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Novel Stilbene-triazine Symmetrical Optical Brighteners: Synthesis and Applications

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Abstract A series of new high light fastness, hot pressing fastness optical brighteners was efficiently synthesized by a three-step approach involving the successive replacement of the three chloro groups of 2,4,6-trichloro-1,3,5-triazine under different conditions of temperature and pH. Thus, 2,4,6-trichloro-1,3,5-triazine was treated with different anilines and the resulting dichlorotriazinyl intermediates (**3a-I**) were further condensed with 4,4-diaminostilbene-2,2′-disulfonic acid to afford bis-monochlorotriazine (**5a-I**) followed by nucleophilic substitution with ethanolamine to furnish the final hybrid brighteners (**7a-I**). All of the newly synthesized compounds were characterized by Fourier-Transform Infrared (FT-IR), UV-visible absorption, NMR spectroscopy and the elemental analyses. The synthesized optical brighteners were also assessed for their efficacy as fluorescent brightening agents.

Keywords Optical brightening agents (OBAs) · UV-visible spectra · Fastness properties

Introduction

Optical brightening agents (OBA) have become an integral part of our everyday life and culture; finding an increasing number of applications in diverse fields. These are commonly used in the HYP-containing pulp also known as bleached chemi-thermo mechanical pulps (BCTMP) and paper industry is to increase their whiteness and brightness stability; in cosmetics and to increase the visibility of fabrics and in night vision devices [1]. Brighteners are also added to laundry soaps, detergents, or cleaning agents, where they adsorb to fabrics or materials during the washing or cleaning process and when illuminated by ultraviolet light they fluoresce and fabrics appear brighter [2].

Brighteners are highly susceptible to adsorption. They are removed from surface and ground water by adsorption onto soil and organic material. They operate through the process of fluorescence. They absorb invisible ultraviolet (UV) radiation at wavelengths below 400 nm and through an electrophysical change, emit light mostly in the blue end of the visible spectrum at about 400–450 nm [3]. Optical brighteners have been used in experimental mycology for quantization of fungal cells or studying cell wall architecture but most important, brighteners are used in histopathology of mycosis in dermatology and diagnosing pneumocystosis. Another conceivable feature of the brighteners in medical mycology is their potential use as homing agents for systemically applied antifungals. This may be particularly effective with those antifungals that act on the cell wall as is the case with the candins [4].

In additions to coumarins, imidazolines, diazoles, triazoles, benzoxazolines and biphenyl-stilbenes; 4,4′-bis-(triazinylamino) stilbene-2,2′-disulfonate derivatives are one of the important classes of OBAs. These are widely used to create intense and bright white shades in textiles, pulps and papers, and are additives to laundry detergents [5]. Triazine-stilbene compounds showed a high degree of whiteness with moderate UV blocking properties [6]. It has been shown that stilbene optical brighteners could enhance the biological activities of NPVs against pests like the tobacco budworm, *Heliothis*

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virescens. These studies served to highlight the potential usefulness of stilbene brighteners with insect pathogenic viruses to control insect pest populations [7].

Fluorescent brighteners having antioxidant properties have been synthesized from 4,4′-bis-(triazin-6-yl) diamino stilbene-2,2′-disulfonate on condensation with cyanuric chloride and the phenol derivatives, 4-amino-2,6-di-tert-butylphenol and 4-(2-aminoethyl)-2,6-di-tertbutyl phenol. Phenolic antioxidants form the stable low-energy radical by the stable resonance hybrids to prevent further oxidation. However, these derivatives have shown lesser color fastness and whiteness as evidenced from their application results on cotton fibers in comparison with standard fluorescent brighteners C186 and C190 [8].

Herein, we wish to report the synthesis of a small library of new triazine derivatives of 4,4′-bis-(1,3,5-triazinylamino)stilbene-2,2-disulfonate and evaluation of their performance by light fastness, chlorinated water fastness, washing fastness and CIE (International Commission on Illumination) Whiteness Index measurement.

Experimental

General

All solvents and reagents were purchased from commercial sources and used as received. NMR spectra were recorded in DMSO-d$_6$ by using Bruker AC 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR Splitting patterns were as follows: s (singlet), d (doublet), dd, (double doublet), t (triplet), m (multiplet) and br (broad). Chemical shifts are reported in δ (ppm) and coupling constants are given in Hertz (Hz). UV/visible absorption spectra were recorded on a Perkin Elmer, L50 Spectrofluorimeter. FT-IR spectra were taken in KBr pellets on a Bruker EQUIOX-55 FT-IR spectrometer.

Preparation of Erlich’s Reagent

Ehrlich’s reagent is prepared by dissolving 2.0 g of p-dimethylaminobenzaldehyde (DMAB) in 50 mL of 95 % ethanol and 50 mL of concentrated hydrochloric acid. It is freshly prepared according to literature procedure [9].

General Procedure for the Synthesis of Optical Brighteners

To a well stirred aqueous solution of cyanuric chloride (**1**) (0.38 g, 0.002 mol) in ice bath at 4°–5 °C was added of sodium lauryl sulfate (0.01 g) and stirred to a fine suspension. To this suspension was added a solution of substituted anilines (**2a-I**) (0.002 mol) at 5 °C and 2–2.5 pH. Condensation was completed after 3 h as checked by Erlich’s reagent to yield the mono condensation bis-dichlorotriazinyl products (**3a-I**).

To a vigorously stirred aqueous solution of 4,4-diaminostilbenedisulfonic acid (**4**) (0.001 mol) maintained at pH 6.5 was added intermediates (**3a-I**) and the resulting solution stirred for 4 h at 40–45 °C to afford the bis-monochlorotriazine products (**5a-I**).

Third condensation with ethanolamine (**6**) (0.002 mol) and (**5a-I**) was achieved by heating the reaction mixture at 90–95 °C for 3 h at pH 9. On completion, the reaction mixture was rotary evaporated to afford the OBAs (**7a-I**) as the solid products [10].

Sulfanilic Acid Derivative of OBA. (7a)

(7a) was prepared according to the general procedure using sodium 4-aminobenzenesulfonate, cyanuric chloride, sodium lauryl sulfate, 4,4-diaminostilbene-disulfonic acid. Mol.Wt: 1078, Yield 84 %; UV-max/nm, (de-ionized water) 461 nm; IR (KBr): 3419 (N-H), 1646 (C=C), 1589, 1412 (C=C, Ar), 1367 (-CH$_3$), 1302 (C-N), 1088 (S=O), 989 (=C-H, bend), 827 (S-O). ^{1}HNMR (300 MHz, DMSO-d$_6$): δ 3.05 (t, 2H, CH$_2$), 3.45 (t, 1H, OH), 3.72 (t, 2H, CH$_2$), 6.92 (d, 2H, *J*=7.48, Ar-H), 7.06 (d, 2H, *J*=7.78 Hz, CH=CH), 7.13 (s, 1H, Ar-H), 7.42 (d, 2H, *J*=7.22, Ar-H), 7.63 (d, 2H, *J*=5.96 Hz, Ar-H), 10.14 (br. s, 6H, NH). Anal. Calcd for $C_{36}H_{34}N_{12}Na_4O_{14}S_4$: C, 40.07; H, 3.18; N, 15.58; S, 11.89. Found: C, 40.02; H, 3.20; N, 15.60; S, 11.91.

5-Nitro-2-(4-nitrophenylamino)benzenesulfonic Acid Derivative of OBA. (7b)

(7b) was prepared according to the general procedure using 5-nitro-2-(4-nitrophenylamino) benzenesulfonic acid. Mol.Wt: 1304, Yield 86 %; UV-max/nm, (de-ionized water) 457 nm; IR (KBr): 3430 (N-H), 1651 (C=C), 1592, 1413 (C=C, Ar), 1584 (C=N), 1488 (N-H), 1360 (-CH$_3$), 1302 (C-N), 1089 (S=O), 825 (S-O), 985 (=C-H, bend). ^{1}HNMR (300 MHz, DMSO-d$_6$): δ 3.15 (t, 2H, CH$_2$), 3.44 (t, 1H, OH), 3.73 (t, 2H, CH$_2$), 6.46–7.98 (Ar-H), 7.07 (d, 2H, *J*=7.76 Hz, CH=CH), 10.21 (br. s, 6H, NH). Anal. Calcd for $C_{48}H_{42}N_{16}Na_2O_{18}S_4$: C, 44.17; H, 3.24; N, 17.17; S, 9.83. Found: C, 44.12; H, 3.22; N, 17.20; S, 9.86.

2-Amino-5-(4-aminophenylamino)benzenesulfonic Acid Derivative of OBA. (7c)

(7c) was prepared according to the general procedure using 2-amino-5-(4-aminophenylamino) benzenesulfonic acid. Mol.Wt: 1244, Yield 89 %; UV-max/nm, (de-ionized water) 459 nm: IR (KBr): 3418 (N-H), 1644 (C=C), 1582, 1411 (C=C, Ar), 1558 (C=N), 1434 (N-H), 1359 (-CH$_3$), 1302 (C-N), 1072 (S=O), 828 (S-O), 982 (=C-H, bend). ^{1}HNMR (300 MHz, DMSO-d$_6$): δ 3.07 (t, 2H, CH$_2$), 3.45 (t, 1H, OH), 3.71 (t, 2H, CH$_2$), 5.99 (s, 2H, NH$_2$), 6.22–7.48 (Ar-H), 7.05 (d, 2H, J=7.77 Hz, CH=CH), 10.32 (br. s, 8H, NH). Anal. Calcd for $C_{48}H_{46}N_{16}Na_2O_{14}S_4$: C, 46.30; H, 3.72; N, 18.00; S, 10.30. Found: C, 46.25; H, 3.69; N, 18.04; S, 10.35.

2-Aminothiazole Derivative of OBA. (7d)

(7d) was prepared according to the general procedure using 2-aminothiazole. Mol.Wt: 886, Yield 82 %; UV-max/nm, (de-ionized water) 461 nm; IR (KBr): 3479 (N-H), 1646 (C=C), 1593, 1404 (C=C, Ar), 1584 (C=N), 1489 (N-H), 1394 (-CH_3), 1320 (C-N), 1088 (S=O), 827 (S-O), 989 (=C-H, bend) ^{1}HNMR (300 MHz, DMSO-d_6): δ 3.04 (t, 2H, CH_2), 3.45 (t, 1H, OH), 3.75 (t, 2H, CH_2), 6.55 (d, 2H, J=7.48, H-tiazole), 7.05 (d, 2H, J=7.76 Hz, CH=CH), 7.52 (d, 2H, J= 5.96 Hz, H-tiazole), 7.13 (s, 1H, Ar-H), 7.42 (d, 2H, J=7.22, Ar-H), 10.31(br. s, 6H, NH). Anal. Calcd for $C_{30}H_{28}N_{14}Na_2O_8S_4$: C, 40.63; H, 3.18; N, 22.11; S, 14.46. Found: C, 40.59; H, 3.15; N, 22.15; S, 14.49.

3-Flouroaniline Derivative of OBA. (7e)

(7e) was prepared according to the general procedure using 3-flouroaniline. Mol.Wt: 908, Yield 89 %; UV-max/nm, (de-ionized water) 460 nm; IR (KBr): 3419 (N-H), 1646 (C=C), 1575, 1412 (C=C, Ar), 1525 (C=N), 1488 (N-H), 1367 (-CH_3), 1259 (C-N), 1088 (S=O), 855 (S-O), 996 (=C-H, bend). ^{1}HNMR (300 MHz, DMSO-d_6): δ 3.01 (t, 2H, CH_2), 3.45 (t, 1H, OH), 3.78 (t, 2H, CH_2), 6.15–7.43 (Ar-H), 7.08 (d, 2H, J=7.79 Hz, CH=CH), 10.24 (br. s, 6H, NH). Anal. Calcd for $C_{36}H_{32}N_{12}Na_2O_8S_2F_2$: C, 47.58; H, 3.55; S, 7.06. Found: C, 47.63; H, 3.49; S, 7.08.

2,5-Dichloroaniline Derivative of OBA. (7f)

(7f) was prepared according to the general procedure using 2,5-dichloroaniline. Mol.Wt: 1010, Yield 86 %; UV-max/nm, (de-ionized water) 459 nm; IR (KBr): 3420 (N-H), 1645 (C=C), 1568, 1410 (C=C, Ar), 1519 (C=N), 1488 (N-H), 1361 (-CH_3), 1302 (C-N), 1089 (S=O), 826 (S-O), 986 (=C-H, bend). ^{1}HNMR (300 MHz, DMSO-d_6): δ 3.07 (t, 2H, CH_2), 3.45 (t, 1H, OH), 3.69 (t, 2H, CH_2), 6.40–7.45 (Ar-H), 7.04 (d, 2H, J=7.75 Hz, CH=CH), 10.39 (br. s, 6H, NH). Anal. Calcd for $C_{36}H_{30}N_{12}Na_2O_8S_2Cl_4$: C, 42.78; H, 2.99; N, 16.63S, 6.35. Found: C, 42.73; H, 3.02; N, 16.58; S, 6.38.

2,3-Dichloroaniline Derivative of OBA. (7g)

(7g) was prepared according to the general procedure using 2,3-dichloroaniline. Mol.Wt: 1010, Yield 82 %; UV-max/nm, (de-ionized water) 460 nm; IR (KBr): 3366 (N-H), 1646 (C=C), 1599, 1406 (C=C, Ar), 1584 (C=N), 1487 (N-H), 1360 (-CH_3), 1302 (C-N), 1065 (S=O), 824 (S-O), 988 (=C-H, bend). ^{1}HNMR (300 MHz, DMSO-d_6): δ 3.06 (t, 2H, CH_2), 3.45 (t, 1H, OH), 3.73 (t, 2H, CH_2), 6.28–7.44 (Ar-H), 7.01 (d, 2H, J=7.73 Hz, CH=CH), 10.35 (br. s, 6H, NH). Anal. Calcd for $C_{36}H_{30}N_{12}Na_2O_8S_2Cl_4$: C, 42.78; H, 2.99; N, 16.63; S, 6.35. Found: C, 42.72; H, 3.01; N, 16.59; S, 6.38.

2,4-Dichloroaniline Derivative of OBA. (7h)

(7h) was prepared according to the general procedure using 2,4-dichloroaniline. Mol.Wt: 1010, Yield 83 %; UV-max/nm, (de-ionized water) 461 nm; IR (KBr): 3418 (N-H), 1650 (C=C), 1587, 1409 (C=C, Ar), 1587 (C=N), 1485 (N-H), 1358 (-CH_3), 1302 (C-N), 1088 (S=O), 828 (S-O), 984 (=C-H, bend). ^{1}HNMR (300 MHz, DMSO-d_6): δ 3.04 (t, 2H, CH_2), 3.45 (t, 1H, OH), 3.71 (t, 2H, CH_2), 6.32–7.43 (Ar-H), 7.02 (d, 2H, J=7.75 Hz, CH=CH), 10.17 (br. s, 6H, NH). Anal. Calcd for $C_{36}H_{30}N_{12}Na_2O_8S_2Cl_4$: C, 42.78; H, 2.99; N, 16.63; S, 6.35. Found: C, 42.75; H, 3.00; N, 16.67; 12.64; S, 6.39.

2,6-Dibromo-4-flouroaniline Derivative of OBA. (7i)

(7i) was prepared according to the general procedure using 2,6-dibromo-4-flouroaniline. Mol.Wt: 1224, Yield 90 %; UV-max/nm, (de-ionized water) 460 nm; IR (KBr): 3393 (N-H), 1644 (C=C), 1590, 1411 (C=C, Ar), 1584 (C=N), 1489 (N-H), 1326 (-CH_3), 1302 (C-N), 1087 (S=O), 823 (S-O), 989 (=C-H, bend). ^{1}HNMR (300 MHz, DMSO-d_6): δ 3.02 (t, 2H, CH_2), 3.45 (t, 1H, OH), 3.74 (t, 2H, CH_2), 6.82–7.45 (Ar-H), 7.03 (d, 2H, J=7.76 Hz, CH=CH), 10.15 (br. s, 6H, NH). Anal. Calcd for $C_{36}H_{28}N_{12}Na_2O_8S_2Br_4F_2$: C, 35.31; H, 2.30; N, 13.73; S, 3.00. Found: C, 35.27; H, 2.32; N, 13.69; S, 3.02.

2,6-Dinitroaniline Derivative of OBA. (7j)

(7j) was prepared according to the general procedure using 2,6-dinitroaniline. Mol.Wt: 1052, Yield 85 %; UV-max/nm, (de-ionized water) 460 nm; IR (KBr): 3419 (N-H), 1644 (C=C), 1588, 1411 (C=C, Ar), 1584 (C=N), 1487 (N-H), 1358 (-CH_3), 1302 (C-N), 1087 (S=O), 824 (S-O), 983 (=C-H, bend). ^{1}HNMR (300 MHz, DMSO-d_6): δ 3.02 (t, 2H, CH_2), 3.45 (t, 1H, OH), 3.70 (t, 2H, CH_2), 6.99–8.75 (Ar-H), 7.04 (d, 2H, J=7.76 Hz, CH=CH), 10.27 (br. s, 6H, NH). Anal. Calcd for $C_{36}H_{30}N_{16}Na_2O_{16}S_2$: C, 41.07; H, 2.87; N, 21.29; S, 6.09. Found: C, 41.12; H, 2.90; N, 21.25; S, 6.12.

2,6-Diaminoanthracene-9,10-dione Derivative of OBA. (7k)

(7k) was prepared according to the general procedure using 2,6-diaminoanthracene-9,10-dione. Mol.Wt: 1163, Yield

87 %; UV-max/nm, (de-ionized water) 581 nm; IR (KBr): 3416 (N-H), 1656 (C=C), 1590, 1416 (C=C, Ar), 1567 (C=N), 1451 (N-H), 1398 (-CH_3), 1328 (C-N), 1050 (S=O), 843 (S-O), 993 (=C-H, bend). ^{1}HNMR (300 MHz, DMSO-d_6): δ 3.03 (t, 2H, CH_2), 3.45 (t, 1H, OH), 3.74 (t, 2H, CH_2), 6.04 (s, 2H, NH_2), 7.04 (d, 2H, J=7.77 Hz, CH=CH), 6.75–7.53 (Ar-H), 10.34 (br. s, 8H, NH). Anal. Calcd for $C_{52}H_{40}N_{14}Na_2O_{12}S_2$: C, 53.70; H, 3.47; N, 16.86; S, 5.51. Found: C, 53.66; H, 3.42; N, 16.88; S, 5.57.

Naphthalene-1,5-diamine Derivative of OBA. (7l)

(7l) was prepared according to the general procedure using naphthalene-1,5-diamine. Mol.Wt: 1002, Yield 86 %; UV-max/nm, (de-ionized water) 459 nm; IR (KBr): 3415 (N-H), 1643 (C=C), 1589, 1410 (C=C, Ar), 1582 (C=N), 1489 (N-H), 1387 (CH_3), 1300 (C-N), 1088 (S=O), 824 (S-O), 986 (=C-H, bend). ^{1}HNMR (300 MHz, DMSO-d_6): δ 3.06 (t, 2H, CH_2), 3.45 (t, 1H, OH), 3.78 (t, 2H, CH_2), 5.98 (s, 2H, NH_2), 6.67–7.42 (Ar-H), 7.05 (d, 2H, J=7.78 Hz, CH=CH), 10.40 (br. s, 8H, NH). Anal. Calcd for $C_{44}H_{40}N_{14}Na_2O_8S_2$: C, 52.69; H, 4.02; N, 19.55; S, 6.39. Found: C, 52.74; H, 4.05; N, 19.49; S, 6.41.

Results and Discussion

A series of twelve new optical brighteners has been synthesized by a three-step synthetic in good yields according to the synthetic route depicted in Scheme 1.

Synthesis of OBAs (7a-I)

The triazine-stilbene fluorescent brighteners are widely used in industrial application as whitening agents [11] and their synthetic procedures are well known. Synthesis of optical brighteners (**7a-I**) has been achieved by reacting 2,4,6-trichloro-1,3,5-triazine (**1**) with twelve different novel organic amines (**2a-l**). This reaction resulted in the formation of dichlorotriazinyl intermediates (**3a-l)**. The chemical structures of the organic amines (**2a-l**) used are given in Table 1. These include a variety of important organic amines viz., mono-, di- and trisubstituted anilines, secondary amines, heterocyclic and bi- and tricyclic amines. The Maintenance of a low temperature of 4–5 °C was found to be critical for the successful coupling of triazine with aromatic amines. Condensation of the dichlorotriazinyl intermediates (**3a-l)** with 4,4-diaminostilbene-2,2′-disulfonic acid (**4**) afforded bis-monochlorotriazine intermediates (**5a-l**) in good yields. Again for conversion, the careful control of pH and temperature was found to be important for the success of reaction. Finally the nucleophilic substitution of (**5a**-l) with ethanolamine (**6**) was achieved at 90–95 °C to furnish the new hybrid optical brighteners (**7a**-l). Deionized water was used throughout all of the synthetic steps.

The structures of the newly synthesized hybrid optical brighteners (**7a**-l) were supported by FTIR, ^{1}HNMR and UV spectral data. The FTIR spectra of all compounds revealed a strong absorption in the range 3479–3366 cm^{-1} indicating the presence of N-H group. The ^{1}HNMR spectra of all compounds showed broad singlet of N-H around 10.14 ppm and

Scheme 1 Three step synthetic pathway to new stilbene-triazine hybrid optical brighteners (**7a-I**)

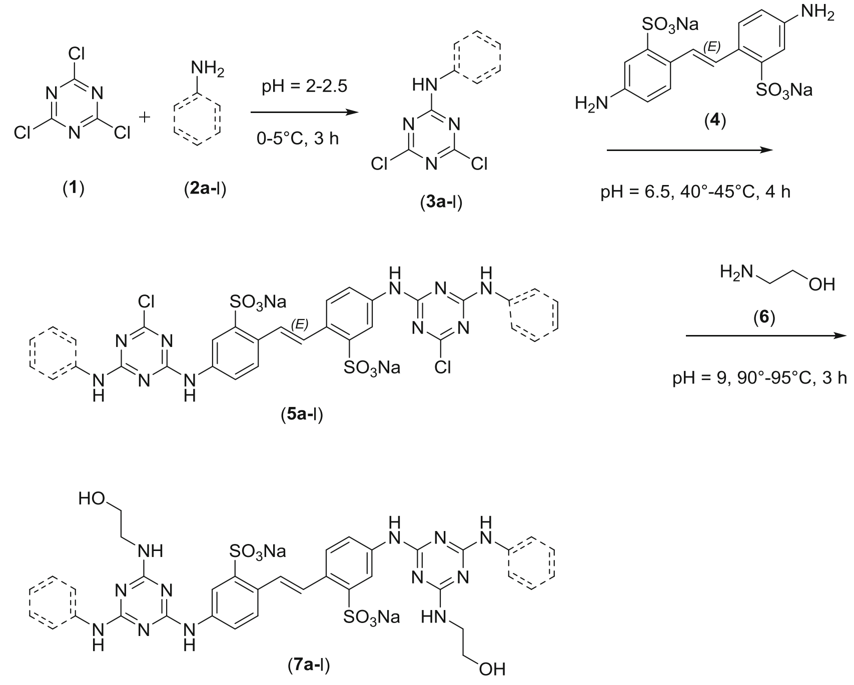
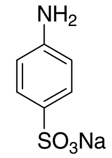
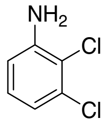
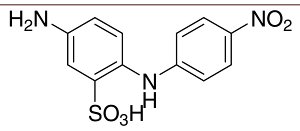
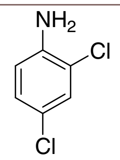
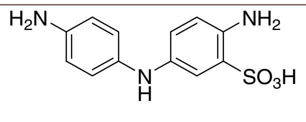
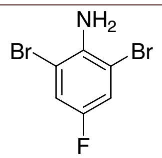
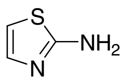
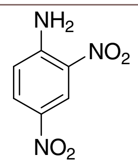
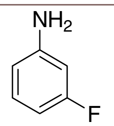
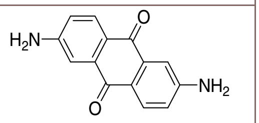
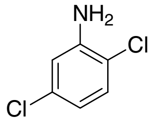
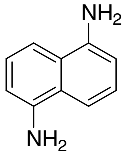


Table 1 Structures of organic amines used in the synthesis of OBAs (**7a-l**)

Compd	amine	Compd	amine
2a		**2g**	
2b		**2h**	
2c		**2i**	
2d		**2j**	
2e		**2k**	
2f		**2l**	

strong aromatic signals in the range of 6.15–8.75 ppm. In UV spectra all compounds displayed characteristic absorptions in the range 457–581 nm.

Stereochemistry of OBAs

Nearly 80 % of all OBAs produced are derived from the stilbene derivatives, which absorb in the ultra violet regions at 340–50 nm and can subsist in the cis and the trans configurations. Optical brighteners in the trans form, can be made both in the liquid and the solid forms, but their protection against light is necessary as they change from trans isomer to cis isomer which cannot penetrate into cotton fibers.

In the present research, synthesized optical brighteners are derived from the heterocyclic moiety containing nitrogen atoms. These synthesized OBAs (**7a-l**) show excellent stability to light which is depicted from their light fastness values which is 4–5 in majority of derivatives (Table 2). There are bulky and polar substituents which prevent their trans to cis geometry transformation. Fluorescence of prepared OBAs (**7a-l**) is also high because of larger conjugation in derivatives (Table 2).

Effect of pH and Temperature on the Synthesis of OBAs

During the preparation of stilbene-triazine compounds a careful control of pH was found be essential in order to avoid

Table 2 Light Fastness data of OBAs (**7a-l**)

Compd	Gray scale reading			
	Wool	Leather	Polyester	Polyamide
7a	4–5	4–5	4–5	4–5
7b	3–4	3–4	3–4	3–4
7c	4–5	4–5	4–5	4–5
7d	4–5	4–5	4–5	4–5
7e	4–5	4–5	4–5	4–5
7f	4–5	4–5	4–5	4–5
7g	4.5	4.5	4.0	4.5
7h	3.5	3.0	3.5	3.5
7i	5.0	5.0	4.5	5.0
7j	3.5	3.5	3.5	3.0
7k	3.0	3.0	3.0	3.0
7l	3.0	3.0	3.0	3.0

Table 3 Hot pressing Fastness data of OBAs (**7a–l**)

Compd	Gray scale reading			
	Wool	Leather	Polyester	Polyamide
7a	4–5	4–5	4–5	4–5
7b	3.0	3.0	3.0	3.0
7c	3–4	3–4	3–4	3–4
7d	3–4	3–4	3–4	3–4
7e	3.5	3.5	3.5	4.0
7f	3.0	3.0	3.0	3.0
7g	4–5	4–5	4–5	4.0
7h	4.0	4.0	4.0	4.0
7i	5.0	5.0	4.5	5.0
7j	4–5	4–5	4–5	4–5
7k	4.0	4.0	4.0	4.0
7l	3.0	4.0	3.0	3.0

formation of unwanted hydrolysis products which can reduce the whiteness. The reactivity was decreased at each chlorine replacement step in the triazine moiety by the introduction of different nucleophiles which decrease the electropositive character of the triazine ring. The three chloro groups of 2,4,6-trichlro-1,3,5-triazine moiety showed different reactivity depending on the nucleophile used and the reaction temperature [12]. It is a well known that the he first substitution takes place around 0–5 °C, second at 30–45 °C and third at 80–90 °C. This difference in reactivity enabled us to successively replace the three chlorine atoms to accomplish the synthesis of OBAs (**7a-l**) in good yields and high purity.

UV/Visible Absorption Study of OBAs

UV/ visible absorption was determined using freshly prepared solutions containing 2×10^{-2} g/L of the compounds in deionized water and adjusting solution to pH 9 with NaOH aq, using a 10 mm quartz cuvette. All compounds have characteristic absorptions in the range 457–581 nm due to main chromophoric groups NH and CH=CH but the compound **7b** showed hypsochromic shift (457 nm) due to the presence of NO_2 group and **7k** showed bathochromic shift because of NH_2 groups which are electron donating and shift wavelength to number (Fig. 1).

Blankophor BBU used commercially to give whiteness and brightness to cellulosic fibers, having a light fastness 5 was used as a standard. Wavelength of maximum absorption (λ_{max}) of hybrid OBAs **7d**, **7f**, **7g** and **7e** is similar to that of the standard, while the λ_{max} of **7a**, **7h** and **7j** has been shifted very little toward the visible region. Compound **7k** (λ_{max} 581 nm) showed marked deviation from the standard due to the presence of more conjugated 2,6-diaminoanthracene-9,10-dione moiety.

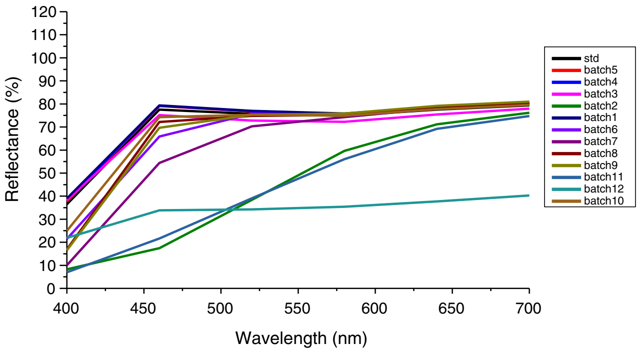


Fig. 1 Combined Reflectance Spectra of Synthesized OBAs

Table 4 Color Fastness to chlorine (ISO 105-EO3) and Whiteness data of OBAs (**7a-l**)

Compd	Concentration (%)	Change of shade	Whiteness (CIE)
7a	0.25	4–5	101.39
7b	0.25	3–4	107.40
7c	0.25	4–5	94.25
7d	0.25	3–4	98.5
7e	0.25	4–5	103.4
7f	0.25	3–4	105.6
7g	0.25	4–5	104.5
7h	0.25	4–5	107.5
7i	0.25	4–5	106.93
7j	0.25	3–4	108.35
7k	0.25	3–4	97.6
7l	0.25	3–4	92.12

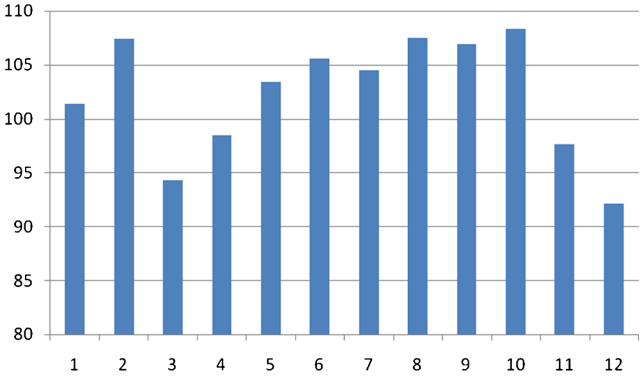


Fig. 2 Graphical representation of whiteness of synthesized OBAs (**7a-l**)

Characterization of OBAs

Optical brighteners (**7a-l**) were applied at concentrations of 0.25 % relative to the weight of cotton fiber and were characterized by various tests which fastness test (color fastness, chlorine fastness, and wash fastness), physical tests, solubility and stability tests, and softening agents effect test.

a) Fastness Properties

i) Color Fastness of textile fibers to Light:

This method is used for determination of the resistance of the color of textile fibers at all stages of processing to the action of an artificial light source. The side to be tested of the specimen of fibers was exposed to light from xenon arc under specified conditions and to a specified depth of color, along with eight dyed wool standards. The fastness was assessed by comparing the fading of cloth with that of the standards. Results of light fastness are shown in Table 2. Light Fastness was measured using Xenon Arc Lamp method according to ISO-105-BO2 [13]. All the synthesized OBAs (**7a-l**) preserved excellent light fastness 4-5.

ii) Color fastness to hot pressing:

This test was conducted to determine the resistance of colors of textile fibers of all kinds and in all forms to ironing and to processing on hot cylinders. Tests are performed on dry as well as on wet textile samples. The end use of the textiles usually determines which test should be performed. A dry specimen or a dry specimen covered with a wet dry cotton adjacent fabric or a wet specimen covered with wet cotton adjacent fabric are pressed with a heating device at a specified temperature for specified time interval. Test results for OBAs applied on wool, leather, polyester and polyamide fibers are given in Table 3.

iii) Chlorine Fastness and Whiteness Index:

Chlorine fastness test was carried out according to ISO-105-EO3 [14]. Whiteness Index (CIE) values were obtained by using standard method [15]. The whiteness was measured using Data Color Spectrophotometer SF 600 with large area view, illuminant D65, and 10° observer. Each sample was measured three times from different surface of fabric. The average results are shown in Table 4**,** Fig. 2.

b) Physical Characterization of OBAs

Physical characterizations of OBAs include the appearance, structure, pH, constitution, storage stability, ionic character and wash fastness properties. Various physical properties of synthesized OBAs are given in Table 5.

c) Solubility and Solution Stability of OBAs

This test was performed to assess, up to what extent

Table 5 Physical Characterization of OBAs (**7a-l**)

Compd	Appearance	Chemical character	Ionic character	pH of 1 % Soln.	Storage stability	Wash fastness property
7a	Light Yellow powder	Stilbene derivative	Anionic	8.5	Virtually unlimited	Good
7b	Light Yellow powder	Stilbene derivative	Anionic	8.0	Virtually unlimited	Good
7c	Light Yellow powder	Stilbene derivative	Anionic	7.5	Virtually unlimited	Good
7d	Light Yellow powder	Stilbene derivative	Anionic	8.5	Virtually unlimited	Good
7e	Light Yellow powder	Stilbene derivative	Anionic	7.25	Virtually unlimited	Good
7f	Light Yellow powder	Stilbene derivative	Anionic	8.0	Virtually unlimited	Good
7g	Light Yellow powder	Stilbene derivative	Anionic	7.5	Virtually unlimited	Good
7h	Light Yellow powder	Stilbene derivative	Anionic	8.5	Virtually unlimited	Good
7i	Light Yellow powder	Stilbene derivative	Anionic	8.0	Virtually unlimited	Good
7j	Light Yellow powder	Stilbene derivative	Anionic	8.0	Virtually unlimited	Good
7k	Light Yellow powder	Stilbene derivative	Anionic	8.5	Virtually unlimited	Good
7l	Light Yellow powder	Stilbene derivative	Anionic	7.5	Virtually unlimited	Good

Table 6 Solubility and solution stability data of OBAs (**7a-l**)

Compd	Solubility (g/l) at 20 °C	Stability of solution					
		Hard water	Acid	Alkali	$Na_2S_2O_4$	H_2O_2	NaClO
7a	300	Very good	Very good	Very good	Very good	Very good	Not stable
7b	300	Very good	Very good	Very good	Very good	Very good	Not stable
7c	300	Very good	Very good	Very good	Very good	Very good	Not stable
7d	300	Very good	Very good	Very good	Very good	Very good	Not stable
7e	300	Very good	Very good	Very good	Very good	Very good	Not stable
7f	300	Very good	Very good	Very good	Very good	Very good	Not stable
7g	300	Very good	Very good	Very good	Very good	Very good	Not stable
7h	300	Very good	Very good	Very good	Very good	Very good	Not stable
7i	300	Very good	Very good	Very good	Very good	Very good	Not stable
7j	300	Very good	Very good	Very good	Very good	Very good	Not stable
7k	300	Very good	Very good	Very good	Very good	Very good	Not stable
7l	300	Very good	Very good	Very good	Very good	Very good	Not stable

OBAs are water soluble, because water is the universal solvent which is most commonly used in textile and leather industries. The solutions of OBAs are treated with different reagents to study their effect on the properties and applications of OBAs on different substrates. Solubility and solution stability data of different synthesized OBAs is given in Table 6.

d) Effect of Softening Agents on OBAs

As a general rule, each fiber has its specific softness value, which depends on its chemical composition and physical structure (less crystallinity = greater softness). The fineness of the fiber or of the filament directly affects the softness of the yarn (woolens, worsteds, microfibers etc.). The yarn twist ratio is inversely proportional to its softness. The weave also contributes to reducing or increasing the fabric softness. Furthermore, a greater number of yarns per centimeter increase the stiffness of the fabric, thus reducing its softness. Softness of fibers includes surface softness, surface smoothness and elasticity (compression and stretching). Softening test was carried out to determine the effect of different types of softening agents, either OBAs precipitate out from solution, lose their properties, or don't penetrate into fiber. All the synthesized OBAs (**7a-l**) showed excellent stability and compatibility toward various softening agents except cationic softeners. The effects of different softening agents on synthesized OBAs are summarized in Table 7.

Table 7 Solution Stability data of OBAs (**7a-l**) toward different softening agents

Compd	Stability of solution			
	Resin Pre condensates	Anionic & non-ionic softeners	Anionic & non-ionic wetting agents	Cationic softeners
7a	Compatible	Compatible	Compatible	Not Compatible
7b	Compatible	Compatible	Compatible	Not Compatible
7c	Compatible	Compatible	Compatible	Not Compatible
7d	Compatible	Compatible	Compatible	Not Compatible
7e	Compatible	Compatible	Compatible	Not Compatible
7f	Compatible	Compatible	Compatible	Not Compatible
7g	Compatible	Compatible	Compatible	Not Compatible
7h	Compatible	Compatible	Compatible	Not Compatible
7i	Compatible	Compatible	Compatible	Not Compatible
7j	Compatible	Compatible	Compatible	Not Compatible
7k	Compatible	Compatible	Compatible	Not Compatible
7l	Compatible	Compatible	Compatible	Not Compatible

Conclusions

Twelve new stilbene-trazine hybrid optical brightening agents were synthesized using industrially important organic amines. The newly synthesized hybrid optical brighteners were applied to fabric on 0.25 % strengths and they exhibited high whiteness values 92.12–108.35, close to commercially available optical brighteners. All of these optical brightening agents exhausted completely in the bath and furnished good whiteness and brightness effects on the fabric and paper. Absorption maxima (λ_{max}) confirmed the presence of absorbing chromophores. Due to their exceptional properties (light fastness, wash fastness, rubbing fastness, stability to light in solution and solid state, compatibility to softeners), these optical brightening agents can potentially be employed for their synthesis on industrial scale to replace the commercially available optical brighteners.

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