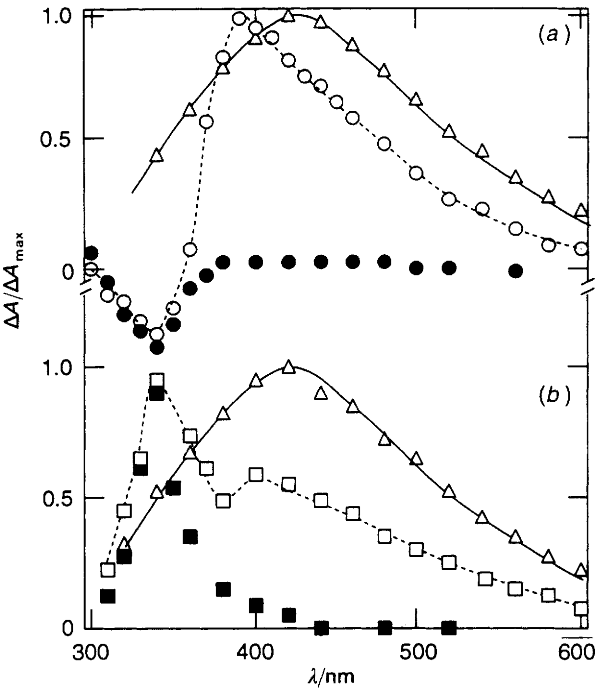


Fig. 5 T–T absorption spectra of (*a*) *trans*-BS and (*b*) *cis*-BS in ethanol solution at room temperature at the pulse end (open circles and squares) and after 0.5 μs (full symbols), and at −196 °C 1 μs after the pulse △, λ_{exc} = 248 nm

to those of *trans*-AS (Table 2). The T–T absorption spectrum of *trans*-BS in several solvents has a similar λ_T, whereas the half-width is somewhat larger [Fig. 5(*a*)] than that of *trans*-AS. The triplet lifetime of *trans*-BS is around 80 ns. Examples of the time dependences of ΔA_{380} in argon-, air- and oxygen-saturated acetonitrile solutions are shown in Fig. 6; the obtained rate constant is $k_{ox} = 8 \times 10^9$ dm^3 mol^{-1} s^{-1}. Furthermore, the k_q values for triplet quenching by ferrocene of (2–3) × 10^9 dm^3 mol^{-1} s^{-1} in the two solvents are well below the diffusion-controlled limit. The Stern–Volmer constant in acetonitrile (Fig. 1) is $\tau_T k_q = 225$ dm^3 mol^{-1}. From the similarity of the Stern–Volmer constants for the quenching of $\Phi_{t \to c}$ and τ_T by ferrocene, a triplet pathway for *trans* → *cis* is concluded.

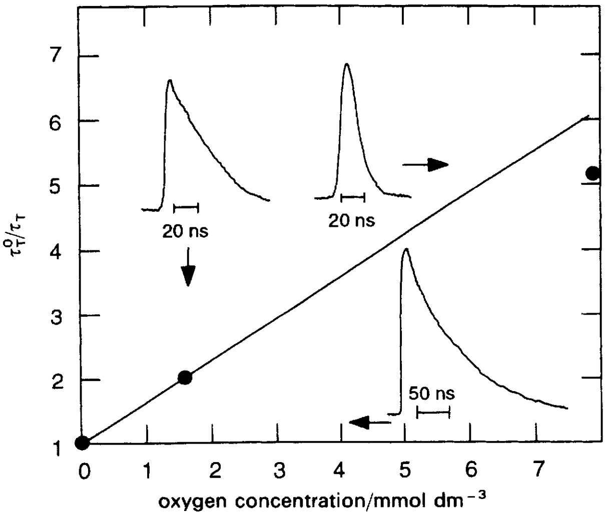


Fig. 6 Plot of k_{obs} (normalized to τ_T^0 = 75 ns) *vs.* the oxygen concentration for *trans*-BS in acetonitrile. Insets: formation and decay of the triplet at 380 nm in argon-, air- and oxygen-saturated solution (λ_{exc} = 353 nm).

Repeated flashing of *trans*-AS or *trans*-BS, thereby gradually converting the sample into a mixture containing both *cis* and *trans* isomers, did not result in a measurable decrease in the transient absorption (ΔA) at λ_T nor generate a change in the spectrum. Consequently, the transient absorption spectra obtained from the two *cis* isomers in the range of no overlap with the $S_0 \to S_1$ absorption can be considered to be the same as those from the *trans* isomers. This is illustrated in Fig. 4(*b*) for *cis*-AS in cyclohexane and in Fig. 5(*b*) for *cis*-BS in ethanol, in comparison with the spectra in Fig. 4(*a*) and 5(*a*), respectively. The *cis* → *trans* isomerization leads to an increase in ΔA in the 300–370 nm range for flashing of the *cis* isomers and the *trans* → *cis* isomerization leads to a decrease in ΔA_{340} for the *trans* sample [Fig. 5(*a*)]. The changes are permanent and thus separated from the transient changes.

Behaviour of the Triplet at Low Temperatures

In glassy media the T–T absorption spectra of both *trans* isomers are similar to those at room temperature, except that their λ_T are red-shifted (Table 3), typically 30–50 nm, when the temperature is decreased to −196 °C. Examples are shown in Fig. 4(*a*) and 5(*a*). Extrapolation of $\Phi_{t \to c}$ (Fig. 2 and 3) shows that *trans* → *cis* photoisomerization does not occur below temperature t_0. The T–T absorption spectrum and $\lambda_T \approx 420$ nm at −196 °C has thus to be attributed to a transition originating from $^3t^*$. A comparison with the spectra of the *cis* isomers [Fig. 4(*b*) and 5(*b*)] reveals that they are identical for each of the two stilbenes. This also holds true for the decay kinetics, no marked difference was found for a given solvent and temperature (below −150 °C, to reduce the isomerization) for either *trans*- or *cis*-BS and in a similar way for *cis*- and *trans*-AS. The observed spectra of the *cis* isomers at −196 °C [Fig. 4(*b*) and 5(*b*)] are due to the $^3c^*$ configuration, because $\Phi_{c \to t}$ is very small. The following results refer to flashing of the *trans* isomers (unless indicated otherwise).

When the temperature is varied from 24 to −196 °C, τ_T increases typically by five orders of magnitude for both ketostilbenes in several media, reaching limiting values of $\tau_T^0 \approx 10$ ms below −180 °C (Table 3). The temperature dependence of the reciprocal triplet lifetime of *trans*-BS (Fig. 3) exhibits three well distinguished parts; one above a critical temperature t_v (*e.g.* −149 and −138 °C in MTHF and ethanol, respectively), one below a second characteristic temperature t_0 (−169 and −155 °C, respectively) and a third region between t_v and t_0. A similar dependence of τ_T^{-1} *vs.* T^{-1} was obtained for *trans*-AS (Fig. 2). In glycerol triacetate (GT) the change in τ_T was obtained in a much narrower temperature range (see Table 3). This indicates that the viscosity, which changes by 12 orders of magnitude between 25 and −76 °C,[33] is the dominant parameter.

The relative triplet yield, as estimated by ΔA_{400}, was found to be nearly constant over a wide temperature range. This was also found for *cis*-AS (or *cis*-BS) in ethanol, starting at −196 °C, where virtually no *cis* → *trans* isomerization occurs (see above), and then increasing the temperature; repeated flashing, however, also yields the *trans* isomer. Triplet population from the *trans* isomers occurs *via* the $^1t^* \to {}^3t^*$ transition (Scheme 1). A significant contribution of a twisting step in S_1, $^1t^* \to {}^1p^*$, as in other cases,[16,25,28,30] is excluded on the basis of the quenching measurements with ferrocene (Fig. 1). Owing to this, the substantial $\Phi_{t \to c}$ (Table 1) and the small Φ_f values, Φ_{isc} is estimated to be in the range 0.7–1.0 for both *trans* isomers.

Based on a rate constant for fluorescence of $k_f = 4 \times 10^8$ s^{-1} ($\Phi_f \approx 0.04$) for *trans*-stilbene at room temperature,[2,7] $k_{isc} \approx k_f/\Phi_f \geqslant 4 \times 10^{11}$ s^{-1} can be estimated for AS or BS using the limit $\Phi_f < 10^{-3}$ (see above) and assuming k_f to be

Table 3 T–T absorption maximum in glassy media and characteristic temperatures for triplet decay[a]

compound	solvent	λ_T^b/nm	t_v/°C	t_0/°C	$k(t_v)/10^6\ s^{-1}$	$1/\tau_T^0$ $^c/10^2\ s^{-1}$
trans-AS	MCH	410				1.1
	MTHF	415	−149	−169	7	1.2
	GT	410	−32	−69	9	1.8
	ethanol	410	−138	−155	10	1.2
trans-BS	MTHF	430	−149	−168	7	0.9
	EPA[d]	430	−134	−173	9	0.8
	GT	430	−50	−70	6	1.5
	ethanol	425	−130	−162	6	1.3
cis-AS	MCH	410				1.2
cis-BS	ethanol	420				1.1
trans-stilbene[e]	GT			−72		1
trans-4-nitrostilbene	GT		−24	−64		
trans-stilbene	ethanol			−168		0.7
trans-4-nitrostilbene	ethanol		−124	−165		

[a] In argon-saturated solutions.[b] λ_T is *ca.* −50 °C for GT and below −150 °C for the other solvents. [c] Reciprocal triplet lifetime below t_0. [d] Diethyl ether, isopentane, ethanol (5 : 5 : 2). [e] Taken from ref. 30 and 21 for stilbene and 4-nitrostilbene, respectively.

the same in the presence and absence of the carbonyl group. The smallness of the changes in ΔA of the T–T absorption spectra with temperature [Fig. 4(*a*) and 5(*a*)] shows that $\Phi_{isc} \approx 1$ holds true over the whole range examined. This contrasts with the case of *trans*-4-R-stilbenes (R: H, F, Cl and Br), where the triplet yield increases with decreasing temperature, *i.e.* T–T absorption becomes significant only when twisting in the excited singlet state ($^1t^* \rightarrow {}^1p^*$) or *via* an upper excited triplet state is hindered by the high viscosity.[30] It is worth pointing out that new insights in the excited singlet state dynamics of *trans*-stilbene have been obtained recently by the investigations of several groups.[7,8]

cis → *trans* Photoisomerization

After population of the $^1c^*$ state, two initial deactivation steps are possible in fluid solution, intersystem crossing at the *cis* side

$$^1c^* \rightarrow {}^3c^* \qquad (2a)$$

followed by rotation about the double bond

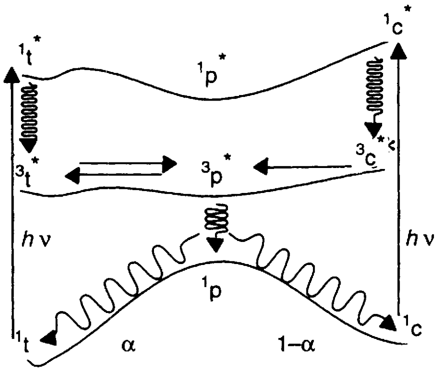
$$^3c^* \rightarrow {}^3p^* \qquad (2b)$$

(Scheme 1) or first twisting in S_1

$$^1c^* \rightarrow {}^1p^* \qquad (3a)$$

and then intersystem crossing.

$$^1p^* \rightarrow {}^3p^* \qquad (3b)$$



Scheme 1

If both partial *cis* → *trans* routes occur on a timescale < 10 ns, they are difficult to distinguish. Identical T–T absorption spectra from $^3c^*$ and $^3p^*$ states would completely hinder a separation. The absence of a marked fluorescence even in rigid media indicates the involvement of n,π* states in the deactivation of $^1c^*$. In this respect, AS and BS behave like a somewhat distorted acetophenone and benzophenone, respectively.†

On the basis of a close similarity of the spectra of the *cis* isomers at 25 and −196 °C, sequence (2) in the *cis* → *trans* pathway at ambient temperatures is likely, although alternative (3) could be involved to a certain extent. The driving force of the electronically excited *cis* form, as compared with the excited *trans* form, to twist about the double bond is generally significantly stronger. This is supported by the much smaller reduction of $\Phi_{c \rightarrow t}$ (at a given low temperature) with respect to $\Phi_{t \rightarrow c}$ on lowering the temperature (Table 1). An impressive example has been reported for BS in the 1 : 1 mixture of MCH and IH, where $\Phi_{c \rightarrow t}$ is only 2.5 times smaller at −180 °C than at room temperature, but the change in $\Phi_{t \rightarrow c}$ is ten times larger.[32] Thus, a clear distinction between sequences (2) and (3) is not possible as yet.

Absorption Spectra and Energetics

The triplet energy, *i.e.* the $T_1 \rightarrow S_0$ transition energy, obtained from phosphorescence at −196 °C, is $E_T = 49$, 47.3 and 46.6 kcal mol^{-1} for the *trans* forms of stilbene, both 4-ketostilbenes and 4-nitrostilbene, respectively.[3,31] The $S_0 \rightarrow S_1$ absorption maximum of the *trans* form of AS (315 nm) or BS (318 nm) also lies between those of stilbene (296 and 307 nm, $\varepsilon_{296} \approx \varepsilon_{307}$) and 4-nitrostilbene (340 nm). It is therefore reasonable to suggest that the singlet energy levels of *trans*-AS and *trans*-BS are also between those of the two others. Concerning the *cis* isomers, the S_1 level also has a small decreasing shift of the same order as above. $E_T = 45$ kcal mol^{-1} above ^1c has been proposed for *cis*-stilbene,[4] no data are available for the other *cis*-stilbenes. Results from photoacoustic calorimetry for the relaxed triplet state are $E_T = 44$ kcal mol^{-1} for both isomers[12] or $E_T = 42.0$ and 46.5 kcal mol^{-1} for *cis*- and *trans*-stilbene, respectively.[13] For comparison, $E_T = 48.4$–49.0 kcal mol^{-1} for *trans*-4,4′-diacetylstilbene.[13]

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† See Φ_{isc} values in ref. 34.

The similarity of the T–T absorption spectra of *trans*- and *cis*-AS (Fig. 4) or BS (Fig. 5) indicates that the energy gap between T_n and T_1 happens to be virtually the same for $^3t^*$, $^3p^*$ and $^3c^*$. This contrasts the cases of stilbene[10] and the 4-nitrostilbenes,[21,24] where the transition energy for $^3t^* \rightarrow T_n$ was suggested to be lower than that for the $^3p^* \rightarrow T_n$ step. Indication for the possibility of only small transition changes between excited states of *cis*- and *trans*-stilbene can be found from the $S_1 \rightarrow S_n$ spectra which have maxima at 660 and 590 nm, respectively.[35]

A further difference caused by the carbonyl group is the absence of structure in the T–T absorption spectrum of *trans*-AS or *trans*-BS [Fig. 4(*a*) and 5(*a*)], whereas those of *trans*-4-R-stilbenes (R: H, F, Cl, Br and OCH_3) are structured, generally showing three peaks.[10,29,30] On the other hand, the T–T absorption spectra of *trans*- and *cis*-BS are quite different from that of benzophenone,[34] indicating that the π system of the styrene part strongly interacts with that of the remaining benzophenone structure. The observation of absorption from $^3c^*$ is new and important. There seems to be a lack of information in the literature concerning the T–T absorption spectrum of *cis*-stilbenes in glassy media, *e.g.* at −196 °C.[34]

Triplet-state Dynamics in the *trans* → *cis* Pathway

The slow decay in the high viscosity range, in particular the limiting τ_T^0 values at temperatures below t_0, is explained for the two ketostilbenes, as generally for 1,2-diarylethylenes,[16,21,30] by intersystem crossing at the *trans* side, $^3t^* \rightarrow {}^1t$. The characteristic temperature, t_0, depends only slightly on the particular 4-R-stilbene molecule (R: H, acetyl, benzoyl and nitro) but strongly on the medium (Table 3). For example, t_0 is −70 and −168 °C for BS in GT and MTHF, respectively.

Evidence for establishment of the $^3t^* \rightleftarrows {}^3p^*$ triplet equilibrium is based on the temperature dependences of τ_T and $\Phi_{t\rightarrow c}$ (Fig. 2 and 3) as follows. When the temperature is increased from t_0 to the second characteristic temperature, t_v, which is only 20–30 °C above t_0, τ_T is decreased. This effect is extremely strong, nearly five orders of magnitude (Fig. 2 and 3), and cannot be due simply to the reduced diffusion at low temperatures;[16,33] obviously inherent geometrical changes are involved. The explanation is that between t_v and t_0 $^3t^*$ is deactivated *via* sequence (4):

$$^3t^* \rightarrow {}^3p^* \rightarrow {}^1p \rightarrow \alpha\,{}^1t + (1-\alpha)\,{}^1c \qquad (4)$$

α is the fraction of triplet decay into the *trans* form (see Scheme 1). Above t_v, the viscosity is low enough, such that the $^3p^* \rightarrow {}^3t^*$ twisting step dominates, as shown for nitrostilbenes[21–24] and naphthylstyrenes.[16] At t_v, the rate constants for the two decay steps of $^3p^*$ are equal. This constitutes a minimum value for the $^3p^* \rightarrow {}^1p$ transition of $k_p = 6 \times 10^6\ s^{-1}$ (Table 3), *i.e.* when this transition is independent of temperature and viscosity. On the other hand, k_p cannot be much larger than the above estimation, as concluded from eqn. (I) for a triplet equilibrium.[21,24]

$$\frac{1}{\tau_T} = k_p \frac{K_1}{1 + K_1} \qquad (I)$$

Here, $K_1 = k_1/k_{-1}$ is the equilibrium constant, k_1 is the rate constant for the $^3t^* \rightarrow {}^3p^*$ conversion and k_{-1} that for the back-conversion. According to eqn. (I), k_p is equal to $1/\tau_T$ [which is in the range $(1.1–1.7) \times 10^7\ s^{-1}$] or smaller, since $K_1/(1 + K_1)$ can vary between 1 and 0. The former case ($K_1 \gg 1$), *i.e.* a shift of the $^3t^* \rightleftarrows {}^3p^*$ equilibrium towards the perpendicular conformation, is supported by the very small effect of temperature on τ_T above t_v. For comparison, the data reported for *trans*-4-nitrostilbene are $k_p \approx 3 \times 10^7\ s^{-1}$ and $0.3 \leqslant K_1 \leqslant 3$ with a trend to smaller values in polar solvents.[24] This trend, which is absent for AS and BS, was also found for stilbene, where $1.9 \leqslant k_p/10^7\ s^{-1} \leqslant 2.2$ and $2.4 \leqslant K_1 \leqslant 10$ has been reported.[10] The latter equilibrium constant had been criticized by Gorman and Rodgers[11] on the basis of singlet oxygen measurements in benzene and a lower value of $K_1 = 1$ was favoured. In contrast, the $^3t^* \rightleftarrows {}^3p^*$ triplet equilibrium does not exist for styrene derivatives.[36]

A limitation for K_1 towards maximum values is obtained from the quenching measurements at room temperature. Assuming that ferrocene, the applied quencher for energy transfer interacts only with $^3t^*$ and that oxygen quenches only $^3p^*$ (the rate constants are k'_q and k'_{ox}, respectively), the experimental slopes of $1/\tau_T$ *vs.* [*Q*] or $[O_2]$ are given by eqn. (II) and (III).

$$k_q = \frac{k'_q}{1 + K_1} \qquad (II)$$

$$k_{ox} = k'_{ox} \frac{K_1}{1 + K_1} \qquad (III)$$

Data in Table 2 show that k_q for quenching by ferrocene is well below the diffusion-controlled limit (rate constant, k_{diff}). A value of $K_1 \geqslant 10$ would not be in agreement with the experimental value $k_q \approx 0.2k_{diff}$. On the other hand, k_{ox} has a trend to values much larger than the $1/9k_{diff}$ limit, which would result from triplet quenching by oxygen *via* energy transfer. Quenching of the $^3p^*$ state of stilbene by oxygen occurs *via* a spin-exchange mechanism.[3,5,6] The k_q and k_{ox} values for AS and BS and $2 \lesssim K_1 \lesssim 6$ are in agreement with the applied model. One could speculate about the role of an extended $^3t^* \rightleftarrows {}^3p^* \rightleftarrows {}^3c^*$ equilibrium and the effect of energy transfer from $^3c^*$ to ferrocene (or azulene), but an answer to this would require a far more in depth study.

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References

1 (*a*) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Dalton, *J. Am. Chem. Soc.*, 1964, **86**, 3197; (*b*) J. Saltiel, D. W. L. Chang, E. D. Megarity, A. D. Rousseau, P. T. Shannon, B. Thomas and A. K. Uriarte, *Pure Appl. Chem.*, 1975, **41**, 559; (*c*) J. Saltiel, P. T. Shannon, O. C. Zafiriou and A. K. Uriarte, *J. Am. Chem. Soc.*, 1980, **102**, 6799; (*d*) J. Saltiel, S. Ganapathy and C. Werking, *J. Phys. Chem.*, 1987, **91**, 2755.

2 J. Saltiel, A. Marinari, D. W-L. Chang, J. C. Mitchener and E. D. Megarity, *J. Am. Chem. Soc.*, 1979, **101**, 2982.

3 J. Saltiel and J. L. Charlton, in *Rearrangements in Ground and Excited States*, ed. P. de Mayo, Academic Press, New York, 1980, vol. 3, p. 25.

4 J. Saltiel, G. R. Marchand, E. Kirkor-Kaminska, W. K. Smothers, W. B. Mueller and J. L. Charlton, *J. Am. Chem. Soc.*, 1984, **106**, 3144.

5 J. Saltiel and B. W. Atwater, *Adv. Photochem.*, 1988, **14**, 1.

6 J. Saltiel and B. Thomas, *Chem. Phys. Lett.*, 1976, **37**, 147.

7 J. Saltiel and Y-P. Sun, in *Photochromism. Molecules and Systems*, ed. H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990, p. 64.

8 (*a*) R. M. Hochstrasser, *Pure Appl. Chem.*, 1980, **52**, 2683; (*b*) S. T. Repinec, R. J. Sension, A. Z. Szarka and R. M. Hochstrasser, *J. Phys. Chem.*, 1991, **95**, 10380; (*c*) S. K. Kim and G. R. Fleming, *J. Phys. Chem.*, 1988, **92**, 2168; (*d*) J. Schroeder, J. Troe and P. Vöhringer, *Chem. Phys. Lett.*, 1993, **203**, 255; (*e*) D. H. Waldeck, *Chem. Rev.*, 1991, **91**, 415, and references therein.

9 M. Sumitani, K. Yoshihara and S. Nagakura, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2503.

10 H. Görner and D. Schulte-Frohlinde, *J. Phys. Chem.*, 1981, **85**, 1835.

11 A. A. Gorman and M. A. J. Rodgers, *Chem. Phys. Lett.*, 1985, **120**, 58.

12 J. A. Lavilla and J. L. Goodman, *Chem. Phys. Lett.*, 1987, **141**, 149.

13 T. Ni, R. A. Caldwell and L. A. Melton, *J. Am. Chem. Soc.*, 1989, **111**, 457.

14 H. Görner, D. W. Eaker and J. Saltiel, *J. Am. Chem. Soc.*, 1981, **103**, 7164.

15 (*a*) S. Lazare, R. Bonneau and R. Lapouyade, *J. Phys. Chem.*, 1984, **88**, 18; (*b*) S. Lazare, R. Lapouyade and R. Bonneau, *J. Am. Chem. Soc.*, 1985, **107**, 6604; (*c*) T. Wismontski-Knittel and P. K. Das, *J. Phys. Chem.*, 1984, **88**, 2803; (*d*) K. A. Muszkat, N. Castel, A. Jakob, E. Fischer, W. Luettke and K. Rauch, *J. Photochem. Photobiol., A: Chem.*, 1991, **56**, 219.

16 F. Elisei, U. Mazzucato and H. Görner, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 1469.

17 (*a*) H. Furuuchi, T. Arai, Y. Kuriyama, H. Sakuragi and K. Tokumaru, *Chem. Phys. Lett.*, 1989, **162**, 211; (*b*) T. Arai, T. Karatsu, H. Misawa, Y. Kuriyama, H. Okamoto, T. Hiresaki, H. Furuuchi, H. Zeng, H. Sakuragi and K. Tokumaru, *Pure Appl. Chem.*, 1988, **60**, 989; (*c*) K. Tokumaru and T. Arai, *J. Photochem. Photobiol., A: Chem.*, 1992, **65**, 1.

18 T. Arai and K. Tokumaru, *Chem. Rev.*, 1993, **93**, 23.

19 P-H. Bong, H. J. Kim, K. H. Chae, S. C. Shim, N. Nakashima and K. Yoshihara, *J. Am. Chem. Soc.*, 1986, **108**, 1006.

20 D. V. Bent and D. Schulte-Frohlinde, *J. Phys. Chem.*, 1974, **78**, 446.

21 D. Schulte-Frohlinde and H. Görner, *Pure Appl. Chem.*, 1979, **51**, 279.

22 H. Görner, *J. Photochem.*, 1980, **13**, 269.

23 H. Görner, *Ber. Bunsenges. Phys. Chem.*, 1984, **88**, 1199.

24 H. Görner and D. Schulte-Frohlinde, *Ber. Bunsenges. Phys. Chem.*, 1984, **88**, 1208.

25 H. Görner, *J. Photochem. Photobiol., A: Chem.*, 1987, **40**, 325.

26 (*a*) H. Gruen and H. Görner, *J. Phys. Chem.*, 1989, **93**, 7144; (*b*) R. Lapouyade, A. Kuhn, J-F. Letard and W. Rettig, *Chem. Phys. Lett.*, 1993, **208**, 48.

27 H. J. Kuhn, R. Straatmann and D. Schulte-Frohlinde, *J. Chem. Soc., Chem. Commun.*, 1976, 824.

28 H. Görner and D. Schulte-Frohlinde, *J. Phys. Chem.*, 1985, **89**, 4105.

29 (*a*) G. Heinrich, H. Blume and D. Schulte-Frohlinde, *Tetrahedron Lett.*, 1967, 4693; (*b*) G. Heinrich, G. Holzer, H. Blume and D. Schulte-Frohlinde, *Z. Naturforsch., Teil B*, 1970, **25**, 496; (*c*) W. G. Herkstroeter and D. S. McClure, *J. Am. Chem. Soc.*, 1968, **90**, 4522; (*d*) J. Saltiel, J. T. D'Agostino, W. G. Herkstroeter, G. Saint-Ruf and N. P. Buu-Hoi, *J. Am. Chem. Soc.*, 1973, **95**, 2543.

30 H. Görner and D. Schulte-Frohlinde, *J. Phys. Chem.*, 1979, **83**, 3107.

31 H. Görner, *J. Phys. Chem.*, 1989, **93**, 1826.

32 D. Gegiou, K. A. Muszkat and E. Fischer, *J. Am. Chem. Soc.*, 1968, **90**, 3907.

33 (*a*) D. Gegiou, K. A. Muszkat and E. Fischer, *J. Am. Chem. Soc.*, 1968, **90**, 12; (*b*) E. Fischer, G. Seger and K. A. Muszkat, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1569; (*c*) G. Fischer and E. Fischer, *Mol. Photochem.*, 1977, **8**, 279.

34 I. Carmichael and G. L. Hug, *J. Phys. Chem. Ref. Data*, 1986, **15**, 1.

35 K. Yoshihara, A. Namiki, M. Sumitani and N. Nakashima, *J. Chem. Phys.*, 1979, **71**, 2892.

36 R. Bonneau and B. Herran, *Laser Chem.*, 1984, **4**, 151.

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