

EFFECT OF SOLVENT ON THE PHOTOCHEMISTRY OF *trans*-4,4'-DIAMINOSTILBENE-2,2'-DISULPHONIC ACID

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Summary

Rate constants for fluorescence, non-radiative decay and *trans*-*cis* photoisomerization of 4,4'-diaminostilbene-2,2'-disulphonic acid (DASDA) have been determined in a range of solvents. The results indicate a marked dependence of the non-radiative rates on solvent polarity, which is discussed in terms of the importance of amino-group lone-pair electron delocalization and intramolecular charge transfer to the photochemistry of DASDA. A comparison is made with the photophysics and photochemical behaviour of the unsulphonated compound.

1. Introduction

The photochemistry of stilbene compounds has been well documented, particularly for *trans*-stilbene itself in which the process of direct *trans*-*cis* photoisomerization is the principal excited state deactivation pathway in solution [1]. It is generally agreed that for *trans*-stilbene direct photoisomerization involves the formation of a twisted excited perpendicular singlet state from the initially populated excited fluorescent state, with subsequent radiationless decay to a perpendicular ground state; further twisting of the perpendicular ground singlet state may produce the *cis* isomer [2 - 5]. Direct photoisomerization of *trans*-stilbene substituted in the 4-position by methyl, methoxy or cyano groups similarly proceeds via a singlet mechanism, but for nitrated molecules a triplet mechanism is favoured [3, 6].

It has been suggested that for *trans*-stilbene significant intramolecular charge transfer (ICT) occurs in the excited singlet state [7], although nominally the molecule is symmetrical. Recent results indicate that the fluorescence quantum yield ϕ_f [8], the excited singlet state lifetime τ and the activation energy E_A for *trans*-*cis* photoisomerization of *trans*-stilbene [5, 9] and diphenylbutadiene [10, 11] are influenced by solvent polarity.

This is readily understood if a greater degree of ICT occurs in the excited perpendicular state than in the fluorescent state, resulting in greater stabilization of the perpendicular state in polar solvents and thereby reducing the energy barrier to photoisomerization [9 - 14].

While solvent polarity is known to influence ϕ_f , τ and E_A of *trans*-stilbene, no effect of solvent polarity has been reported on the wavelength λ_A of absorbance [15], the wavelength λ_F of fluorescence [8] or the quantum yield ϕ_t of *trans*-*cis* photoisomerization [16, 17]. The invariance of ϕ_t appears to contradict the large change in E_A found recently [5, 9]. The best-known solvent polarity effects are those reported for nitrated stilbenes for which increasing solvent polarity is associated with higher ϕ_f values and lower values of ϕ_t owing to greater stabilization of the *trans* triplet state relative to the perpendicular triplet state [6]. Recently we noted that solvent polarity has the opposite effect on ϕ_f and ϕ_t for 4,4'-diaminostilbene (DAS) [18] and this observation was attributed in part to possible ICT character in the excited perpendicular state. Delocalization of amino-group non-bonding electrons was considered to be responsible for the much reduced ϕ_t obtained for DAS in solvents of low polarity compared with *trans*-stilbene [18] and also for the variation in ϕ_t for related compounds [19].

Few photophysical studies have been reported on stilbene sulphonic acids which are an important class of fluorescent dyes. *trans*-4,4'-Diaminostilbene-2,2'-disulphonic acid (*trans*-DASDA) is known to photoisomerize to a non-fluorescent *cis* isomer in aqueous solution [20]. This study reports the effect of solvent polarity on the photophysics and photoisomerization process in DASDA and relates the results to DAS. The effect of protonating the amino groups is also examined for both DASDA and DAS. It is expected that substantial changes will occur in the absorption and emission spectra because of the importance of non-bonding electrons from the amino groups on the photochemistry of these molecules.

2. Experimental details

Corrected fluorescence quantum yields ϕ_f were obtained relative to quinine bisulphate (Eastman) in 1 N H_2SO_4 (May and Baker Analytical Reagent for which $\phi_f = 0.546$ [21]) employing a Perkin-Elmer MPF-44A fluorescence spectrophotometer using sample absorbances of 0.06 or less in 1 cm. The fluorescence lifetimes τ were determined by employing a picosecond laser-streak camera system [22] using 353 nm excitation and a microcomputer for data storage. Fluorescence decay analysis was carried out on a Vax computer using a non-linear least-squares curve fitting program. Good fits to a single exponential decay were always observed (*e.g.* Fig. 1) and degassing of the solution to remove oxygen by a freeze-pump-thaw procedure had no effect on τ in ethanol. Concentrations used were 10^{-5} M or less for these measurements.

The photoisomerization quantum yields were determined by monitoring the decrease in absorbance using a Cary 17 spectrophotometer after

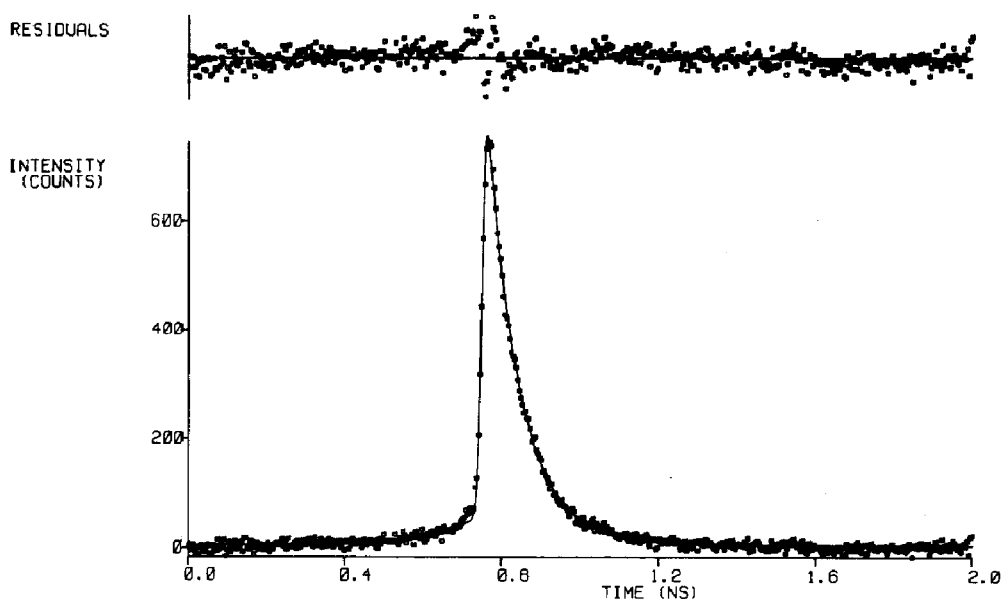


Fig. 1. Fluorescence decay curve of DASDA in methanol (lifetime, 0.071 ns).

irradiation in the fluorescence spectrophotometer at 340 nm to less than 15% degradation. The photon flux at 340 nm had been determined shortly before these experiments using potassium ferrioxalate actinometry [23]. The DASDA solutions absorbed more than 85% of the light and were agitated with dry air during photolysis. Appropriate corrections were made for the contribution by the *cis* isomer to absorbance at the absorbance maxima λ_A of the *trans*-DASDA solutions by determining the extinction coefficient ϵ_c of the *cis* isomer at this wavelength. This was achieved by redetermining ϕ_f for a photostationary mixture of *trans*- and *cis*-DASDA and evaluating the fraction of light absorbed by the *trans* isomer. The extinction coefficients ϵ_t and ϵ_c determined for the *trans* and *cis* isomers are summarized in Table 1.

TABLE 1

Dependence of the absorption maxima λ_A and fluorescence maxima λ_F on solvent polarity ($E_T(30)$), with the molar absorptivities ϵ_t and ϵ_c for the *trans* and *cis* isomers at λ_A for the *trans* isomer of DASDA

Solvent	$E_T(30)^a$ (kJ mol ⁻¹)	λ_A (nm)	λ_F (nm)	ϵ_t (M ⁻¹ cm ⁻¹)	ϵ_c (M ⁻¹ cm ⁻¹)
Water	264	339	446	34100	9200
Methanol	232	345	424	38000	10450
Ethanol	217	342	422	35200	12700
DMF	183	348	423	38900	10700
Glycerol	238	342	452		

^aSee ref. 25.

Activation energies for non-radiative decay were determined in the temperature range 25 - 70 °C by observing the temperature dependence of the fluorescence intensity I_f and plotting $\ln(I_f^0/I_f - 1)$ vs. $1/T$ as described previously [24]. The limiting fluorescence intensity I_f^0 was taken to correspond to $\phi_f^0 = 1.0$, so $I_f^0 = (\phi_f^0/\phi_f)I_f$. Low temperature measurements were carried out in an Oxford Instruments model DN 704 liquid nitrogen cryostat with a DTC-2 temperature controller.

The *trans*-DASDA and *trans*-DAS dihydrochloride were used as received (T.C.I.). Solutions of these compounds gave coincident absorbance and excitation maxima and there was no evidence of fluorescent impurities. Thin-layer chromatography analysis using 0.5 M NaOH in ethanol-water (7:3) eluant on alumina plates was also negative to impurity. Water was obtained from a Milli-Q reagent water system (Millipore) while methanol and ethanol (99.3%) were redistilled before use from spectroscopic grade solvent. Dimethylformamide (DMF) was spectroscopic grade (Ajax) while 1,4-dioxan (Ajax Laboratory Reagent) and glycerol (Merck Analytical Reagent) gave no impurity fluorescence at the instrument sensitivities employed. Poly(vinyl alcohol) (PVA, Polysciences Inc., 99% hydrolysed) was used to prepare polymer films by evaporation from 4 wt.% PVA in an aqueous solution of DASDA.

All solutions were prepared immediately prior to use by dissolution of the DASDA or DAS salt in 1 drop of 0.1 M NaOH and dilution as required. For fluorescence studies this gave a solution pH of about 9.5.

3. Results and discussion

3.1. Effect of solvent polarity on the photochemistry and photophysics of DASDA

The photoisomerization of DASDA from the *trans* to the *cis* isomer is illustrated by the change in the absorption spectrum with irradiation in the first absorption band of the *trans* isomer in water (Fig. 2). The *cis* isomer has its absorption maximum at much shorter wavelengths than the *trans* isomer and the spectral characteristics obtained in a range of solvents are summarized in Table 1 as a function of solvent polarity. The values of the extinction coefficients ϵ_t and ϵ_c refer to the absorption maxima λ_A of the *trans* isomer and are required to obtain the quantum yields ϕ_t of *trans*-*cis* photoisomerization given in Table 2.

Although ϕ_t remains reasonably constant, the values of ϕ_f and τ increase significantly with a decrease in solvent polarity. Values of ϕ_f and τ have also been determined in 1,4-dioxan, but ground state association and high sensitivity to traces of water made the results ($\phi_f \approx 0.5$ and $\tau \approx 1.1$ ns) less reliable. The effect of solvent polarity on ϕ_f and τ is similar to that observed for DAS [18], although ϕ_t was observed to decrease for DAS in less polar solvents (from 0.52 in water to 0.096 in dioxan).

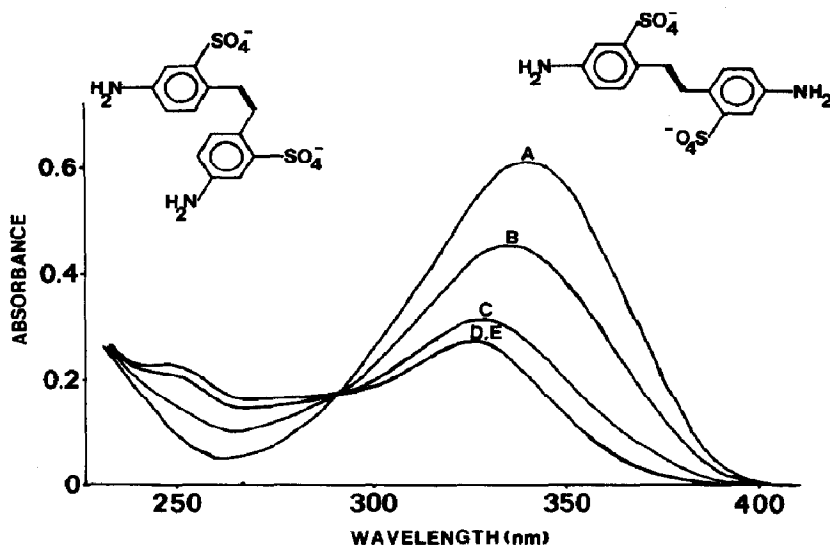


Fig. 2. Effect of total irradiation time on the absorption spectrum of DASDA in water using a 150 W xenon lamp and Corning 9863 filter: curve A, before irradiation; curve B, 0.25 min; curve C, 1 min; curve D, 5 min; curve E, 15 min.

TABLE 2

Solvent dependence of the fluorescence lifetime τ , quantum yields of fluorescence ϕ_f and trans-cis photoisomerization ϕ_t , and the rate constants k_r , k_{nr} and k_t for radiative, non-radiative and photoisomerization processes in DASDA

Solvent	ϕ_f (25 °C)	ϕ_t (25 °C)	τ (ns)	Rate constants $\times 10^{-8}$ (s ⁻¹)			k_t/k_{nr}
				k_r	k_{nr}	k_t	
Water	0.018	0.38 ± 0.02	0.052 ± 0.002	3.5	189	73	0.39
Methanol	0.035	0.39 ± 0.01	0.071 ± 0.004	4.9	136	55	0.40
Ethanol	0.054	0.37 ± 0.01	0.101 ± 0.001	5.3	93	37	0.39
DMF	0.156	0.28 ± 0.01	0.246 ± 0.005	6.3	34	11.4	0.33
Glycerol	0.22		0.47 ± 0.05	4.6	17		

The rate constants k_r , k_{nr} and k_t for the radiative, non-radiative and trans-cis photoisomerization processes are summarized in Table 2 and it is apparent that k_{nr} and k_t are the principle solvent-polarity-sensitive rate constants. Values for the ratio k_t/k_{nr} (the branching ratio α'') indicate that, from water to DMF, the effect of solvent polarity on the two rate constants is similar. This strongly suggests that the major non-radiative pathway for deactivation of excited DASDA is the formation of the excited perpendicular singlet state with subsequent formation of the cis isomer with a branching ratio of about 0.39. We can compare this result with $\alpha'' = 0.54$ reported for

trans-stilbene [2, 9, 26] and $\alpha'' = 0.50$ for DAS [18]. The lower value of α'' for DASDA may be associated with the introduction of sulphonate groups in the 2,2'-positions of DAS resulting in increased steric hindrance to twisting from the ground perpendicular state to the *cis* isomer.

From the results obtained for DASDA in glycerol (Table 2), it is found that solvent viscosity also affects k_{nr} , as would be expected from the viscosity dependence of photoisomerization for *trans*-stilbene [8, 27]. However, the viscosity does not differ sufficiently in the remaining solvents of Table 2 to affect the trend observed for k_{nr} with solvent polarity.

For k_r a much smaller dependence on solvent polarity is noted. In a solid PVA film, in which photoisomerization is prevented and $\phi_f \approx 1.0$, we have obtained $\tau = 0.99 \pm 0.01$ ns, giving a limiting value of $k_r = 1 \times 10^9$ s⁻¹. A variation in k_r with solvent polarity has been observed for *trans*-stilbene [8] and DAS [18]. These changes in k_r cannot be attributed to an increase in solvent refractive index [28], as this does not occur continuously down Table 2. It is possible that some mixing of electronic character from the ¹A_g* state into the ¹B_u* fluorescent state occurs at higher solvent polarity, similar to the coupling between these states suggested to explain variations in k_r with solvent in diphenylhexatriene [29].

Related to the effect of solvent polarity on k_t and k_{nr} is its effect on the activation energy E_A of non-radiative decay. E_A could be evaluated by observing the decrease in fluorescence intensity with an increase in temperature between 25 and 70 °C. For DASDA in ethanol (Fig. 3) E_A was determined to be 19.1 ± 0.4 kJ mol⁻¹, while a value of 10.7 ± 0.3 kJ mol⁻¹ was obtained with water as the solvent. It should be noted that for ethanol there is a smaller change in viscosity with rise in temperature than for water [30], which suggests a real solvent polarity effect on the energy barrier to non-radiative decay and hence photoisomerization.

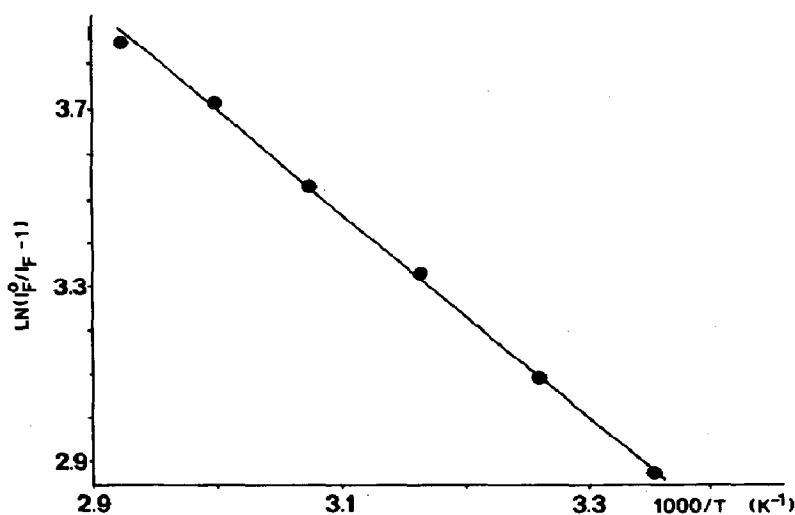


Fig. 3. Plot of $\ln(I_f^0/I_f - 1)$ vs. $1000/T$ for the variation of DASDA fluorescence intensity with temperature in ethanol (activation energy, 19.1 ± 0.4 kJ mol⁻¹).

The larger values of ϕ_f and τ for DASDA in low polarity solvents compared with *trans*-stilbene ($\phi_f \approx 0.05$ [8] and $\tau \approx 0.084$ ns [31]) may be attributed to delocalization of the non-bonding electrons from the amino groups, as suggested for DAS [18, 32]. The amino group is also considered to be responsible for a decrease in ϕ_f for quaternary salts of 4-dialkylamino-4'-azostilbene [19]. The 40 - 50 nm λ_A red shift for DAS relative to *trans*-stilbene in solution is attributable to the presence of amino groups [33, 34] and electron delocalization from these groups would increase the electron density of the central ethylenic linkage in the excited state to increase the barrier to rotation about this bond relative to *trans*-stilbene.

Solvent interaction, particularly hydrogen bonding with the amino-group lone-pair electrons, may reduce delocalization [35] and therefore increase k_t in polar protic solvents. It is also possible that the perpendicular excited state may have increased charge transfer character and would be stabilized in polar solvents relative to the fluorescent state. This would lower the barrier to photoisomerization, and the large difference observed for ϕ_f and τ between aprotic DMF and dioxan solutions of DASDA supports this latter interpretation. For DASDA the value of k_{nr} is also larger than that obtained for DAS [18] by a factor of more than 2.5 in the solvents used. This would be consistent with increased ICT character in the perpendicular state of DASDA compared with DAS, which may be associated with the presence of electron withdrawing sulphonate groups. An increase in the amount of mixing of electronic character from $^1A_g^*$ into $^1B_u^*$ with increase in solvent polarity may result in a "less allowable" radiative transition to the 1A_g ground state and therefore a decrease in k_r [29]. The increase in k_{nr} with more polar solvents is also consistent with stabilization of the $^1A_g^*$ perpendicular state relative to the 1B_u fluorescent state [36] according to the accepted potential energy diagrams for stilbene [2, 37]. For *trans*-stilbene the effect of solvent polarity on τ is smaller than for DASDA [11]; however, since ϕ_f is reported to remain constant [16, 17], k_t would be expected to increase in solvents of higher polarity. An increase in k_t for *trans*-stilbene in more polar solvents is indicated from recent results, in agreement with the observed drop in E_A [5, 9].

3.2. Effect of acidification of solutions of DASDA and DAS on their absorption and emission spectra

The importance of delocalization of amino-group lone-pair electrons to the photochemistry of DASDA suggests that protonation of these groups will have a large effect on the absorption maxima λ_A . A blue shift of 44 nm in λ_A has previously been reported for the first absorption band of DAS in water upon protonation [18] ($pK_a \approx 3.95$ for the amino groups [38]). The resulting absorption spectrum of acidified DAS in water (Fig. 4) closely resembles the absorption spectrum reported for *trans*-stilbene [15]. Protonation of DASDA in water results in a similar blue shift of λ_A to 296 nm at a pH value of 3.5 or below. However, a consequence of protonation is precipitation of DASDA owing to the insolubility of the zwitterionic ground state

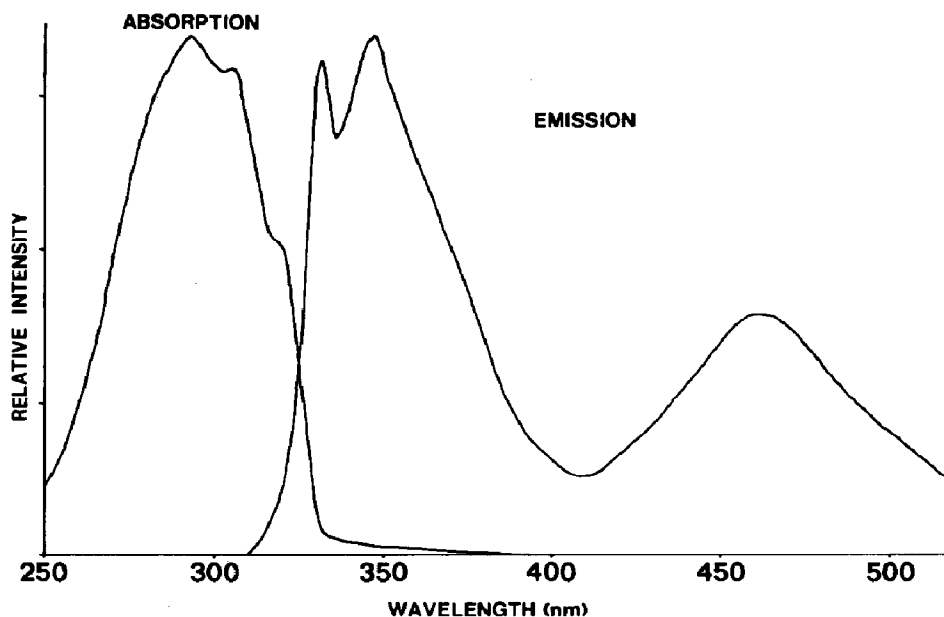


Fig. 4. Absorption and emission spectra for acidified DAS in water.

species. Another example of this effect of protonation is provided by acidified sulphanilic acid (*i.e.* anilino-4-sulphonate) which is insoluble in water but dissolves in base [39]. For this reason studies on the effect of protonation are more easily carried out using DAS.

For acidified DAS in water (pH about 2) fluorescence maxima occur at two wavelengths: 349 nm and 461 nm (Fig. 4). Both bands have an excitation maximum ($S_1^* \leftarrow S_0$) at 292 nm. The 349 nm fluorescence, by analogy with *trans*-stilbene ($\lambda_F \approx 350$ nm [15, 40]), is likely to be the fluorescence from fully protonated DAS. However the 461 nm band is shifted 34 nm to longer wavelengths compared with DAS in water (Table 3). Acidified DASDA in water also has two fluorescence bands with excitation maxima ($S_1^* \leftarrow S_0$) at 293 nm. Fluorescence occurs at 360 nm and 480 nm showing, as with DAS, a 34 nm red shift of the 480 nm fluorescence band relative to that of DASDA in water (Table 1).

TABLE 3

Effect of acidification of DAS on the fluorescence emission maxima λ_F and excitation maxima λ_{ex} in different solvents

Solvent	DAS		Acidified DAS	
	λ_{ex} (nm)	λ_F (nm)	λ_{ex} (nm)	λ_F (nm)
Water	334	427	292	349, 461
Methanol	344	415	295	347, 447
Ethanol	345	414	294	349, 444
DMF	360	410, 420	291	356, 441

The excited singlet state of aromatic amine salts is generally much more acidic than the ground state and, within the lifetime of the excited state, loss of a proton may result in emission from the unprotonated species [41]. A possible explanation for the longer wavelength of the second emission band of DAS and DASDA after protonation in the ground state, compared with the emission from the non-protonated molecules, is a contribution to the emission from a partially deprotonated species in which only one amino group has lost a hydrogen ion. If this species exists its dipole moment will be much larger than that of the non-protonated form, resulting in a large red shift of emission. It can be observed from the significant Stokes shift of fluorescence in water for DAS (Table 3) and DASDA (Table 1), relative to less polar solvents, that in the first excited singlet state a significant dipole moment is already present and the charge distribution in the molecule cannot be completely symmetrical.

3.3. Effect of cooling DAS and DASDA on the excitation and emission spectra in solution

The influence of temperature on degassed ethanolic solutions of DAS and DASDA is presented in Figs. 5 and 6. It can be noted that the shoulder present in the excitation spectrum for DAS at about 330 nm is absent in DASDA. Also, while the DAS excitation spectrum shifts about 9 nm to longer wavelengths on cooling to 86 K, in approximate agreement with the small (4 nm) shift observed for *trans*-stilbene absorbance [15, 42], the excitation maximum λ_{ex} of DASDA shows a considerable red shift of 25 nm. The bulky sulphonate groups present in DASDA are likely to distort the

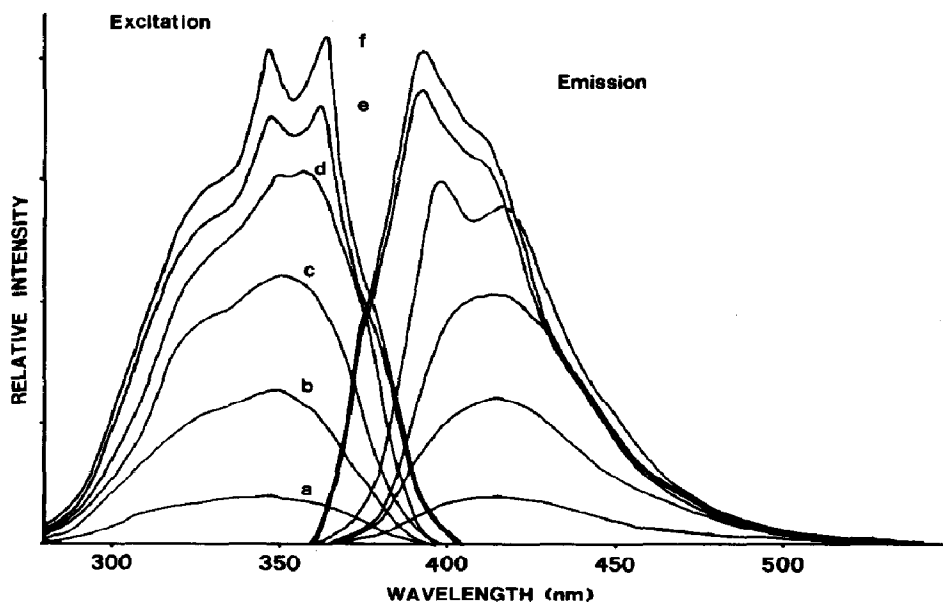


Fig. 5. Dependence of fluorescence emission and excitation spectra of DAS in ethanol on the temperature: curve a, 298 K; curve b, 240 K; curve c, 200 K; curve d, 150 K; curve e, 100 K; curve f, 86 K.

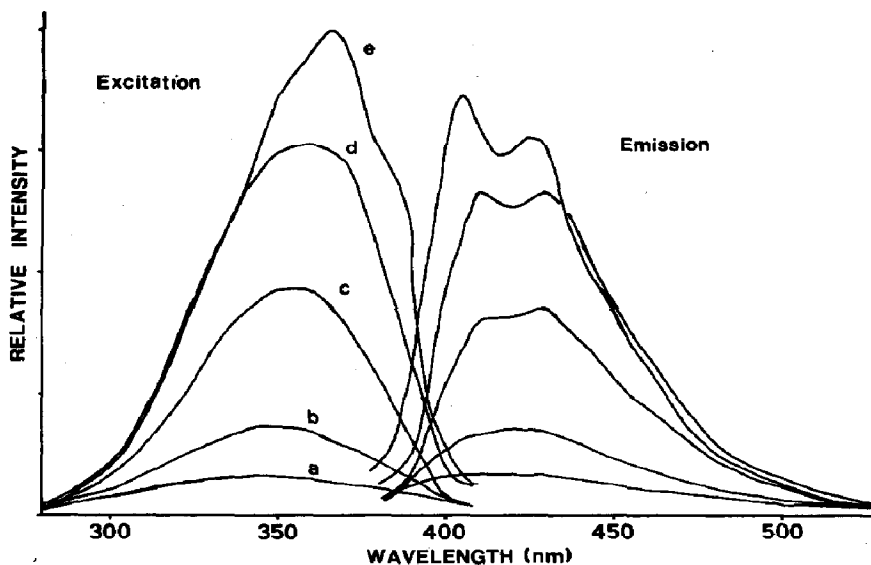


Fig. 6. Dependence of fluorescence emission and excitation spectra of DASDA in ethanol on the temperature: curve a, 295 K; curve b, 250 K; curve c, 200 K; curve d, 150 K; curve e, 100 K.

ground state conformation of the molecule owing to steric hindrance [33]. It is likely that at very low temperatures a lower energy less sterically hindered ground state configuration [43] is populated relative to the range of configurations populated at room temperature [44], leading to a red shift of λ_{ex} .

In contrast to the excitation spectra, the fluorescence spectra of both compounds show a similar shift to shorter wavelengths with decreasing temperature. This may be compared with results reported for *trans*-stilbene fluorescence in which the emission spectra shift to significantly longer wavelengths on cooling [15, 40], owing to the increase in solvent refractive index. An increase in the excited state dipole moment for DAS and DASDA relative to the ground state is indicated from a reduction in the Stokes shift of emission with change of solvent from water to methanol (Table 1) [45]. Therefore changes in the fluorescence spectra of DAS and DASDA in ethanol with reduction in temperature may be attributed to restrictions on solvent relaxation about the initially excited Franck-Condon state.

4. Conclusions

Studies on the effect of solvent polarity and temperature on the fluorescence of DASDA indicate that a significant increase in dipole moment occurs for this molecule on excitation to the fluorescent singlet state. The principle process of excited state deactivation for DASDA is twisting to the

perpendicular configuration, resulting in formation of the cis isomer with a branching ratio of about 0.39. Delocalization of amino-group lone-pair electrons is of considerable importance to the photochemistry of DASDA and is responsible for the larger values of ϕ_f , τ , λ_A and λ_F relative to *trans*-stilbene. This is supported by studies on the effect of protonation of the amino groups on the excitation and emission spectra. With an increase in solvent polarity there is a decrease in ϕ_f and τ and an increase in k_t . To some extent solvent interaction, particularly hydrogen bonding with the amino-group lone-pair electrons, may be responsible for the increase in k_t as the solvent polarity increases. However, there are indications that ICT character is present in the excited perpendicular state of DASDA which stabilizes this state relative to the fluorescent state in more polar solvents. The observed reduction in k_t and E_A for photoisomerization in the more polar solvents is consistent with this proposal.

Acknowledgments

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References

- 1 D. Gegiou, K. A. Muszkat and E. Fischer, *J. Am. Chem. Soc.*, **90** (1968) 3907.
- J. Salties and J. L. Charlton, *Rearrangements in Ground and Excited States*, Vol. 3, Academic Press, New York, 1980.
- J. Salties, A. Marinari, D. W.-L. Chang, J. C. Mitchener and E. D. Megarity, *J. Am. Chem. Soc.*, **101** (1979) 2982.
- 2 D. J. S. Birch and J. B. Birks, *Chem. Phys. Lett.*, **38** (1976) 432.
- 3 H. Görner, *J. Photochem.*, **13** (1980) 269.
- 4 M. Sumitani and K. Yoshihara, *Bull. Chem. Soc., Jpn.*, **55** (1982) 85.
- 5 V. Sundstrom and T. Gillbro, *Chem. Phys. Lett.*, **109** (1984) 538.
- 6 H. Görner, *Ber. Bunsenges. Phys. Chem.*, **88** (1984) 1199, 1208.
- 7 K. Yoshihara, A. Namiki, M. Sumitani and N. Nakashima, *J. Phys. Chem.*, **71** (1979) 2892.
- 8 L. A. Brey, G. B. Schuster and H. G. Drickamer, *J. Am. Chem. Soc.*, **101** (1979) 129.
- 9 V. Sundstrom and T. Gillbro, *Ber. Bunsenges. Phys. Chem.*, **89** (1985) 222.
- 10 S. P. Velsko and G. R. Fleming, *J. Chem. Phys.*, **76** (1982) 3553.
- 11 G. R. Fleming, *Proc. 14th Australian Spectroscopy Conf., Canberra, 1985*, p. 54.
- 12 Y. Maeda, T. Okada and N. Mataga, *J. Phys. Chem.*, **88** (1984) 2714.
- 13 N. Mataga, *Pure Appl. Chem.*, **56** (1984) 1255.
- 14 J. Hicks, M. Vandersall, Z. Babarogic and K. B. Eisenthal, *Chem. Phys. Lett.*, **116** (1985) 18.
- 15 R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36** (1961) 2326.
- 16 D. Gegiou, K. A. Muszkat and E. Fischer, *J. Am. Chem. Soc.*, **90** (1968) 12.
- 17 D. Schulte-Frohlinde, H. Blume and H. Gusten, *J. Phys. Chem.*, **66** (1962) 2486.
- 18 K. J. Smit and K. P. Ghiggino, *Chem. Phys. Lett.*, **122** (1985) 369.
- 19 H. Görner and H. Gruen, *J. Photochem.*, **28** (1985) 329.

- 20 F. Mashio and Y. Kimura, *Kogyo Kagaku Zasshi*, 62 (1959) 113; *Chem. Abstr.*, 57 (1959) 8481f.
- 21 W. H. Mehuish, *J. Phys. Chem.*, 65 (1961) 229.
- 22 G. R. Fleming, J. M. Morris and G. W. Robinson, *Aust. J. Chem.*, 30 (1977) 2337.
- 23 C. A. Parker, *Photoluminescence of Solutions*, Elsevier, Amsterdam, 1968, p. 208.
- 24 R. Sakurovs and K. P. Ghiggino, *Aust. J. Chem.*, 34 (1981) 1367.
- 25 C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, 18 (1979) 98.
- 26 M. Sumitani, N. Nakashima, K. Yoshihara and S. Nagakura, *Chem. Phys. Lett.*, 51 (1977) 183.
- 27 P. E. Brown and D. G. Whitten, *J. Phys. Chem.*, 89 (1985) 1217.
- 28 J. Olmsted III, *Chem. Phys. Lett.*, 38 (1976) 287.
- 29 J. B. Birks, G. N. R. Tripathi and M. D. Lumb, *Chem. Phys.*, 33 (1978) 185.
- 30 J. Timmermans, *Physico-chemical Constants of Binary Systems*, Vol. 4, Wiley, New York, 1975, p. 49.
- 31 H. P. Good, U. P. Wild, E. Haas, E. Fischer, E.-P. Resewitz and E. Lippert, *Ber. Bunsenges. Phys. Chem.*, 86 (1982) 126.
- 32 M. Furst, H. Kallmann and F. Brown, *J. Chem. Phys.*, 26 (1957) 1321.
- 33 H. Inoue, E. A. Saumi, T. Hinohara, S. Sekiguchi and K. Matsui, *Kogyo Kagaku Zasshi*, 73 (1970) 187; *Chem. Abstr.*, 73 (1970) 26586c.
- 34 A. E. Lutskii, A. S. Golberkova, Z. M. Kanevskaya, L. Ya. Malkes and L. V. Shubina, *Teor. Eksp. Khim.*, 2 (1966) 117; *Chem. Abstr.*, 65 (1966) 6522a.
- 35 K. J. Smit and K. P. Ghiggino, *Proc. 14th Australian Spectroscopy Conf., Canberra, 1985*, p. 98.
- 36 R. S. Becker and K. Freedman, *J. Am. Chem. Soc.*, 107 (1985) 1477.
- 37 G. Orlandi and W. Siebrand, *Chem. Phys. Lett.*, 30 (1975) 352.
- 38 H. Veschambre and A. Kergomard, *Bull. Soc. Chim. Fr.*, (1966) 336.
- 39 R. T. Morrison and R. N. Boyd, *Organic Chemistry*, Allyn and Bacon, Boston, 1973, 3rd edn., p. 760.
- 40 S. Malkin and E. Fischer, *J. Phys. Chem.*, 68 (1964) 1153.
- 41 J. A. Barltrop and J. D. Coyle, *Excited States in Organic Chemistry*, Wiley, London, 1975, pp. 49 - 51.
- 42 R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, (1953) 2755.
- 43 H. H. Jaffe and M. Orchin, *Theory and Applications of UV Spectroscopy*, Wiley, New York, 1962, pp. 424 - 435.
- 44 J. Kordas, P. Avouris and M. A. El-Bayoumi, *J. Phys. Chem.*, 79 (1975) 2420.
- 45 H. H. Jaffe and M. Orchin, *Theory and Applications of UV Spectroscopy*, Wiley, New York, 1962, p. 191.