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Photophysical and photochemical properties of some triazine–stilbene fluorescent brighteners

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Abstract

The study presents the photophysical and photochemical characteristics in aqueous solution of some triazine–stilbene fluorescent brighteners containing 2-hydroxyethylamino groups and their *trans–cis* isomers in equilibrium. It has been established that the type of substituent in the triazine ring does not affect significantly the absorption–fluorescence assignments or the relative distribution of the *trans*- and *cis*-isomers. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Triazine–stilbene fluorescent brighteners (FBs) are widely used in the textile and paper industry to reduce yellowness and to increase fabric brightness. They absorb light in the near ultraviolet region of the spectrum (about 340–380 nm) and re-emit the light as violet-blue fluorescence in the visible region. There is extensive literature data on FBs containing different amino and alkoxy derivatives in the triazine ring [1–4]. In solution these FBs have low light resistance, determined by the possibility of their existence in two stereoisomeric *cis* and *trans* forms. Exposure to light causes *trans–cis* isomerism, with shift of the absorption maxima and formation of an equilibrium mixture usually with predomination of the *cis*-form. Isomerization to the *cis*-form results in the loss of fluorescence [5]. The equilibrium ratio of the two forms depends on the type of substitutents in the triazine ring [6]. It is know that the photophysics and photochemistry of triazine–stilbene fluorescent brighteners are markedly determined by solvent polarity. With decrease in the solvent polarity, the quantum yield of fluorescence increases, while the photoisomerization yield decreases [7]. We have previously reported the synthesis of some FBs containing unsaturated polymerisable groups, their photophysical properties [8–10] and applications [11–16].

In this paper we present some photophysical and photochemical properties of three triazine–stilbene fluorescent brighteners.

2. Results and discussion

2.1. Synthesis of triazine–stilbene fluorescent brighteners

Triazine–stilbene fluorescent brighteners with the following structure have been studied (Scheme 1):

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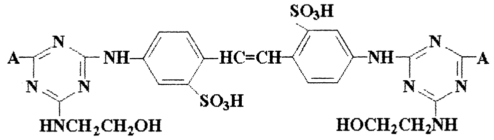


Scheme 1.

where A is -morpholino (**1**), -N(CH_3)$_2$ (**2**), -N(C_2H_5)$_2$ (**3**).

FBs **1–3** were prepared by established methods, whereby 0.005 mol of 4,4′-diaminostilbene-2,2′-disulphonic acid in water–acetone solution (1:1) was reacted with 0.01 mol of cyanuric chloride at 0–5°C for 2 h, maintaining pH 6 by addition of 10% aq. sodium hydroxide. When the first condensation stage was complete, the temperature was increased to 30–35°C and 0.01 mol of the respective amine AH was then added at pH 6. Stirring was continued for a further 3 h and after this second acylation stage the temperature was increased to 80–85°C and 0.015 mol of 2-hydroxyethylamine was added. The mixture was stirred for 5 h at pH 7. After cooling to ambient temperature the product was isolated by addition of sodium chloride. Relevant characterisation data are shown in Tables 1 and 2.

The rate of reaction and the purity of the final product was monitored by TLC using *n*-butanol: pyridine:25 vol% NH_3 (1:1:1) on silica gel plates. The chromatograms were developed by irradiation at 366 nm. The R_f values for the *trans*- and *cis*-isomers are listed in Table 1; the two isomers have different R_f values, indicating different absorbancies. The *cis*-form has disturbed coplanarity of the molecule, of a weaker substantiality, and lower R_f values [17].

2.2. Spectral characteristics

Table 2 shows the basic electronic characteristics and fluorescence data of the FBs **1–3** in aqueous medium; values of the ground state position of the absorption maxima (λ_A) and the molecular extinction coefficient (ε) of the FBs are given together with values of fluorescence maxima (λ_F), Stoke's shift ($\Delta\nu$), wavelength (λ_{S1}) and the energy of the singlet state (E_{S1}), quantum yield of fluorescence (Φ_F) and the energy yield (E_F).

In aqueous solution the FBs absorb in the UV-region (λ_A 346–350 nm). Fluorescence emission is observed in the region 385–500 nm with a well pronounced maximum at 436–440 nm. The nature of substituent A in the triazine ring does not influence the absorption and fluorescence maxima. FBs pass from the basic singlet state S_0 to the first excited state S_1 on light absorption. The energy of the excited state E_{S1} and the corresponding λ_{S1} are estimated from the intersection of the fluorescence and absorption spectra. The energy of the excited state E_{S1} in water is 300–304 kJ.mol^{-1}. The FBs studied do not phosphoresce in ethanol solution at 77 K, which indicates that when excited they are in the singlet state S_1. The FBs molecule is deactivated by fluorescence light emission and passes from the S_1 to the basic S_0 state.

The Stoke's shift is given by Eq. (1):

$$\Delta\nu = (1/\lambda_A - 1/\lambda_F) \times 10^7, \mathrm{cm}^{-1} \tag{1}$$

The Stoke's shift is 5800–5965 cm^{-1}. The significant Stoke's shift is due to the energy losses during the transition into the excited state. This is evidence of notable steric changes which the

Table 1
Characterisation data of the fluorescent brighteners

FB	Yield %	R_f		Analysis calcd % (found)			IR (KBr) cm^{-1}					
		cis	*trans*	C	H	N	ν_{OH}	$\nu_{N=C}$	ν_{CH}	ν_{CH3}	$\nu_{S=O}$	δ_{CH}
1	82	0.42	0.78	44.65 (44.49)	4.42 (4.36)	19.53 (19.44)	3425	1621	1580	—	1079	790
2	74	0.24	0.56	43.30 (43.12)	4.38 (4.21)	21.65 (21.50)	3414	1615	1584	1358	1020	800
3	71	0.30	0.64	46.15 (45.98)	5.05 (4.98)	20.19 (20.08)	3444	1617	1570	1359	1023	802

Table 2
Absorption and fluorescence characteristics of fluorescent brighteners in aqueous solution (see text)

FBs	**1**	**2**	**3**
λ_A (nm)	350	346	348
log ε	4.83	4.91	4.89
λ_F (nm)	440	436	436
E_{S1} (kJ mol^{-1})	300	302	304
$\Delta\nu$ (cm^{-1})	5814	5965	5800
Φ_F	0.29	0.26	0.24
E_F	0.23	0.21	0.19

molecules undergo during the transition from the ground to the excited state.

The ability of the molecules to emit the absorbed light energy is characterised quantitatively by the quantum fluorescent yield Φ_F. This is calculated on the basis of the absorption and fluorescence spectra of the FBs dissolved in water at a concentration of 10^{-6} mol l^{-1} using sodium salycilate ($\Phi_0 = 0.55$) as a standard [18]. Φ_F values are 0.25–0.29, which shows that the fluorescence involves non-emission deactivation of the S_1 state.

Besides Φ_F, the energy yield of fluorescence E_F can be also used [19] [Eq. (2)]:

$$E_F = \Phi_F \lambda_A / \lambda_F \qquad (2)$$

These values ($\Delta\nu$, Φ_F and E_F) reveal the domination of non-radiative deactivation processes during the transition $S_1 \rightarrow S_0$ which are parted by isomerization in the non-fluoerescent *cis*-form.

2.3. *Trans–cis isomerization in aqueous solution*

Irradiation of triazine–stilbene fluorescent brigthteners in solution is known to result in *trans* (*E*)–*cis* (*Z*) photoisomerization [20–22]. *Trans–cis* isomerization has been studied in aqueous solution at 2.10^{-3} wt% concentration of the FBs and exposure of the solution to monochromatic light of a wavelength which overlaps with the absorption maximum of the *trans*-isomer. The irradiation was carried out in an inert atmosphere to avoid photochemical breakdown. The course of isomerization was followed spectrometrically.

The obtained percentage content of the isomers of FBs **1–3** in solution after exposure to light is estimated according to Eqs. (3) and (4) [23]:

$$C_T = \frac{A_T(A'_c - A_c)}{A'_c A_T - A_c A'_T} 100\% \qquad (3)$$

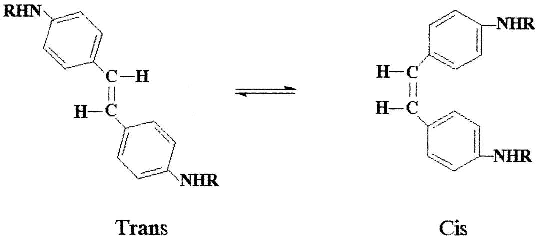
and

$$C_C = 100 - C_T\% \qquad (4)$$

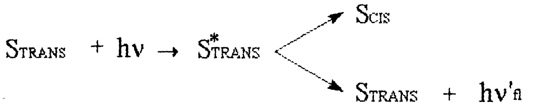
where A_T and A_C are the absorption of the *trans*- and *cis*-isomers before exposing the solution, A'_T and A'_C are the respective absorption after exposure, and C_T and C_C are the percentage concentrations of the *trans*- and *cis*-isomers in the solution.

The double bond in the stilbene molecule favours *trans–cis* isomerization of FBs. The two isomeric forms have different absorption maxima in the UV region. The *trans*-isomer absorption maximum is at 340–355 nm while the *cis*-isomer has a maximum hypsochromically shifted to the 250–280 nm region [24]. In daylight, the photostationary state favours the *cis*-isomer. In solution the *trans*-form absorbs the excited energy, and by a rotation the molecule transforms into a *cis*-state which is richer in energy (Scheme 2). This leads to disintegration of the molecular compactness. Thus, *cis*-isomers lose their fluorescence properties and their ability to brighten material; thus the FBs become less effective.

The processes operative in the photoexcited *trans*-form FBs leading to a *cis*-conformation can be represented by Scheme 3:



Scheme 2.



Scheme 3.

and for the *cis*-form:

$$S_{\mathrm{CIS}} + h\nu \rightarrow S^*_{\mathrm{CIS}} \rightarrow S_{\mathrm{CIS}}$$

Therefore the mechanism of the emissionless deactivation of the singlet state FBs is in fact a conformation transition of a singlet excited state of the *trans*-isomer being in the slightly fluorescing *cis*-form accompanied by a well pronounced non-radiative emission $S_1 \rightarrow S_0$.

In isomeric mixtures the *trans*-isomer is predominantly excited and its concentration decreases with irradiation time, while that of *cis*-isomer increases until equilibrium is reached. Table 3 presents the results for C_T and C_C of the two isomers for the FBs **1–3**; in the equilibrium the *trans*-isomer prevails (62–66%). No considerable difference between C_T and C_C and the type of the third substitutent in the triazine ring was observed.

The λ_A values at the isobestic points are in the region 304–307 nm. The FBs concentration at these isobestic points does not depend on the composition of *trans*- and *cis*-isomers in the solution, and can be used for quantitative measurements.

2.4. Fluorescence and whiteness degree

It is known that the effect of FBs is due to fluorescent emission in the blue region which enhances the whiteness degree (*W* CIE).

The whiteness *W* was calculated according to the CIE equation [Eq. (5)]:

$$W = Y + 800(x_n - x) + 1700(y_n - y) \quad (5)$$

Figs. 1 and 2 show the changes in the whiteness degree with increase in the concentration of FBs on cotton and polyamide fabrics. It is apparent that the whiteness degree increases with increasing concentration of FBs. Its maximum is reached at 0.5–0.6 wt% for both materials; it then drops regardless of the FBs content. The increase of the whiteness degree after the maximum concentration is a result of the effect of "fluorescence concentration quenching".

Table 3
Absorption maxima of *trans* (λ_T) and *cis* (λ_C) forms of the fluorescent brighteners and their concentration (C_T and C_C) in aqueous solution

FBs	λ_T (nm)	λ_C (nm)	Isobestic point (nm)	C_T (%)	C_C (%)
1	350	252	304	62	38
2	346	263	307	63	37
3	348	265	306	66	34

It was interesting to investigate the fluorescence of polyamide and cotton materials after their treatment with 0.5 wt% FBs at $\lambda = 350$ nm. As seen from the results in Table 4, the differences in the fluorescence maximum of FBs in aqueous solution, and after laying them over the samples, the shift ($\Delta\lambda_F$) in the fluorescent spectrum is no bigger than 4 nm. The fluorescence of polyamide and cotton fabrics is considerably higher (more than 60–80 times) than that of an aqueous solution of the FBs. It is due only to the polymeric textile matrix, the surface of which absorbs only the high fluorescing *trans*-isomer. In textile materials, the isomerization in the non-fluorescing *cis* form is hindered compared to the facile transfer in aqueous solution. The results give grounds for the

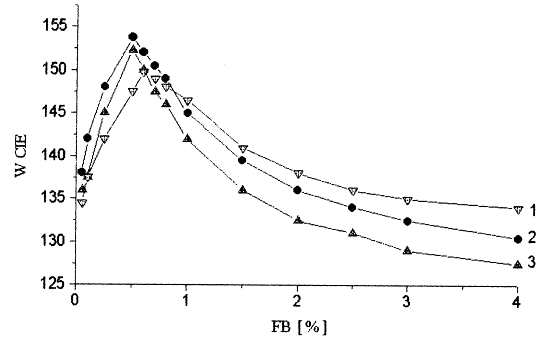


Fig. 1. Degree of whiteness *W* CIE of cotton fibres as a function of the concentration of the fluorescent brighteners.

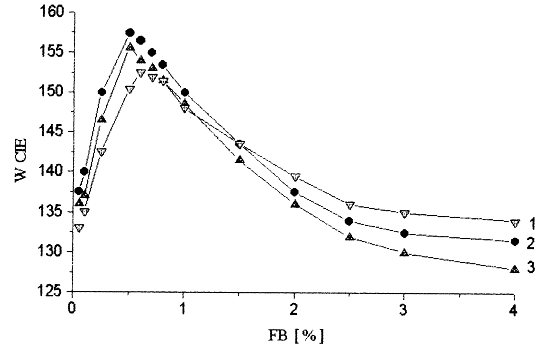


Fig. 2. Degree of whiteness *W* CIE of polyamide fibres as a function of the concentration of the fluorescent brighteners.

Table 4
Fluorescence maxima of the fluorescent brighteners in aqueous solution, polyamide and cotton materials and whiteness degree (see text)

FB	Water	Polyamide		Cotton		Whiteness (CIE)	
	λ_F (nm)	λ_F (nm)	$\Delta\lambda_F$ (nm)	λ_F (nm)	$\Delta\lambda_F$ (nm)	W_C	W_{PA}
1	440	441	−1	442	−2	150.5	147.8
2	436	440	−4	438	−3	157.4	153.4
3	436	439	−3	440	−4	155.6	152.3

suggestion that the fluorescent activity of FBs, after their application to textiles, will be much higher than that of the isomer in aqueous solution.

3. Experimental

3.1. General method for the synthesis of triazine–stilbene fluorescent brighteners

3.1.1. 4,4′-bis[2-Morpholino-4-(2-hydroxyethyl-amino)-1,3,5-triazin-6-yl-amino]-stilbene-2,2′-di-sulphonic acid (1)

Cyanuric chloride (0.01 mol) was dissolved in 50 ml acetone and to the solution was added a 50 ml aq. solution of 0.005 mol 4,4′-diaminostilbene-2,2′-disulphonic acid at 0–5°C. After stirring for 2 h, whilst maintaining pH 6 by addition of 10% aq. sodium hydroxide, the liquor was heated to 30–35°C; 0.01 mol morpholine was added and stirring continued for 3 h at pH 6. The temperature was raised to 80–85°C, 0.01 mol 2-hydroxyethylamine was added and the mixture was stirred for 5 h at pH 7. The reaction mixture was cooled and the product isolated by addition of sodium chloride; the precipitated product was filtered, washed with acetone and dried under vacuum at 40°C.

FBs **2** and **3** were synthesised using the same procedure using the dimethylamine and diethylamine.

Reaction yields and characterisation data of FBs **1–3** are given in Table 1.

3.2. Materials and methods

The textile materials used were 100% polyamide-6 and 100% pure chemically bleached cotton. The FBs **1–3** were applied at concentrations of 0.05, 0.1, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 3.0 and 4% relative to the weight of textile materials, using the procedure previously described [14]. The degree of whiteness (*W* CIE) was determined using a Texflach ACS/DATACOLORR spectrophotometer and a CIE D_{65} light source.

3.2.1. Infrared (IR) spectra

IR-spectra were recorded in KBr pellets on a Perkin–Elmer 1600 FTIR spectrophotometer.

3.2.2. Electronic absorption measurements

UV spectra were recorded from aqueous solutions at a concentration 5.10^{-5} mol l^{-1} on a Hewlett–Packard 8452A spectrophotometer.

3.2.3. Emission measurements

Fluorescence measurements were recorded on a Perkin–Elmer MPF 44 spectrophotometer in aqueous solution, cotton and polyamide fabrics at room temperature; phosphorescence measurements were recorded in ethanol solution at 77 K.

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