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The synthesis and properties of triazine–stilbene fluorescent brighteners containing the phenolic antioxidant [II]

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Abstract

New 18 triazine–stilbene fluorescent brighteners containing the phenolic antioxidant have been synthesized. The obtained compounds (**7a–i** and **8a–i**) were characterized by the analysis of proton NMR spectrum and confirmed by UV spectrum. The physical properties of the new compounds were performed by fastness and whiteness measurement and 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

Fluorescent brightener is a dye which is frequently used for commercial purpose. Fluorescent brightener is used to brighten not only textiles but also paper and plastic [1–3]. Fluorescent brightener is a strongly fluorescent substance that emits light in the blue violet region of the visible spectrum. A typical fluorescent brightener absorbs light in ultraviolet ray (330–380 nm) and emits visible blue lights (400–450 nm) [4]. It is necessary that the fluorescent brightener has a planar molecular structure with conjugated double bonds and electron-donating groups to show the high fluorescence activity [5]. Fluorescent brightener should present a high quality of whiteness and fastness. However, as the fluorescent brightener is exposed to the sunlight, the whiteness of it is diminished. This happens because the chemical structure of fluorescent brightener is destroyed by the autoxidation which is developed from free radical generated from the sunlight.

Previously, we reported disodium 4,4′-bis(triazinylamino)stilbene-2,2′-disulfonate derivatives containing the 4-amino-2,6-di-*tert*-butylphenol (**1**) or 4-(2-aminoethyl)-2,6-di-*tert*-butylphenol (**2**) as phenolic antioxidants [6].

As the work continued for the development of new antioxidant fluorescent brighteners, 18 new triazine–stilbene fluorescent brighteners containing the phenolic antioxidant on triazine moiety have been synthesized. The structures of obtained compounds were characterized by the analysis of proton NMR spectrum and confirmed by UV spectrum. The physical properties of the new compounds were performed by various fastness and whiteness measurements.

2. Result and discussion

2.1. Synthesis of triazine–stilbene fluorescent brighteners containing the phenolic antioxidant derivatives

The synthesis of the triazine–stilbene fluorescent brighteners containing the phenolic antioxidant derivatives was started from the reaction of disodium

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4,4′-diaminostilbene-2,2′-disulfonate (**3**) with two equivalent of 2,4,6-trichloro-1,3,5-triazine (**4**). It is well known that three chloro groups of compound (**4**) show the different chemical reactivities with the nucleophiles depending on the reaction temperature [7,8].

After stirring disodium 4,4′-diaminostilbene-2,2′-disulfonate (**3**) with 2 equivalent of 2,4,6-trichloro-1,3,5-triazine (**4**) at 0–5 °C, the resulting disodium 4,4′-bis (2,4-dichloro-1,3,5-triazin-6-yl)diaminostilbene-2,2′-disulfonate (**5**) was treated with amine derivative at 30 °C without separation. The substitution of an aliphatic or an aromatic amine derivative with a second chloride on triazine moiety was established within 3–4 h.

Finally, 4-amino-2,6-di-*tert*-butylphenol (**1**) [6,9–12] or 4-(2-aminoethyl)-2,6-di-*tert*-butylphenol (**2**) [6,13,14] was added in situ to the reaction mixture. The third substitution reaction occurred when the temperature reached at 80 °C. The synthetic procedures of triazine–stilbene fluorescent brighteners containing the phenolic antioxidant derivatives are summarized in Scheme 1 and relevant data are given in Table 1.

2.2. Colour assessment and various fastness

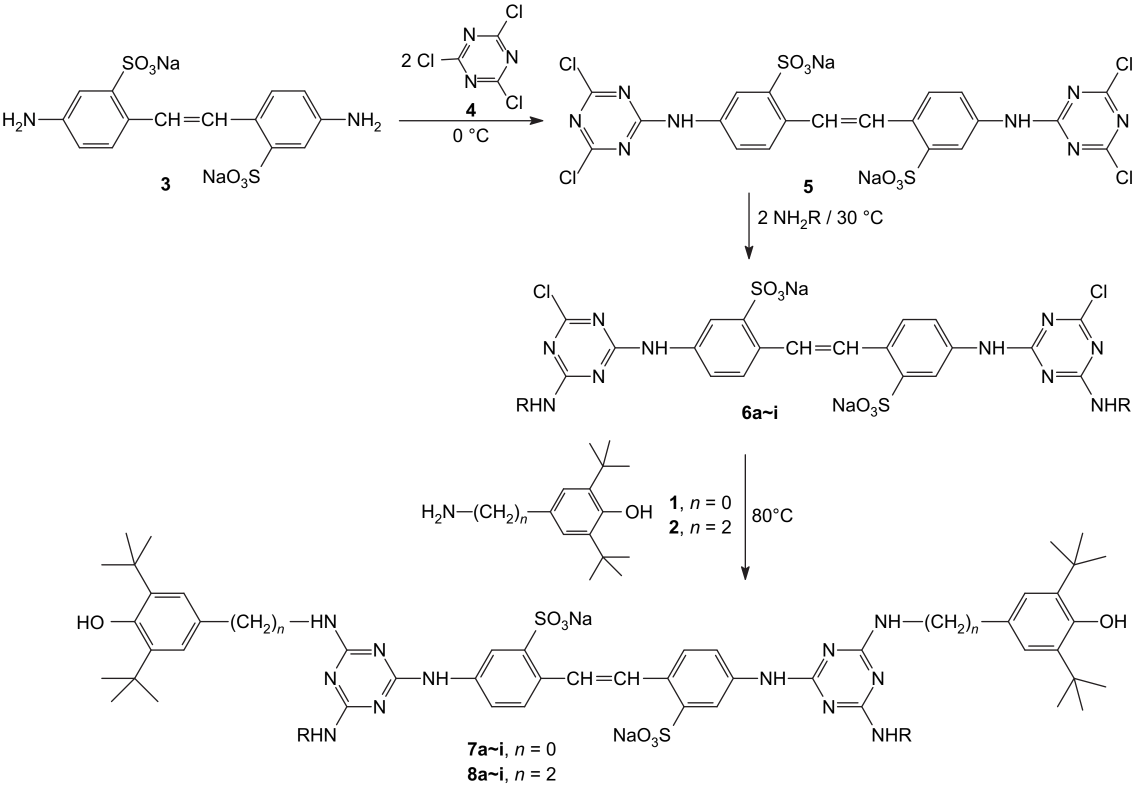
Characteristics of the compounds (**7a–i** and **8a–i**) are compared with **CI86** and **CI90** which are used for commercial purpose. The chemical structures of **CI86** and **CI90** are shown in Fig. 1.

The newly synthesized compounds (**7a–i** and **8a–i**) 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 whiteness and CIE L^*, a^*, b^* coordinates were determined. The data obtained are presented and compared with those of **CI86** and **CI90** in Table 2. It is apparent that the compounds (**7a–i** and **8a–i**) showed a lower degree of whiteness than **CI86** and **CI90**.

The data of light fastness and chlorinated water fastness appear in Table 3. The compound **8f** presented excellent resistance to the light. The rest of compounds showed the same degree of light fastness of **CI86** and **CI90.** The fastnesses of compound **7i** and **8g–i** to chlorinated water are at around a similar level to **CI86** and **CI90**, and that of the rest of compounds are below the level of **CI86** and **CI90**. The compounds (**7a–i** and **8a–i**) provided the better rubbing fastness than **CI86** and **CI90** as shown in Table 3.

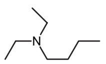
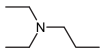
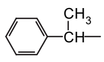
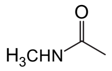
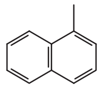
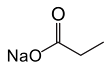
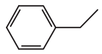
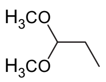
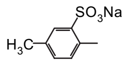
Washing fastness data are given in Table 4. The results from the washing fastness test showed that all the compounds (**7a–i** and **8a–i**) preserved excellent fastness, especially superior for cotton than **CI86** and **CI90**.

Generally, the fastnesses of compounds (**7a–i** and **8a–i**) are at an advanced level which can be commercially viable, but the whitenesses of the compounds are found at relatively lower level. That is because the solubility of antioxidant is not good and thus the solubility of the compound is fairly low.



Scheme 1.

Table 1
Characterization data of the triazine–stilbene fluorescent brighteners containing the phenolic antioxidant derivatives (**7a–i** and **8a–i**)

R	Entry	Yield (%)	UV (λ_{max}) (nm in MeOH)	Entry	Yield (%)	UV (λ_{max}) (nm in MeOH)
	**7a**	96	361	**8a**	68	353
	**7b**	98	356	**8b**	63	358
	**7c**	63	350	**8c**	96	350
	**7d**	83	350	**8d**	39	343
	**7e**	43	350	**8e**	82	348
	**7f**	96	351	**8f**	54	352
	**7g**	46	349	**8g**	92	347
	**7h**	21	351	**8h**	81	344
	**7i**	98	344	**8i**	75	347

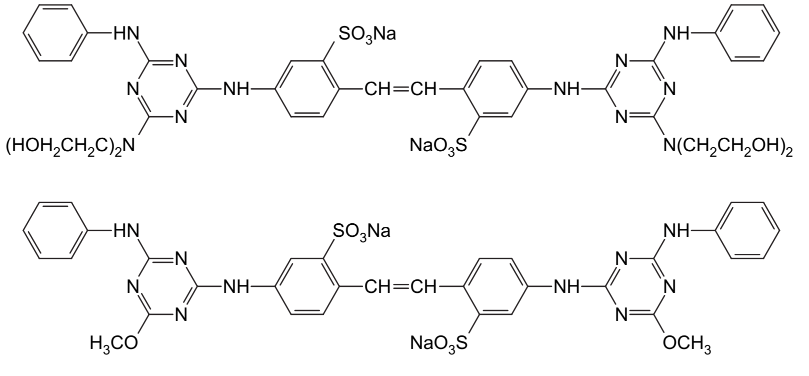
3. Conclusion

Various triazine–stilbene derivatives containing the phenolic antioxidant derivatives (**1** and **2**) were prepared as antioxidant fluorescent brighteners (**7a–i** and **8a–i**) in good yield. On the basis of the results obtained from the various physical tests, compounds (**7a–i** and **8a–i**) showed the lower degree of whiteness than **CI86** and **CI90**. Also light fastness and chlorinated water fastness showed the same degree of **CI86** and **CI90**. On the other hand, in rubbing fastness and washing fastness, the compounds (**7a–i** and **8a–i**) showed excellent fastness.

4. Experimental

4.1. Materials and analysis

All chemicals, which were purchased from commercial sources (Aldrich, Merck, Duksan, Yakuri, Junsei, etc.), were of analytical grade. The solvents



CI86

CI90

Fig. 1. The structures of **CI86** and **CI90**.

Table 2
Colour fastness of cotton fiber dyed with compounds (**7a–i** and **8a–i**)

Entry	o.w.f (%)	Whiteness	L^*	a^*	b^*	Entry	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	95.52	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
7a	0.05	88.88	90.72	0.65	−2.07	**8a**	0.05	79.58	91.14	0.32	−0.15
	0.1	92.48	90.90	0.69	−2.57		0.1	79.29	90.98	0.22	−0.16
	0.3	89.24	91.02	0.08	−1.57		0.3	76.13	90.96	−0.21	0.51
	0.5	86.16	90.85	0.08	−0.91		0.5	70.32	90.92	−0.57	1.70
	1	79.36	90.35	−0.33	0.45		1	65.83	90.70	−0.95	2.53
7b	0.05	82.74	90.18	0.70	−1.15	**8b**	0.05	74.83	90.75	0.21	0.67
	0.1	87.24	90.83	0.65	−1.74		0.1	76.33	91.03	0.05	0.49
	0.3	87.69	90.83	0.23	−1.54		0.3	67.18	90.95	−0.37	2.38
	0.5	89.17	91.18	0.25	−1.65		0.5	69.58	90.28	−0.40	1.56
	1	83.57	90.64	0.16	−0.55		1	51.12	89.50	−0.82	5.02
7c	0.05	83.77	91.07	0.06	−0.69	**8c**	0.05	76.96	91.25	0.17	0.45
	0.1	85.07	91.02	−0.17	−0.80		0.1	80.04	90.32	0.25	−0.17
	0.3	86.26	91.08	−0.47	−0.85		0.3	86.86	91.41	1.15	−1.52
	0.5	84.09	90.74	−0.61	−0.49		0.5	78.53	91.39	−0.05	0.19
	1	80.87	90.96	−0.98	0.41		1	38.89	91.17	−3.70	8.31
7d	0.05	77.48	90.87	−0.30	0.61	**8d**	0.05	77.68	91.05	0.36	0.20
	0.1	81.83	91.44	−0.45	0.07		0.1	75.74	90.75	0.18	0.47
	0.3	81.28	91.19	−0.65	0.22		0.3	75.61	91.28	0.16	0.74
	0.5	80.15	90.95	−0.81	0.42		0.5	75.41	91.09	0.17	0.71
	1	78.88	91.10	−0.97	0.82		1	77.06	90.07	0.31	0.30
7e	0.05	82.34	90.66	0.23	−0.66	**8e**	0.05	74.65	90.09	0.51	0.40
	0.1	83.92	90.93	−0.05	−0.69		0.1	77.92	90.28	0.92	−0.20
	0.3	80.84	90.78	−0.53	0.15		0.3	77.95	89.71	1.53	−0.45
	0.5	80.88	90.71	−0.51	0.12		0.5	69.36	89.77	1.00	1.37
	1	78.46	90.98	−0.77	0.87		1	51.57	88.55	1.49	4.49
7f	0.05	78.77	90.88	0.15	0.17	**8f**	0.05	71.93	91.16	0.01	1.46
	0.1	82.26	90.74	0.14	−0.58		0.1	71.81	91.08	−0.03	1.45
	0.3	87.93	91.11	0.02	−1.38		0.3	53.86	90.29	−0.79	4.82
	0.5	87.54	90.77	−0.14	−1.33		0.5	62.68	90.68	−0.37	3.17
	1	84.95	90.66	−0.24	−0.70		1	56.91	90.62	−0.63	4.34
7g	0.05	82.40	90.46	0.35	−0.84	**8g**	0.05	82.28	91.30	0.56	−0.66
	0.1	89.25	90.85	0.23	−1.84		0.1	84.89	91.17	0.69	−1.26
	0.3	88.10	90.97	−0.20	−1.33		0.3	84.14	91.31	0.70	−1.03
	0.5	88.11	91.02	−0.35	−1.24		0.5	82.56	90.89	0.62	−0.88
	1	87.86	91.56	−0.75	−0.79		1	79.25	90.87	0.59	−0.19
7h	0.05	76.84	90.85	0.17	0.37	**8h**	0.05	78.99	90.65	0.57	−0.26
	0.1	78.26	91.09	0.02	0.31		0.1	74.84	90.77	0.30	0.68
	0.3	81.49	91.13	−0.01	−0.24		0.3	78.87	90.99	0.53	−0.07
	0.5	82.16	90.87	0.02	−0.39		0.5	64.63	90.56	−0.09	2.73
	1	85.09	91.45	−0.34	−0.56		1	60.79	90.24	−0.24	3.38
7i	0.05	83.20	91.45	0.56	−0.78	**8i**	0.05	77.64	90.29	0.30	0.33
	0.1	84.39	91.38	0.64	−1.06		0.1	71.71	91.26	−0.25	1.57
	0.3	94.87	91.51	1.16	−3.22		0.3	69.87	91.04	−0.33	1.85
	0.5	94.72	91.37	1.07	−3.25		0.5	59.87	90.67	−0.81	3.77
	1	96.43	91.44	1.07	−3.58		1	56.93	90.71	−0.98	4.40

were purified by distillation and the other reagents were used without further purification. The ^{1}H NMR spectrum was measured at 300 MHz using a Varian Mercury 300. The UV spectrum was 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 150 S. 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 a SF600 Data color.

*4.2. General procedure for the preparation of triazine–stilbene fluorescent brighteners containing the phenolic antioxidant derivatives (**7a–i** and **8a–i**)*

To a stirred suspension of 2,4,6-trichloro-1,3,5-triazine (**4**, 3.95 g, 21.4 mmol), $CaCO_3$ (1.07 g, 10.7 mmol)

Table 3
Various fastness of cotton fiber dyed with compounds (**7a–i** and **8a–i**)

Compound	Chlorinated water fastness	Light fastness	Rubbing fastness	
			Dry	Wet
CI86	3	2	3–4	2
CI90	3–4	2	3–4	2
7a	1–2	2	4	3
7b	2	2	4	3
7c	2–3	2	4	2–3
7d	1–2	2	4	2–3
7e	1–2	2	4	3–4
7f	1–2	2	4	3
7g	2	2	4	3
7h	1	2	4–5	2–3
7i	4	2	3–4	3–4
8a	2	2	4	3
8b	2	2	4	4
8c	3–4	2	3	3–4
8d	2	2	3	4
8e	2–3	2	3–4	4–5
8f	4–5	5	4–5	4–5
8g	3	2	3–4	4
8h	3–4	2	4	3–4
8i	3–4	2	4	4

and small amounts of dispersant agent in water (50 mL) a solution of disodium 4,4′-diaminostilbene-2,2′-disulfonate (**3**, 10.6 mmol) was added dropwise at the temperature range 0–5 °C. After the addition was completed, the reaction mixture was stirred for 2 h below 5 °C. To the reaction mixture $CaCO_3$ (1.07 g, 10.7 mmol), and an antifoaming agent and amine derivative (21.4 mmol) were added, 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 a phenolic derivative (**1** or **2**, 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.

Table 4
Washing fastness of cotton fiber dyed with compounds (**7a–i** and **8a–i**)

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
7a	4–5	3	4–5	4–5	4–5	4–5
7b	4–5	3–4	4–5	4–5	4–5	4–5
7c	4–5	2–3	4–5	4–5	4–5	4–5
7d	4–5	1–2	4–5	4–5	4–5	4–5
7e	4–5	3	4–5	4–5	4–5	4–5
7f	4–5	1–2	4–5	4–5	4–5	4–5
7g	4–5	2–3	4–5	4–5	4–5	4–5
7h	4–5	1–2	4–5	4–5	4–5	4–5
7i	4–5	2–3	4–5	4–5	4–5	4–5
8a	4–5	4	4–5	4–5	4–5	4–5
8b	4–5	4–5	4–5	4–5	4–5	4–5
8c	4–5	2	4–5	4–5	4–5	4–5
8d	4–5	4	4–5	4–5	4–5	4–5
8e	4–5	4–5	4–5	4–5	4–5	4–5
8f	4–5	4–5	4–5	4–5	4–5	4–5
8g	4–5	4	4–5	4–5	4–5	4–5
8h	4–5	4	4–5	4–5	4–5	4–5
8i	4–5	4–5	4–5	4–5	4–5	4–5

*4.2.1. Synthesis of the compound **7a***

Yields 96%; ^{1}H NMR (DMSO–d_6) δ 1.14(t, 12H, $-CH_3$), 1.35(s, 36H, *tert*-butyl), 1.91(m, 8H, $-CH_2$), 3.10(s, 12H, $-CH_2$), 6.65(s, 2H, –OH), 6.99(s, 4H, ArH), 7.36(d, 2H, ArH), 7.57(d, 2H, –CH=CH–), 7.78(d, 2H, ArH), 7.99(s, 2H, ArH), 8.83(s, 2H, –NH), 9.07(s, 2H, –NH), 10.26(s, 2H, –NH).

*4.2.2. Synthesis of the compound **7b***

Yields 98%; ^{1}H NMR (DMSO–d_6) δ 1.15(t, 12H, $-CH_3$), 1.39(s, 36H, *tert*-butyl), 3.19(m, 16H, $-CH_2$), 6.65(s, 2H, –OH), 7.32(s, 4H, ArH), 7.55(d, 2H, ArH), 7.81(s, 2H, –CH=CH–), 7.99(d, 2H, ArH), 8.29(s, 2H, ArH), 9.03(s, 2H, –NH), 9.41(s, 2H, –NH), 10.40 (s, 2H, –NH).

*4.2.3. Synthesis of the compound **7c***

Yields 63%; ^{1}H NMR (DMSO–d_6) δ 1.38(s, 36H, *tert*-butyl), 1.41(s, 6H, $-CH_3$), 5.24(s, 2H, –CH), 6.67(s, 2H, –OH), 7.21(s, 4H, ArH), 7.36(m, 10H, ArH), 7.45(d, 2H, ArH), 7.67(s, 2H, –CH=CH–), 7.80(d, 2H, ArH), 8.06(s, 2H, ArH), 8.41(s, 2H, –NH), 10.30(s, 4H, –NH).

*4.2.4. Synthesis of the compound **7d***

Yields 83%; ^{1}H NMR (DMSO–d_6) δ 1.23(s, 6H, $-CH_3$), 1.39(s, 36H, *tert*-butyl), 6.67(s, 2H, –OH), 6.93(s, 4H, ArH), 7.49(d, 2H, ArH), 7.68(s, 2H, –CH=CH–), 7.76(d, 2H, ArH), 8.07(s, 2H, ArH), 8.39(s, 2H, –NH), 10.30(s, 4H, –NH).

*4.2.5. Synthesis of the compound **7e***

Yields 43%; ^{1}H NMR (DMSO–d_6) δ 1.37(s, 36H, *tert*-butyl), 6.70(s, 2H, –OH), 6.93(s, 2H, ArH), 7.01(s, 2H, ArH), 7.07(d, 2H, ArH), 7.61(s, 14H, Naphthyl), 7.70(m, 2H, –CH=CH–), 7.74(s, 2H, ArH), 7.95(d, 2H, ArH), 9.03(s, 2H, –NH), 9.15(s, 2H, –NH), 10.24(s, 2H, –NH).

*4.2.6. Synthesis of the compound **7f***

Yields 96%; ^{1}H NMR (DMSO–d_6) δ 1.39(s, 36H, *tert*-butyl), 3.81(d, 4H, $-CH_2$), 6.62(s, 2H, –OH), 7.19(s, 4H, ArH), 7.37(d, 2H, ArH), 7.59(s, 2H, –CH=CH–), 7.82(d, 2H, ArH), 8.02(s, 2H, ArH), 8.98(s, 2H, –NH), 9.99(s, 2H, –NH). 10.14(s, 2H, –NH).

*4.2.7. Synthesis of the compound **7g***

Yields 46%; ^{1}H NMR (DMSO–d_6) δ 1.37(s, 36H, *tert*-butyl), 4.57(d, 4H, $-CH_2$), 6.591(s, 2H, –OH), 7.39(m, 10H, ArH), 7.52(s, 4H, ArH), 7.62(d, 2H, ArH), 7.80(s, 2H, $-CH{=}CH-$), 8.03(d, 2H, ArH), 8.28(s, 2H, ArH), 8.79(s, 2H, $-NH$), 10.12(s, 2H, $-NH$), 10.26(s, 2H, $-NH$).

4.2.8. Synthesis of the compound **7h**

Yields 21%; ^{1}H NMR (DMSO$-d_6$) δ 1.39(s, 36H, *tert*-butyl), 1.90(s, 2H, $-CH$), 3.50(s, 12H, $-CH_3$), 4.53(d, 4H, $-CH_2$), 6.63(s, 2H, $-OH$), 7.38(s, 4H, ArH), 7.63(d, 2H, ArH), 7.72(s, 2H, $-CH{=}CH-$), 7.81(d, 2H, ArH), 8.05(s, 2H, ArH), 8.39(s, 2H, $-NH$), 8.96(s, 2H, $-NH$), 10.30(s, 2H, $-NH$).

4.2.9. Synthesis of the compound **7i**

Yields 98%; ^{1}H NMR (DMSO$-d_6$) δ 1.39(s, 36H, *tert*-butyl), 2.09(s, 6H, $-CH_2$), 6.67(s, 2H, $-OH$), 7.26(d, 4H, ArH), 7.50(s, 4H, ArH), 7.65(s, 2H, $-CH{=}CH-$), 7.83(d, 4H, ArH), 8.07(s, 4H, ArH), 9.05(s, 2H, $-NH$), 9.47(s, 2H, $-NH$), 10.26(s, 2H, $-NH$).

4.2.10. Synthesis of the compound **8a**

Yields 68%; ^{1}H NMR (DMSO$-d_6$) δ 1.15(t, 12H, $-CH_3$), 1.37(s, 36H, *tert*-butyl), 1.89(m, 8H, $-CH_2$), 2.72(s, 4H, $-CH_2$), 3.12(s, 12H, $-CH_2$), 3.39(s, 4H, $-CH_2$), 6.70(s, 2H, $-OH$), 6.93(s, 4H, ArH). 7.32(d, 2H, ArH), 7.52(d, 2H, $-CH{=}CH-$), 7.71(d, 2H, ArH), 7.96(s, 2H, ArH), 8.83(s, 2H, $-NH$), 9.11(s, 2H, $-NH$), 10.22(s, 2H, $-NH$).

4.2.11. Synthesis of the compound **8b**

Yields 63%; ^{1}H NMR (DMSO$-d_6$) δ 1.15(s, 12H, $-CH_3$), 1.31(s, 36H, *tert*-butyl), 2.74(t, 8H, $-CH_2$), 2.97(t, 4H, $-CH_2$), 3.16(t, 8H, $-CH_2$), 3.69(s, 4H, $-CH_2$), 6.77(s, 2H, $-OH$), 6.93(s, 4H, ArH), 7.35(s, 2H, ArH), 7.52(d, 2H, $-CH{=}CH-$), 7.55(s, 2H, ArH), 7.94(s, 2H, ArH), 8.56(s, 2H, $-NH$), 9.14(s, 2H, $-NH$), 9.24(s, 2H, $-NH$).

4.2.12. Synthesis of the compound **8c**

Yields 96%; ^{1}H NMR (DMSO$-d_6$) δ 1.36(s, 36H, *tert*-butyl), 1.44(s, 6H, $-CH_3$), 2.71(t, 4H, $-CH_2$), 3.46(t, 4H, $-CH_2$), 5.21(m, 2H, $-CH$), 6.70(s, 2H, $-OH$), 6.93(s, 4H, ArH), 7.19(s, 2H, ArH), 7.40(m, 10H, ArH), 7.69(s, 2H, $-CH{=}CH-$), 7.99(d, 2H, ArH), 8.20(s, 2H, ArH), 8.97 (s, 2H, $-NH$), 10.06(s, 2H, $-NH$), 10.25(s, 2H, $-NH$).

4.2.13. Synthesis of the compound **8d**

Yields 39%; ^{1}H NMR (DMSO$-d_6$) δ 1.31(s, 6H, $-CH_3$), 1.36(s, 36H, *tert*-butyl), 2.74(m, 4H, $-CH_2$), 3.45(m, 4H, $-CH_2$), 6.70(s, 2H, $-OH$), 6.93(s, 4H, ArH), 7.57(d, 2H, ArH), 7.75(s, 2H, $-CH{=}CH-$), 8.02(d, 2H, ArH), 8.16(s, 2H, ArH), 9.92(s, 2H, $-NH$), 10.02(s, 4H, $-NH$).

4.2.14. Synthesis of the compound **8e**

Yields 82%; ^{1}H NMR (DMSO$-d_6$) δ 1.35(s, 36H, *tert*-butyl), 2.74(m, 4H, $-CH_2$), 3.50(s, 4H, $-CH_2$), 6.68(s, 2H, $-OH$), 6.74(s, 4H, ArH), 6.93(d, 2H, ArH), 7.07(d, 2H, $-CH{=}CH-$), 7.51(m, 14H, naphthyl), 7.72(d, 2H, ArH), 7.95(s, 2H, ArH), 9.03(s, 2H, $-NH$), 9.15(s, 2H, $-NH$), 10.24(s, 2H, $-NH$).

4.2.15. Synthesis of the compound **8f**

Yields 54%; ^{1}H NMR (DMSO$-d_6$) δ 1.36(s, 36H, *tert*-butyl), 2.71(t, 4H, $-CH_2$), 3.50(s, 4H, $-CH_2$), 3.84(d, 4H, $-CH_2$), 6.54(s, 2H, $-OH$), 7.20(s, 4H, ArH), 7.32(d, 2H, ArH), 7.60(s, 2H, $-CH{=}CH-$), 7.81(d, 2H, ArH), 8.01(s, 2H, ArH), 8.92(s, 2H, $-NH$), 9.99(s, 2H, $-NH$), 10.12(s, 2H, $-NH$).

4.2.16. Synthesis of the compound **8g**

Yields 92%; ^{1}H NMR (DMSO$-d_6$) δ 1.36(s, 36H, *tert*-butyl), 2.71(t, 4H, $-CH_2$), 3.51(s, 4H, $-CH_2$), 4.56(d, 4H, $-CH_2$), 6.67(s, 2H, $-OH$), 6.93(s, 4H, ArH), 7.23(d, 2H, ArH), 7.32(m, 10H, ArH), 7.51(s, 2H, $-CH{=}CH-$), 7.73(s, 2H, ArH), 8.03(s, 2H, ArH), 8.28(s, 2H, $-NH$), 8.67(s, 2H, $-NH$), 10.12(s, 2H, $-NH$).

4.2.17. Synthesis of the compound **8h**

Yields 81%; ^{1}H NMR (DMSO$-d_6$) δ 1.37(s, 36H, *tert*-butyl), 2.74(t, 4H, $-CH_2$), 3.43(m, 4H, $-CH_2$), 3.95(s, 12H, $-CH_3$), 4.55(m, 4H, $-CH_2$), 6.84(s, 2H, $-OH$), 6.93(d, 2H, ArH), 7.06(s, 4H, ArH), 7.56(d, 2H, $-CH{=}CH-$), 7.75(d, 2H, ArH), 8.03(s, 2H, ArH), 8.12 (s, 2H, $-NH$), 10.00(s, 2H, $-NH$), 10.13(s, 2H, $-NH$).

4.2.18. Synthesis of the compound **8i**

Yields 75%; ^{1}H NMR (DMSO$-d_6$) δ 1.34(s, 36H, *tert*-butyl), 2.22(s, 6H, $-CH_2$), 2.95(t, 4H, $-CH_2$), 3.49(t, 4H, $-CH_2$), 6.64(s, 2H, $-OH$), 6.81(s, 4H, ArH), 6.91(s, 4H, ArH), 7.47(m, 2H, $-CH{=}CH-$), 7.69(d, 4H, ArH), 7.95(s, 4H, ArH), 9.29(s, 2H, $-NH$), 9.58(s, 2H, $-NH$), 10.31(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. Colour 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, 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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