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UV-visible absorption and fluorescence studies of 4,4′-diamino-*trans*-stilbene and its protonated species

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Abstract

4,4′-Diaminostilbene (DAS), its monoprotonated and diprotonated forms exhibit fluorescence. Their UV absorption and fluorescence emission spectra in different solvents and proton concentrations have been measured. 4-Trimethylammonium-4′-aminostibene hydrogen sulfate has been synthesized as a model for the monoprotonated DAS form. pK_a values in the ground state have been measured spectrophotometrically. The Stokes shifts in solvents of different polarities, the quantum yields and the apparent rate constants of *trans-cis* isomerization have been determined. Solvent polarity has a strong influence on spectroscopic properties.

Keywords: Spectroscopy; Photophysics; 4,4′-Diaminostilbene; 4-Trimethylammonium-4′-aminostilbene hydrogen sulfate; Molecular probe

1. Introduction

The unique photophysical and photochemical properties of stilbene derivatives have attracted considerable interest to this class of compounds [1–4]. Both 4,4′-donor and acceptor-substituted stilbenes have been investigated during the last few decades [5–7]. Among others, 4,4′-diamino-*trans*-stilbene (DAS) is the model chromophore for a variety of stilbene-based dyes and its photophysical behavior is different from that of *trans*-stilbene owing to the involvement of non-binding electrons of amino groups. The bathochromic shift of a long-wavelength emission band has been explained by the conjugation effect [8,9]. Indeed, the results of further investigation [10,11] have demonstrated that the delocalization of amino groups lone-pair electrons is of considerable importance to the photochemical properties of DAS and large increases in the fluorescence quantum yield, the lifetime and the location of absorption and emission maxima compared with those for unsubstituted *trans*-stilbene have been observed.

DAS can serve as an efficient molecular probe because of the high sensitivity of quantum yield and the rate of *trans–cis* photoisomerization to the molecular environment. DAS was used as a reactive label to probe cure reactions in an epoxy network [12]. Recently we became interested in the interaction of DAS with polystyrene sulfonate (PSS). It was found that protonated species of DAS are involved in this interaction. However, for the further investigation of these phenomena it is necessary to gain deeper insight into the spectroscopic behavior of different protonated species of DAS in solutions. DAS, its monoprotonated (DASH$^+$) and diprotonated (DASH$_2^{2+}$) forms present formally donor–donor, donor–acceptor and acceptor–acceptor *p*-disubstituted *trans*-stilbenes, and therefore these species should possess different spectroscopic and photochemical properties.

Although DAS has been the subject of several studies and applications, some basic points are still unclear. Thus the available literature data on protonated forms of DAS are somewhat contradictory. The two-step proton dissociation constant for DAS (pK_{a1} = 3.9 and pK_{a2} = 5.2) has been reported [13]. On the contrary, only one value (pK_a = 3.95) has been determined in a 50% methanol–water mixture [14]. The latter pK_a value is not reasonable (cf. pK_a = 4.65 for aniline [15] and pK_{a1} = 2.4 and pK_{a2} = 6.1 for *p*-phenylenediamine [16]). Apparently, DAS should undergo two-step protonation, although the expected separation between the first and the second protonation values is smaller than for *p*-phenylenediamine owing to the diminished interaction between the two amino groups. No detailed studies of the photochemical behavior of the protonated DAS species have hitherto been undertaken.

The spectroscopic properties of DAS and its derivatives together with their different protonated species have been investigated and discussed in the present communication. The

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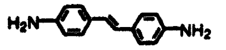
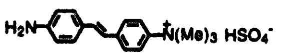
diprotonated species of DAS were compared with the unsubstituted *trans*-stilbene. The monoprotonated species of DAS were compared with the 4-trimethylammonium-4′-aminostilbene hydrogen sulfate (TAAS) which is a monocationic salt and was synthesized in our laboratory for comparison. UV absorption and fluorescence emission spectra are reported for those species. In addition, the fluorescence quantum yield and *trans–cis* photoisomerization have been measured.



DAS



TAAS$^+$

DASH$^+$

TAASH^{2+}

DASH$_2^{2+}$

2. Experimental section

2.1. Synthesis of 4-trimethylammonium-4′-aminostilbene hydrogen sulfate

4-Amino-4′-dimethylaminostilbene (**I**). This has been synthesized by the reduction of 4-nitro-4′-dimethylaminostilbene with stannous chloride dihydrate in concentrated hydrochloric acid according to [17].

4-Acetamido-4′-dimethylaminostilbene (**II**). This has been synthesized according to [18] with a 78% yield (melting point (m.p.), 234–237 °C).

4-Acetamido-4′-trimethylammoniumstilbene p-toluene sulfonate (**III**). This was prepared in analogy to the procedure in [18], using methyl *p*-toluene sulfonate and used on the next step without further purification.

4-Trimethylammonium-4′-aminostilbene hydrogen sulfate (**IV**): The mixture of **III** (0.5 g, 1.1 mmol) and 20% sulfuric acid (10 ml) was refluxed for 3 h. Ammonium hydroxyde was added to this solution dropwise at room temperature until pH 7. The precipitate was filtered and washed several times with distilled water. The salt **IV** was purified by dissolving in acetic acid and precipitating by ether. Compound **IV** melted with decomposition at 196 °C. Anal. Found: C, 55.31; H, 6.70; N, 7.72. $C_{17}H_{22}N_2SO_4 \cdot H_2O$ calc.: C, 55.42; H, 6.57; N, 7.60%. Nuclear magnetic resonance (NMR) (dimethylsulfoxide-d6): δ 3.58 (9 H, s, CH_3); 5.42 (2 H, broad, NH_2); 6.56 (2 H, d, CH); 6.99–7.90 (8 H, m, CH_{arom}) ppm.

2.2. Reagents and experimental methods

DAS dihydrochloride (Aldrich) was dissolved in water, filtered and ammonium hydroxide was added to afford neutral DAS, which was doubly recrystallized from *o*-dichlorobenzene in the dark under argon. The concentrations of stock solutions of DAS and TAAS were 2.5×10^{-4} M. HCl (2×10^{-3} M) was added to these solutions to ensure full dissolution. The concentration for measurement was around 1×10^{-5} M. Doubly distilled water was filtered through a millipore water system (220 nm pore size) until 10^{-18} Ω cm resistance has been obtained. Standard Titrisol buffer solution (Merck) was used to maintain the solution pH from 2 to 6. In the measurement of pK_a, HAc–NaAc buffer was used for pH control and to keep the ionic strength constant. UV and fluorescence spectra were measured in water or an ethanol–water mixture. No proton quenching effect has been observed under the conditions of our experiment. Other chemical reagents were of analytical grade. Ethanol was distilled to remove traces of fluorescent impurities.

UV absorption spectra were recorded on Hewlett-Packard UV b4527 diode array spectrophotometer. The calculations of the overlapping pK_a for DAS have been done by the computer program [19]. Fluorescence intensity measurements were carried out on SLM 4800 spectrophotometer. A 150 W Xenon lamp was used for photoisomerization experiments. The corrected fluorescence quantum yields were determined by the secondary standard method, using quinine sulfate in 1.0 N H_2SO_4 ($\Phi_r = 0.546$) [20] as a reference and using sample absorbance less than 0.06 in 1 cm. The equation ($\Phi_2 = \Phi_1 S_2 A_1 / S_1 A_2$) was applied to calculate the quantum yield. Molecular orbital calculations by the AM [21] method have been performed using HyperChem software [22] after the full geometry optimization.

3. Results and discussion

The neutral DAS is only slightly soluble in water. However, in order to study the interaction of DAS with polyions in aqueous solution we prefer to deal with the experimental measurement in water. Therefore it is necessary to estimate the solubility of DAS. The solubility of DAS has been evaluated in different organic solvents and water. DAS is easily soluble in ethanol, acetonitrile and toluene, but it is poorly soluble in cyclohexane. In comparison with the calibration curve in which the absorption of DAS was measured in 4% EtOH the solubility of DAS in water has been estimated to be about 2×10^{-5} M. The solubility of DAS can reach 2.5×10^{-4} M in aqueous solution at pH 2–3. In this case the most of the DAS is present as the protonated species. This solubility is sufficient for using DAS as a probe.

pK_a values for DAS were determined spectrophotometrically at the analytical wavelength of 340 nm. The absorption values at different pH values were measured in an acetate buffer solution at constant ionic strength ($I = 0.01$) at 25 °C. pK_a values of 5.12 and 3.87 have been calculated for the first motonation and second protonation correspondingly. The calculated value of the absorption coefficient for the monoprotonated species ($DASH^+$) is 21 820 M^{-1} cm^{-1}. The same experimental conditions were used to determine pK_a

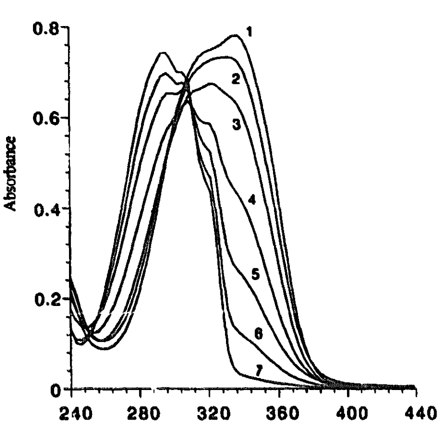


Fig. 1. Absorption spectra of DAS in a 4% ethanol–water mixture at 298 K ([DAS] = 2.7×10^{-5} M l^{-1}) The pH values of solution as follows: curve 1, 6.0; curve 2; 5.0; curve 3; 4.6; curve 4; 4.1; curve 5; 3.6; curve 6; 3.0; curve 7; 2.0.

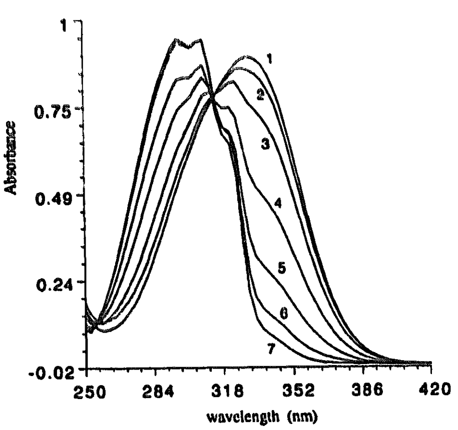


Fig. 2. Absorption spectra of TAAS in a 4% ethanol–water mixture at 298 K ([TAAS] = 2.7×10^{-5} M l^{-1}). The pH values of solution are as follows: curve 1; 5.5; curve 2; 5.0; curve 3; 4.6; curve 4; 4.0; curve 5, 3.6; curve 6; 3.0; curve 7; 2.5.

value of TAAS. The pK_a value of 3.92 for TAAS, which is close to the second pK_a of DAS has been obtained.

The UV absorption spectra of DAS and TAAS at different proton concentrations are shown in Figs. 1 and 2 respectively. The absorption band of DAS at pH 6 is essentially the same as that of neutral DAS in dichloromethane, whereas the absorption spectra of the diprotonated species ($DASH_2^{2+}$) at pH 2.0 is similar to the spectra of unsubstituted *trans*-stilbene [23], including the presence of the fine vibrational structure. The doubly charged species of TAAS ($TAASH^{2+}$) have the same spectroscopic features as $DASH_2^{2+}$ and *trans*-stilbene. It is difficult to define the spectra of the DAS monocation, because the separation between the two pK_a values of DAS is small. At any pH value between pK_{a1} and pK_{a2}, the solution always contains three species. There are two isosbestic points in the absorption spectra (in Fig. 1 between curves 1, 2 and 3 and between curves 4, 5, 6 and 7). The well-defined isosbestic point in Fig. 2 shows that there are only two species present in TAAS solution. The spectroscopic behavior of $TAAS^+$ salt should resemble that of the monoprotonated species of DAS ($DASH^+$).

The general absorption features of DAS can be reproduced by quantum-mechanical calculations. Thus, MNDO-type AM1 calculations have been used for the full geometry optimization of DAS, $DASH^+$ and $DASH_2^{2+}$ molecules and their absorption spectra were calculated using 4×4 configuration interaction (CI) (a further increase of the number of orbitals in the CI procedure did not lead to a considerable change in the calculated spectra). Whereas the absorption of neutral DAS and its dication are qualitatively reproduced by the calculations (Table 1), the predicted red shift of monoprotonated DAS cannot be observed experimentally, although a considerable red shift for donor-acceptor-substituted stilbenes compared with the corresponding symmetrically substituted stilbenes is well documented. This behavior of DAS can be attributed to the strong solvent effect which can be evaluated by solvatochromism studies.

Four solvents of different polarity have been chosen. Trifluoroacetic acid (TFA), perchloric acid or hydrochloric acid were added to generate protonated species of DAS and TAAS. The absorption bands maxima of DAS and TAAS, including their protonated species in solvents of different polarities, are compiled in Table 1. As expected, the protonation gives rise to significant changes in band positions. However, the positions of absorption and fluorescence bands corresponding to the doubly charged forms $DASH_2^{2+}$ and $TAASH^{2+}$ do not vary with the solvent polarity and are essentially the same for both compounds (322, 308 and 296 nm absorption and 350 nm fluorescence) (cf. [23–25] for *trans*-stilbene). A negative solvatochromism for the long-wave absorption and a positive solvatofluorochromism for fluorescence are observed for neutral DAS. The behavior of TAAS (which we can consider to be the analog of monoprotonated $DASH^+$) is somewhat more complicated. Thus, a bathochromic shift of the long-wave absorption band is observed within the toluene–acetonitrile–ethanol series; the absorption band undergoes a sharp hypsochromic shift in water (Table 1). Evidently, the absorption of monoprotonated $DASH^+$ is overlapped by the absorption of neutral and diprotonated DAS species. A normal bathochromic trend is observed for fluorescence of TAAS.

The basicities of aromatic amines should undergo considerable changes upon excitation. In case of aromatic diamines this behavior has been demonstrated by Dogra and coworkers [16,26] in a series of articles. The difference between pK_{a1} and pK_{a2} for DAS in the excited state should also be several orders higher than that of ground state, and separate fluorescent bands corresponding to DAS, $DASH^+$ and $TAASH^{2+}$ are observed.

The AM1 semiempirical approach has been successfully applied for the calculation of proton affinities for various organic bases [21]. The calculated proton affinity (PA) of DAS is higher than that of aniline, but lower than that of *p*-phenylenediamine (PDA). These results are in agreement with the pK_a values found experimentally (Table 2). The

Table 1
Absorption and fluorescence maxima of DAS and TAAS in different solvents and at various proton concentrations

Solvent	DAS			DASH$^+$			DASH$_2^{2+}$			TAAS$^+$		TAASH^{2+}	
	λ_{abs} (cm)	λ_{cal} (cm)	λ_{flu} (cm)	λ_{abs} (cm)	λ_{cal} (cm)	λ_{flu} (cm)	λ_{abs} (cm)	λ_{cal} (cm)	λ_{flu} (cm)	λ_{abs} (cm)	λ_{flu} (cm)	λ_{abs} (cm)	λ_{flu} (cm)
Toluene	348	360	399	–	429	424 [a]	322 [b]	341	351 [b]	330	440	326 [b]	354 [b]
	326	323			305		308			286	325	310	
	282	296			274	296					288		
		230			271		264	266					
Acetonitrile	346		408	–			322 [c]		348 [c]	342	458	322 [c]	349 [c]
	320					308			322	326	308		
	256						296			248		286	
Ethanol	344		414	–		443 [d]	322 [d]		350 [d]	350	461	322 [d]	349 [d]
	322						310			246	326	308	
Water	336 [e]		427 [e]	–		460 [f]	322 [f]		350 [f]	332 [e]	476 [e]	322 [f]	349 [f]
	320						308			240	329	308	
							296					296	

The underlined band maxima were used to calculate the Stokes shift. λ_{cal} is the absorption maximum wavelength calculated by AM1 method.

[a] 0.0002 (v/v) TFA.

[b] 1.0 (v/v) TFA.

[c] 0.5MHClO$_4$.

[d] 0.1 M HCl.

[e] pH = 6.0.

[f] pH = 2.0.

Table 2
Comparison of calculated proton affinities and pK_a values

Derivative	PA (kcal mol^{-1})		pK_a	pK_a^*
	Ground state	Excited state	Ground state	Excited state
trans-DAS	217.9	225.9	5.12	–
trans-DASH$^+$	171.7	162.2	3.87	–
Aniline	212.2 [a]	237.8	4.6[15]	–
p-phenylenediamine [[24](d)]	222.1	237.4	6.08	6.2 [b] (1.3 [c])
p-phenylendiamine H$^+$	130.2	76.9	3.29	−5.1 [b] (−5.9 [c])

[a] Experimental value: 209.5 (kcal mol^{-1}).

[b] Fluorometric method.

[c] Förster method.

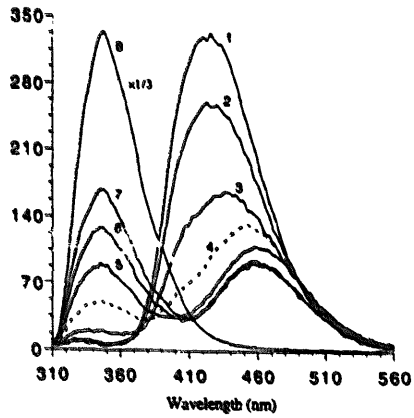


Fig. 3. Emission spectra of DAS in water solution at 298 K. (excitation wavelength, 298 nm; [DAS] = 5 × 10^{-6} M l^{-1}). The pH values of solution are as follows: curve 1, curve 6.0; curve 2, 5.1; curve; 3, 4.6; curve 4, 4.1; curve 5, 3.6; curve 6, 3.0; curve 7, 2.0; curve 8, 5.0 M HClO$_4$.

calculated proton affinity of DASH$^+$ is higher than that of the protonated form of PDA. This behavior can be attributed to the diminished conjugation of amino groups in DAS compared with PDA. The calculated proton affinity of both DAS and PDA in the excited state is higher than in the ground state. It is noteworthy that this trend is consistent with measurement for PDA by the fluorimetric method (pK_{a1}^* = −5.1; pK_{a2}^* = 6.2) but contradicts values calculated using the Förster cycle method [16] (Table 2). The proton affinities of DAS and PDA monocations in the excited state are considerably smaller than in the ground state, which also corresponds to our experiment. The monocation of DAS is a stronger base than the monocation of PDA owing to the diminished conjugation of amino groups in DAS.

The emission spectra of DAS and TAAS in solution of different pH are shown in Figs. 3 and 4 respectively. In Fig. 3,

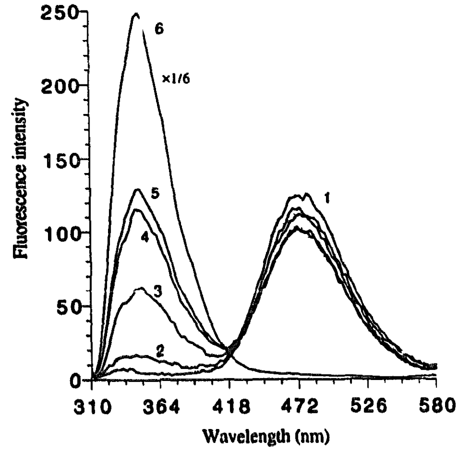


Fig. 4. Emission spectra of TAAS in water solution at 298 K. excitation wavelength 298 nm; [TAAS] = 1×10^{-5} M l^{-1}). The pH values of solution are as follows: curve 1, 6.0; curve 2, 5.0; curve 3; 4.0; curve 4, 3.0; curve 5, 2.0; curve 6, 5.0 M $HClO_4$.

the emission band of DAS at pH 2.0 consists of two bands at 350 and 460 nm. The 350 nm fluorescence, by analogy with *trans*-stilbene ($\lambda_F = 350$ nm [25,27] is likely to be the fluorescence from the fully protonated DAS. Practically, when the proton concentration in solution is increased to 5 M $HClO_4$, the emission band at 460 nm disappeared and the intensity of the band at 350 nm grows proportionally. A good isosbestic point is found between these two bands. The results suggest that the emission maxima at wavelengths of 350 nm and 460 nm correspond to di-protonated and monoprotonated species respectively. A similar situation was also found in Fig. 4. The emission bands with maxima at 349 nm and 476 nm correspond to charged species ($TAASH^{2+}$) and monocationic species ($TAAS^+$) respectively. The dication of DAS and TAAS possesses a strong photoacid behavior in the excited state and a fast conversion of dictation to monocation occurs. Therefore two separated emission bands are obtained in an aqueous solution of low pH or in some protonic solvent (e.g. ethanol). The broad bands between 427 and 460 nm (Fig. 3) always consist of two bands which can be separated as a band at 427 nm and a band at 460 nm. The band at 427 nm corresponds to the emission from the neutral species of DAS [11].

The emission band maxima of DAS, TAAS and their protonated species in different solvents are given in Table 1. The emission spectra of dicationic species ($DASH_2^{2+}$ and $TASSH_2^+$) do not exhibit any noticeable solvatofluorochromism, similarly to their absorption spectra. However, a red shift of about 30 nm is observed for DAS and $DASH^+$ moving from toluene to water solutions, indicating a positive solvatofluorochromism. The opposite trends observed for DAS and $TAAS^+$ (negative solvatochromism and positive solvatofluorochromism) give rise to the strong increase in the Stokes shifts in solutions of increasing polarity, whereas the Stokes shifts of $DASH_2^{2+}$ and $TAASH^{2+}$ remains almost constant (Table 3).

Table 3
Stokes shift with different solvent polarities

Solvent	E_T (30) [28] (kJ mol^{-1})	DAS	Stokes shift × 10^{-3} (cm^{-1})			
			$DASH^+$	$DASH_2^{2+}$	$TAAS^+$	$TAASH^{2+}$
Toluene	142	3.67	–	3.98	7.58	4.01
Acetonitrile	192	4.39	–	3.73	7.40	3.81
Ethanol	217	4.92	–	3.69	6.83	3.81
Water	264	6.34	–	3.90	9.11	3.81

Table 4
The molar extinction coefficients, quantum yields and the apparent isomerization rate constants of DAS, TAAS and their different charge species in aqueous solution

Species	ϵ (M^{-1} cm^{-1})	Θ_f	K_{is}^{ap} (s^{-1})
DAS	27600 (336 nm)	0.040	0.012 [a]
$DASH^+$	21800 [b] (340 nm)	0.016	0.044 [c]
$DASH_2^{2+}$	25800 (296 nm)	0.018	0.042 [d]
$TAAS^+$	22500 (332 nm)	0.014	0.035 [a]
$TAASH^{2+}$	23800 (296 nm)	0.020	0.053 [d]

[a] At pH 11, and an excitation wavelength of 350 nm.
[b] The result was obtained by the computer simulation.
[c] At pH 3.2, and an excitation wavelength of 350 nm.
[d] At 60% $HClO_4$, and an excitation wavelength of 310 nm.

The excitation wavelength of 296 nm was chosen to measure the quantum yields of $DASH_2^{2+}$ and $TAASH^{2+}$ in 60% $HClO_4$ and the excitation wavelengths of 336 nm and 350 nm for the quantum yields of DAS and $TAAS^+$ at pH 11 solution respectively. $DASH^+$ at pH 3.2 was irradiated at 350 nm. The results are presented in Table 4. The accuracy of quantum yield determination was about 20%, attributed to the rapid photoisomerization which takes place during the measurement. The fluorescence decay measurements have also been performed for these two compounds and their charged species in aqueous solution (Table 4).

The kinetics of photoisomerization of *trans*-DAS into the *cis* isomer have also been studied. The process of the isomerization can be monitored by ^1H NMR, absorption and fluorescence spectra. Whereas exposing the solution of DAS in dichloromethane or chloroform to light leads to the fast decomposition of DAS (probably owing to photo-oxidation), in a water–ethanol solution smooth isomerization has been observed by ^1H NMR. The characteristic signal of vinylic protons of *trans*-DAS at 6.86 decreases and the corresponding doublet of the *cis* isomer appears at 6.33. An analogous shift is observed for multiple signals of aromatic protons. This technique can also be used to detect the protonation process of DAS. The kinetic measurements of *trans–cis* isomerization of both DAS and TAAS monitored by fluorescence intensity show that the decay process is followed by first-order kinetics (Fig. 5). The apparent rate constant K_{is}^{ap} was of photoisomerization calculated according to [3] and the relevant data are collected in Table 4. These results suggest that there is no considerable difference between the

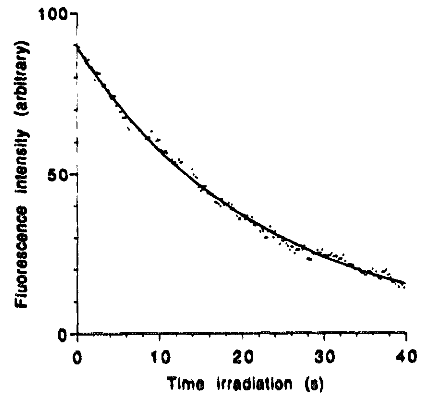


Fig. 5. The dependence of the $DASH_2^{2+}$ fluorescence intensity on time of irradiation at 296 K in 60% $HClO_4$ aqueous solution excitation wavelength 310 nm). The solid line is the best fit to equation $f = A \exp(-K_{is}^{ap} t) + B$ with $K_{is}^{ap} = 4.2 \times 10^{-2}\ s^{-1}$. A and B are constant.

rates of *trans–cis* photoisomerization for the differently charged species of DAS and TAAS.

4. Conclusion

Two pK_a values of 5.12 and 3.87 for DAS and one pK_a value of 3.92 for TAAS have been determined. The solubility of neutral DAS in water was estimated to reach 2×10^{-5} M. The negative solvatochromism and positive solvatofluorochromism of DAS and $TAAS^+$ lead to the large Stokes shift in polar solvents. Unlike *p*-phenylenediamine, DAS, its monocation and dication are fluorescent and highly sensitive to properties of surroundings. Therefore, DAS can be used as an efficient probe for polyelectrolyte investigations.

Acknowledgements

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