

Synthesis, Characterization and Applications of Some New Reactive Dyes Based on 5,5'-Methylenebis (2-Aminobenzenesulfonic Acid)

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Received: May 08, 2017; Accepted: June 08, 2017; Published: June 14, 2017

Abstract

Coupling of 2-chloro anilino cyanurated acids with 5,5'-methylenebis(2-sulfobenzenediazonium) chloride to give the corresponding methylene based reactive dyes in good yields. They were characterized by nitrogen elemental analysis, IR and ¹H NMR spectra. The dyeing performance of synthesized dyes has been examined on silk, wool and cotton. The synthesized dyes gave moderate to good light fastness, good to excellent wash fastness and rubbing fastness.

Keywords: 5,5'-methylenebis (2-aminobenzenesulfonic acid); Dyeing; Silk; Cotton; Wool; Fastness properties

Introduction

The structural development of new reactive dyes has been a subject of interest and many novel structures are useful in commercial application to wool, silk and cotton as well as their blends with other fibers has been discovered [1]. Reactive dyes have an efficient utilization and also a facile ease of washing out of the non-fixed portions which is the requirement of dyeing. They should have a high reactivity and good yield and should have produced high degrees of fixing in particular dyeing [2].

In the dye stuff research, reactive dyes are the newest addition and is the center of attention [3,4]. Hot brand reactive dyes are commercially important in reactive dyeing [5]. Due to their higher fixation yields on various fibres, they have been extensively recognized [6]. The popularity of reactive dyes is increased due to the ease of dyeing cellulosic fibres as they

Citation: Gamit EA, Patel SM, Savant SS, et al. Synthesis, Characterization and Applications of Some New Reactive Dyes based on 5, 5'-methylenebis (2-aminobenzenesulfonic acid). Int J Chem Sci 2017;15(2):142.

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have wide range of shades, easy application and very good wet fastness properties. The structural improvement of reactive chromogens, number and selection of reactive groups led to an increment in their use [7].

The chemicals containing s-Triazine nucleus have been widely applied in different fields viz, dyes, drugs, explosives, polymers, pesticides and trade good chemicals [8] as a result, experimental and theoretical research on these types of compounds have been widely carried out [9,10]. The s-triazine ring is an important conjugated heterocycle whose electronics properties are suitably different from those of benzene due to the alternate substitution of -CH- group by N atoms [11].

Materials and Methods

All the raw materials used were of commercial grade and were further purified by recrystallization and re-distillation before used. All the acid couplers were received from Atul Ltd., Valsad (TABLE 1). Melting points of all synthesized dyes were taken by open capillary method which expressed in °C and are uncorrected. Thin layer chromatography was carried out on silica gel G F254-coated aluminium sheets. IR spectra were recorded on a Perkin-Elmer Model 377 system using the KBr pellet. ¹H-NMR (400 MHz) in D₂O solvent, TMS is an internal standard, for UV-vis absorption spectra, thermo scientific evolution 300. Spectrophotometer is used at the wavelength of maximum absorption (λ_{max}) using water as solvent. The rota dyer instrument was used for dyeing in laboratory.

Synthesis

Synthesis of 5,5'-methylenebis-(2-aminobenzenesulfonic acid) [3]

At 50°C concentrated hydrochloric acid (50 mL) is added to the aqueous solution of 0.1 mol Orthonilic acid [1] (17.3 g), followed by the addition of 35 mL 3% aqueous formaldehyde [2] solution at 60°C with constant stirring. The reaction mass was stirred for an hour with maintaining the temperature at 60°C, which is then neutralized with 10% sodium hydroxide solution to obtain 5, 5'-methylenebis-(2-aminobenzenesulfonic acid) [3]. It was then filtered, washed with hot water, dried and recrystallized from alcohol. Yield: 88%, m.p. 130°C.

Tetrazotization of 5,5'-methylenebis-(2-aminobenzenesulfonic acid) [4]

To the suspension of 5, 5'-methylenebis-(2-aminobenzenesulfonic acid) [3] (3.58 g, 0.01 mol) in water (60 mL), conc. hydrochloric acid (1.5 mL) was added drop wise with stirring. To obtain clear solution, the temperature of mixture was gradually raised up to 70°C. Then the reaction mass was cooled at 0°C -5°C in an ice bath and NaNO₂ (1.38 g, 0.02 mol) in water (16 mL) was mixed to the above solution over a period of five minutes with stirring. The mixture is stirred further for an hour by maintaining the temperature, with positive test for nitrous acid on starch iodide paper. The excess of nitrous acid was destroyed by sulphamic acid solution in water. The clear solution of titled product was obtained and used for coupling reaction.

Cyanuration of Bronner acid [7a]

In 25 mL acetone, Cyanuric chloride [6] (1.85 g, 0.01 mol) is added and stirred at below 5°C for an hour. To this solution, a solution of Bronner acid [5a] (2.23 g, 0.01 mol) in aqueous sodium carbonate (10% w/v), was then added in small portions. The pH was maintained 7.0 by subsequent addition of 1% w/v Na₂CO₃ solution. The reaction mass was further stirred at 0-

5°C for 4 h to obtain a clear solution. The cyanurated bronner acid solution thus obtained was used for condensation reaction.

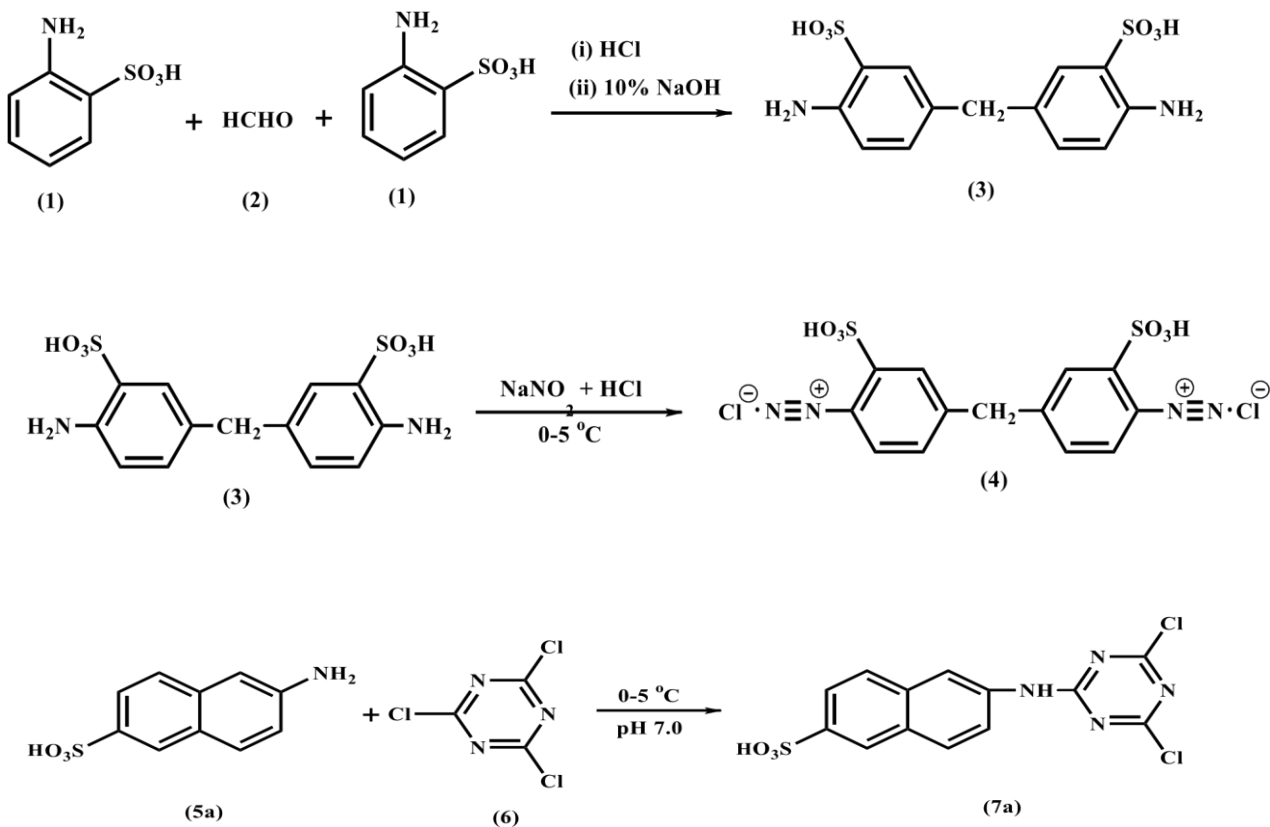
Synthesis of 2-chloro anilino cyanurated Bronner acid (9a)

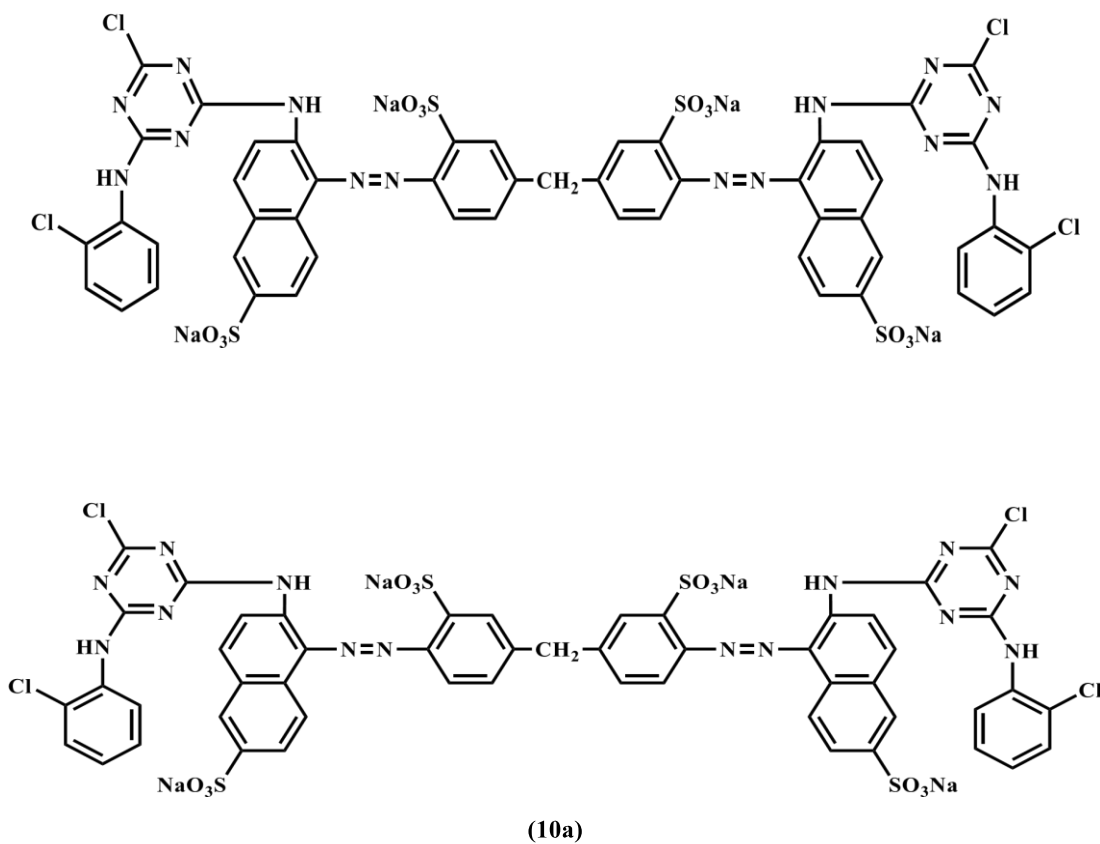
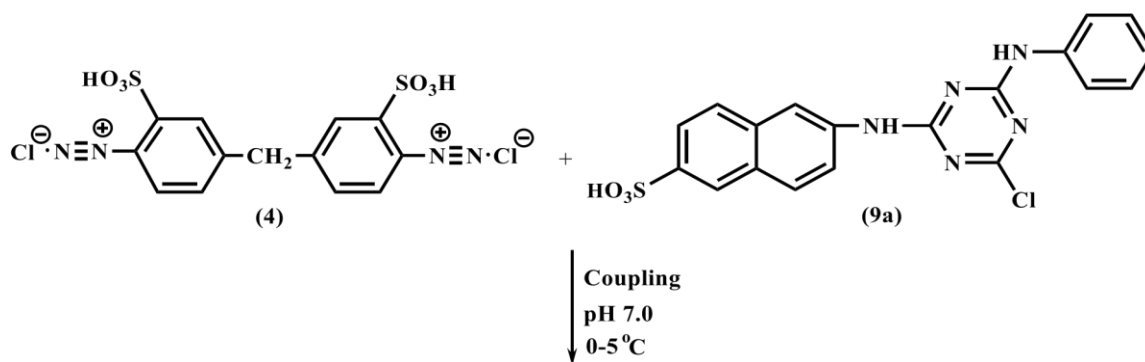
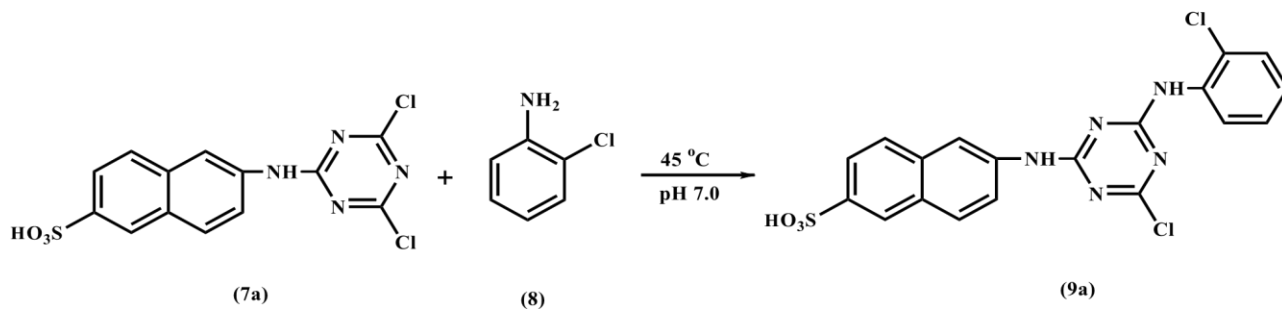
The temperature of ice-cooled well stirred solution of compound [7a], (2.23 g, 0.01 mol) was gradually raised to 45°C for 30 min. To this mixture, the 2-chloro aniline [8] (1.275 g, 0.01 mol) was added gradually by maintaining the temperature at 45°C, during a period of 30 min. The pH was maintained at 7.0 by sodium bicarbonate solution (1% w/v). After the addition was done, stirring was continued for further 3 h. The 2-chloro anilino cyanurated Bronner acid solution was formed and proceeds further for coupling reaction.

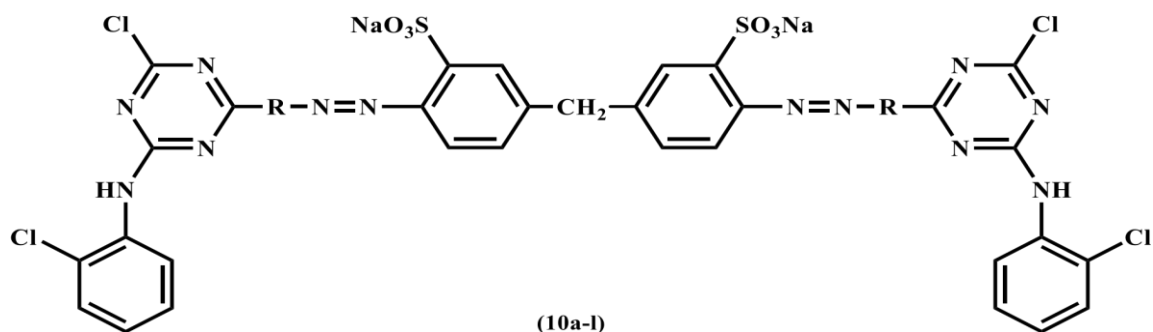
Coupling of tetrazotized solution with 2-chloro anilino cyanurated acid coupling component (10a-1)

A freshly prepared tetrazo solution [4] (4.53 g, 0.01 mol) was added to an ice cooled solution of compound [9a] (9.24 g, 0.02 mol) over a period of 10-15 min. The pH was maintained at 7.5 to 8.5 by simultaneous addition of 10% w/v Na₂CO₃. Yellow solution was formed during coupling. By maintaining the same temperature, the stirring was continued for 3-4 h. The solution of NaCl was added for the precipitation of coloring material. The reaction mass then stirred for 1 h, filtered and washed with 5% w/v NaCl solution. The compounds [10a-1] was dried at 80-90°C and extracted by DMF. By adding excess of chloroform to the extract, the synthesized dye was precipitated. A yellow dye was then filtered, washed with chloroform and dried yield 88%.

Reaction scheme







Where, R=

- | | |
|-----------------------------|------------------|
| a: Bronner acid; | g: Tobias acid; |
| b: Koch acid; | h: Laurent acid; |
| c: Sulpho tobias acid; | i: J-acid; |
| d: K-acid; | j: M-acid; |
| e: <i>N</i> -methyl-J-acid; | k: H-acid; |
| f: Chicago acid; | l: Peri acid |

TABLE 1. Physical properties of reactive dye.

No.	-R	Molecular formula	Mol. weight	Yield (%)	% of Nitrogen		R _f value
					Found	Required	
10 _a	Bronner acid	C ₅₁ H ₃₀ O ₁₂ N ₁₄ C ₁₄ S ₄ Na ₄	1393	89	14.02	14.08	0.48
10 _b	Koch acid	C ₅₁ H ₂₆ O ₂₄ N ₁₄ C ₁₄ S ₈ Na ₈	1801	88	17.97	18.01	0.37
10 _c	Sulpho tobias acid	C ₅₁ H ₃₀ O ₁₂ N ₁₄ C ₁₄ S ₄ Na ₄	1392	90	14.03	14.08	0.36
10 _d	K-acid	C ₅₁ H ₂₈ O ₂₀ N ₁₄ C ₁₄ S ₆ Na ₆	1629	84	12.00	12.04	0.44
10 _e	<i>N</i> -methyl acid	C ₅₃ H ₃₄ O ₁₄ N ₁₄ C ₁₄ S ₄ Na ₄	1453	90	13.47	13.50	0.39
10 _f	Chicago acid	C ₅₁ H ₂₈ O ₂₀ N ₁₄ C ₁₄ S ₆ Na ₆	1629	88	11.98	12.04	0.44
10 _g	Tobias acid	C ₅₁ H ₃₂ O ₆ N ₁₄ C ₁₄ S ₂ Na ₂	1188	91	14.02	14.08	0.40
10 _h	Laurent acid	C ₅₁ H ₃₀ O ₁₂ N ₁₄ C ₁₄ S ₄ Na ₄	1393	88	16.42	16.49	0.43
10 _i	J-acid	C ₅₁ H ₃₀ O ₁₄ N ₁₄ C ₁₄ S ₄ Na ₄	1425	90	13.68	13.76	0.34
10 _j	M-acid	C ₅₁ H ₃₀ O ₁₄ N ₁₄ C ₁₄ S ₄ Na ₄	1425	88	13.70	13.76	0.35
10 _k	H-acid	C ₅₁ H ₂₈ O ₂₀ N ₁₄ C ₁₄ S ₆ Na ₆	1629	90	12.00	12.04	0.38
10 _l	Peri acid	C ₅₁ H ₃₀ O ₁₂ N ₁₄ C ₁₄ S ₄ Na ₄	1393	88	14.01	14.08	0.40

Result and Discussion

Characterization

All the synthesized dyes have been characterized by visible absorption spectra, some representative IR spectra and PMR spectra.

Visible absorption spectra: The visible absorption spectra of all synthesized dyes have been recorded in water and observed in the range of 550-383 nm. The color observed for each dye is due to the presence of substituents and oscillation of electrons.

IR Spectra: IR spectra of dye 10_c showed N-H stretching vibration of secondary amine at 3365 cm⁻¹, C-H stretching vibration of -CH₂- group at 2865 cm⁻¹, C=C stretching vibration of aromatic ring at 1570 cm⁻¹, N=N stretching vibration of azo group at 1462 cm⁻¹, C-N stretching vibration of tertiary amine group at 1542 cm⁻¹, S=O stretching vibration of -SO₃Na group at 1180 and 1090 cm⁻¹, C-Cl stretching vibration of chloro group at 716 cm⁻¹.

IR spectra of dye 10_i showed O-H stretching vibration of -OH group at 3490 cm⁻¹, N-H stretching vibration of secondary amine at 3365 cm⁻¹, C-H stretching vibration of -CH₂- group at 2860 cm⁻¹, C=C stretching vibration of aromatic ring at 1580 cm⁻¹, N=N stretching vibration of azo group at 1452 cm⁻¹, C-N stretching vibration of tertiary amine group at 1531 cm⁻¹, S=O stretching vibration of -SO₃Na group at 1190 and 1080 cm⁻¹, C-Cl stretching vibration of chloro group at 723 cm⁻¹.

IR spectra of dye 10_j showed N-H stretching vibration of secondary amine at 3355 cm⁻¹, C-H stretching vibration of -CH₂- group at 2860 cm⁻¹, C=C stretching vibration of aromatic ring at 1575 cm⁻¹, N=N stretching vibration of azo group at 1450 cm⁻¹, C-N stretching vibration of tertiary amine group at 1533 cm⁻¹, S=O stretching vibration of -SO₃Na group at 1190 and 1090 cm⁻¹, C-Cl stretching vibration of chloro group at 720 cm⁻¹.

¹H NMR Spectra: ¹H NMR Spectra of dye 10_a showed signals at 3.89 (s, 2H, -CH₂), 4.17 (s, 4H, -NH), 6.2-8.6 (m, 24 H, Ar-H). ¹H NMR Spectra of dye 10_k showed signals at 3.952 (s, 2H, -CH₂), 3.958 (s, 2H, -OH) 4.12 (s, 4H, -NH), 6.7-8.3 (m, 20H, Ar-H). ¹H NMR Spectra of dye 10_l showed signals at 3.92 (s, 2H, -CH₂), 4.15 (s, 4H, -NH), 6.4-8.5 (m, 24H, Ar-H).

Applications

Dyeing of fibres

All the dyes were applied on wool, cotton and silk fibres by using the standard procedure [12].

Exhaustion and fixation study: The percentage exhaustion of 2% dyeing on silk fabric ranges from 68-74%, for wool ranges from 67-74% and for cotton ranges from 64-75%. The percentage fixation of 2% dyeing on silk fabric ranges from 80-92%, for wool ranges from 80-93% and for cotton ranges from 81-96% (TABLE 2), (FIG. 1 and FIG. 2).

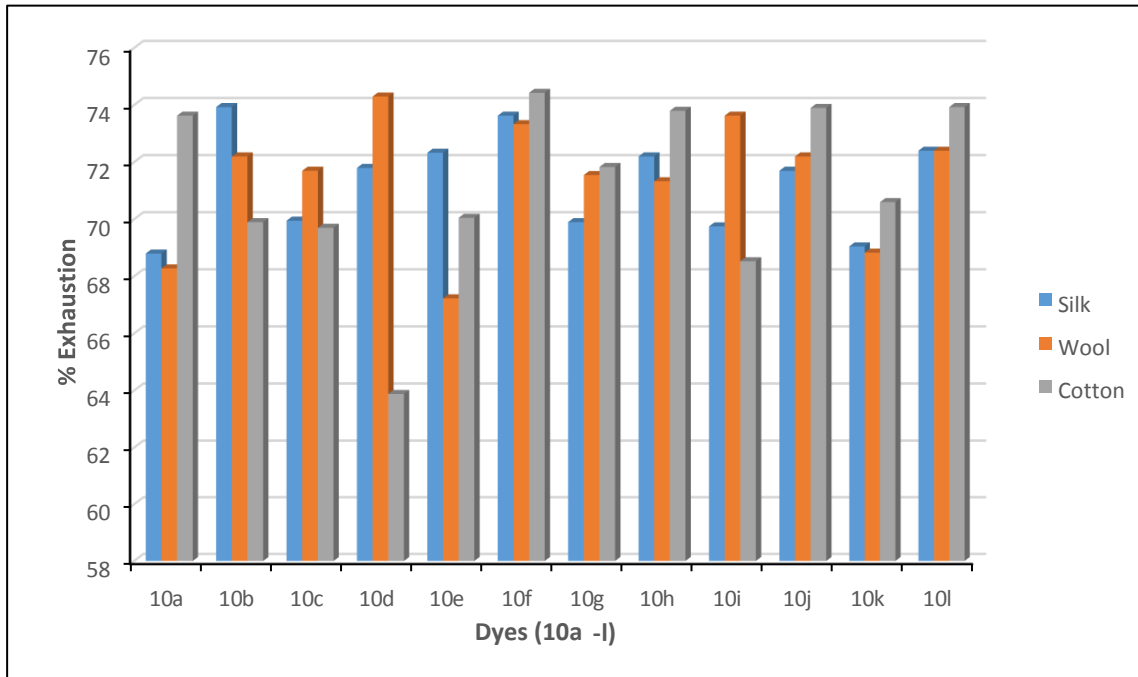


FIG. 1. % Exhaustion of dye 10a-1.

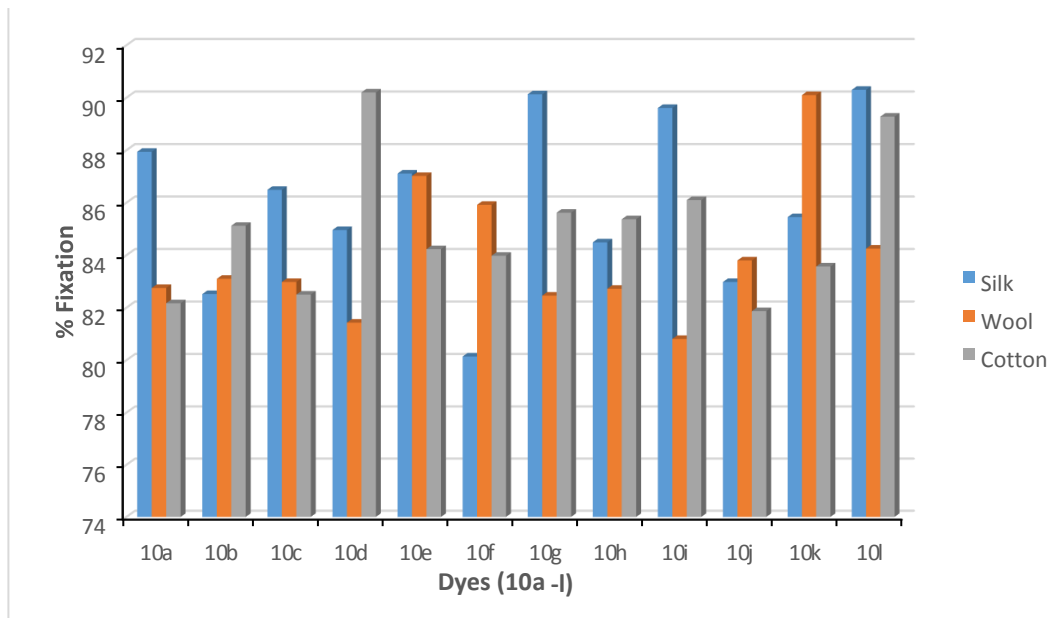


FIG. 2. % Fixation of dye 10a-1.

TABLE 2. Exhaustion and fixation data.

Dye No.	Shade on silk fabric	Shade on wool fabric	Shade on cotton fabric	λ_{max}	% Exhaustion			% Fixation		
					S	W	C	S	W	C
10 _a	Orange brown	Dark yellow	Yellow	458	68.80	68.28	73.63	87.94	82.75	82.17
10 _b	Light brown	Light brown	Light maroon	496	73.93	72.20	69.90	82.52	83.10	85.12
10 _c	brown	yellow	Maroon	441	69.95	71.70	69.70	86.49	82.98	82.50
10 _d	Yellow	Light yellow	Light yellow	476	71.80	74.30	63.88	84.96	81.43	90.20
10 _e	Maroon	Red	Maroon	503	72.33	67.23	70.05	87.11	87.02	84.23
10 _f	Red	Orange	Yellow	448	73.63	73.33	74.43	80.14	85.92	83.98
10 _g	Brown	yellow	Dark maroon	426	69.90	71.55	71.83	90.13	82.46	85.62
10 _h	Light orange	Light yellow	Light yellow	478	72.20	71.33	73.80	84.49	82.72	85.37
10 _i	Red	Red	Yellow	434	69.75	73.63	68.53	89.61	80.81	86.10
10 _j	orange	Orange	Orange	496	71.70	72.20	73.90	82.98	83.80	81.87
10 _k	Violet	Light violet	violet	426	69.05	68.83	70.60	85.45	90.10	83.57
10 _l	Light brown	Yellow	Light brown	451	72.40	72.40	73.93	90.30	84.25	89.28

S: silk; W: wool; C: cotton

Fastness properties [13]

Fastness to light was assessed in accordance with BS: 1006-1978 (Standard Test Method, 1994) [14]. The rubbing fastness test was carried out by using Crock meter (Atlas) in accordance with the AATCC-1961(AATCC Test, 1961) and the wash fastness was carried out in accordance with IS:765-1979 (Indian Standard,1979) [15]. All the dyes show generally fair to good light fastness properties. The washing and rubbing fastness properties ranges from very good to excellent fastness on silk, wool and cotton (TABLE 3).

TABLE 3. Fastness properties.

Dye	Light Fastness			Wash Fastness			Rubbing Fastness					
							Dry			Wet		
	S	W	C	S	W	C	S	W	C	S	W	C
10 _a	4	3	4	4	4	4	4	3	5	3	5	3
10 _b	4	4	5	4	4	5	4	3	3	4	4	4
10 _c	5	5	5	5	5	5	5	3	4	3	4	3
10 _d	4	5	4	4	4	4	4	4	3	3	3	5
10 _e	4	4	5	4	4	4	3	5	3	5	5	5
10 _f	3	5	3	5	5	4	4	4	3	4	5	4
10 _g	4	4	4	4	4	4	5	4	4	3	4	5
10 _h	5	5	3	5	5	5	4	5	3	5	3	5
10 _i	4	3	4	4	4	4	5	5	4	4	3	4
10 _j	3	4	3	4	4	4	4	5	5	5	3	5
10 _k	5	4	4	5	5	5	5	3	3	5	4	5
10 _l	5	5	5	3	3	4	4	3	5	5	3	5

S: silk; W: wool; C: cotton

Light fastness: 1-Poor; 2-Slight; 3-Moderate; 4-Fair; 5-Good; 6-Very good; 7-Excellent; 8-maximum

Wash and Rubbing fastness: 1-Poor; 2-Fair; 3-Good; 4-Very good; 5-Excellent

Conclusion

Tetrazotization of 5, 5'-methylenebis-(2-aminobenzenesulfonic acid) followed by coupling with various 2-chloro anilino cyanurated acid coupling components gave corresponding bisazo reactive dyes (10a-l). These dyes gave violet to yellow shade on silk, wool and cotton fibres. The dyeing performance of all these dyes on various fibres gave moderate to good light fastness, good to excellent wash fastness and rubbing fastness. The presence of triazine group of dye molecule improves the exhaustion, fixation and fastness properties. Thus, exhaustion and fixation of these dyes are very good in order.

Acknowledgement

Authors are thankful to Department of Chemistry, Veer Narmad South Gujarat University, Surat, Gujarat, India for providing research facility, Atul Products Ltd., Atul, Valsad, India for providing dyeing facility, fastness, colorimetric data and SAIF, Chandigarh for spectral data.

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