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The synthesis and properties of triazine-stilbene fluorescent brighteners containing the phenolic antioxidant

Seong-Il Um[a], Joon-Kyun Lee[a], Yonghan Kang[a,*], Dae-Jin Baek[b]

[a]*Department of Chemistry and Applied Chemistry, Hanyang University, Ansan, Kyunggi-do 426-791, South Korea*
[b]*Department of Chemistry, Hanseo University, Soesan, Choongchungnam-do 356-706, South Korea*

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Abstract

Disodium 4,4′-bis(1,3,5-triazin-6-yl)diaminostilbene-2,2′-disulfonate derivatives (**11a–h**) which were substituted with 4-amino-2,6-di-*tert*-butylphenol (**3**) or 4-(2-amino-ethyl)-2,6-di-*tert*-butylphenol (**6**) as an antioxidant on triazine moiety were prepared. The obtained compounds were characterized by the analysis of the proton NMR spectrum and confirmed by UV spectrum. The physical properties of the new compounds (**11a–h**) were performed by fastness test and whiteness measurement, compared with those of **CI86** and **CI90**.

Keywords: Antioxidant; Triazine-stilbene FBs; Whiteness; Fastness; 4-Amino-2,6-di-*tert*-butylphenol; 4-(2-Aminoethyl)-2,6-di-*tert*-butylphenol

1. Introduction

Disodium 4,4′-bis(triazinylamino)stilbene-2,2′-disulfonate derivatives are most widely used as fluorescent brighteners for the whitening of both cotton and wool [1–3]. They increased the whiteness by a process of absorption of the light in ultraviolet region (330–380 nm) and emission of the visible blue light (400–450 nm) [4]. It is necessary for the fluorescent brighteners to show the high fluorescence activity a planar molecular structure with conjugated double bonds and electron-donating groups [5]. Fluorescent brighteners, furthermore, should present a high quality of whiteness and fastness.

In some cases, if the matter which was treated with a fluorescent brightener is exposed outside, a free radical could be produced due to the solar light. As a result, the chemical skeleton of the fluorescent brightener is destroyed and the whiteness is decreased rapidly. Recently, our research interests are focused on the development of the fluorescent brightener that could be capable of being exposed under the sun for a long time.

In this study, disodium 4,4′-bis(1,3,5-triazin-6-yl)diaminostilbene-2,2′-disulfonate derivatives which were substituted with the phenol derivatives on triazine moiety were prepared as the antioxidant fluorescent brighteners. The newly synthesized compounds (**11a–h**) were characterized by analysis of the proton NMR spectrum and confirmed by UV spectrum. The physical properties of the new compounds (**11a–h**) were performed by fastness test and whiteness measurement, compared with those of **CI86** and **CI90**.

2. Result and discussion

2.1. Synthesis of phenolic antioxidant derivatives

Oxygen is an essential element for life, but it also has the possibility of forming a toxic substance called oxygen free radical. Antioxidants could decrease the

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* Corresponding author. Tel.: +82 31 400 5495; fax: +82 31 407 3863.

E-mail address: yhmkang@hanyang.ac.kr (Y. Kang).

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energy of free radical or stop forming it at the first place. Also it interrupts the oxidation chain-reaction in order to minimize free radical's inhibition reaction [6,7].

Phenolic antioxidants form the stable low-energy free radical by the stable resonance hybrids to prevent further oxidation (Fig. 1).

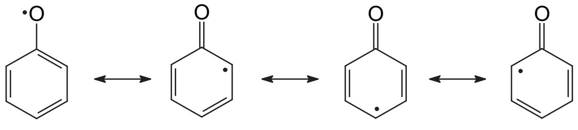


Fig. 1. The resonance structures of the phenoxy free radical.

Also if alkyl group is substituted in phenolic compound, phenoxy free radical would be more stable because of the electron donating character of alkyl group. BHA (butylated hydroxyanisole) and BHT (butylated hydroxytoluene) are representative models for phenolic antioxidant compound (Fig. 2) [8].

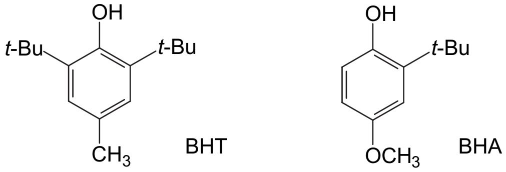


Fig. 2. The structures of BHT and BHA.

4-Amino-2,6-di-*tert*-butylphenol (**3**) [9–12] and 4-(2-aminoethyl)-2,6-di-*tert*-butylphenol (**6**) [13,14] were selected as the analogous compounds of BHT and prepared as shown in Scheme 1.

4-Amino-2,6-di-*tert*-butylphenol (**3**) was prepared from the nitrosation of 2,6-di-*tert*-butylphenol (**1**) followed by reduction with sodium hydrosulfite. Compound (**3**) was easily oxidized in air, so it had to be used for the next step without further purification.

The reaction of 2,6-di-*tert*-butylphenol (**1**) with paraformaldehyde in the presence of concentrated hydrochloric acid provided 4-chloromethyl-2,6-di-*tert*-butylphenol (**4**) which was converted to 4-cyanomethyl-2,6-di-*tert*-butylphenol (**5**) by the treatment with potassium cyanide. The reduction of 4-cyanomethyl group of the compound (**5**) with lithium aluminum hydride afforded 4-aminoethyl-2,6-di-*tert*-butylphenol (**6**).

2.2. Synthesis of triazine-stilbene fluorescent brighteners containing the phenolic antioxidant derivatives

The triazine-stilbene fluorescent brighteners are widely used in industrial application as whitening agents [15] and their synthetic procedures are well known. The syntheses of the triazine-stilbene fluorescent brighteners containing the phenolic antioxidant derivatives were started from the reaction of disodium 4,4′-diaminostilbene-2,2′-disulfonate (**7**) with 2,4,6-trichloro-1,3,5-triazine (**8**). Three chloro groups of compound (**8**) showed different chemical reactivities with the nucleophiles depending on the reaction temperature (Fig. 3) [16,17].

After stirring disodium 4,4′-diaminostilbene-2,2′-disulfonate (**7**) with 2 equivalents of 2,4,6-trichloro-1,3,5-triazine (**8**) at 0–5 °C, the resulting disodium 4,4′-bis(2,4-dichloro-1,3,5-triazin-6-yl)diaminostilbene-2,2′-disulfonate (**9**) was treated with aniline derivatives (aniline, sodium *o*-aminobenzenesulfonate, *p*-aminobenzenesulfonate, and *m*-aminobenzenesulfonate) at 30 °C without separation. While the substitution of *o*-aminobenzenesulfonate with the chloro group of the intermediate (**9**) took at least 13 h, the substitution of the other aniline derivatives was established within 3–4 h. It is assumed that the *ortho* positioned sulfonate group *o*-aminobenzenesulfonate caused the steric hindrance to prevent the nucleophilic substitution of amino group.

Finally, 4-amino-2,6-di-*tert*-butylphenol (**3**) or 4-(2-aminoethyl)-2,6-di-*tert*-butylphenol (**6**) was added in situ to the reaction mixture. The third substitution reaction occurred when a temperature of 80 °C was reached.

The synthetic procedures of triazine-stilbene fluorescent brighteners containing the phenolic antioxidant derivatives are summarized in Scheme 2 and relevant data are given in Table 1.

2.3. Color assessment and various fastness

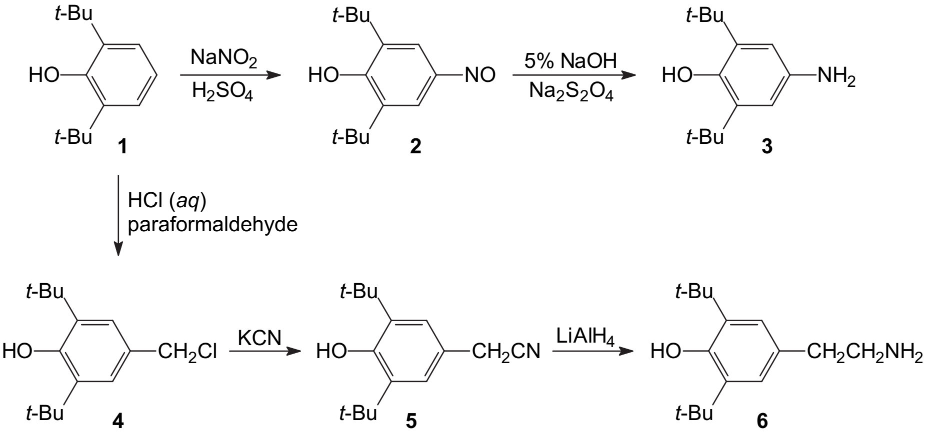
Characteristics of the compounds (**11a–h**) are compared with those of **CI86** and **CI90** which are used for commercial purpose. The structures of **CI86** and **CI90** are shown in Fig. 4.

The compounds (**11a–h**) were applied at concentrations of 0.05%, 0.1%, 0.3%, 0.5%, and 1% relative to the weight of cotton fiber. The degree of the whiteness and the CIE $L^*a^*b^*$ coordinates were determined. The data obtained are presented in Table 2. It is apparent that the compounds (**11a–h**) showed lower degree of whiteness than **CI86** and **CI90**. The compounds (**11a–h**) gave the range of the attractive color shade from bluish white to white. The compounds **11a**, **11b**, **11d**, and **11f** presented good resistance to light, but the compound **11c** showed lower light fastness than **CI86** and **CI90**. While the compounds (**11a–h**) afforded low fastness in the chlorinated water, they provided better rubbing fastness than **CI86** and **CI90** as shown in Table 3.

Washing fastness data are given in Table 4. The results of the washing fastness test showed that all the compounds (**11a–h**) preserved excellent fastness, especially superior for cotton.

3. Conclusion

Triazine-stilbene derivatives containing the phenolic antioxidant derivatives (**11a–h**) were prepared as



Scheme 1.

antioxidant fluorescent brighteners in good yield. On the basis of the results obtained from the various physical tests, compounds (**11a–h**) showed lower degree of whiteness than **CI86** and **CI90**. On the other hand, in light fastness, rubbing fastness and washing fastness, the compounds (**11a–h**) preserved excellent fastness.

4. Experimental

4.1. Materials and analysis

All chemicals were used as purchased from commercial sources (Aldrich, Merck, Duksan, Yakuri, Junsei) and were of analytical grade. The solvents were purified by distillation and the other reagents were used without further purification. The ^{1}H NMR spectra were measured at 300 MHz using a Varian Mercury 300. The UV spectra were obtained on a Shimadzu UV-2401PC. TLC was carried out using Merck silica gel plates (F254) with distilled solvents. Light fastness results were obtained on a Xenotest 150S. Washing fastness and chlorinated water fastness were tested on an Atras LP2. Rubbing fastness results were obtained on an Atras CM-5. The computer color matching (CCM) data were obtained on an SF600 Data color.

4.2. Synthesis of the compounds

4.2.1. Synthesis of 2,6-di-tert-butyl-4-nitrosophenol (2)

To a stirred solution of 2,6-di-*tert*-butylphenol (**1**) (5.16 g, 25.0 mmol) in ethanol (25 mL) containing conc. sulfuric acid (0.75 mL) was added dropwise to a solution of sodium nitrite (1.78 g, 25.8 mmol) in water (5 mL) at 0 °C. After addition was completed, the reaction mixture was stirred at 0 °C for 2 h. The yellow precipitate was collected by filtration and washed with water and dried. The crude product was recrystallized from carbon tetrachloride to afford 2,6-di-*tert*-butyl-4-nitrosophenol (**2**, 5.40 g, 92%) as a yellow solid: mp 217–219 °C; ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 18H, *tert*-butyl), 6.91 (d, 1H, ArH), 7.54 (d, 1H, ArH).

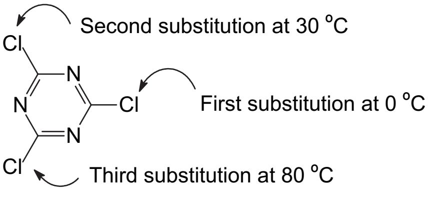


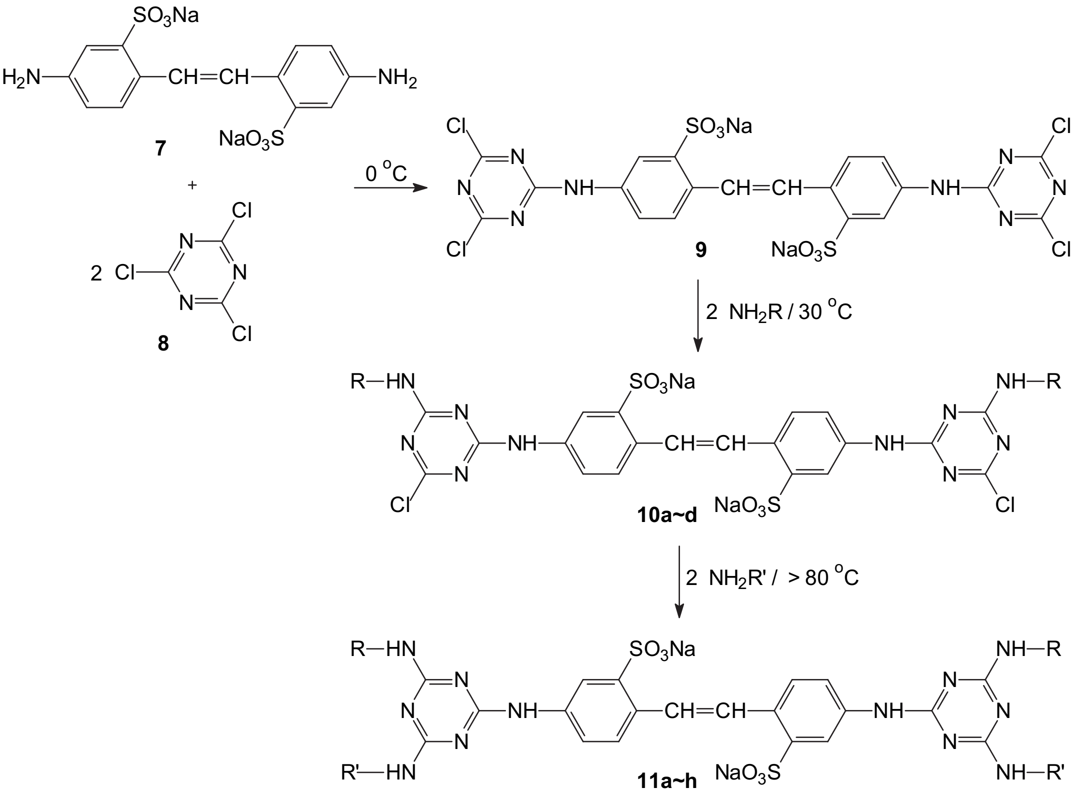
Fig. 3. Differential reactivity of 2,4,6-trichloro-1,3,5-triazine (**8**).

4.2.2. Synthesis of 4-amino-2,6-di-tert-butylphenol (3)

A solution of 2,6-di-*tert*-butyl-4-nitrosophenol (**2**) (5.18 g, 22.0 mmol) in 5% sodium hydroxide solution (30 mL) was heated to 50–60 °C, and then sodium hydrosulfite (10.0 g) was added portionwise. After addition was completed, the reaction mixture was stirred at 50–60 °C for 1 h. The reaction mixture was diluted with water (20 mL). After being cooled to room temperature, the cream-colored precipitate was filtered, washed with water and dried to provide 4-amino-2,6-di-*tert*-butylphenol (**3**, ~98%). The crude product (**3**) was used for the next step without further purification. The color of the product (**3**) turned red rapidly on standing because aminophenol derivatives are extremely sensitive to air-oxidation.

4.2.3. Synthesis of 4-chloromethyl-2,6-di-tert-butylphenol (4)

To a solution of 2,6-di-*tert*-butylphenol (**1**) (10.0 g, 48.5 mmol) in *n*-heptane (50 mL) were added paraformaldehyde (30 g) and conc. hydrochloric acid (75 mL). The vigorously stirred reaction mixture was gently refluxed under nitrogen for 13 h. After being cooled to room temperature, the organic layer was separated from liquid layer and washed with water until the washing liquid was neutral. The organic layer was dried over anhydrous magnesium sulfate and evaporated to give 4-chloromethyl-2,6-di-*tert*-butylphenol (**4**, ~99%) as an



Scheme 2.

orange syrup which was used for the next step without further purification.

4.2.4. Synthesis of 4-cyanomethyl-2,6-di-tert-butylphenol (5)

To a solution of potassium cyanide (6.30 g, 96.7 mmol) in 70% aqueous ethanol (250 mL) was added dropwise a solution of 4-chloromethyl-2,6-di-*tert*-butylphenol (**4**) (12.4 g, 48.7 mmol) in *n*-heptane (100 mL) at 0 °C. After addition was completed, the reaction mixture was heated under reflux for 2 h. After being cooled to room temperature, the precipitate was collected by filtration and washed with water to afford 4-cyanomethyl-2,6-di-*tert*-butylphenol (**5**, 10.0 g, 84%) as a yellow solid: mp 107–109 °C; ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 18H, *tert*-butyl), 3.65 (s, 2H, $-CH_2CN$), 5.25 (s, 1H, −OH), 7.09 (s, 2H, ArH).

4.2.5. Synthesis of 4-(2-aminoethyl)-2,6-di-tert-butylphenol (6)

To a stirred suspension of lithium aluminum hydride (3.20 g, 84.3 mmol) in anhydrous diethyl ether (100 mL) was added dropwise 4-cyanomethyl-2,6-di-*tert*-butylphenol (**5**) (9.82 g, 40.0 mol) in anhydrous diethyl ether (75 mL) at 0 °C under nitrogen. The vigorously stirred reaction mixture was gently refluxed under nitrogen for 4 h. After being cooled to 0 °C, the excess lithium aluminum hydride was decomposed by adding 1 N sodium hydroxide solution and water. The resulting mixture was filtered, and organic layer was separated, washed with water, dried over magnesium sulfate, and evaporated. The residue was recrystallized from ligroin to give 4-(2-aminoethyl)-2,6-di-*tert*-butylphenol (**6**, 7.50 g, 75%) as a yellow solid: mp 105–106 °C; ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 18H, *tert*-butyl), 2.66 (t, 2H, $-CH_2-C$), 2.93 (t, 2H, $-CH_2N-$), 5.09 (s, 1H, −OH), 7.09 (s, 2H, ArH).

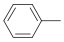
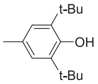
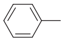
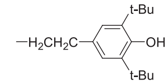
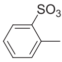
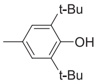
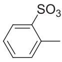
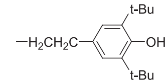
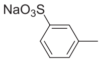
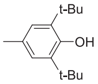
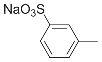
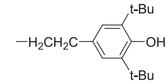
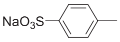
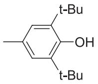
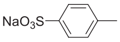
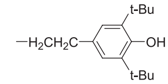
4.2.6. Preparation of disodium 4,4′-diaminostilbene-2,2′-sulfonate (7)

To a suspension of 4,4′-diaminostilbene-2,2′-disulfonic acid (95%, 4.15 g, 10.7 mmol) was added portionwise sodium carbonate (1.15 g, 10.9 mmol), and then stirred until a clear solution was obtained. The solution was used for the next step without further purification.

4.2.7. General procedure for the preparation of triazine-stilbene fluorescent brighteners containing the phenolic antioxidant derivatives (11a–h)

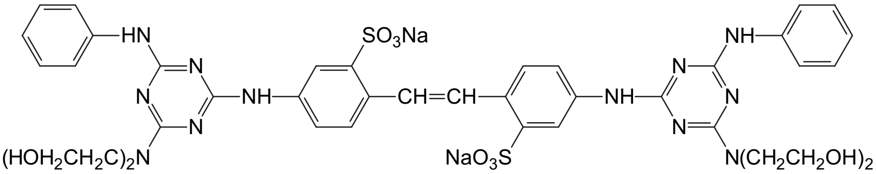
To a stirred suspension of 2,4,6-trichloro-1,3,5-triazine (**8**, 3.95 g, 21.4 mmol), $CaCO_3$ (1.07 g, 10.7 mmol) and small amounts of dispersant agent in water (50 mL) was added dropwise a solution of disodium 4,4′-diaminostilbene-2,2′-disulfonate (**7**, 10.6 mmol) at a range of 0–5 °C. After addition was completed, the reaction mixture was stirred 2 h below 5 °C. To the reaction mixture were added $CaCO_3$ (1.07 g, 10.7 mmol),

Table 1
Characterization data of the triazine-stilbene fluorescent brighteners containing the phenolic antioxidant derivatives (**11a–h**)

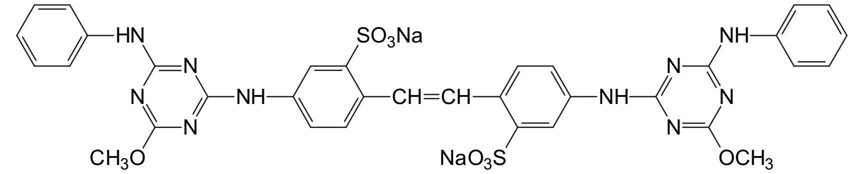
Compound	R	R'	Yield (%)	UV (λ_{max}) (nm, in MeOH)
11a			83	344, 268
11b			94	351, 268
11c			67	349, 278
11d			74	342, 273
11e			84	347, 269
11f			77	337, 271
11g			81	342, 285
11h			82	344, 280

antifoaming agent and aniline (or sodium aminobenezenesulfonate derivative) (21.4 mmol), and then allowed to warm to 30 °C. After being stirred at 30 °C for 3 h, $CaCO_3$ (1.07 g, 10.7 mmol) and phenolic derivative (**3** or **6**, 21.4 mmol) were added portionwise to the resulting reaction mixture. After being heated under reflux for 3 h, the reaction mixture was allowed to cool to room temperature. The precipitate was filtered and dried.

*4.2.7.1. Synthesis of the compound **11a**.* Yields 83%; ^1H NMR (DMSO-d_6) δ 1.39 (s, 18H, *tert*-butyl), 6.51



CI86



CI90

Fig. 4. The structures of **CI86** and **CI90**.

Table 2
Color fastness of cotton fiber dyed with compounds (**11a**–**h**)

No.	o.w.f. (%)	Whiteness	L^*	a^*	b^*	No.	o.w.f. (%)	Whiteness	L^*	a^*	b^*
CI86	0.05	123.69	91.91	2.55	−9.06	**CI90**	0.05	120.93	92.59	2.83	−8.74
	0.1	132.07	91.77	2.78	−10.75		0.1	128.36	91.45	3.10	−10.30
	0.3	141.05	92.52	2.17	−12.00		0.3	138.43	92.45	2.90	−11.83
	0.5	142.28	92.85	1.52	−11.90		0.5	139.06	92.45	2.67	−11.84
	1	138.00	93.02	0.22	−10.56		1	138.67	92.22	2.03	−11.62
11a	0.05	92.57	91.18	0.26	−2.34	**11e**	0.05	78.52	90.92	0.00	0.25
	0.1	90.79	91.35	−0.01	−1.83		0.1	82.19	90.77	−0.12	−0.40
	0.3	83.83	91.25	−1.10	0.06		0.3	84.51	91.04	−0.44	−0.52
	0.5	81.12	91.08	−1.45	0.68		0.5	84.37	91.04	−0.56	−0.40
	1	80.22	90.92	−1.44	0.78		1	82.05	91.00	−0.91	0.21
11b	0.05	78.34	90.97	−0.11	0.40	**11f**	0.05	78.69	91.09	0.02	0.22
	0.1	78.02	90.88	−0.03	0.32		0.1	78.01	90.87	−0.03	0.30
	0.3	76.76	90.78	−0.53	0.86		0.3	73.16	90.63	−0.43	1.47
	0.5	74.71	90.71	−0.91	1.39		0.5	71.53	90.28	−0.37	1.73
	1	71.29	90.8	−1.35	2.31		1	65.54	90.96	−1.63	3.41
11c	0.05	77.70	90.81	−0.44	0.62	**11g**	0.05	88.22	91.29	0.37	−1.59
	0.1	84.62	91.28	0.81	−1.12		0.1	90.53	91.04	0.49	−2.15
	0.3	78.00	90.84	−0.77	0.80		0.3	91.53	91.41	−0.31	−1.75
	0.5	77.93	90.87	−0.90	0.87		0.5	88.79	91.20	−0.61	−1.13
	1	78.38	91.13	−0.91	0.89		1	88.70	91.61	−0.81	−0.83
11d	0.05	75.71	91.06	0.04	0.76	**11h**	0.05	76.91	90.74	0.08	0.39
	0.1	76.93	90.88	0.14	0.52		0.1	78.16	90.75	−0.21	0.36
	0.3	73.52	91.08	−0.74	0.62		0.3	74.15	90.62	−0.60	1.30
	0.5	71.65	90.74	−0.89	1.90		0.5	70.11	90.71	−0.98	2.28
	1	64.18	90.69	−1.47	3.58		1	69.31	90.47	−0.97	2.34

(s, 2H, −OH), 6.93 (t, 6H, ArH), 7.05 (s, 4H, ArH), 7.23 (d, 4H, ArH), 7.37 (d, 2H, ArH), 7.67 (s, 2H, −CH=CH), 7.80 (d, 2H, ArH), 8.08 (s, 2H, ArH), 8.90 (s, 2H, −NH), 9.19 (s, 2H, −NH), 10.27 (s, 2H, −NH).

*4.2.7.2. Synthesis of the compound **11b**.* Yields 94%; ^{1}H NMR (DMSO-d_6) δ 1.36 (s, 18H, *tert*-butyl), 2.77 (s, 2H, $-CH_2-$), 3.51 (t, 2H, $-CH_2N-$), 6.71 (s, 2H, −OH), 6.93 (s, 4H, ArH), 6.95 (m, 10H, ArH), 7.61 (d, 2H, ArH), 7.23 (s, 2H, −CH=CH−), 7.82 (d, 2H, ArH), 8.01 (s, 2H, ArH), 8.97 (s, 2H, −NH), 9.08 (s, 2H, −NH), δ 10.25 (s, 2H, −NH).

Table 3
Various fastness of cotton fiber dyed with compounds (**11a**–**h**)

Compound	Chlorinated water fastness	Light fastness	Rubbing fastness	
			Dry	Wet
CI86	3	2	3–4	2
CI90	3–4	2	3–4	2
11a	1–2	3	4	3
11b	2	3	4–5	4
11c	2–3	1	4	3–4
11d	3	3	4–5	3–4
11e	3–4	2	4	2–3
11f	3	3	4	3–4
11g	2–3	2	4–5	3–4
11h	1–2	2	4	3

*4.2.7.3. Synthesis of the compound **11c**.* Yields 67%; ^{1}H NMR (DMSO-d_6) δ 1.39 (s, 18H, *tert*-butyl), 6.51 (s, 2H, −OH), 6.62 (d, 2H, ArH), 6.92 (t, 2H, ArH), 7.29 (s, 4H, ArH), 7.37 (t, 2H, ArH), 7.68 (d, 2H, ArH), 7.75 (s, 2H, −CH=CH−), 7.82 (d, 2H, ArH), 8.07 (s, 2H, ArH), 8.62 (s, 2H, −NH), 9.08 (s, 2H, −NH), δ 10.27 (s, 2H, −NH).

*4.2.7.4. Synthesis of the compound **11d**.* Yields 74%; ^{1}H NMR (DMSO-d_6) δ 1.36 (s, 18H, *tert*-butyl), 2.75 (s, 2H, $-CH_2-$), 3.50 (t, 2H, $-CH_2NH$), 6.71 (t, 2H, ArH), 6.93 (t, 2H, ArH), 6.96 (s, 4H, ArH), 7.21 (t, 2H, ArH), 7.56 (d, 2H, ArH), 7.68 (s, 2H, −CH=CH−), 7.80 (d, 2H, ArH), 7.79 (s, 2H, ArH), 8.59 (d, 2H, ArH),

Table 4
Washing fastness of cotton fiber dyed with compounds (**11a**–**h**)

Compound	Acetate	Cotton	Nylon	PET	Acrylic	Wool
CI86	4–5	1	3	4–5	4–5	4–5
CI90	4	1	3	4–5	4–5	4–5
11a	4–5	2	4–5	4–5	4–5	4–5
11b	4–5	3–4	4–5	4–5	4–5	4–5
11c	4–5	2–3	4–5	4–5	4–5	4–5
11d	4–5	2	4–5	4–5	4–5	4–5
11e	4	1–2	4–5	4–5	4–5	4–5
11f	4	3–4	4–5	4–5	4–5	4–5
11g	4–5	2	4–5	4–5	4–5	4–5
11h	4–5	2–3	4–5	4–5	4–5	4–5

9.66 (s, 2H, −NH), 9.73 (s, 2H, −NH), 10.25 (s, 2H, −NH).

*4.2.7.5. Synthesis of the compound **11e**.* Yields 84%; ^{1}H NMR (DMSO-d_6) δ 1.39 (s, 18H, *tert*-butyl), 6.69 (s, 2H, −OH), 7.21 (d, 2H, ArH), 7.37 (s, 4H, ArH), 7.37 (t, 2H, ArH), 7.62 (s, 2H, −CH=CH−), 7.81 (m, 4H, ArH), 8.06 (s, 4H, ArH), 8.28 (d, 2H, ArH), 8.90 (s, 2H, −NH), 9.16 (s, 2H, −NH), 10.26 (s, 2H, −NH).

*4.2.7.6. Synthesis of the compound **11f**.* Yields 77%; ^{1}H NMR (DMSO-d_6) δ 1.36 (s, 18H, *tert*-butyl), 2.79 (s, 2H, $-CH_2-$), 3.55 (t, 2H, $-CH_2NH$), 6.67 (s, 2H, −OH), 6.93 (d, 2H, ArH), 6.98 (s, 4H, ArH), 7.19 (t, 2H, ArH), 7.60 (d, 2H, ArH), 7.73 (s, 2H, −CH=CH−), 7.80 (d, 2H, ArH), 8.01 (s, 4H, ArH), 8.20 (d, 2H, ArH), 9.17 (s, 2H, −NH), 9.23 (s, 2H, −NH), 10.26 (s, 2H, −NH).

*4.2.7.7. Synthesis of the compound **11g**.* Yields 81%; ^{1}H NMR (DMSO-d_6) δ 1.40 (s, 18H, *tert*-butyl), 6.74 (s, 2H, −OH), 7.24 (d, 4H, ArH), 7.29 (s, 4H, ArH), 7.50 (d, 2H, ArH), 7.66 (s, 2H, −CH=CH−), 7.81 (d, 2H, ArH), 8.03 (s, 2H, ArH), 8.35 (d, 4H, ArH), 8.92 (s, 2H, −NH), 9.15 (s, 2H, −NH), 10.27 (s, 2H, −NH).

*4.2.7.8. Synthesis of the compound **11h**.* Yields 82%; ^{1}H NMR (DMSO-d_6) δ 1.37 (s, 18H, *tert*-butyl), 2.80 (s, 2H, $-CH_2-$), 3.51 (t, 2H, $-CH_2NH$), 6.67 (s, 2H, −OH), 6.93 (d, 4H, ArH), 6.97 (s, 4H, ArH), 7.50 (d, 2H, ArH), 7.59 (s, 2H, −CH=CH−), 7.80 (d, 2H, ArH), 8.01 (s, 2H, ArH), 8.38 (d, 4H, ArH), 9.15 (s, 2H, −NH), 9.24 (s, 2H, −NH), 10.26 (s, 2H, −NH).

4.3. Dyeing properties

4.3.1. Dyeing procedure

Dyeing of cotton was carried out precisely at 80 °C for 1 h. It was prepared with a paste of finely powdered dye, 0.1% aqueous NaOH solution and water at 40 °C and it was raised to 80 °C for cotton at the rate of 1 °C/min.

4.3.2. Color fastness test

The light fastness test was assessed by using Xenon arc lamp method in accordance with ISO 105-B02. The rubbing fastness test was carried out using crock meter method in accordance with ISO 105-X12 and the wash fastness test in accordance with ISO 105-C01 and chlorinated water fastness test in accordance with KS K 0725. The results are given in Tables 3 and 4.

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References

[1] Milligan B, Holt A. Aust J Chem 1974;27:195–203.
[2] Grabchev I. Dyes Pigments 1995;29:155–60.
[3] Konstantinova TM, Konstantinov HrI, Betcheva RI. Dyes Pigments 1999;43:197–201.
[4] Grabchev I, Philipova T. Dyes Pigments 2000;44:175–80.
[5] Hurd RP, Reagan BM. J Soc Dyers Colour 1990;106:49–54.
[6] Jirackova L, Pospisil J. Eur Polym J 1973;9:71–6.
[7] Prusikova M, Jirackova L, Pospisil J. Collect Czech Chem Commun 1972;37:3788–99.
[8] Pospisil J, Kotulak L, Kahovec J. Eur Polym J 1970;6:841–52.
[9] Kjaer AM, Ulstrup J. J Am Chem Soc 1987;109:1934–42.
[10] Vaughan WR, Finch GK. J Org Chem 1956;21:1201–10.
[11] Ecke GG, Mich F, Kolka AJ. US patent 2,932,942; 1960.
[12] Galvin M. US patent 3,004,042; 1961.
[13] Neureiter NP. J Org Chem 1963;28:3486–90.
[14] Dreckmann-Behrendt B,Witte E, Wolff H, Dresel H. European patent 0404039; 1990.
[15] Alsins J, Bjorling M, Furo I, Egle V. J Phys Org Chem 1999;12: 171–5.
[16] Hoog P, Gomez P, Driessen W, Reedijk J. Tetrahedron Lett 2002; 43:6783–6.
[17] Yang X, Lowe CR. Tetrahedron Lett 2003;44:1359–62.