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# Synthesis of 4,4′-bis[(4-morpholino-6-arylureido/thioureido-*s*-triazin-2-yl)amino] stilbene-2,2′-disulphonic Acid Derivatives and their Use as Fluorescent Brightening Agents for Cotton and Nylon Fibres

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## ABSTRACT

*4,4′-Diaminostilbene-2,2′-disulphonic acid was condensed with two moles of cyanuric chloride to give 4,4′-[(4,6-dichloro-s-triazin-2-yl)amino] stilbene-2,2′-disulphonic acid, which was then condensed with two moles of morpholine to afford 4,4′-bis[(4-morpholino-6-chloro-s-triazin-2-yl)amino] stilbene-2,2′-disulphonic acid. This compound was then further condensed with two moles of an arylurea and arylthiourea to give 4,4′-bis[(4-morpholino-6-arylureido-s-triazin-2-yl)amino] stilbene-2,2′-disulphonic acid and 4,4′-bis[(4-morpholino-6-asylthiouscido-s-triazin-2-yl)amino] stilbene-2,2′-disulphonic acids respectively. These compounds were applied as fluorescent brightening agents on cotton and nylon fibres and gave excellent results.*

## 1 INTRODUCTION

Fluorescent brightening agents (FBAs) are applied to textiles to reduce yellowness and to increase fabric brightness.[1] They function by absorbing ultra-violet radiation and re-emitting it as visible blue light. When initially introduced into the textile industry, FBAs were mainly used on cellulosics, but are now frequently applied in a variety of textiles including cellulosics, during manufacturing and are incorporated into laundry detergents.[2]

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The molecular requirements necessary for high fluorescence activity include a planer structure with conjugated double bonds and electron-donating groups, e.g. hydroxyl and amino.[3] A wide range of chemical structures has been investigated and those structures containing the bistriazinylaminostilbene chromophore are an important chemical class for cotton, wool and other fibres.[4–12] However, the stilbenes vary in substantivity and may photodegrade, resulting in a loss in fluorescence, yellowing, degradation of the substrate and acceleration of dye fading, depending on the functional group present.

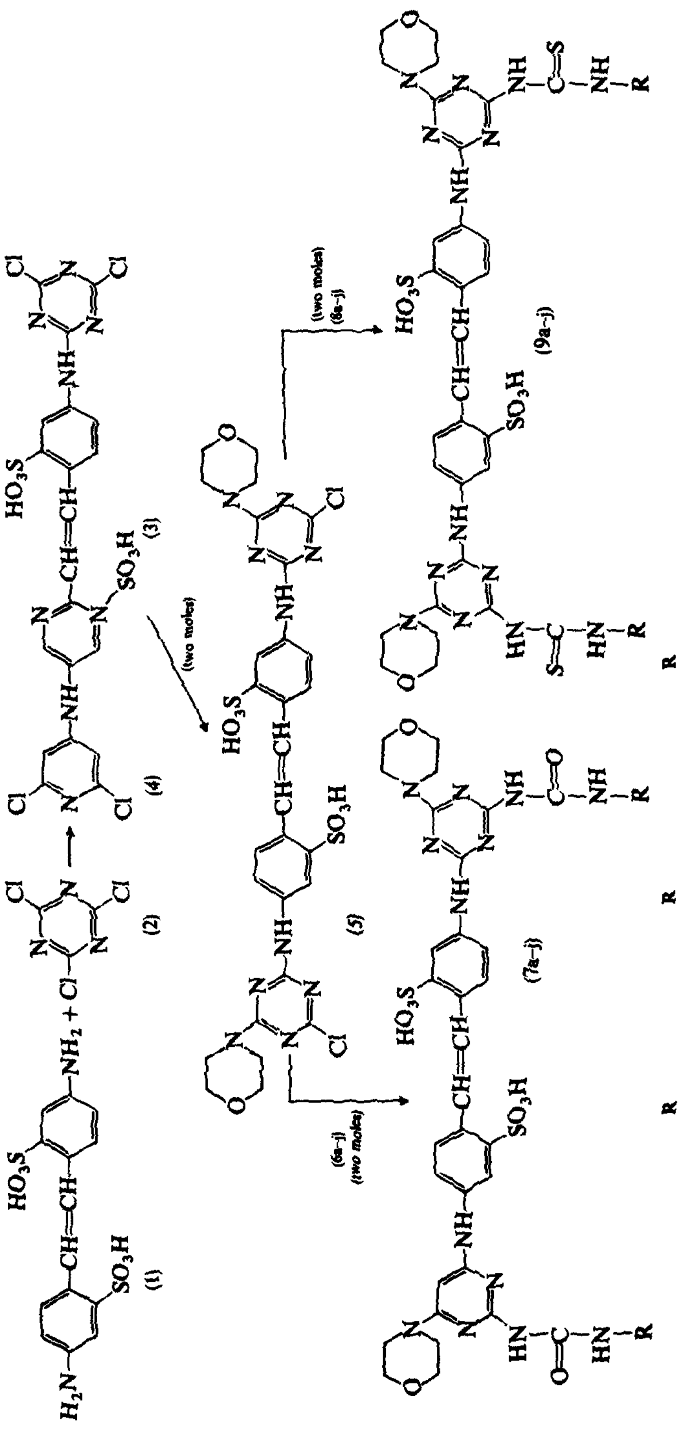
The present study reports the synthesis, application, absorption characteristics and fastness properties of some bistriazinyl aminostilbene FBAs.

## 2 RESULTS AND DISCUSSION

To obtain the compounds which were anticipated to possess fluorescent properties, compounds containing the *s*-triazine system as one substituent in 4,4′-diaminostilbene-2,2′-disulphonic acid with variations in the other substituent were synthesised. The substituent selected in the 4-position of the bistriazinylaminostilbenes was a group such as morpholino, and the substituents used in the 6-position of the bistriazinylaminostilbenes were various arylurea and thiourea derivatives. 4,4′-Diaminostilbene-2,2′-disulphonic acid (1) (see Scheme 1) was condensed with two molecules of cyanuric chloride (2) to give 4,4′-bis(4,6-dichloro-s-triazin-2-yl)amino stilbene-2,2′-disulphonic acid (3). Reaction of (3) with two molecules of morpholine (4) gave rise to the corresponding compound (5).

In a similar fashion, compound (5) was condensed with two molecules of compounds (6a–j) and (8a–j) and gave, respectively, the compounds (7a–j) and (9a–j). The structures were established on the basis of elemental analysis, UV spectra, enhancement of fluorescence, IR and PMR spectrum (7a and 9d). Scheme 1 shows the reactions employed. Table 1 shows characterisation data of compounds (7a–j) and (9a–j). The compounds (7a–j) and (9a–j) were colourless to pale yellow in colour and they were obtained in good yield (69–80%) (Table 1). The absorption maxima of these compounds, recorded in DMF, varied from 300 nm to 354 nm and the emission maxima were in the range of 432–465 nm.

The compounds when applied to cotton and nylon fibres as fluorescent brighteners showed a whitening effect with bluish fluorescence in the case of compounds (7e), (7f), (9e) and (9f); greenish-blue fluorescence in the case of compounds (7g), (7h), (7i), (7j), (9g), (9h), (9i) and (9j) and bluish-violet fluorescence in the case of (7a), (7b), (7c), (7d), (9a), (9b), (9c) and (9d). The



R
(a) Phenyl
(b) *o*-tolyl
(c) *p*-toolyl
(d) *p*-tolyl

R
(e) *o*-methoxyphenyl
(f) *p*-methoxyphenyl
(g) *o*-chlorophenyl
(h) *m*-chlorophenyl

R
(i) *p*-chlorophenyl
(j) *p*-bromophenyl

Scheme 1

**TABLE 1**
Characterisation Data of Compounds (7a–j) and (9a–j)

| *Compound* | *R* | *Yield (%)* | *Melting point (°C)* | *Molecular formula* | *Analysis (%)*[a] | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | *N* | | *S* | |
| | | | | | *Calc.* | *Found* | *Calc.* | *Found* |
| 7a | Phenyl | 75 | 122 | $C_{42}H_{42}N_{14}O_{10}S_2$ | 20·29 | 20·34 | 6·62 | 6·61 |
| 7b | *o*-Tolyl | 79 | 196 | $C_{44}H_{46}N_{14}O_{10}S_2$ | 19·72 | 19·76 | 6·44 | 6·49 |
| 7c | *m*-Tolyl | 76 | 192 | $C_{44}H_{46}N_{14}O_{10}S_2$ | 19·72 | 19·65 | 6·44 | 6·43 |
| 7d | *p*-Tolyl | 75 | 148 | $C_{44}H_{46}N_{14}O_{10}S_2$ | 19·72 | 19·69 | 6·44 | 6·41 |
| 7e | *o*-Methoxyphenyl | 70 | 118 | $C_{44}H_{46}N_{14}O_{12}S_2$ | 19·10 | 19·03 | 6·24 | 6·25 |
| 7f | *p*-Methoxyphenyl | 77 | 125 | $C_{44}H_{46}N_{14}O_{12}S_2$ | 19·10 | 19·09 | 6·24 | 6·23 |
| 7g | *o*-Chlorophenyl | 80 | 216 | $C_{42}H_{40}N_{14}O_{10}S_2Cl_2$ | 18·94 | 18·99 | 6·18 | 6·17 |
| 7h | *m*-Chlorophenyl | 71 | 212 | $C_{42}H_{40}N_{14}O_{10}S_2Cl_2$ | 18·94 | 18·84 | 6·18 | 6·09 |
| 7i | *p*-Chlorophenyl | 77 | 210 | $C_{42}H_{40}N_{14}O_{10}S_2Cl_2$ | 18·94 | 18·87 | 6·18 | 6·15 |
| 7j | *p*-Bromophenyl | 77 | 201 | $C_{42}H_{40}N_{14}O_{10}S_2Br_2$ | 17·44 | 17·49 | 5·69 | 5·71 |
| 9a | Phenyl | 78 | 159 | $C_{42}H_{42}N_{14}O_8S_4$ | 19·64 | 19·53 | 12·83 | 12·89 |
| 9b | *o*-Tolyl | 72 | 199 | $C_{44}H_{46}N_{14}O_8S_4$ | 19·10 | 19·07 | 12·48 | 12·46 |
| 9c | *m*-Tolyl | 69 | 175 | $C_{44}H_{46}N_{14}O_8S_4$ | 19·10 | 19·07 | 12·48 | 12·46 |
| 9d | *p*-Tolyl | 70 | 220 | $C_{44}H_{46}N_{14}O_8S_4$ | 19·10 | 19·19 | 12·48 | 12·54 |
| 9e | *o*-Methoxyphenyl | 79 | 140 | $C_{44}H_{46}N_{14}O_{10}S_4$ | 18·53 | 18·59 | 12·10 | 12·13 |
| 9f | *p*-Methoxyphenyl | 80 | 165 | $C_{44}H_{46}N_{14}O_{10}S_4$ | 18·53 | 18·56 | 12·10 | 12·09 |
| 9g | *o*-Chlorophenyl | 78 | 201 | $C_{42}H_{40}N_{14}O_8S_4Cl_2$ | 18·36 | 18·26 | 12·00 | 11·98 |
| 9h | *m*-Chlorophenyl | 70 | 212 | $C_{42}H_{40}N_{14}O_8S_4Cl_2$ | 18·36 | 18·24 | 12·00 | 12·07 |
| 9i | *p*-Chlorophenyl | 74 | 225 | $C_{42}H_{40}N_{14}O_8S_4Cl_2$ | 18·36 | 18·34 | 12·00 | 12·04 |
| 9j | *p*-Bromophenyl | 78 | 197 | $C_{42}H_{40}N_{14}O_8S_4Br_2$ | 16·96 | 16·92 | 11·07 | 11·01 |

[a] Satisfactory C and H analyses obtained.

compounds, on assessment, for relative use as fluorescent brighteners could be sub-divided into grades one (for compounds (7a) and (9a)), two (for compounds (7g), (7h), (7i), (7j), (9g), (9h), (9i) and (9j)) and three (for compounds (7b), (7c), (7d), (7e), (7f), (9b), (9c), (9d), (9e) and (9f)).

## 3 EXPERIMENTAL

All melting points are uncorrected. Absorption and fluorescence emission spectra were recorded on a Hitachi U-320 spectrophotometer and a Jobin Yvon JY 3CS spectrophotofluorimeter respectively. IR spectra were recorded on a Perkin Elmer 377 spectrophotometer and $^1H$ NMR spectra on a Varian 90 MHz instrument EM-360-L using TMS as internal standard and $CDCl_3 + DMSO\text{-}d_6$ as solvent. Fastness tests were assessed by the standard methods of testing (BS: 1006-1978 and IS: 765-1979).

### 3.1 Preparation of starting materials

4,4′-Diaminostilbene-2,2′-disulphonic acid (1),[13] arylureas (6a–j)[14] and arylthioureas (8a–j)[15] were prepared by known methods.

### 3.2 4,4′-Bis[(4,6-dichloro-s-triazin-2-yl)amino)] stilbene-2,2′-disulphonic acid (3)

Finely powdered (2) (4·78 g, 0·026 mol) was added to acetone (80 ml) with vigorous stirring to obtain a fine suspension and the solution cooled to 0°C. A solution of (1) (4·81 g, 0·013 mol) in sodium carbonate (30%, w/v) was added with constant stirring to the above suspension. The reaction mixture was stirred for 3 h at 0–5°C maintaining pH 7 by simultaneous addition of sodium carbonate (10%, w/v). The product was filtered, washed with cold water, dried and crystallised from ethanol, m.p. 245°C, yield 63%, (calc.: C, 36·03; H, 1·80; N, 16·81; S, 9·60; Cl, 21·32. Found: C, 36·02; H, 1·79; N, 16·84; S, 9·59; Cl, 21·36%); IR (KBr); 770 (C–Cl), 805 ($C_3N_3$), 1005 (—CH=CH—), 1200 (sulphonic SO) and 1595 (—NH—). $^1H$ NMR ($CDCl_3 + DMSO\text{-}d_6$), 6·66 (1H, S, —C$\underline{H}$=CH—), 7·25 (1H, S, —CH=C$\underline{H}$—), 7·09 (2H, bs, —NH—) and 7·0–7·24 (6H, m, Ar$\underline{H}$).

### 3.3 4,4′-Bis[(4-morpholino-6-chloro-s-triazin-2-yl)amino] stilbene-2,2′-disulphonic acid (5)

To a stirred solution of (3) (6·66 g, 0·01 mol) in acetone (50 ml) at 35°C, a solution of (4) (1·72 ml, 0·02 mol) in acetone (8 ml) was added slowly in

## TABLE 2

Absorption-Emission and Fastness Evaluation Data of Compounds (7a–j) and (9a–j)

| *Compound* | *Absorption max (nm)* | *Emission max (nm)* | *Log E* | *Light fastness* | | *Wash fastness* | | *Perspiration fastness* | | | | *Chlorine fastness* | | *Sublimation fastness* | | *Pick-up value* | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | *C* | | *N* | | | | | | | |
| | | | | *C* | *N* | *C* | *N* | *Acid* | *Alkaline* | *Acid* | *Alkaline* | *C* | *N* | *C* | *N* | *C* | *N* |
| 7a | 300 | 432 | 4·21 | 4 | 3–4 | 3 | 4 | 3–4 | 3 | 4 | 4 | 4–5 | 5 | 3 | 3 | 3–4 | 4 |
| 7b | 335 | 454 | 4·43 | 4 | 5–6 | 4 | 5–6 | 4–5 | 5 | 5–6 | 5–6 | 5 | 5–6 | 4 | 4 | 3–4 | 4 |
| 7c | 310 | 446 | 4·35 | 4–5 | 5–6 | 4 | 5 | 5 | 5 | 5 | 4–5 | 4–5 | 5 | 3–4 | 4 | 4 | 2–3 |
| 7d | 345 | 460 | 4·49 | 4 | 6 | 4–5 | 5 | 5 | 5 | 4–5 | 5–6 | 5 | 5–6 | 3 | 4 | 3 | 3 |
| 7e | 333 | 446 | 4·37 | 4 | 4–5 | 3–4 | 5 | 5 | 4–5 | 5–6 | 5–6 | 5 | 5–6 | 3 | 4 | 2 | 2 |
| 7f | 330 | 465 | 4·54 | 4 | 4–5 | 3–4 | 4 | 3–4 | 5 | 4 | 5 | 4 | 4 | 3 | 4 | 2 | 1–2 |
| 7g | 315 | 454 | 4·42 | 3–4 | 4 | 3 | 3–4 | 3–4 | 4 | 4–5 | 4–5 | 4 | 4 | 3 | 4 | 2 | 2 |
| 7h | 317 | 457 | 4·45 | 3 | 3–4 | 3 | 3–4 | 3 | 3 | 4 | 3 | 3 | 3 | 3 | 2–3 | 2 | 2 |
| 7i | 326 | 458 | 4·67 | 3 | 3 | 3–4 | 3–4 | 3 | 4 | 3–4 | 3–4 | 3 | 3–4 | 2 | 2 | 1–2 | 1–2 |
| 7j | 354 | 444 | 4·30 | 3–4 | 4–5 | 4 | 4 | 4 | 4 | 4 | 4 | 3 | 3 | 2–3 | 2 | 2 | 2 |
| 9a | 305 | 445 | 4·34 | 4 | 3 | 3–4 | 4–5 | 4 | 4 | 4–5 | 4–5 | 5 | 5–6 | 3 | 2–3 | 3–4 | 4 |
| 9b | 312 | 451 | 4·46 | 4 | 5 | 5 | 6 | 4 | 5 | 6 | 6 | 5 | 6 | 4 | 4 | 3–4 | 4 |
| 9c | 338 | 458 | 4·63 | 4 | 5 | 5 | 5–6 | 4–5 | 5 | 6 | 5–6 | 5 | 5–6 | 4 | 4 | 3–4 | 3–4 |
| 9d | 342 | 457 | 4·80 | 4–5 | 5 | 5 | 6 | 4 | 5 | 5–6 | 6 | 5 | 5 | 3–4 | 4 | 3–4 | 4 |
| 9e | 330 | 447 | 4·70 | 4 | 4–5 | 4–5 | 5 | 4 | 5 | 5 | 5 | 5 | 4 | 4 | 4 | 3 | 3 |
| 9f | 334 | 452 | 4·57 | 3–4 | 4 | 4 | 4–5 | 4 | 5 | 5 | 5 | 4–5 | 5 | 3 | 3 | 2–3 | 2 |
| 9g | 319 | 461 | 4·56 | 3–4 | 4 | 4 | 3–4 | 4 | 3–4 | 5 | 4 | 4 | 4 | 2 | 3 | 2 | 1–2 |
| 9h | 314 | 453 | 4·36 | 3 | 4 | 3 | 4 | 3 | 4 | 3–4 | 4 | 3–4 | 4 | 3 | 3 | 2 | 1–2 |
| 9i | 320 | 449 | 4·39 | 3 | 4 | 3 | 4 | 3 | 3–4 | 4 | 3–4 | 4 | 3 | 3 | 2 | 2 | 1–2 |
| 9j | 345 | 463 | 4·46 | 3 | 5 | 4 | 4 | 3–4 | 4 | 3–4 | 4 | 3–4 | 3–4 | 3 | 2–3 | 1–2 | 1–2 |

C, Cotton; N, nylon.

30 min, maintained pH 7. The temperature was gradually raised to 45°C in 2 h. The mixture was then poured onto crushed ice, filtered and the product crystallised from absolute alcohol, m.p. 213°C, yield 79%, calc.: C, 43·80; H, 3·65; N, 18·25; S, 8·34; Cl, 9·25. Found: C, 43·79; H, 3·63, N, 18·21; S, 8·36; Cl, 9·27%. IR (KBr), 765 (C–Cl), 1010 ($-CH{=}CH-$), 1200 (sulphonic SO), 1290 (morpholine $C-O-C$) and 1590 ($-NH-$). $^1H$ NMR ($CDCl_3 + DMSO\text{-}d_6$), 2·15 (8H, S, $-O-C\underline{H}_2-CH_2-N$ ), 2·25 (8H, S, $-O-CH_2-C\underline{H}_2-N<$), 6·84 (1H, S, $-C\underline{H}{=}CH-$), 7·15 (1H, S, $-CH{=}C\underline{H}-$), 7·3 (2H, bs, $-NH-$) and 6·96–7·16 (6H, m, Ar$\underline{H}$).

### 3.4 4,4′-Bis[(4-morpholino-6-arylureido-s-triazin-2-yl)amino)] stilbene-2,2′-disulphonic acid (7a–j) and 4,4′-Bis[(4-morpholino-6-aryl thioureido-s-triazin-2-yl)amino] stilbene-2,2′-disulphonic acid (9a–j)

#### *3.4.1 General procedure*

A mixture of (5) (3·84 g, 0·005 mol) and (6a–j) (0·01 mol) in dioxan (70 ml) was refluxed for 3 h at 90–95°C maintaining pH 7. The mixture was poured onto crushed ice, filtered and the product recrystallised from ethanol to give (7a–j). IR (KBr), 805 ($C_3N_3$), 1015 ($-CH{=}CH-$), 1205 (Sulphonic SO), 1290 (morpholine ($C-O-C$), 1550–1560 ($-NH-$) and 3315–3345 ($-NH.CO.NH-$). $^1H$ NMR ($CDCl_3 + DMSO\text{-}d_6$): compound (7a) showed signals at 2·07 (8H, S, $-O-C\underline{H}_2-CH_2-N<$), 2·25 (8H, S, $-O-CH_2-C\underline{H}_2-N<$), 6·56 (1H, S, $-C\underline{H}{=}CH-$), 7·0 (1H, S, $-CH{=}C\underline{H}-$), 6·96–7·20 (16H, m, Ar$\underline{H}$), 7·31 (2H, bS, $-N\underline{H}-$) and 8·4 (4H, S, $-N\underline{H}-CO$).

Following the same procedure, (5) (3·84 g, 0·005 mol) was condensed with (8a–j) (0·01 mol) to give (9a–j). IR (KBr), 790 ($C_3N_3$), 1025 ($-CH{=}CH-$), 1165–1170 (thioureido CS), 1200 (sulphonic SO), 1275 (morpholine $C-O-C$) and 1595–1600 ($-NH-$). $^1H$ NMR ($CDCl_3 + DMSO\text{-}d_6$) of a typical compound (9d) showed signals at 1·45 (6H, S, $CH_3$), 2·12 (8H, S, $-O-C\underline{H}_2-CH_2-N<$), 2·34 (8H, S, $-O-CH_2-C\underline{H}_2-N<$), 4·09 (4H, S, N$\underline{H}$CS), 6·84 (1H, S, $-C\underline{H}{=}CH-$), 6·96 (1H, S, $-CH{=}C\underline{H}-$), 7·15–7·96 (14H, m, Ar$\underline{H}$) and 7·49 (2H, bs, $-N\underline{H}-$).

The characterisation data of compounds (7a–j) and (9a–j) are given in Table 1, and UV absorption–emission and fastness properties in Table 2.

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