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Fluorescence and Photoisomerization of Two Stilbene-Based Dyes

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SUMMARY

The effect of solvent on the fluorescence and direct trans–cis *photoisomerization of two stilbene-based fluorescent whitening agents has been investigated. With increasing solvent polarity there is an increase in the rate of photoisomerization resulting in reduced fluorescence quantum yields. This solvent polarity dependence is particularly marked for the bis(triazinylamino)stilbene dye and the results are discussed with reference to previous studies on model compounds. A comparison is made between the fluorescence lifetimes determined for the dyes in solution, embedded in poly(vinyl alcohol) film and adsorbed onto wool fabric. Fluorescence lifetimes of the dyes on wool fabric are shorter than expected and possible explanations for this observation are presented.*

1 INTRODUCTION

Stilbene-based fluorescent whitening agents are widely used in the fluorescent whitening of textiles and an extensive amount of research has been undertaken to improve the performance of these dyes and to understand their photochemistry.[1] A knowledge of the photophysical and photochemical properties of fluorescent whitening agents is particularly

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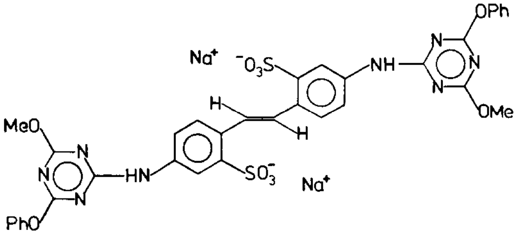
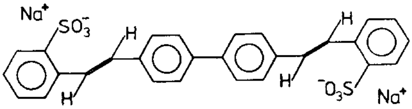
relevant for explaining the poor lightfastness of fluorescently whitened wool fabric compared with the unwhitened fabric.[1-5]

In solution, stilbene-based fluorescent dyes are known to lose their fluorescence rapidly. The principal mechanism for photofading of these dyes is photoisomerization from the fluorescent *trans* isomer to the non-fluorescent *cis* isomer.[1,2,6,7] This process has been reported for dyes based on both the bis(triazinylamino)stilbene[2] and bis-styrylbiphenyl[7] structures investigated in this work and denoted **I** and **II**, respectively. Whilst further degradation of both dyes occurs, this may not be observed until a photostationary mixture of *trans* and *cis* isomers has been formed. *Trans–cis* photoisomerization has been found to be an important process in the photochemistry of *trans*-stilbene,[8] *trans*-4,4′-diaminostilbene (DAS)[9] and *trans*-4,4′-diaminostilbene-2,2′-disulphonic acid (DASDA)[10] which may be considered as model compounds.

I



II



Viscous media should inhibit twisting from the *trans* to the *cis* isomer in the excited state and a decrease in photoisomerization is expected and has been observed for **I** on wool.[2] However, solvent polarity also influences the photochemistry of **I** as indicated by the reported increase in fluorescence quantum yield (ϕ_f) when the solvent is changed from water to 1,4-dioxane.[3] The influence of solvent polarity on ϕ_f for stilbene dyes has been employed in the application of these molecules as fluorescent probes of protein environments.[11] Previous studies have not shown to what extent the photoisomerization process in stilbene dyes is affected by solvent polarity or the mechanism responsible for the solvent polarity-dependence of ϕ_f. These issues are addressed here with respect to **I** and **II** and the results related to recent investigations on model compounds. The fluorescence lifetimes of the dyes on wool fabric have also been determined and compared with the results obtained in solution and in polymer films.

2 EXPERIMENTAL

The sodium salt of *trans*-4,4′-bis(4″-methoxy-6″-phenoxy-*s*-triazin-2″-ylamino)stilbene-2,2′-disulphonic acid (**I**, Reg. No. [54262-22-5], Leucophor PAF, Sandoz) was used as received. Studies were also made on the collidine salt of **I**, synthesized at the CSIRO, Division of Protein Chemistry,[2] to support the results obtained using the sodium salt. The sodium salt of all *trans*-4,4′-bis(2-sulphostyryl)biphenyl (**II**, Reg. No. [60317-04-6], Uvitex NFW, Ciba–Geigy) was recrystallized three times from ethanol/water before use.

Corrected fluorescence quantum yields (ϕ_f) were obtained relative to quinine bisulphate (Eastman) in 1M-H_2SO_4 (May and Baker AR) for which $\phi_f = 0{\cdot}546$.[12] Fluorescence spectra were recorded on a Perkin–Elmer MPF-44A fluorescence spectrophotometer using solution absorbances of less than 0·06 in 1-cm pathlength cells. The fluorescence lifetime (τ) was determined using a picosecond laser/streak camera system described in detail elsewhere.[13] The third harmonic of a single pulse from a mode-locked Nd^{3+}/phosphate glass laser was used for excitation (λ_{exc} 353 nm) and the fluorescence emitted from the sample above 400 nm was detected by a Photochron II streak camera. The digitized fluorescence decay profile provided by the streak camera/optical multichannel analyzer combination was analyzed on a VAX computer using non-linear least-squares reconvolution fitting procedures. In solution and in polymer films, good fits were obtained to a single exponential decay (Fig. 1). Degassing of the solutions through several freeze–pump–thaw cycles to remove oxygen did not significantly affect ϕ_f or τ.

The photoisomerization quantum yields (ϕ_t) were determined by monitoring the decrease in absorbance, using a Cary 17 spectrophotometer, after irradiation at 340 nm in the fluorescence spectrophotometer to less than 10% degradation. The photon flux incident on the samples at 340 nm had been determined shortly before using potassium ferrioxalate actinometry.[14] The dye solutions absorbed more than 80% of the exciting light and were agitated with dry air during photolysis. Appropriate corrections were made for the contribution of the *cis* isomers of **I** and **II** to the absorbance at the absorbance maxima of the *trans* isomer (λ_A). This correction required determining the extinction coefficients of the *cis* isomers (ε_c), which was achieved by measuring ϕ_f for a photostationary mixture of *trans* and *cis* isomers of each dye and evaluating the fraction of light absorbed by the fluorescent *trans* isomer.[9] The extinction coefficients used to determine ϕ_t are collected in Table 1 and are of similar magnitude to the values of ε_c derived from a study on related stilbene dyes.[15]

Plain weave 64’s merino wool fabric was cleaned by Soxhlet extraction

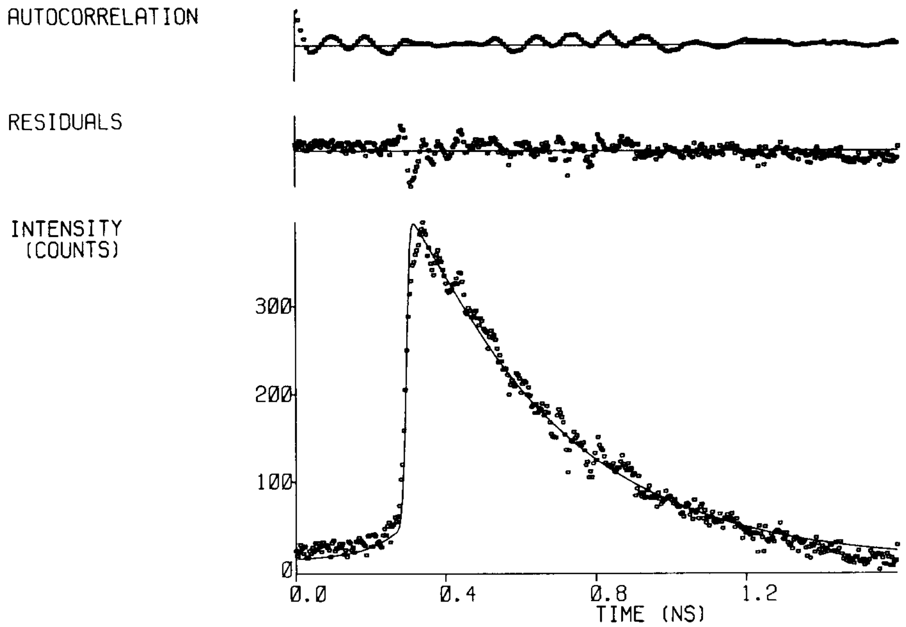


Fig. 1. Fluorescence decay profile of **I** in water fitted to a single exponential decay function with $\tau = (0{\cdot}37 \pm 0{\cdot}02)$ ns. □, Experimental data; ——, fitted curve. Residuals and autocorrelation plots indicate goodness-of-fit.

TABLE 1
Dependence of Absorption (λ_A) and Fluorescence (λ_F) Maxima of **I** on Solvent

Solvent	$E_T(30)$[a] (*kJ/mol*)	λ_A (*nm*)	λ_F (*nm*)	*Molar extinction coefficient*[b] (M^{-1} *cm*$^{-1}$)	
				ε_t	ε_c
Water	264	343	427	57 200	10 500
Methanol	232	348·5	403, 425	59 400	10 600
Ethanol	217	347·5	403, 425	55 200	9 900
n-Propanol	212	341	403, 425	—	—
n-Butanol	210	337	406, 425	—	—
DMF	183	354	404, 427	59 000	10 300
Dioxane	151	352·5, 365	402, 425	—	—
Ethylene glycol	236	352	409, 430	53 700	8 400
Glycerol	238	354	411, 428	—	—

[a] $E_T(30)$, solvent polarity parameter.[16]
[b] Molar extinction coefficients for the *trans* (ε_t) and *cis* (ε_c) isomers of **I** are given at λ_A.

with petroleum ether (60/80 May and Baker, AR), ethanol and triply distilled water before use. The wool fabric was then dyed in accordance with the literature procedure.[4] Polymer films of poly(vinyl alcohol) (PVA, Polysciences Inc., 99% hydrolysed) were prepared by evaporation of a 4% aqueous solution of PVA with dissolved dye onto glass slides. Dye absorbances of 0·04 and 0·08 were used for **I** and **II**, respectively, in the polymer films.

Water was obtained from a milli-Q reagent water system (Millipore) whilst methanol and ethanol (99·3%) were redistilled from spectroscopic grade solvents before use. Other solvents used were dimethylformamide (DMF, Ajax, spectroscopic grade), deuterated water (AAEC, 99·75%), *n*-propanol (Merck, extra pure), *n*-butanol (Ajax, AR), 1,4-dioxane (Ajax, LR), ethylene glycol (BDH, AR), acetonitrile (Ajax, AR) and glycerol (Merck, AR). At the instrument sensitivities employed, solvent impurity emissions were negligible for all solvents. For solvents less polar than methanol (other than dioxane) the dyes were dissolved in a small quantity of methanol before dilution with the required solvent. In dioxane, **I** was dissolved by heating alone. Solutions were always prepared immediately prior to measurements under dimmed lighting to minimize photoisomerization of the whitening agent.

3 RESULTS AND DISCUSSION

3.1 Studies on the bis(triazinylamino)stilbene dye (I)

The absorption and fluorescence spectral properties of **I** in a variety of solvents are summarized in Table 1. No significant spectral differences were observed between the sodium and collidine salts of **I**. The molar extinction coefficient (ε_t) for the collidine salt determined in this work compares well with the literature value of 52 400 M^{-1} cm^{-1} at 342·5 nm.[3] However, comparison of the molar extinction coefficients of the collidine salt with the sodium salt indicated that the latter commercial product contained about 40% by wt of a non-absorbing component, possibly inorganic salts. The values of ε_t reported in Table 1 for the sodium salt have therefore been normalized to the value obtained for the collidine salt in water. The sodium salt was generally more soluble in the solvents studied but no significant differences in photophysical properties between the collidine and sodium salts were noted in this work.

With decreasing solvent polarity, as measured by the $E_T(30)$ solvent polarity parameter of Reichardt,[16] there are minor changes in the position of the absorption spectrum maximum (λ_A) of **I** similar to that noted previously for the model compound DASDA.[10] The small shifts in the absorption maximum are most likely due to the influence of hydrogen bonding on delocalization of secondary amino group lone-pair electrons[6b,9] and solvent polarity effects on the relative stabilization of ground and excited states involved in the transition.[3,17] The fluorescence spectrum becomes quite structured in lower-polarity solvents (see Fig. 2) and a blue shift in emission is apparent in changing from water to less polar solvents. The smaller Stokes shift and increased structure in lower-polarity solvents is indicative of reduced solvent relaxation around the excited state.[17] In the viscous solvents ethylene glycol and glycerol, the red-shifted values of λ_A and λ_F compared with methanol, which is of similar polarity, may be attributed to the effects of higher refractive index on absorption and emission.[18]

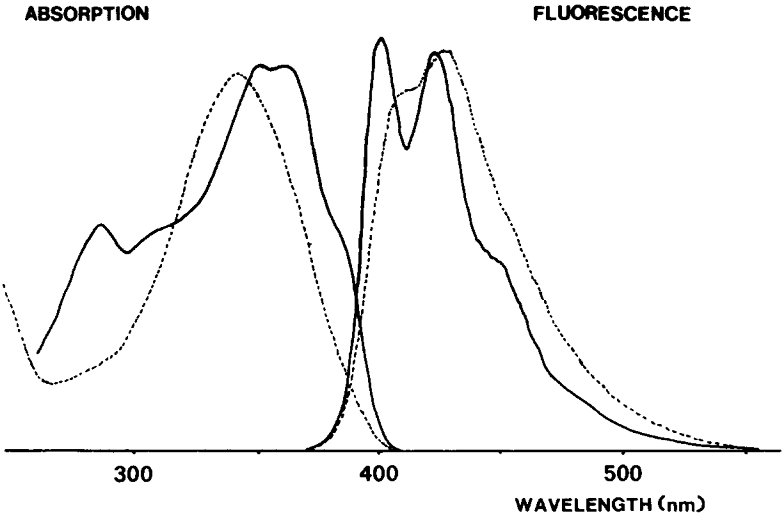


Fig. 2. Absorption and fluorescence spectra for **I** in water (----) and dioxane (——).

In contrast to the relatively small effects of solvent polarity on spectral properties of **I** are the large effects of solvent on the fluorescence quantum yield (ϕ_f), lifetime (τ) and *trans–cis* photoisomerization yield (ϕ_t) (Table 2). With decreasing solvent polarity there is a marked increase in fluorescence yield and lifetime and a corresponding decrease in the photoisomerization yield. The values of ϕ_f obtained here in water and dioxane are in reasonable agreement with the literature values of 0·23 and 0·99, respectively.[3] Results for ϕ_f, ϕ_t and τ in water and methanol did not depend on whether the collidine or sodium salts of **I** were used and observations in water and deuterated water were identical. In ethylene glycol and glycerol the higher

TABLE 2

Fluorescence Quantum Yield (ϕ_f), *trans–cis* Photoisomerization Quantum Yield (ϕ_t), Fluorescence Lifetime (τ) and the Rate Constants for Radiative (k_r), Non-radiative (k_{nr}) and Photoisomerization (k_t) Processes for **I** in Different Solvents at 25°C

Solvent	ϕ_f	ϕ_t	τ (*ns*)	$10^{-8} \times$ *rate constant* (s^{-1})			
				k_r	k_{nr}	k_t	k_t/k_{nr}
Water	0·20	0·184 ± 0·015	0·37 ± 0·02	5·4	22·0	5·0	0·23
Methanol	0·49	0·135 ± 0·010	0·59 ± 0·02	8·3	8·6	2·3	0·27
Ethanol	0·59	0·091 ± 0·007	0·69 ± 0·03	8·5	6·0	1·3	0·21
DMF	0·71	0·049 ± 0·004	0·68 ± 0·03	10·4	4·3	0·72	0·16
Dioxane	0·94	—	0·98 ± 0·01	9·6	0·6	—	—
Ethylene glycol	0·70	0·058 ± 0·005	0·68 ± 0·03	10·3	4·4	0·85	0·19
Glycerol	0·74	—	0·72 ± 0·03	10·3	3·6	—	—

values of ϕ_f and smaller values of ϕ_t may be attributed to inhibition of molecular twisting required for *trans–cis* photoisomerization in these high-viscosity solvents.[19,20]

The rate constants for fluorescence (k_r), non-radiative decay (k_{nr}) and *trans–cis* photoisomerization (k_t) may be obtained from the following relationships:

$$\phi_f = k_r/(k_r + k_{nr}) = k_r\tau \qquad \phi_t = k_t\tau$$

The calculated values for the rate constants are summarized in Table 2 and it is apparent that solvent polarity has the most significant effects on k_{nr} and k_t. Both rate constants decrease markedly as solvent polarity is reduced. Quite similar behaviour has been observed previously for the model compounds DAS[9] and DASDA.[10] The ratio k_t/k_{nr}, called the branching ratio for *cis* isomer formation, is also given in Table 2 and represents the fraction of molecules undergoing non-radiative decay which complete the twisting process to form the *cis* isomer. The branching ratio for **I** is approximately 0·21 in the solvents studied which may be compared with values of 0·54, 0·50 and 0·40 found for *trans*-stilbene,[22] DAS[9] and DASDA,[10] respectively. The lower branching ratio for **I** compared with the model compounds can be associated with steric restrictions on the isomerization process imposed by the bulkier substituents.

The results obtained can be discussed with reference to the accepted energy diagram for *trans*-stilbene as a function of the angle of rotation about the central ethylenic bond presented in Fig. 3. For *trans*-stilbene excitation of the *trans* isomer to the $^1B_u^*$ state may lead to either fluorescence or intramolecular rotation to a twisted 'perpendicular'

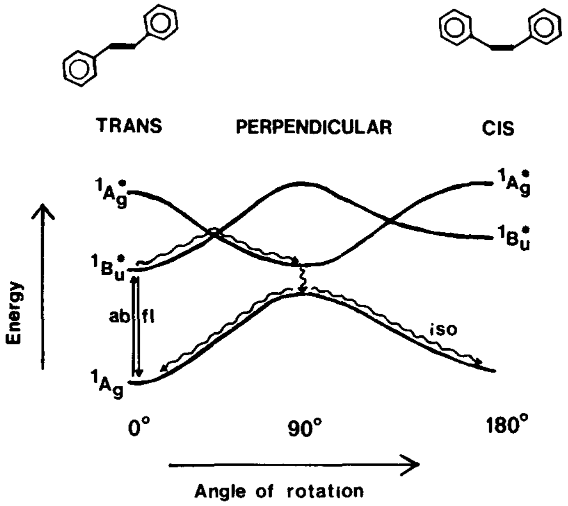


Fig. 3. Energy diagram for *trans*-stilbene as a function of angle of rotation about the central ethylenic bond. Absorption (ab), fluorescence (fl) and isomerization (iso) processes are indicated. Adapted from refs 20–22.

configuration. The perpendicular excited state ($^1A_g^*$) may then decay non-radiatively to the ^1A_g ground state from which either further rotation to form the *cis* isomer or relaxation to reform the *trans* isomer may occur. If the excited perpendicular configuration of **I** has intramolecular charge transfer (ICT) character then this state will be stabilized in solvents of increasing polarity. Solvent stabilization of the perpendicular excited state relative to the fluorescent state will reduce the energy barrier to photoisomerization and thus increase k_t and k_{nr}, resulting in a decrease in fluorescence yield. The activation energy for the non-radiative decay process (E_a) can be determined by observing the temperature-dependence of fluorescence intensity as described previously.[9,10] Fluorescence measurements of **I** over the temperature range 25–65°C gave values for E_a of $28{\cdot}4 \pm 1{\cdot}1$ kJ/mol and $17{\cdot}8 \pm 0{\cdot}3$ kJ/mol in ethanol and water, respectively. These results indicate a reduction in the energy barrier to photoisomerization in more polar solvents. Such a mechanism has also been proposed to explain the similar solvent-dependence of rate constants observed for DAS[9] and DASDA.[10] In the related molecules *trans*-stilbene,[19,24,27] diphenylbutadiene[28] and the Schiff base of *cis*-retinal,[29–31] larger rates of non-radiative decay due to a solvent-dependent reduction in the energy barrier to photoisomerization have also been reported. In the case of **I**, an additional effect due to hydrogen bonding in protic solvents may also be operative. In this case, hydrogen bonding to the secondary amino groups in polar protic solvents will reduce electron delocalization from the amino nitrogen, which may lead to an increase in k_t due to lower electron density in the region of the ethylenic bond in the excited state.

A small increase in k_r is also observed as the polarity of the solvent decreases. Similar behaviour was found for DAS[9] and DASDA[10] and attributed to mixing of the $^1A_g^*$ and $^1B_u^*$ states in solvents of increasing polarity, thus influencing the 'allowedness' of the radiative transition.

3.2 Studies on the bis-styrylbiphenyl dye (II)

The absorption and emission spectral properties of **II** in a range of solvents are summarized in Table 3. The absorption spectrum is structureless and displays little solvent-dependence. However, the fluorescence maximum undergoes a marked blue shift in solvents less polar than water, accompanied by increased spectral structure (Fig. 4). This behaviour is similar to that observed for **I** and suggests that a change in electronic charge distribution occurs upon excitation leading to solvent relaxation around the excited solute in polar aqueous media. The molar extinction coefficient for the absorption maximum of the *trans* isomer of **II** in water (ε_t) is in good agreement with a value of 65 000 M^{-1} cm^{-1} at 349 nm reported previously.[6c]

TABLE 3

Dependence of the Absorption (λ_A) and Fluorescence (λ_F) Maxima of **II** on Solvent

Solvent	$E_T(30)$[a] (*kJ/mol*)	λ_A (*nm*)	λ_F (*nm*)	*Molar extinction coefficient*[b] (M^{-1} *cm*$^{-1}$)	
				ε_t	ε_c
Water	264	348	430	64 000	18 500[c]
Methanol	232	348	404, 422	64 800	—
Ethanol	217	348	402, 423	61 500	—
Butanol	210	350	404, 425	58 400	—
Acetonitrile	191	349	403, 422	—	—
DMF	183	354·5	407, 428	—	—

[a] $E_T(30)$, solvent polarity parameter.[16]

[b] Molar extinction coefficients for the *trans* (ε_t) and *cis* (ε_c) isomers of **II** are given at λ_A.

[c] ε_c assumed invariant of solvent for correction of ϕ_t values in Table 4 (see Section 2). This correction did not significantly affect ϕ_t for **II**.

Values for ϕ_f, ϕ_t, τ, k_r, k_{nr} and k_t (for **II**) in several solvents are reported in Table 4. The fluorescence quantum yields are generally much higher than those observed for **I** and smaller rate constants for photoisomerization are

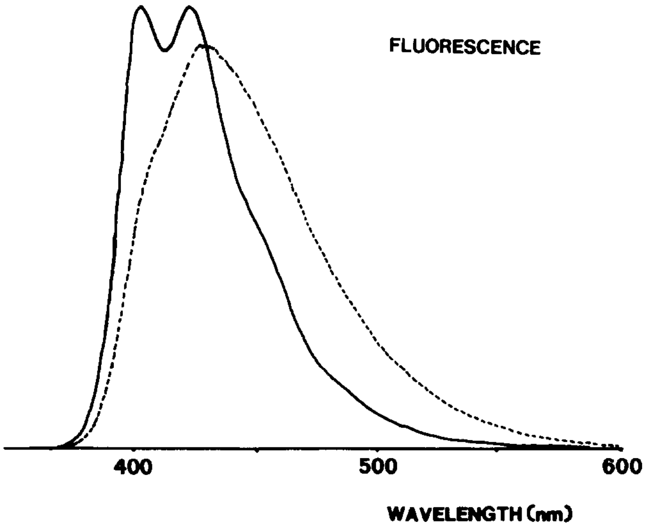


Fig. 4. Fluorescence spectra for **II** in water (– – – –) and ethanol (——).

obtained. It should be noted that no isobestic point in the absorption spectrum was observed as the *trans* isomer was photodegraded. This behaviour arises because more than one *cis* isomer product can result from the irradiation of **II** and a mixture of *cis–trans* and *cis–cis* isomers will be formed.[1] The value of ϕ_t includes degradation to all the photoisomerization products. Since the fluorescence yield is already quite high in water, significant solvent polarity effects on the photoisomerization rate constant are not apparent. However, two observations may be made. The radiative rate constant, k_r, displays a similar solvent dependence to that found for **I** and the model compounds DAS[9] and DASDA,[10] indicating a similar effect is operating in these stilbene-based compounds. In addition, the large

TABLE 4

Fluorescence Quantum Yield (ϕ_f), *trans–cis* Photoisomerization Quantum Yield (ϕ_t), Fluorescence Lifetime (τ) and the Rate Constants for Radiative (k_r), Non-radiative (k_{nr}) and Photoisomerization (k_t) Processes for **II** in Different Solvents at 25°C

Solvent	ϕ_f	ϕ_t	τ (*ns*)	*10^{-8} × rate constant (s^{-1})*			
				k_r	k_{nr}	k_t	k_t/k_{nr}
Water	0·82	0·019	1·18 ± 0·05	6·9	1·5	0·16	0·10
Methanol	0·95	0·016	0·98 ± 0·01	9·7	0·5	0·16	0·32
Ethanol	0·95	< 0·01	0·92 ± 0·01	10·3	0·54	—	—

change in the branching ratio, k_t/k_{nr}, upon changing the solvent from water to methanol suggests that an additional non-radiative pathway, apart from photoisomerization, is operative in aqueous media. Laser flash photolysis experiments conducted in this laboratory (Smit and Ghiggino, unpublished observations) have indicated the presence of long-lived transient species in aqueous solutions of **II** upon excitation. These transient species are possibly radical cations and may account for the smaller branching ratio in water, where photoionization will be favoured.

3.3 Studies on I and II in poly(vinyl alcohol) (PVA) films and on wool fabric

In rigid PVA films no decrease in *trans* isomer absorption was observed for **I** and **II** following irradiation with the full output of a 150-W xenon lamp for 45 and 400 min, respectively. This result indicates that photoisomerization is prevented in the highly viscous polymer environment and that ϕ_t is essentially zero. In PVA film the fluorescence decay was exponential for **I** and **II** with lifetimes of 0·78 ± 0·03 ns and 0·72 ± 0·02 ns, respectively. The corresponding values for k_r, assuming $\phi_f \simeq 1$, are $12{\cdot}8 \times 10^8$ and $13{\cdot}9 \times 10^8\,s^{-1}$.

On wool fabric, *trans–cis* photoisomerization of **II** has been observed although it occurs to a much smaller extent than in solution.[2] The fluorescence excitation and emission spectra of the dyes on wool are similar to those obtained in PVA films.[3] Weak fluorescence from unwhitened wool is observed with excitation at 353 nm although no amino acids in the keratin protein absorb at this wavelength. The naturally occurring pigments in wool which absorb in the blue and near-ultraviolet regions of the spectrum have not been positively identified[5] although melanin-type precursors are likely to be present. The fluorescence from unwhitened wool with excitation at 353 nm is broad and structureless with a maximum near 420 nm. The fluorescence decay profile could not be adequately described by a single exponential function but was more closely fitted by the sum of two exponential decays (Fig. 5) yielding the lifetimes in Table 5.

With 0·02% on-weight-of-fabric (o.w.f.) of **I** the fluorescence observed is due to the whitener, as natural wool fluorescence is minimal at the much lower instrument sensitivities employed. Again, two fluorescence lifetimes are required to describe adequately the fluorescence decay profile with the short τ component of 0·33 ns accounting for 64% of the initial emission intensity. For **II** at 0·02% o.w.f., two lifetimes were also required with the short τ component of 0·39 ns accounting for 80% of the initial fluorescence (Fig. 6). Fluorescence decay data for **I** and **II** on wool are given in Table 5. The non-exponential fluorescence decay profiles for the whiteners on wool may be attributed to the different binding sites of the dyes in the fibre

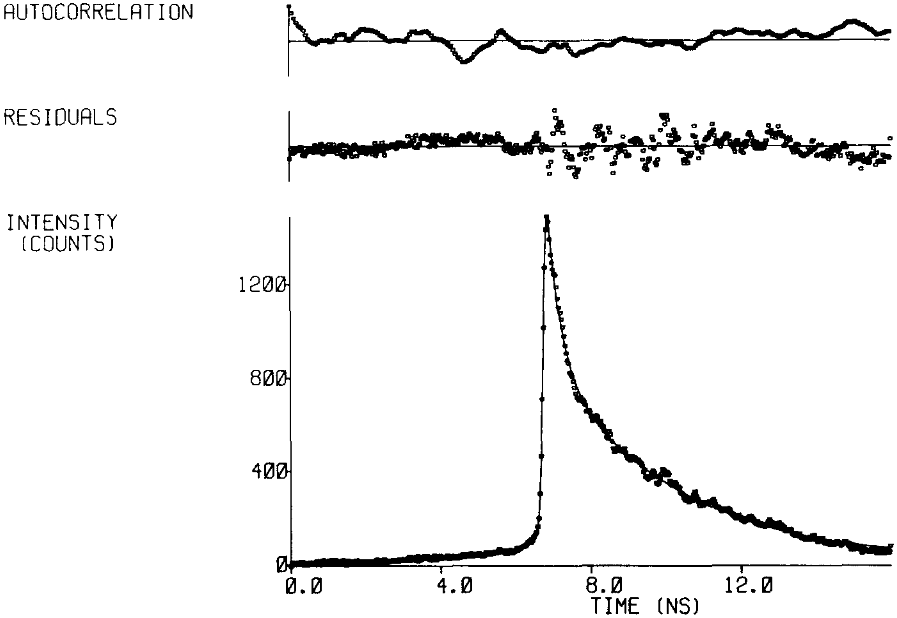


Fig. 5. Fluorescence decay profile of unwhitened wool fabric excited at 353 nm. □, Experimental data; ——, fitted curve to a double exponential function with $\tau_1 = (0{\cdot}35 \pm 0{\cdot}10)$ ns, $\tau_2 = (3{\cdot}3 \pm 0{\cdot}5)$ ns and $F = 0{\cdot}57 \pm 0{\cdot}05$ (cf. Table 5).

leading to emission from dye molecules in different microenvironments.[3] However, the majority of initial fluorescence from **I** and **II** on the fabric arises from excited dye molecules which have considerably shorter decay lifetimes than were obtained in PVA film or observed in any of the solvents (cf. Tables 2 and 4). This result suggests that a majority of excited state dye molecules are undergoing quenching interactions with the surrounding

TABLE 5

Fluorescence Lifetimes for Unwhitened Wool Fabric and Wool Fluorescently Whitened with **I** and **II**

Decay profiles fitted to a double exponential function of the form $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where τ_1, τ_2 are the two lifetimes. $F = A_1/(A_1 + A_2)$ is the initial fraction of the short-lived fluorescent component. Excitation wavelength 353 nm.

Sample	τ_1 *(ns)*	τ_2 *(ns)*	*F*
Unwhitened wool	0·35 ± 0·10	3·3 ± 0·5	0·57 ± 0·05
0·02% **I** on wool	0·33 ± 0·15	1·7 ± 0·7	0·64 ± 0·25
0·02% **II** on wool	0·39 ± 0·06	1·15 ± 0·10	0·80 ± 0·02

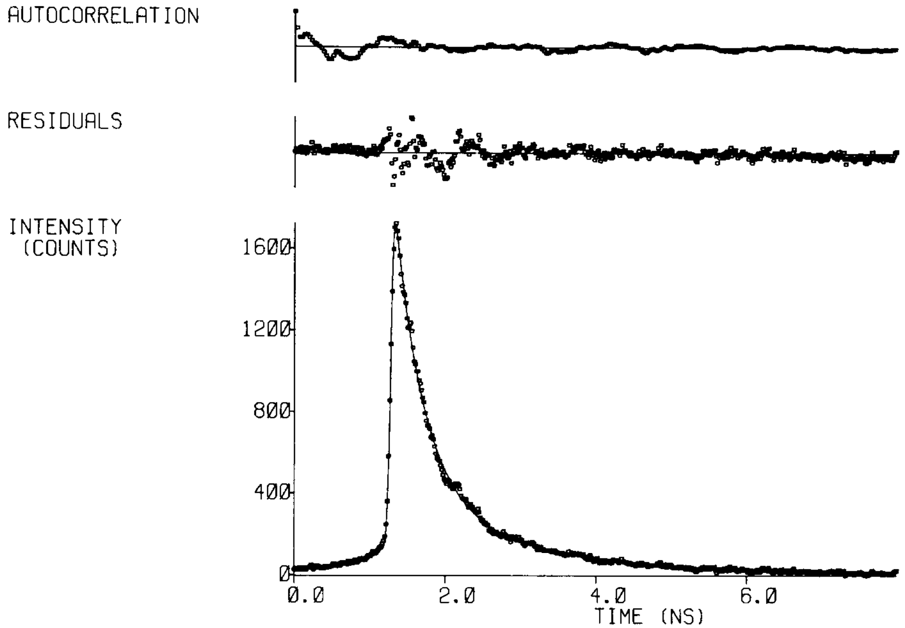


Fig. 6. Fluorescence decay profile of **II** on wool fabric at 0·02% o.w.f. with excitation at 353 nm. □, Experimental data; ——, fitted curve with $\tau_1 = (0{\cdot}39 \pm 0{\cdot}06)$ ns, $\tau_2 = (1{\cdot}15 \pm 0{\cdot}10)$ ns and $F = 0{\cdot}80 \pm 0{\cdot}02$ (cf. Table 5).

fibre environment. One possibility is that non-radiative singlet energy transfer occurs from the whitener to the pigments present in wool. The absorption spectra of the natural pigments in wool overlap the fluorescence spectrum of the dye and thus fulfil the conditions required for non-radiative energy transfer.[32] It has also been observed that in fluorescently whitened wool degraded by sunlight, the yellow products formed efficiently quench the fluorescence from the whiteners.[2]

4 CONCLUSION

The photophysics and photochemistry of the bis(triazinylamino)stilbene dye (**I**) are markedly dependent on solvent polarity. With decreasing solvent polarity the quantum yield of fluorescence increases while the photoisomerization yield is reduced. This behaviour is similar to that observed for the model compounds DAS[9] and DASDA[10] and may be attributed to increased stabilization of the excited perpendicular configuration in more polar solvents. The effect of hydrogen bonding with the solvent on delocalization of the amino group electrons may also be significant. The fluorescence yields of the bis-styrylbiphenyl dye (**II**) are much higher than those of **I** and only small solvent effects are apparent. The fluorescence lifetimes of **I** and **II** on wool fabric are considerably shorter than expected, indicating significant quenching interactions with the fibre environment. Non-radiative singlet–singlet energy transfer to natural wool pigments is possible and could provide a pathway for the sensitized photodegradation of fluorescently whitened wool.

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