Synthesis and Fluorescent Brightening Properties of Symmetrically Substituted 4,4′-*Bis*(1,3,5-Triazinyl)-Diaminostilbene-2,2′-Disulfonic Acid Derivatives

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Summary: Disodium-4,4′-*bis*(1,3,5-triazinylamino)stilbene-2,2′-disulfonates **5a-5d** were synthesized by reacting 4,4′-diaminostilbene-2-2′-disulfonic acid **1** with 2,4,6-trichloro-1,3,5-triazine **2** *via* the intermediacies of **3** and **4a-4d**. The intermediate **3** was reacted with different amines at different temperature conditions to afford other intermediates **4a-4d** and finally the desired fluorescent brightener's **5a-5d**. The structures of the products were characterized by UV-visible, IR and H^1-NMR spectroscopy techniques. Elemental analyses were found to be in good agreement with the calculated values. These compounds were applied on cotton fiber as fluorescent brighteners and their physical properties were performed by wash-, chlorine-, and light-fastness. The whiteness of the fiber was measured by spectrophotometer.

Keywords: Fluorescent brightening agents, UV-visible spectra, Fastness properties, Whiteness properties.

Introduction

The whitening effect of fluorescent brightening agents (FBAs) was discovered by Krais in 1929 [1]. Fluorescent brightening agents are used to enhance the whiteness and brightness of the textiles, papers, plastics, and leathers. These are important constituents of house hold detergents [2]. FBAs are also used in lasers, sensors, tracers, protein staining and as UV absorbers [3-8]. FBAs are also known as fluorescent whitening agents which absorb light in the ultra-violet region with the emission in the blue-violet region of the EMR spectrum. A typical FBA absorbs light between 340 and 380 nm and emits light between 425 and 450 nm [9].

The application of FBAs depends on the type of fibers on which it is applied and can be classified as direct or substantive, disperse and cationic. Most of the FBAs are imidazole, triazole, coumarin, naphthalimide, benzoxazol and stilbene derivatives [10]. Different symmetrically substituted 4,4′-*bis*(1,3,5-triazinyl)diaminostilbene-2,2′-disulfonic acid derivatives act as fluorescent brighteners to whiten the cotton, paper, and viscose [11-13].

In this study, we prepared few new FBAs which are substituted with different amines to triazine moieties. These compounds were applied on cotton fiber and their performances were evaluated by various fastness tests and International Commission on Illumination (CIE) whiteness was measured. Attempts were made to correlate these compounds with their performances.

Results and Discussion

Chemistry

2,4,6-Trichloro-1,3,5-triazine is a trifunctional compound in which three reactive chlorine atoms can be replaced by a nucleophile in a stepwise fashion under different temperature conditions as shown in Scheme-1. Different amines (Table-1) were introduced to triazine moiety by nucleophilic aromatic substitution (NAS), replacing the chlorine groups periodically. The three chloro groups of 2,4,6-trichloro-1,3,5-triazine moiety showed different reactivity pattern and hence needed different temperature conditions to be replaced (Fig. 1). After each replacement of chlorine, the electrphilicity of triazine moiety decreased and therefore temperature was raised for the next substitution. The structures and IUPAC names of compounds **5a-5d** are shown in Table-2.

Table-1: Differently substituted amines.

Compounds	R^1-NH_2	R^2-NH_2
5a	2-Methoxyaniline-5-Sulfonic acid	Aniline
5b	2-Methoxyaniline-5-Sulfonic acid	Diethanolamine
5c	2-Methoxyaniline-5-Sulfonic acid	Monoethanolamine
5d	2-Methoxyaniline-5-Sulfonic acid	Dodecylamine

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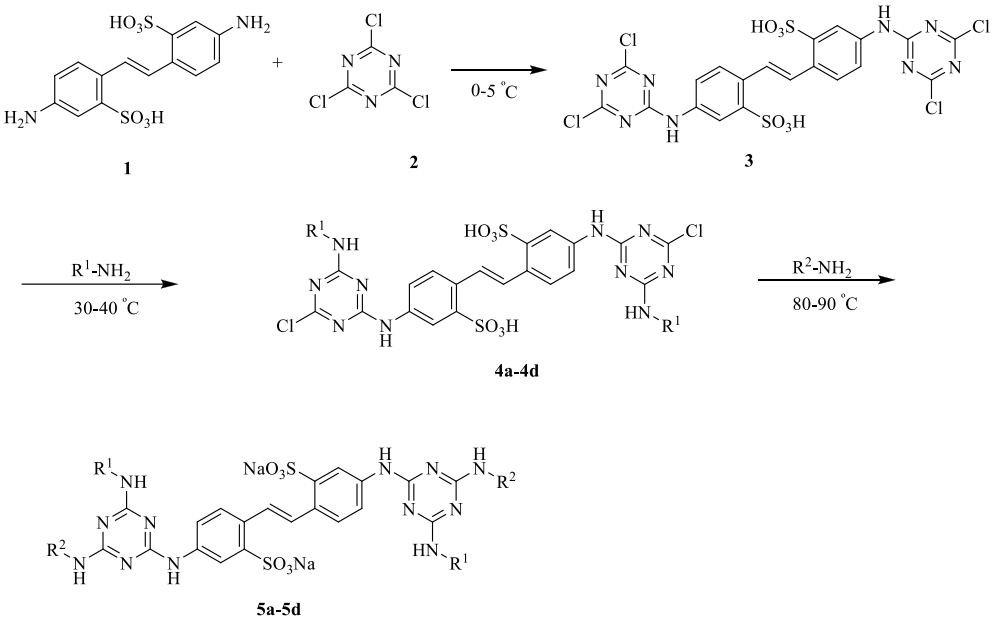
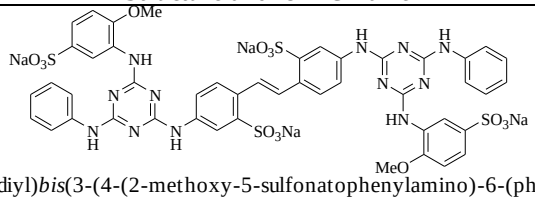
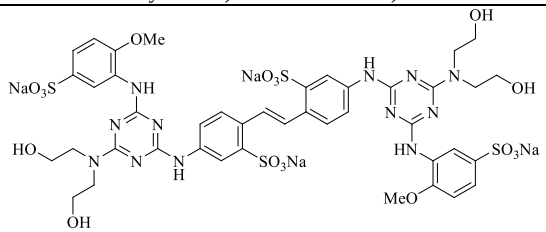
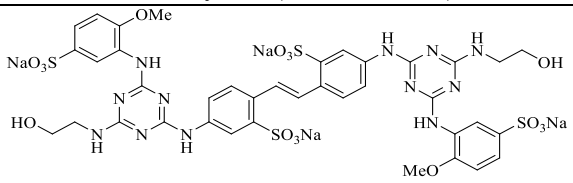
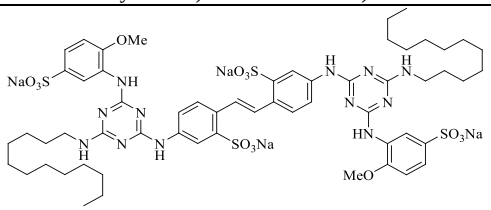


Scheme-1: Synthesis of compounds **5a-5d.**

Table-2: Structure and IUPAC names of compounds **5a-5d.**

Compounds	Structure and IUPAC Name
5a	 Sodium (*E*)-6,6'-(ethene-1,2-diyl)*bis*(3-(4-(2-methoxy-5-sulfonatophenylamino)-6-(phenylamino)-1,3,5-triazin-2-ylamino)benzenesulfonate)
5b	 Sodium (*E*)-6,6'-(ethene-1,2-diyl)*bis*(3-(4-(bis(2-hydroxyethyl)amino)-6-(2-methoxy-5-sulfonatophenylamino)-1,3,5-triazin-2-ylamino)benzenesulfonate)
5c	 Sodium (*E*)-6,6'-(ethene-1,2-diyl)*bis*(3-(4-(2-hydroxyethylamino)-6-(2-methoxy-5-sulfonatophenylamino)-1,3,5-triazin-2-ylamino)benzenesulfonate)
5d	 Sodium (*E*)-6,6'-(ethene-1,2-diyl)*bis*(3-(4-(dodecylamino)-6-(2-methoxy-5-sulfonatophenylamino)-1,3,5-triazin-2-ylamino)benzenesulfonate)

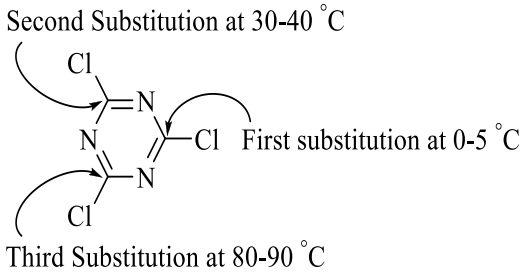


Fig. 1: Differential reactivity of 2,4,6-trichloro-1,3,5-triazine.

Fastness Properties

The color fastness to washing was assessed using multi-fabric specimen (acetate, cotton, nylon, polyesters, acrylic, and wool) according to ISO 105-CO6 [14]. Washing fastness of the compounds **5a-5d** was found to be excellent. Change of shade rating is good. The results are listed in Table-3. Light fastness was measured using Xenon Arc Lamp method according to ISO-105-BO2 [15]. Chlorine fastness test was carried out according to ISO-105-EO3 [16]. The results are depicted in Table-4 and Table-5. Compounds **5a-5d** showed fair to good color fastness to light as shown in Table-4 and color fastness to chlorine are good as shown in Table-5.

Colour Assessment

AATCC Method 110-2000 [17] was used to determine the degree of whiteness and the CIE *L* a* b* c* h* coordinates. Values are measured by using Datacolor SF600 spectrophotometer with illuminant D65, large area view (30mm) and 10° observer. Each sample was measured in triplicate at a different surface of fabric and the average value was taken. Results are presented in Table-6. The value of whiteness increased from 0.05% to 0.1% on the weight of fabric (o.w.f) and decreased after 0.1% o.w.f. It shows that increase in the concentration results in decrease in the whiteness. This is due to increase in the aggregation of the FBAs on the substrate, resulting in a shift in fluorescence hue. The whiteness of synthetic compounds **5a-5d** was in the range of 95.46 - 109.84 with 0.1% o.w.f FBA. Three basic characters of color are measured as lightness (*L**), chroma (*c**) and hue (*h*). The darkness or lightness (*L**) of the dyed samples was measured and the results were found to be almost same for the compounds **5a-5d**. Chroma (c^*) is the brightness or dullness of color. Compound **5a** is brighter than **5c**, **5b** and **5d**, respectively. Hue (*h*) is the basic element of the color. Results showed that compounds **5a-5d** have approximately same hue (*h*).

Experimental

Materials and Analysis

The ultra-violet spectra were run in de-ionized water on a lambda-5UV/Visible Spectrophotometer (Perkin-Elmer). IR spectra (KBr) were recorded on a Bruker FT-IR IFS48 Spectrometer. Elemental analyses were carried out on an elemental analyzer-1106 (Carlo Erba). ^{1}H-NMR Spectra were recorded on Avance Bruker AM 300 MHz equipment. TLC sheets (2.0 × 5.0 cm) were pre-coated with silica gel having fluorescent indicator 254 nm to a thickness of 0.25 mm (Fluka). Preparative TLC analyses were carried out with Silica Gel GF 254 nm plates (Analtech). The chromatograms were visualized under an ultra-violet light of wavelengths of 254 and 365 nm. EUTECH pH meter was used during the process. The starting materials 4,4′-diaminostilbene-2,2′-disulfonic acid and 2,4,6-trichloro-1,3,5-triazine were of commercial grade and acquired from Clariant, Pakistan. Other chemicals were of analytical grade and obtained from Merck and Aldrich. Application of compounds **5a-5d** was carried out on Datacolor Ahiba IR. Chlorinated water fastness and washing fastness were determined on GyroWash2. Results of light fastness were measured on Xenon Test 150S. Degree of whiteness and CIE *L** a* b* c* h coordinates were determined on the Datacolor Spectrophotometer SF-600.

Table-3: The Washing Fastness of Fabric Dyed with Compounds **5a-5d** according to ISO 105-CO6.

Compound	Acetate	Cotton	Nylon	PET	Acrylic	Wool	Change of Shade
5a	**5**	**4 – 5**	**5**	**5**	**5**	**5**	**4-5**
5b	**5**	**4 – 5**	**5**	**5**	**5**	**5**	**4-5**
5c	**5**	**4 – 5**	**5**	**5**	**5**	**5**	**4-5**
5d	**5**	**4 – 5**	**5**	**5**	**5**	**5**	**4-5**

Table-4: Color Fastness to Light ISO 105-BO2.

Compounds	Concentration; %	Light Fastness
5a	**0.20**	**3-4**
5b	**0.20**	**3-4**
5c	**0.20**	**3**
5d	**0.20**	**3-4**

Table-5: Color Fastness to Chlorine ISO 105-EO3.

Compounds	Concentration; %	Chlorinated water fastness
5a	0.20	4-5
5b	0.20	4-5
5c	0.20	4-5
5d	0.20	4-5

Table-6: CIELab Coordinates by Datacolor Spectrophotometer.

Compounds	Conc.;%	Whiteness (CIE)	Light Source	*L**	*a**	*b**	*c**	*h*
Cotton Fabric		75.27	D65-10°					
5a	0.05	107.19	D65-10°	93.16	2.81	-5.20	5.91	298.38
	0.1	109.84		93.30	2.22	-5.72	6.13	291.21
	0.2	107.40		93.30	1.97	-5.18	5.54	290.79
	0.5	98.59		92.56	1.05	-3.60	3.75	286.26
5b	0.05	95.49	D65-10°	93.03	1.35	-2.70	3.02	296.50
	0.1	96.14		93.15	0.96	-2.79	2.95	289.02
	0.2	94.25		93.57	0.38	-2.17	2.21	279.93
	0.5	85.26		93.05	0.47	-0.68	0.87	271.32
5c	0.05	107.89	D65-10°	93.41	2.14	-5.24	5.66	292.18
	0.1	107.85		93.08	1.99	-5.38	5.73	290.28
	0.2	106.93		93.47	1.32	-5.00	5.17	284.83
	0.5	98.66		93.55	0.06	-3.15	3.15	271.11
5d	0.05	94.48	D65-10°	92.94	1.64	-2.52	3.01	303.00
	0.1	95.46		93.21	1.32	-2.61	2.92	296.83
	0.2	93.36		93.28	0.75	-2.12	2.25	289.53
	0.5	85.77		93.15	0.16	-0.54	0.56	286.17

Whitening of Fabric

Scoured and bleached knitted cotton fabric was dyed with the different concentration of a paste of finely powdered compounds **5a-5d** (FBAs) at 0.05, 0.1, 0.2, and 0.5% o.w.f. Commercially available Glauber's salt was used to improve the exhaustion at concentration of 5 g/L. The liquor to fabric ratio (L:R) was adjusted to 1:15. The temperature was raised at the rate of 2 °C/min initiating from 30 to 60 °C and the bath was maintained at temperature of 60 °C for 30 min. After this, the dyeing bath was dropped and rinsed with cold water. The treated fabric was air dried at room temperature.

General method of synthesis of compounds **5a-5d**

In a 250 mL flask with an agitator, pH meter, thermometer and a reflux condenser were charged with acetone (25 mL) and ice (20 g) and was added 2,4,6-trichloro-1,3,5-triazine (20 mmol) and stirred. The pH was maintained at 3 to 4 by using drop wise addition of aqueous $NaHCO_3$ solution. 4,4'-Diaminostilbene-2,2'-disulfonic acid disodium salt (10 mmol) was added slowly to above-mentioned mixture. Temperature was maintained at 0-5 °C by using an ice salt bath and the stirring was continued for 1 h. To the reaction mixture, differently substituted amines (20 mmol) was added in acetone (30 mL) and was heated to 30-40 °C for 2 h while pH was maintained at 5-6. First substituted product was separated out as solid by adding aqueous NaCl solution and solid was filtered through suction filtration. The wet cake was used without drying in the next step. The wet cake was transferred into another flask and de-ionized water (150 mL) and differently substituted amines (20 mmol) in acetone (30 mL) were added and stirred the reaction at an elevated temperature 80-90 °C. Stirring was continued for 3-4 h while pH was maintained in the range of 8-9. Advancement in the reaction at each stage was monitored using TLC (2-Propanol:MeCN:NH_4OH 50:20:30). After completion of the reaction, the solvent was evaporated under vacuum on a rotary evaporator. The crude solid product was dissolved in DMF and filtered. The residue was discarded. The filtrate was evaporated to get a solid mass. The solid mass was thoroughly washed using ultrasonic bath.

Sodium (E)-6,6'-(ethene-1,2-diyl)bis(3-(4-(2-methoxy-5-sulfonatophenylamino)-6-(phenylamino)-1,3,5-triazin-2-ylamino)benzenesulfonate) **(5a).**

Yield: 60%; ^{1}H-NMR: (500 MHz, DMSO-d_6): δ_H 7.84-6.66 (m, 22H, Aromatic), 5.18 (m, 2H, Vinylic), 3.80 (s, 6H, 2 x OCH_3). UV-visible spectra, λ_{max}, de-ionized water (347nm); logε = 4.39; IR (KBr): 3406 (N–H), 1574 (C=C, Ar), 1366 (N-C, Stretch), 1180 (S=O), 1029 (S-O), 757 (=C-H, Bend). Anal. Calcd for $C_{46}H_{36}N_{12}Na_4O_{14}S_4$: C, 46.00; H, 3.02; N, 13.99; Na, 7.66; O, 18.65; S, 10.68, Found C = 46.08 %, H = 3.11%, N = 14.02%.

Sodium (E)-6,6'-(ethene-1,2-diyl)bis(3-(4-(bis(2-hydroxyethyl)amino)-6-(2-methoxy-5-sulfonatophenylamino)-1,3,5-triazin-2-ylamino)benzenesulfonate) **(5b)**

Yield: 63%; ^{1}H-NMR: (300 MHz, DMSO-d_6): δ_H 8.03-7.02 (m, 12H, Aromatic), 5.16 (m, 2H,

Vinylic), 3.82 (s, 6H, 2 x OCH_3). UV-visible spectra, λ_{max}, de-ionized water (347nm); logε = 4.63; IR (KBr): 3407 (N-H), 1587 (C=C, Ar), 1303 (N-C, Stretch), 1179 (S=O), 1026 (S-O), 795 (=CH, Bend). Anal. Calcd for $C_{42}H_{44}N_{12}Na_4O_{18}S_4$: C, 41.18; H, 3.62; N, 13.72; Na, 7.51; O, 23.51; S, 10.47, Found C = 41.24%, H = 3.69%, N = 13.76%.

Sodium (E)-6,6'-(ethene-1,2-diyl)bis(3-(4-(2-hydroxyethylamino)-6-(2-methoxy-5-sulfonatophenylamino)-1,3,5-triazin-2-ylamino)benzenesulfonate) **(5c)**

Yield: 65%; ^{1}H-NMR: (300 MHz, DMSO-d_6): δ_H 9.40-8.28 (m, 8H, Aminic and Hydroxylic), 7.99-6.94 (m, 12H, Aromatic), 5.18 (m, 2H, Vinylic), 3.88 (s, 6H, 2 x OCH_3). UV-visible spectra, λ_{max}, de-ionized water (356nm); logε = 4.65; IR (KBr): 3407 (N-H), 1589 (C=C, Ar), 1302 (N-C, Stretch), 1181 (S=O), 1026 (S-O), 799(=CH, Bend). Anal. Calcd for $C_{38}H_{36}N_{12}Na_4O_{16}S_4$: C, 40.14; H, 3.19; N, 14.78; Na, 8.09; O, 22.51; S, 11.28, Found C = 40.20%, H = 3.27%, N = 14.73%.

Sodium (E)-6,6'-(ethene-1,2-diyl)bis(3-(4-(dodecylamino)-6-(2-methoxy-5-sulfonatophenylamino)-1,3,5-triazin-2-ylamino)benzenesulfonate) **(5d)**

Yield: 64%; ^{1}H-NMR: (300 MHz, DMSO-d_6): δ_H 10.24 (m, 6H, Aminic), 8.05-7.53 (m, 12H, Aromatic), 5.16 (m, 2H, Vinylic), 3.87 (s, 6H, 2 x OCH_3). UV-visible spectra, λ_{max}, de-ionized water (343nm); logε = 4.62; IR (KBr): 3448 (N-H), 1573 (C=C, Ar), 1309 (N-C, Stretch), 1181 (S=O), 1031 (S-O), 795 (=CH, Bend). Anal. Calcd for $C_{58}H_{76}N_{12}Na_4O_{14}S_4$: C, 50.28; H, 5.53; N, 12.13; Na, 6.64; O, 16.17; S, 9.26, Found C = 50.39%, H = 5.69%, N = 12.19%.

Conclusions

The prepared optical brightening agents were applied on the cotton fabric. Optical and dyeing properties of these compounds were studied. On the account of various results acquired from different physical tests, these compounds were found to be suitable for whitening the cotton fabric with a moderate degree of whiteness. Compounds **5a-5d** showed a high degree of wash fastness. Light fastness found to be moderate. Chlorine fastness of the compounds was excellent in contrast to reported results.

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