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The Synthesis and Properties of Asymmetrically Substituted 4,4'-Bis(1,3,5-triazine-6-yl)diaminostilbene-2,2'-disulfonic Acid Derivatives as Fluorescent Brighteners [II]

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In this work, the key intermediate, 4-amino-4'-(2-amino-4-anilino-1,3,5-triazine-6-yl)-aminostilbene-2,2'-disulfonic acid, was prepared from 4-(2-amino-4-anilino-1,3,5-triazine-6-yl)amino-4'-nitrostilbene-2,2'-disulfonate by using Tin(II) chloride as the reducing agent. Using this intermediate, nineteen new asymmetrically substituted bistriazinylstilbene fluorescent brightening agents were synthesized. Chemical structures of the obtained compounds **5a-s** were analyzed by proton NMR spectrum. The physical properties of the new compounds **5a-s** were characterized by fastness test and whiteness measurement test and the obtained data were compared to measurements obtained from **CI 86**.

Key Words : Bistriazinylstilbene fluorescent brightening agents, 2,4,6-trichloro-1,3,5-triazine, Asymmetrical, Whiteness, Fastness

Introduction

Fluorescent brightening agents (FBAs) are fluorescent organic compounds with affinity for various organic materials such as fiber, paper, and plastic. Typical FBAs are direct dyes which can absorb ultraviolet ray (330-380 nm) and emit visible blue lights (400-450 nm).[1] FBAs are substances which normally have a planar molecular structure with conjugated double bonds and electron-donating groups to show the high fluorescent activity.[2] Various bistriazinylstilbene derivatives are widely used as commercial FBAs for cotton and wool.[3-6] Their chemical structures, however, are symmetrically substituted bistriazinylstilbenes.

In the past, we have reported on the synthesis of some asymmetrically substituted triazinylstilbene FBAs.[7] In the previous report, the key intermediate, 4-amino-4'-(2-amino-4-anilino-1,3,5-triazine-6-yl)aminostilbene-2,2'-disulfonic acid (**2**), was prepared from disodium 4-(2-amino-4-anilino-1,3,5-triazine-6-yl)amino-4'-nitrostilbene-2,2'-disulfonate (**1**) by using Fe powder as the reducing agent in acidic medium. After the reduction, the removal of unreacted metal powder from the product caused isolated yield to be low.

Recently, our research group became interested in asymmetrically substituted bistriazinyl-stilbene FBAs again because we were expecting high fluorescent activities from asymmetrically substituted substituents on bistriazinylstilbenes.

In this study, the reduction method for 4-nitro group of 4-(2-amino-4-anilino-1,3,5-triazine-6-yl)amino-4'-nitrostilbene-2,2'-disulfonate (**1**) was developed by carrying out reduction reactions with various reducing agents. When metals, such as zinc, tin, or Fe, were used, reducing compound **1** to **2** showed high yield with 80-85%. But an excess amount of metals had to be used in the process, requiring an additional purification step to remove the unreacted metals. $SnCl_2$ was the more convenient reducing agent compared to the metals. When $SnCl_2$ was used in acidic medium, the compound **1** was reduced to **2** with excellent yield. Also, because only compound **2** precipitated in acid form as bright, yellow power, the workup process was very simple.

Nineteen bistriazinylstilbene FBAs **5a-s** were synthesized from 4-amino-4'-(2-amino-4-anilino-1,3,5-triazine-6-yl)amino-stilbene-2,2'-disulfonic acid (**2**). All of the compounds **5a-s** have four different amino groups on bistriazine moiety. Of the four amino groups, one group contains a *tert*-aminoalkyl group, which can be used as cationic FBAs. Chemical structures of the compounds **5a-s** were analyzed by proton NMR spectrum. The physical properties of the new compounds were characterized by various fastness test and whiteness measurement test then compared to **CI 86**, a symmetrically substituted bistriazinylstilbene FBA.

Experimental

All chemicals, purchased from commercial sources (Aldrich, Merck, Duksan, Yakuri, Junsei, *etc*.), were analytical grade. The solvents were purified by distillation and other reagents were used without further purification. ^{1}H NMR spectrum was measured at 300 MHz using Varian Mercury 300. The UV spectrum was obtained from Shimadzu UV-2401PC. TLC was carried out using Merck silica gel plates (F254) with distilled solvents. Elemental analyses were performed by Fisons EA 1108. The dyeing process was carried out using a High Temperature-Atmospheric Dyeing machine in basic condition because the synthesized compounds **5a-s** have very low water solubility, which can cause spots to form on dyed materials. Dyeing solution was prepared by adding compounds **5a-s** to NaOH solution (1 g NaOH/1 L water) at 0.05, 0.1, 0.3, 0.5, and 1% o.w.f. concentration. The cotton was first soaked in the solution at 40 °C then the temperature was raised to 80 °C at the rate of 1 °C/min. The

dyeing process continued for 1 h at 80 °C then cooled to room temperature. Light fastness results were obtained from Xenotest 150S by using Xenon arc lamp method in accordance with ISO 105-B02. Rubbing fastness results were obtained from Atras CM-5 by using crock meter method following ISO 105-X12 and washing fastness and chlorinated water fastness were tested with Atras LP2 in accordance with ISO 105-C01. The chlorinated water fastness tested in accordance with KS K 0725. The results are given in Tables 3 and 4. The computer color matching (CCM) data were obtained from SF600 Data color.

4'-Amino-4-(2-amino-4-anilino-1,3,5-triazine-6-yl)aminostilbene-2,2'-disulfonic acid (1). To a stirred suspension of cyanuric chloride (7.6 g, 40 mmol), $CaCO_3$ (2 g, 20 mmol), and a small amount of dispersant agent in water (40 mL), a solution of 4-amino-4'-nitrostilbene-2,2'-disulfonic acid (18.6 g, 40 mmol, 86% purity) and Na_2CO_3 (4.24 g, 40 mmol) in water (400 mL) was added at 0 °C. After completing the addition, the reaction mixture was stirred for 2 h below 5 °C. $CaCO_3$ (2 g, 20 mmol), antifoaming agent, and anilin (3.7 mmol, 40 mmol) were added to the mixture and then warmed to 30 °C. After being stirred at 30 °C for 6 h, ammonia water (30 mL, 25%) was added to the resulting reaction mixture and then heated under reflux for 7 h. After cooling to room temperature, 10% hydrochloric acid solution (200 mL) was added. The resulting precipitate was filtered then washed with 10% NaCl solution. The wet cake was suspended in 400 mL ethanol and then acidic $SnCl_2$ solution, which $SnCl_2$ dihydrate was dissolved in 200 mL *conc.* hydrochloric acid, was added. The reaction mixture was heated at 70-80 °C for 2 h. After completing the reduction, the precipitate was filtered, washed with water, and then dried to provide 4'-amino-4-(2-amino-4-anilino-1,3,5-triazine-6-yl)aminostilbene-2,2'-disulfonic acid (**1**, 19.8 g, 89%) as yellow powder.

General Method for the Synthesis of the Asymmetrically Substituted Bistriazinylstilbene FBAs 5a-s: To a stirred suspension of cyanuric chloride (4.43 g, 24 mmol), $CaCO_3$ (1.20 g, 12 mmol), and a small amount of dispersant agent in water (40 mL), a solution of 4'-amino-4-(2-amino-4-anilino-1,3,5-triazine-6-yl)aminostilbene-2,2'-disulfonic acid (**2**, 13.35 g, 24 mmol) and Na_2CO_3 (2.55 g, 24 mmol) in water (400 mL) was added at 0 °C. After completing the addition, the reaction mixture was stirred for 2 h below 5 °C. $CaCO_3$ (1.20 g, 20 mmol), antifoaming agent, and amine derivative (24 mmol) were added to the mixture then warmed to 30 °C. After being stirred at 30 °C for 3-12 h, $CaCO_3$ (1.20 g, 20 mmol) was added and *N*,*N*-diethylethylenediamine or 3-(diethylamino)propylamine (24 mmol) was added portionwise to the resulting reaction mixture and then heated at 90-95 °C for 7 h. After adding sodium chloride (45 g), the mixture was allowed to cool to room temperature. The precipitate was filtered then dried to provide the compounds **5a~s** as sodium salts.

Synthesis of the Compound 5a: Yields 80%; ^{1}H NMR (DMSO-d_6) δ 1.14 (s, 6H, -CH_3), 1.83 (s, 1H, -CH), 2.21 (s, 3H, -CH_3), 3.13 (s, 4H, -CH_2), 3.62 (s, 4H, -CH_2), 6.62 (s, 1H, -NH), 6.84 (d, 1H, -CH=CH-), 6.96 (d, 1H, -CH=CH-), 7.31 (m, 5H, ArH), 7.49 (s, 2H, -NH), 7.61 (d, 2H, ArH), 7.84 (t, 1H, ArH), 8.00 (s, 2H, ArH), 8.02 (d, 4H, ArH), 8.18 (s, 2H, -NH_2), 8.92 (s, 1H, -NH), 9.01 (s, 1H, -NH), 9.22 (s, 1H, -NH); Anal. Calcd for $C_{40}H_{43}N_{13}Na_2O_6S_2$: C, 52.68; H, 4.75; N, 19.97. Found C, 52.39; H. 4.99; N, 20.18.

Synthesis of the Compound 5b: Yields 88%; ^{1}H NMR (DMSO-d_6) δ 1.13 (s, 6H, -CH_3), 1.82 (s, 1H, -CH), 2.20 (s, 3H, -CH_3), 3.01 (s, 6H, -CH_2), 3.62 (s, 4H, -CH_2), 6.61 (s, 1H, -NH), 6.84 (d, 1H, -CH=CH-), 6.96 (d, 1H, -CH=CH-), 7.31 (m, 5H, ArH), 7.49 (s, 2H, -NH), 7.62 (d, 2H, ArH), 7.81 (t, 1H, ArH), 8.00 (s, 2H, ArH), 8.02 (d, 4H, ArH), 8.18 (s, 2H, -NH_2), 8.92 (s, 1H, -NH), 9.01 (s, 1H, -NH), 9.23 (s, 1H, -NH); Anal. Calcd for $C_{41}H_{45}N_{13}Na_2O_6S_2$: C, 53.18; H, 4.90; N, 19.66. Found C, 52.87; H. 5.20; N, 19.98.

Synthesis of the Compound 5c: Yields 80%; ^{1}H NMR (DMSO-d_6) δ 1.13 (s, 6H, -CH_3), 1.82 (s, 1H, -CH), 2.35 (s, 3H, -CH_3), 3.14 (s, 4H, -CH_2), 3.62 (s, 4H, -CH_2), 6.61 (s, 1H, -NH), 6.82 (d, 1H, -CH=CH-), 6.91 (d, 1H, -CH=CH-), 7.01 (d, 2H, ArH), 7.12 (d, 2H, ArH), 7.32 (m, 5H, ArH), 7.51 (s, 2H, -NH), 7.62 (d, 2H, ArH), 8.01 (s, 2H, ArH), 8.14 (d, 2H, ArH), 8.25 (s, 2H, -NH_2), 9.01 (s, 1H, -NH), 9.20 (s, 1H, -NH), 10.25 (s, 1H, -NH); Anal. Calcd for $C_{39}H_{41}N_{13}Na_2O_6S_2$: C, 52.17; H, 4.60; N, 20.28. Found C, 52.48; H. 4.39; N, 19.99.

Synthesis of the Compound 5d: Yields 80%; ^{1}H NMR (DMSO-d_6) δ 1.13 (s, 6H, -CH_3), 1.82 (s, 1H, -CH), 2.35 (s, 3H, -CH_3), 3.13 (s, 6H, -CH_2), 3.32 (s, 4H, -CH_2), 6.61 (s, 1H, -NH), 6.84 (d, 1H, -CH=CH-), 6.96 (d, 1H, -CH=CH-), 7.01 (d, 2H, ArH), 7.21 (d, 2H, ArH), 7.54 (m, 5H, ArH), 7.62 (s, 2H, -NH), 7.81 (d, 2H, ArH), 8.02 (s, 2H, ArH), 8.21 (d, 2H, ArH), 8.25 (s, 2H, -NH_2), 9.04 (s, 1H, -NH), 9.21 (s, 1H, -NH), 10.25 (s, 1H, -NH); Anal. Calcd for $C_{40}H_{43}N_{13}Na_2O_6S_2$: C, 52.68; H, 4.75; N, 19.97. Found C, 52.58; H. 4.99; N, 19.79.

Synthesis of the Compound 5e: Yields 84%; ^{1}H NMR (DMSO-d_6) δ 1.13 (s, 6H, -CH_3), 1.81 (s, 1H, -CH), 2.42 (s, 3H, -CH_3), 3.11 (s, 4H, -CH_2), 3.30 (s, 4H, -CH_2), 5.01 (s, 1H, -NH), 6.84 (d, 1H, -CH=CH-), 6.96 (d, 1H, -CH=CH-), 6.94 (d, 2H, ArH), 7.04 (d, 2H, ArH), 7.11 (t, 1H, ArH), 7.38 (m, 5H, ArH), 7.27 (m, 5H, ArH), 7.59 (d, 2H, ArH), 7.64 (s, 1H, ArH), 7.49 (s, 2H, -NH), 7.60 (d, 2H, ArH), 8.01 (s, 2H, ArH), 8.02 (d, 2H, ArH), 8.25 (s, 2H, -NH_2), 9.03 (s, 1H, -NH), 9.16 (s, 1H, -NH), 9.28 (s, 1H, -NH); Anal. Calcd for $C_{39}H_{41}N_{13}Na_2O_6S_2$: C, 52.17; H, 4.60; N, 20.28. Found C, 52.48; H. 4.39; N, 19.99.

Synthesis of the Compound 5f: Yields 84%; ^{1}H NMR (DMSO-d_6) δ 1.14 (s, 6H, -CH_3), 1.82 (s, 1H, -CH), 3.12 (s, 6H, -CH_2), 2.25 (s, 3H, -CH_3), 3.30 (s, 4H, -CH_2), 5.03 (s, 1H, -NH), 6.84 (d, 1H, -CH=CH-), 6.96 (d, 1H, -CH=CH-), 6.91 (d, 2H, ArH), 7.04 (d, 2H, ArH), 7.11 (t, 1H, ArH), 7.27 (m, 5H, ArH), 7.33 (m, 5H, ArH), 7.59 (d, 2H, ArH), 7.64 (s, 1H, ArH), 7.49 (s, 2H, -NH), 7.63 (d, 2H, ArH), 8.01 (s, 2H, ArH), 8.03 (d, 2H, ArH), 8.25 (s, 2H, -NH_2), 9.04 (s, 1H, -NH), 9.12 (s, 1H, -NH), 9.28 (s, 1H, -NH); Anal. Calcd for $C_{40}H_{43}N_{13}Na_2O_6S_2$: C, 52.68; H, 4.75; N, 19.97. Found C, 52.49; H. 4.49; N, 19.89.

Synthesis of the Compound 5g: Yields 85%; ^{1}H NMR

(DMSO-d_6) δ 1.13 (s, 6H, -CH_3), 1.82 (s, 1H, -CH), 3.13 (s, 4H, -CH_2), 3.61 (s, 4H, -CH_2), 5.02 (s, 1H, -NH), 6.75 (d, 1H, -CH=CH-), 6.88 (d, 1H, -CH=CH-), 6.90 (d, 2H, ArH), 6.98 (d, 2H, ArH), 6.99 (t, 1H, ArH), 7.21 (m, 5H, ArH), 7.58 (d, 2H, ArH), 7.68 (s, 1H, ArH), 7.77 (s, 2H, -NH), 7.82 (d, 2H, ArH), 7.93 (s, 2H, ArH), 8.11 (d, 2H, ArH), 8.25 (s, 2H, -NH_2), 9.04 (s, 1H, -NH), 9.13 (s, 1H, -NH), 9.72 (s, 1H, -NH-); Anal. Calcd for $C_{38}H_{38}N_{13}Na_3O_9S_3$: C, 46.29; H, 3.88; N, 18.47. Found C, 46.01; H. 3.98; N, 18.19.

Synthesis of the Compound 5h: Yields 85%; ^{1}H NMR (DMSO-d_6) δ 1.14 (s, 6H, -CH_3), 1.81 (s, 1H, -CH), 3.10 (s, 6H, -CH_2), 3.32 (s, 4H, -CH_2), 5.02 (s, 1H, -NH), 6.84 (d, 1H, -CH=CH-), 6.96 (d, 1H, -CH=CH-), 6.98 (d, 2H, ArH), 7.04 (d, 2H, ArH), 7.14 (t, 1H, ArH), 7.32 (m, 5H, ArH), 7.27 (m, 5H, ArH), 7.49 (s, 2H, -NH), 7.59 (d, 2H, ArH), 7.64 (s, 1H, ArH), 7.69 (d, 2H, ArH), 8.01 (s, 2H, ArH), 8.03 (d, 2H, ArH), 8.25 (s, 2H, -NH_2), 9.01 (s, 1H, -NH), 9.14 (s, 1H, -NH), 9.28 (s, 1H, -NH); Anal. Calcd for $C_{39}H_{40}N_{13}Na_3O_9S_3$: C, 46.84; H, 4.03; N, 18.21. Found C, 47.11; H. 3.98; N, 18.09.

Synthesis of the Compound 5i: Yields 85%; ^{1}H NMR (DMSO-d_6) δ 1.13 (s, 6H, -CH_3), 1.83 (s, 1H, -CH), 3.12 (s, 4H, -CH_2), 3.32 (s, 4H, -CH_2), 5.04 (s, 1H, -NH), 6.84 (d, 1H, -CH=CH-), 6.93 (d, 1H, -CH=CH-), 6.98 (d, 2H, ArH), 7.04 (d, 2H, ArH), 7.26 (m, 5H, ArH), 7.38 (d, 2H, ArH), 7.48 (d, 2H, ArH), 7.59 (s, 2H, -NH), 7.77 (d, 2H, ArH), 7.83 (s, 2H, ArH), 7.98 (d, 2H, ArH), 8.24 (s, 2H, -NH_2), 9.16 (s, 1H, -NH), 9.21 (s, 1H, -NH), 9.38 (s, 1H, -NH); Anal. Calcd for $C_{38}H_{38}N_{13}Na_3O_9S_3$: C, 46.29; H, 3.88; N, 18.47. Found C, 46.09; H. 4.09; N, 18.72.

Synthesis of the Compound 5j: Yields 85%; ^{1}H NMR (DMSO-d_6) δ 1.14 (s, 6H, -CH_3), 1.83 (s, 1H, -CH), 2.35 (s, 3H, -CH_3), 3.14 (s, 4H, -CH_2), 3.34 (s, 4H, -CH_2), 6.62 (s, 1H, -NH), 6.84 (d, 1H, -CH=CH-), 6.96 (d, 1H, -CH=CH-), 7.02 (d, 2H, ArH), 7.18 (d, 1H, ArH), 7.21 (m, 5H, ArH), 7.24 (s, 2H, -NH), 7.47 (d, 2H, ArH), 7.58 (s, 2H, ArH), 7.76 (d, 2H, ArH), 7.99 (s, 2H, -NH_2), 9.02 (s, 1H, -NH), 9.64 (s, 1H, -NH), 10.27 (s, 1H, -NH-); Anal. Calcd for $C_{39}H_{40}N_{13}Na_3O_9S_3$: C, 46.84; H, 4.03; N, 18.21. Found C, 46.99; H. 4.19; N, 18.00.

Synthesis of the Compound 5k: Yields 83%; ^{1}H NMR (DMSO-d_6) δ 1.14 (s, 6H, -$\underline{CH_3}$), 1.82(s, 1H, -CH), 2.35 (s, 3H, -CH_3), 3.14 (s, 6H, -$\underline{CH_2}$), 3.33 (s, 4H, -$\underline{CH_2}$), 6.64 (s, 1H, -NH), 6.84 (d, 1H, -$\underline{CH}$=CH-), 6.96 (d, 1H, -CH=$\underline{CH}$-), 7.04 (d, 2H, ArH), 7.24 (d, 1H, ArH), 7.52 (m, 5H, ArH), 7.74 (s, 2H, -NH), 7.91 (d, 2H, ArH), 8.03 (s, 2H, ArH), 8.24 (d, 2H, ArH), 8.56 (s, 2H, -NH_2), 9.34 (s, 1H, -NH) 9.52 (s, 1H, -NH), 10.25 (s, 1H, -NH); Anal. Calcd for $C_{40}H_{42}N_{13}Na_3O_9S_3$: C, 47.38; H, 4.17; N, 17.96. Found C, 47.12; H. 4.29; N, 18.11.

Synthesis of the Compound 5l: Yields 86; ^{1}H NMR (DMSO-d_6) δ 1.14 (s, 6H, -CH_3), 1.83 (s, 1H, -CH), 3.13 (s, 4H, -CH_2), 3.32 (s, 4H, -CH_2), 5.70 (s, 1H, -NH), 6.66 (d, 1H, -CH=CH-), 6.89 (d, 1H, -CH=CH-), 6.91 (d, 2H, ArH), 7.00 (d, 2H, ArH), 7.08 (d, 1H, ArH), 7.12 (d, 1H, ArH), δ 7.20 (d, 1H, ArH), 7.26 (m, 5H, ArH), 7.32 (d, 1H, ArH), 7.41 (d, 1H, ArH), 7.54 (d, 1H, ArH), 7.63 (d, 1H, ArH), 7.72 (s, 2H, -NH), 7.84 (d, 2H, ArH), 7.91 (s, 2H, ArH), 8.01 (d, 2H, ArH), 8.26 (s, 2H, -NH_2), 9.02 (s, 1H, -NH), 9.24 (s, 1H, -NH), 9.32 (s, 1H, -NH-); Anal. Calcd for $C_{42}H_{41}N_{13}Na_2O_6S_2$: C, 54.01; H, 4.42; N, 19.50. Found C, 54.29; H. 4.17; N, 19.23.

Synthesis of the Compound 5m: Yields 85%; ^{1}H NMR (DMSO-d_6) δ 1.13 (s, 6H, -CH_3), δ 1.83 (s, 1H, -CH), δ 3.13 (s, 4H, -CH_2), 3.32 (s, 4H, -CH_2), 5.71 (s, 1H, -NH), 6.66 (d, 1H, -CH=CH-), 6.91 (d, 1H, -CH=CH-), 7.14 (d, 2H, ArH), 7.21 (d, 2H, ArH), 7.32 (m, 5H, ArH), 7.38 (d, 1H, ArH), 7.44 (d, 1H, ArH), 7.54 (d, 1H, ArH), 7.62 (d, 1H, ArH), 7.71 (d, 1H, ArH), 7.80 (d, 1H, ArH), 7.81 (d, 1H, ArH), 7.85 (s, 2H, -NH), 7.92 (d, 2H, ArH), 7.98 (s, 2H, ArH), 8.06 (d, 2H, ArH), 8.27 (s, 2H, -NH_2), 8.93 (s, 1H, -NH-), 9.04 (s, 1H, -NH), 9.24 (s, 1H, -NH); Anal. Calcd for $C_{43}H_{43}N_{13}Na_2O_6S_2$: C, 54.48; H, 4.57; N, 19.21. Found C, 54.40; H. 4.39; N, 19.44.

Synthesis of the Compound 5n: Yields 86%; ^{1}H NMR (DMSO-d_6) δ 1.05 (s, 6H, -CH_3), 1.82 (s, 1H, -CH), 2.54 (s, 2H, -CH_2), 3.42 (s, 4H, -CH_2), 3.52 (s, 4H, -CH_2), 6.62 (s, 1H, -NH), 6.84 (d, 1H, -CH=CH-), 6.96 (d, 1H, -CH=CH-), 7.22 (m, 5H, ArH), 7.51 (s, 2H, 2(-NH-)), 7.72 (d, 2H, ArH), 7.91 (s, 2H, ArH), 8.12 (s, 2H, -NH_2), 9.04 (s, 1H, -NH-) 9.16 (s, 1H, -NH-), 10.14 (s, 1H, -NH); Anal. Calcd for $C_{34}H_{36}N_{13}Na_3O_8S_2$: C, 46.00; H, 4.09; N, 20.51. Found C, 46.22; H. 4.19; N, 20.27.

Synthesis of the Compound 5o: Yields 80%; ^{1}H NMR (DMSO-d_6) δ 1.14 (s, 6H, -CH_3), 1.84 (s, 1H, -CH), 2.72 (s, 2H, -CH_2), 3.12 (s, 6H, -CH_2), 3.52 (s, 4H, -CH_2), 6.64 (s, 1H, -NH), 6.84 (d, 1H, -CH=CH-), 6.96 (d, 1H, -CH=CH-), 7.25 (m, 5H, ArH), 7.50 (s, 2H, -NH), 7.82 (d, 2H, ArH), 8.02 (s, 2H, ArH), 8.25 (s, 2H, -NH_2), 8.83 (s, 1H, -NH), 9.05 (s, 1H, -NH), 9.16 (s, 1H, -NH); Anal. Calcd for $C_{35}H_{38}N_{13}Na_3O_8S_2$: C, 46.61; H, 4.25; N, 20.19. Found C, 46.90; H. 4.29; N, 19.93.

Synthesis of the Compound 5p: Yields 85%; ^{1}H NMR (DMSO-d_6) δ 1.13 (s, 6H, -CH_3), 1.82 (s, 1H, -CH), 2.72 (s, 2H, -CH_2), 3.04 (s, 1H, -CH_2), 3.15 (s, 6H, -CH_2), 3.24 (s, 6H, -CH_3), 3.50 (s, 4H, -CH_2), 4.51 (s, 1H, -CH), 6.62 (s, 1H, -NH), 6.84 (d, 1H, -CH=CH-), 6.96 (d, 1H, -CH=CH-), 7.21 (m, 5H, ArH), 7.52 (s, 2H, -NH), 7.81 (d, 2H, ArH), 8.02 (s, 2H, ArH), 8.25 (s, 2H, -NH_2), 8.81 (s, 1H, -NH), 9.02 (s, 1H, -NH), 9.14 (s, 1H, -NH); Anal. Calcd for $C_{36}H_{43}N_{13}Na_2O_8S_2$: C, 48.26; H, 4.84; N, 20.32. Found C, 48.46; H. 4.69; N, 20.07.

Synthesis of the Compound 5q: Yields 82%; ^{1}H NMR (DMSO-d_6) δ 1.14 (s, 6H, -CH_3), 1.82 (s, 1H, -CH), 2.74 (s, 2H, -CH_2), 3.02 (s, 1H, -CH_2), 3.12 (s, 6H, -CH_2), 3.24 (s, 6H, -CH_3), 3.54 (s, 4H, -CH_2), 4.52 (s, 1H, -CH), 6.62 (s, 1H, -NH), 6.84 (d, 1H, -CH=CH-), 6.96 (d, 1H, -CH=CH-), 7.23 (m, 5H, ArH), 7.51 (s, 2H, -NH), 7.81 (d, 2H, ArH), 8.00 (s, 2H, ArH), 8.25 (s, 2H, -NH_2), 8.82 (s, 1H, -NH), 9.02 (s, 1H, -NH), 9.14 (s, 1H, -NH-) Anal. Calcd for $C_{37}H_{45}N_{13}Na_2O_8S_2$: C, 48.84; H, 4.98; N, 20.01. Found C, 48.79; H. 5.19; N, 20.28.

Synthesis of the Compound 5r: Yields 80%; ^{1}H NMR (DMSO-d_6) δ 1.14 (s, 6H, -CH_3), 1.23 (s, 2H, -CH_2), 1.45 (s,

2H, -CH_2), 1.74 (s, 2H, -CH_2), 2.01 (s, 2H, -CH_2), 2.52 (s, 2H, -CH_2), 2.77 (s, 2H, -CH_2), 3.22 (s, 4H, -CH_2), 3.52 (s, 4H, -CH_2), 6.62 (s, 1H, -NH), 6.84 (d, 1H, -CH=CH-), 6.96 (d, 1H, -CH=CH-), 7.24 (m, 5H, ArH), 7.52 (s, 2H, -NH), 7.82 (d, 2H, ArH), 8.02 (s, 2H, ArH), 8.25 (s, 2H, -NH_2), 8.82 (s, 1H, -NH), 9.02 (s, 1H, -NH), 9.14 (s, 1H, NH); Anal. Calcd for $C_{39}H_{46}N_{13}Na_3O_8S_2$: C, 48.90; H, 4.84; N, 19.01. Found C, 48.67; H. 4.70; N, 18.90.

Synthesis of the Compound 5s: Yields 85%; ^{1}H NMR (DMSO-d_6) δ 0.96 (s, 6H, -CH_3), 1.18 (s, 1H, -CH), δ 1.25 (s, 2H, -CH_2), 1.43 (s, 2H, -CH_2), 1.75 (s, 2H, -CH_2), 2.08 (s, 2H, -CH_2), 2.53 (s, 2H, -CH_2), 3.13 (s, 6H, -CH_2), 3.52 (s, 4H, -CH_2), 6.61 (s, 1H, -NH), 6.84 (d, 1H, -CH=CH-), 6.96 (d, 1H, -CH=CH-), 7.20 (m, 5H, ArH), 7.51 (s, 2H, -NH), 7.82 (d, 2H, ArH), 8.01 (s, 2H, ArH), 8.27 (s, 2H, -NH_2), 8.83 (s, 1H, -NH), 9.03 (s, 1H, -NH-), 9.15 (s, 1H, -NH-); Anal. Calcd for $C_{40}H_{48}N_{13}Na_3O_8S_2$: C, 49.43; H, 4.98; N, 18.73. Found C, 49.63; H. 4.86; N, 18.88.

Result and Discussion

Using the same procedure from the previous report,[7] the starting material, disodium 4-(2-amino-4-anilino-1,3,5-triazine-6-yl)amino-4'-nitrostilbene-2,2'-disulfonate (**1**) was prepared by reacting 4-amino-4'-nitrostilbene-2,2'-disulfonic acid with 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride, CNC), followed by adding aniline at 40 °C then ammonia water at 80 °C.

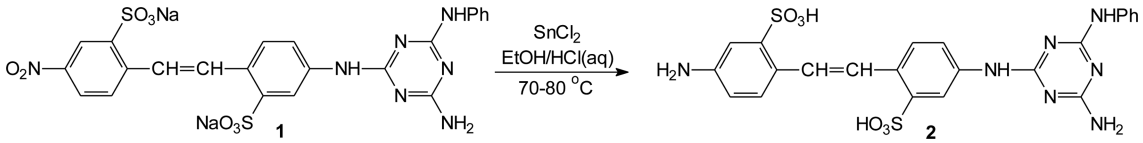
Treating the nitro group of compound **1** with $SnCl_2$ in ethanol/hydrochloric acid solution at 70-80 °C produced 4-amino-4'-(2-amino-4-anilino-1,3,5-triazine-6-yl)aminostilbene-2,2'-disulfonic acid (**2**) with 89% yield (Scheme 1).

The synthesis of asymmetrically substituted bistriazinylstilbene fluorescent brighteners **5a-s** started with 4-amino-4'-(2-amino-4-anilino-1,3,5-triazine-6-yl)amino-stilbene-2,2'-disulfonic acid (**2**). After stirring the disodium salt of 4-amino-4'-(2-amino-4-anilino-1,3,5-triazine-6-yl)aminostilbene-2,2'-disulfonic acid (**1**) with equivalent amount of CNC at 0-5 °C, disodium 4-(2,4-dichloro-1,3,5-triazine-6-yl)-amino-4'-(2-amino-4-anilino-1,3,5-triazine-6-yl)amino-stilbene-2,2'-disulfonate (**3**) was obtained. Then without separation, compound **3** was treated with aliphatic or aromatic amine derivative at 30-40 °C. Finally, *N*,*N*-diethylethylenediamine or 3-(diethylamino)propylamine was added to the reaction mixture. The third substitution reaction occurred when the temperature reached over 80 °C. The general synthetic route of asymmetrical substituted bistriazinylstilbene derivatives **5a-s** is presented in Scheme 2 and relevant data are given in Table 1.

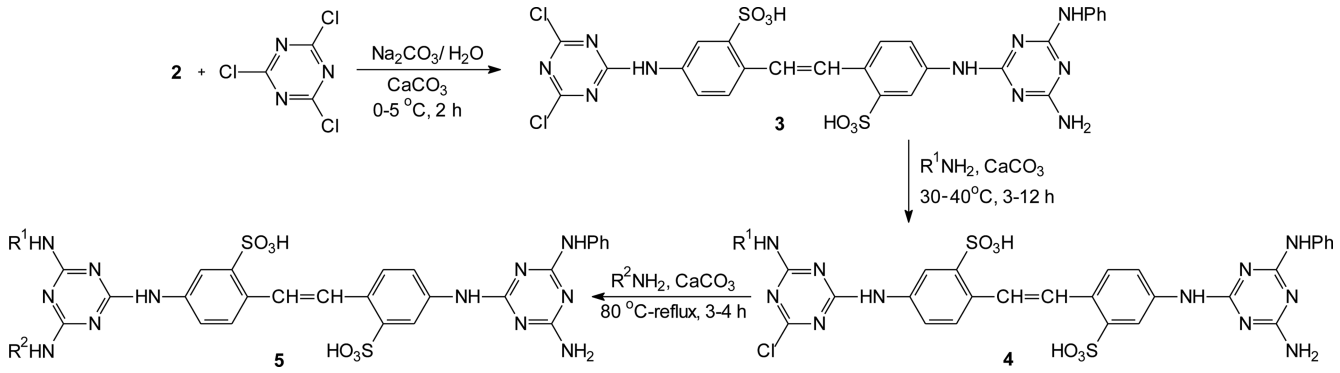
Characteristics of the compounds **5a-s** are compared with those of **CI 86**, which is used for commercial purpose. The chemical structure of **CI 86** is shown in Figure 1.

The newly synthesized compounds **5a-s** were applied at concentrations of 0.05%, 0.1%, 0.3%, 0.5%, and 1%, relative to the weight of cotton fiber. The degrees of whiteness and CIE *L*a*b** coordinates were determined. The data obtained are presented and compared in Table 2. Whiteness increased in the concentration range of 0.1-0.5% and decreased after 0.5%. The whiteness of synthesized compounds is in the range of 52-129, while the whiteness of **CI 86** is in the range of 123-142. In particular, compounds **5g**, **5h**, **5n** and **5o** showed the same value of whiteness as **CI 86**. These four compounds have either *m*-(sodium sulfo)aniline group (**5g** and **5h**) or *N*-(sodium carboxymethyl)amino group (**5n** and **5o**), which are capable of hydrogen bonding to the hydroxyl group of cotton fiber. However, **5i** and **5j** that have *para*- or *ortho*-(sodium sulfo)aniline groups showed low measurement of whiteness compared to **CI 86**.

The data for chlorinated water fastness, light fastness, and rubbing fastness are shown in Table 3. The results show that the value of chlorinated water fastness of compounds **5e**, **5f**, **5k**, and **5s** are higher than the value of **CI 86**. On the other hand, rest of the compounds showed the same or lower value than **CI 86**. Light fastness of the compound **5n** was higher

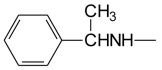
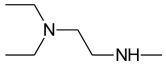
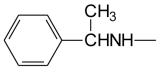
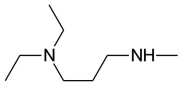
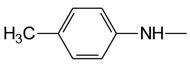
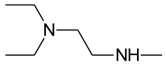
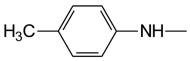
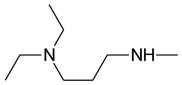
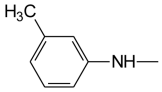
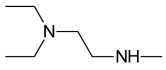
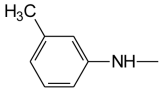
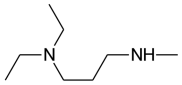
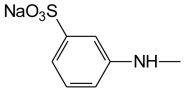
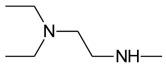
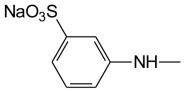
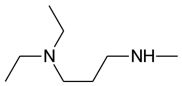
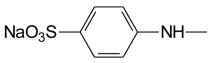
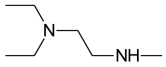
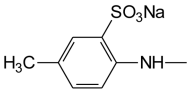
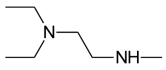
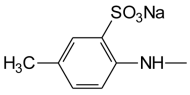
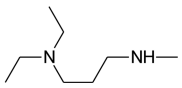
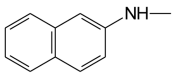
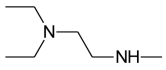
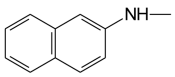
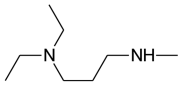
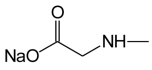
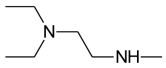
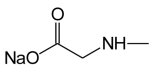
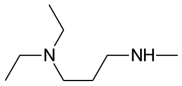
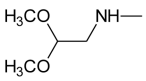
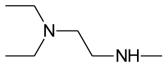
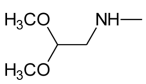
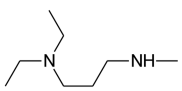
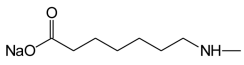
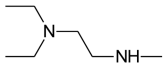
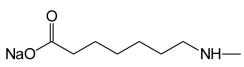
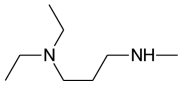


Scheme 1



Scheme 2

Table 1. Characterization data of the asymmetrically substituted bistriazinylstilbene fluorescent brighteners **5a-s**

Entry	R_1-NH-	R_2-NH-	Yield (%)	UV/λ_{max} nm (logε)
5a			80	282(4.44), 353(4.67)
5b			78	282(4.16), 352(4.51)
5c			80	282(4.44), 352(4.54)
5d			80	272(4.33), 351(4.72)
5e			84	278(4.22), 352(3.99)
5f			84	276(4.42), 349(4.03)
5g			85	289(4.99), 350(4.22)
5h			85	274(4.39), 352(4.34)
5i			85	280(4.51), 353(4.49)
5j			85	273(3.85), 352(3.72)
5k			83	283(3.85), 352(3.72)
5l			86	282(4.23), 353(4.44)
5m			85	282(4.73), 352(3.94)
5n			86	274(4.73), 353(4.45)
5o			80	277(4.09), 353(4.35)
5p			85	273(4.70), 352(4.03)
5q			82	283(4.44), 352(3.86)
5r			80	282(5.01), 352(4.29)
5s			85	292(5.02), 347(4.25)

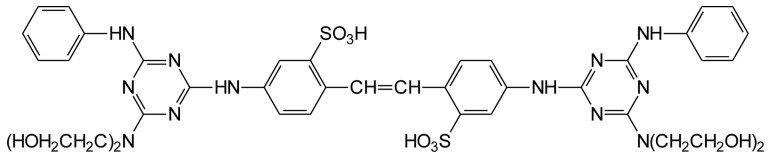


Figure 1. The structure of **CI 86**.

Table 2. Colour fastness of cotton fiber dyed with compounds **5a-s**

Entry	o.w.f (%)	Whiteness	*L**	*a**	*b**	Entry	o.w.f (%)	Whiteness	*L**	*a**	*b**
	0.05	123.69	91.91	2.55	-9.06		0.05	95.07	90.65	1.59	-3.61
	0.1	132.07	91.77	2.78	-10.75		0.1	96.82	90.82	1.92	-3.87
CI 86	0.3	141.05	92.52	2.17	-12.00	**5a**	0.3	87.83	90.08	2.64	-2.29
	0.5	142.28	92.85	1.52	-11.90		0.5	74.99	89.64	3.26	0.17
	1	138.67	93.02	0.22	-10.56		1	52.18	88.41	4.55	4.25
	0.05	97.48	90.91	1.64	-4.01		0.05	103.48	90.82	2.55	1.89
	0.1	97.74	90.83	1.92	-4.06		0.1	111.01	91.19	2.78	2.35
5b	0.3	89.42	90.35	2.60	-2.50	**5c**	0.3	109.33	91.04	2.17	2.87
	0.5	79.53	89.79	3.07	-0.69		0.5	101.99	90.42	1.52	3.07
	1	57.23	88.74	4.27	3.41		1	83.52	89.66	0.22	3.69
	0.05	109.50	91.03	2.18	-6.04		0.05	97.78	91.43	1.38	-3.87
	0.1	113.93	90.88	2.66	-7.31		0.1	108.37	91.88	1.96	-6.15
5d	0.3	105.64	91.05	3.18	-5.38	**5e**	0.3	109.23	91.80	1.98	-5.93
	0.5	92.63	90.04	3.59	-3.05		0.5	103.95	91.55	1.67	-5.11
	1	64.59	88.75	4.66	2.19		1	93.76	91.20	1.30	-3.09
	0.05	96.77	91.47	1.36	-3.64		0.05	108.23	91.91	2.55	-9.06
	0.1	102.35	92.67	1.66	-4.71		0.1	117.34	91.77	2.78	-10.75
5f	0.3	104.30	91.91	1.74	-5.04	**5g**	0.3	124.79	92.52	2.17	-12.00
	0.5	100.05	92.00	1.56	-4.08		0.5	129.43	92.85	1.52	-11.90
	1	88.02	91.37	1.26	-1.78		1	129.73	93.02	0.22	-10.56
	0.05	105.54	91.28	1.80	-5.52		0.05	104.65	91.60	1.80	-5.27
	0.1	113.46	91.59	2.17	-7.22		0.1	108.08	91.38	2.00	-6.04
5h	0.3	123.59	91.76	2.49	-8.90	**5i**	0.3	116.27	91.51	2.34	-7.62
	0.5	124.73	91.72	2.22	-9.02		0.5	118.60	91.47	2.52	-8.04
	1	124.95	92.00	1.87	-8.74		1	118.81	91.70	2.26	-7.87
	0.05	76.96	91.29	0.19	0.46		0.05	97.98	91.54	1.35	-3.86
	0.1	77.67	91.29	0.25	0.31		0.1	102.31	91.98	1.54	-4.59
5j	0.3	79.05	91.27	0.30	0.01	**5k**	0.3	94.53	91.40	1.50	-3.16
	0.5	82.73	91.61	0.47	-0.60		0.5	88.53	91.53	1.44	-1.81
	1	82.47	91.15	0.60	-0.76		1	67.63	90.29	1.27	2.05
	0.05	106.10	91.91	1.80	-5.50		0.05	107.76	91.65	1.58	-4.62
	0.1	108.23	91.77	1.83	-5.93		0.1	108.47	91.98	1.90	-5.91
5l	0.3	97.96	92.52	1.47	-3.89	**5m**	0.3	96.23	91.62	1.55	-3.43
	0.5	86.21	92.85	1.07	-1.38		0.5	93.71	91.30	1.53	-3.03
	1	67.65	90.82	0.87	2.28		1	83.34	90.81	1.78	-1.04
	0.05	100.62	91.23	1.49	-4.52		0.05	97.61	91.06	1.41	-3.97
	0.1	105.55	91.20	1.86	-5.53		0.1	101.72	91.02	1.55	-4.78
5n	0.3	114.51	91.31	2.02	-7.27	**5o**	0.3	114.47	91.21	2.13	-7.32
	0.5	118.25	91.88	1.96	-7.74		0.5	119.88	91.59	2.43	-8.27
	1	121.78	91.95	1.86	-8.32		1	123.73	92.15	2.15	-8.72
	0.05	92.54	91.40	1.19	-2.77		0.05	95.51	91.59	1.35	-3.30
	0.1	91.24	91.28	1.23	-2.53		0.1	92.53	91.53	1.27	-2.68
5p	0.3	78.74	90.84	1.08	-0.06	**5q**	0.3	89.20	91.42	1.03	-2.02
	0.5	69.69	90.86	0.80	1.86		0.5	78.15	91.20	0.86	0.24
	1	47.25	90.41	0.68	6.38		1	72.42	88.87	2.17	14.99
	0.05	90.53	91.23	1.12	-2.42		0.05	90.27	91.39	1.08	-2.39
	0.1	92.77	91.47	1.27	-2.78		0.1	92.77	91.55	1.12	-2.64
5r	0.3	82.45	91.56	0.25	-0.56	**5s**	0.3	94.44	91.67	1.30	-3.04
	0.5	77.66	91.08	1.07	0.29		0.5	88.01	91.66	1.28	-1.65
	1	58.57	90.69	1.11	4.15		1	77.92	91.35	1.17	0.36

Table 3. Various fastness of cotton fiber dyed with compounds **5a-s**

Compound	Chlorinated water fastness	Light fastness	Rubbing fastness	
			Dry	Wet
CI 86	3	2	3-4	2
5a	1-2	2	4-5	3
5b	1-2	2	4-5	3
5c	1-2	2	4	3-4
5d	1-2	2	4-5	3
5e	4	2	4-5	2-3
5f	4	2	4	3
5g	1-2	2	4-5	2-3
5h	1-2	2	4-5	2-3
5i	1-2	2	4	3
5j	1-2	2	4-5	4-5
5k	4	2	4-5	4-5
5l	2	2	4-5	2-3
5m	2	2	4-5	3
5n	1-2	3	4	2-3
5o	1-2	2	4-5	2-3
5p	3	2	4-5	3-4
5q	2-3	2	4-5	3-4
5r	3	2	4-5	3-4
5s	3-4	2	4	3

Table 4. Washing fastness of cotton fiber dyed with compounds **5a-s**

Compound	Acetate	Cotton	Nylon	PET	Acrylic	Wool
CI 86	4-5	1	3	4-5	4-5	4-5
5a	4-5	2	4-5	4-5	4-5	4-5
5b	4-5	2	4-5	4-5	4-5	4-5
5c	4-5	1-2	4-5	4-5	4-5	4-5
5d	4-5	1	4-5	4-5	4-5	4-5
5e	4-5	2	4-5	4-5	4-5	4-5
5f	4-5	2	4-5	4-5	4-5	4-5
5g	4-5	1	4-5	4-5	4-5	4-5
5h	4-5	1	4-5	4-5	4-5	4-5
5i	4-5	1	4-5	4-5	4-5	4-5
5j	4-5	4	4-5	4-5	4-5	4-5
5k	4-5	2-3	4-5	4-5	4-5	4-5
5l	4-5	2	4-5	4-5	4-5	4-5
5m	4-5	3	4-5	4-5	4-5	4-5
5n	4-5	1	4-5	4-5	4-5	4-5
5o	4-5	1	4-5	4-5	4-5	4-5
5p	4-5	2-3	4-5	4-5	4-5	4-5
5q	4-5	2-3	4-5	4-5	4-5	4-5
5r	4-5	2-3	4-5	4-5	4-5	4-5
5s	4-5	2-3	4-5	4-5	4-5	4-5

than **CI 86** and rest of the compounds had the same or lower value than **CI 86**. All of the compounds showed better rubbing fastness than **CI 86**. Washing fastness data are given in Table 4. The results from the washing fastness test showed that all the compounds **5a-s** have better washing fastness compared to **CI 86**.

Conclusion

The treatment of the nitro group of disodium 4-(2-amino-4-anilino-1,3,5-triazine-6-yl)amino-4'-nitrostilbene-2,2'-disulfonate (**1**) with $SnCl_2$ in ethanol-hydrochloric acid solution at 70-80 °C produced 4-amino-4'-(2-amino-4-anilino-1,3,5-triazine-6-yl)amino-stilbene-2,2'-disulfonic acid (**2**) with excellent yield. Asymmetrically substituted bistriazinylstilbene fluorescent brighteners were synthesized in good yield by using 4-amino-4'-nitrostilbene-2,2'-disulfonic acid (**1**) as the staring material.

At the triazine moiety, newly synthesized compounds **5g** and **5h** contain *m*-(sodium sulfo)anilino group and **5n** and **5o** contain *N*-(sodium carboxymethyl)amino group. These compounds showed almost the same value of whiteness as **CI 86**. From this result, it was confirmed that high whiteness can be obtained by using a substituent that can form a hydrogen bond with the OH group of cotton fiber.

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