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Synthesis and characterization of some bi-functional reactive dyes and their application on various fibers

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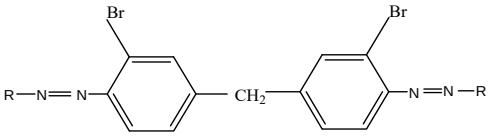
Abstract
Various bi-functional reactive dyes have been prepared by coupling diazotized 4,4'methylene-bis-ortho-bromo aniline with cyanurated coupling components and their dyeing performance as reactive dyes has been assessed on silk, wool and cotton fiber. All the dyes gave yellow to marron shades with good to very good light fastness on each fiber. The purity of dyes was checked by thin layer chromatography. The IR spectra showed all characteristic bands and a representative dye's PMR spectra showed all the signals. The percentage dyebath exhaustion on different fibers was reasonably good and acceptable. The dyed fibers showed moderate to very good fastness to light, washing and rubbing.

Keywords: Bi-functional reactive dyes, diazotization, dyeing, fixation, exhaustion, fibers

Introduction
The most recent technological contribution to textile has been the development of bifunctional reactive dyes. Several new bi-functional reactive systems have been introduced from time to time, which covers the subject of innumerable patents and publication [1-3]. It is for the first time that dyeing has been by chemical reaction between the dye and the fiber, enabling one to get an assortment of bright, attractive shades of adequate fastness with considerable ease of dyeing. It can also be easily understood that dyes with two reactive groups give a higher fixation yield than dyes with one reactive group for if one of the two dye-fiber bonds is hydrolyzed one is still left for fixation [4, 5]. Patel *et al*. has synthesized bisazo bi-functional dyes based on 4.4'-azo-bis-aniline [6, 7].
We report here the synthesis and study of the dyeing properties of the bi-functional reactive dyes based on 4, 4'mehtylene-bis-ortho-bromo aniline. The bi-functional reactive dyes of the following structure were prepared.



Where R= Cyanurated coupling components such as cyanurated K-acid, J-acid, T-acid, Gamma acid, Sulfotobias acid, Tobias acid, Bronner's acid, Chicago acid, Laurent's acid, Peri acid.

Experimental
Synthesis of 4, 4'-methylene-bis-ortho-bromo aniline
Synthesis of 4, 4'-methylene-bis-acetanilide
A mixture of acetic anhydride (36 ml) and glacial acetic acid (60 ml) and 4,4'mehtylene-bis-anilne (17.2 gm, 0.1 mole) was refluxed for 30 minutes on a hot water bath. The product was precipitated by pouring the mixture into cold water and crystallized from 75% acetic acid, yield 80%, m.p. 236-237 ºC.

Analysis:
$C_{17}H_{18}N_2O_2$ Found:N 9.91% Required: N, 9.92%

Synthesis of 4, 4'-methylene-bis-otho-bromo acetanilide
4, 4'-methylene-bis-otho-bromo acetanilide (0.28 gm, 0.001 mole) was dissolved in acetic acid (30 ml) and bromine in acetic acid (2.0 ml, 10%) was slowly added to it. The reaction mixture was kept for 4 hours in water bath. Then it was treated with ice-water. The solid separated was filtered, washed with sodium thiosulphate solution and then with water, dried and crystallized from absolute alcohol, yield 80%, m.p. 193 ºC.

Analysis:
$C_{17}H_{16}N_2O_2Br_2$Found: N 6.35% Required: N, 6.36%

Synthesis of 4,4'-methylene-bis-ortho-bromo aniline
4, 4'-methylene-bis-ortho-bromo acetanilide (4.40 gm, 0.01 moles) and 70% of H_2SO_4 was refluxed for 30 minutes on hot water-bath. Pour the clear hot solution into ice cold water and precipitate by adding excess of 10% NaOH solution and crystallized from alcohol, yield 60%, m.p. 110 ºC.

Analysis:
C13H12N2Br2 Found:N, 7.85%Required: N, 7.86%

Preparation of cyanurated H-acid
Cyanuric chloride (3.70 gm, 0.02 moles) was stirred in acetone (40 ml) at a temperature below 5°C for a period of an hour. A neutral solution of H-acid (6.38 gm, 0.02 mole) in aqueous sodium carbonate solution (10% W/V) was then added in small lots in about an hour. The pH was maintained neutral by simultaneous addition of sodium carbonate solution (1% W/V). The temperature was maintained below 5°C throughout this reaction. The reaction mass was then stirred at 0-5°C for further 4 hours. The cyanurated H-acid solution thus formed was used for subsequent condensation reaction.

Condensation of 4,4'-methylene-bis-ortho-bromo aniline with cyanurated H-acid (A)
To an ice cooled and well stirred solution of cyanurated H-acid (9.34 gm, 0.02 mole), a solution of 4,4'-methylene-bis-ortho-bromo aniline (3.56 gm, 0.01 mole) in water (20 ml) was then added. The solution was stirred for nearly an hour at 0-5 ºC. The temperature was then gradually raised to 35 ºC and pH adjusted between 7 and 8 by the addition of dilute sodium bicarbonate solution. The mixture was stirred over night, filtered, washed and the resultant product was used for the subsequent coupling reaction (A).

Diazotization of K-acid (B)
K-acid (7.32 gm, 0.02 moles) was suspended in water, hydrochloric acid was added drop wise into this well stirred suspensions. The solution was cooled to 0-5 ºC in an ice-bath. A solution of $NaNO_2$ in water previously cooled to 0 ºC was the added over a period of 5 minutes with stirring. The stirring was continued for an hour, maintaining the same temperature. If positive test for nitrous acid with required amount of a solution of sulphamic acid. The clear solution at 0-5 ºC was used for subsequent coupling reaction.
Using the similar process different diazotized coupling component were prepared and subsequently used for coupling reaction.

Coupling of A and B (Formation Dyes (D_1 to D_{10})
A solution of diazotized K-acid (B) (0.02 mole) was added to well stirred solution of compound (A) (0.01 mole) in water at pH 7-8. The pH was maintained throughout the reaction. The dye formed was stirred for further 2-3 hours and then salted out by the addition of sodium chloride. It was filtered, dried and crystallized from DMF- acetone, yield 83%.

Analysis:
$C_{59}H_{28}O_{28}N_{14}S_8Na_8Cl_2Br_2$ Found:N, 9.55%Required: N, 9.56%

Dyeing of Fibers
All the dyes D_1 to D_{10} were applied on silk, wool and cotton fibers using reported procedure [8].

Fastness Test
Fastness to light was assessed in accordance with BS: 1006-1978. The rubbing fastness test was carried out with crockmeter (Atlas) in accordance with AATCC (1961) and the wash fastness test in accordance with IS: 765-1979.

Result and Discussion
All the dyes were yellow to maroon color and obtained in excellent yield (75-85%). The purity of all dyes has been checked by thin layer chromatography [9]. The adsorption spectra of all the dyes were recorded on Beckman DB-GT grafting spectrophotometer. The characterization data of dyes are given in table-1.

Conclusion
Various bi-functional reactive dyes based on 4,4'-methylene-bis-ortho-bromo-aniline have been synthesized. These dyes mostly yellow, orange, brown and marron shades on cotton, wool and silk fabric having good fastness properties. The variations in the hues of the dyed fabric result from the both the nature and position of the substituent present on the coupler ring. The exhaustion and fixation of these dyes are very good; this indicates that the dyes have good affinity and solubility with the fabric. The remarkable degree of levelness after washing indicates the good penetration and affinity of these dyes to the fabric. The intrinsic conjugation in the diazo structure results in very good colour strength.

Infrared Spectra
The IR spectra of dyes D_1 to D_{10} were recorded on Perkin-Elmer spectrophotometer (model
830) using KBr pellets. Dyes D_1 to D_{10} showed characteristic bend at 2910-2890 (-CH_2-) [10], 830-800 (s-Triazine), 560-510 (C-Br), 1635-1580 (-NH-), 1390-1360 (-N=N-), 1210-1110 (S=O), 3420-3410 cm^{-1} due to (O-H) stretching vibration.

PMR Spectra
The PMR spectra (300 MHz, $CDCl_3$) of representative dye, showed signals at 2.10 (-CH_2-), 3.61 (-OH) 8.10-6.84 (aromatic proton) and 9.2 (-NH-).

Fastness Properties
The percentage exhaustion, fixation and fastness properties of dyes D_1 to D_{10} are given table2 and 3. All the dyes D_1 to D_{10} are showed good affinity for silk, wool and cotton fibers and gave moderate to very good light, washing and rubbing fastness and good to very good exhaustion and fixation.

Table1: Characterization

Dye No.	Coupling Component	Molecular Formula	Molecular Weight gm	Yield %	% Nitrogen		Rf Value
					Found	Required	
D_1	K-acid	C59H28O28N14S8Na8Cl2Br2	2050	83	9.55	9.56	0.45
D_2	J-acid	C59H30O22N14S6Na6Cl2Br2	1846	87	10.60	10.61	0.46
D_3	T-acid	C59H28O32N14S10Na10Cl2Br2	2224	85	8.80	8.81	0.37
D_4	Gamma acid	C59H30O22N14S6Na6Cl2Br2	1846	87	16.59	16.61	0.38
D_5	Sulfotobias acid	C59H34O24N14S8Na8Cl2Br2	1992	88	9.82	9.83	0.42
D_6	Tobias acid	C59H36O20N14S6Na6Cl2Br2	1820	70	10.75	10.76	0.40
D_7	Bronner's acid	C59H36O20N14S6Na6Cl2Br2	1820	83	10.74	10.76	0.47
D_8	Chicago acid	C59H28O28N14S8Na8Cl2Br2	2050	79	9.54	9.56	0.45
D_9	Laurent's acid	C59H36O20N14S6Na6Cl2Br2	1820	80	10.75	10.76	0.47
D_{10}	Peri acid	C59H36O20N14S6Na6Cl2Br2	1820	85	10.74	10.76	0.38

Table2: Shade, Percentage, Exhaustion and Fixation of reactive dyes on silk, wool and cotton fibers.

Dye No.		% Exhaustio	n		% Fixation	
	Silk	Wool	Cotton	Silk	Wool	Cotton
D_1	78.50	66.50	46.00	89.00	88.50	63.00
D_2	73.70	67.00	48.50	92.50	84.00	66.00
D_3	76.70	64.50	49.50	84.50	81.50	65.50
D_4	68.60	67.50	49.00	84.70	80.00	62.00
D_5	72.30	65.00	50.50	93.20	82.50	63.50
D_6	69.00	66.00	48.00	87.50	83.50	63.50
D_7	73.00	68.00	45.50	82.60	80.00	61.50
D_8	75.00	67.50	51.00	87.50	80.50	60.00
D_9	71.00	64.00	47.50	91.50	82.50	65.60
D_{10}	74.00	66.50	49.50	90.50	77.80	64.00

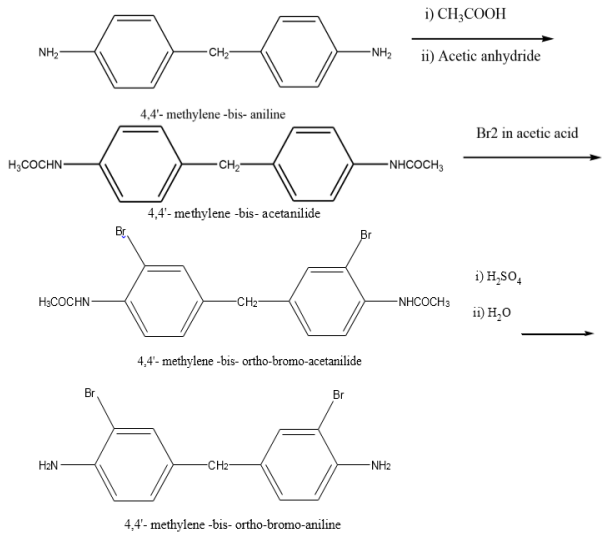
Table3: Fastness properties of reactive dyes on silk, wool and cotton fibers.

Dye No.	Light Fastness			Wash Fastness				Rubbing Fastness				
								Dry		Wet		
	S	W	C	S	W	C	S	W	C	S	W	C
D_1	5	5	5	4	4	5	5	4	4	4	5	5
D_2	4	4	4	5	5	4	3-4	4-5	5	5	4-5	4
D_3	3	4	5	4-5	4	4	4	4-5	5	4	4	4-5
D_4	5	5	4	4	3-4	4-5	4	5	5	5	5	5
D_5	4-5	4	4-5	5	4	5	5	4	4	5	4	4
D_6	3	5	5	4	5	4	4-5	4	4	5	4	5
D_7	3-4	4	4	4-5	4	4	3-4	4	3-4	4	5	4-5
D_8	5	3-4	3-4	4	4	4-5	4	5	4-5	3-4	5	4
D_9	4	4-5	5	3-4	4	4	5	4	5	5	4	4
D_{10}	5	4	4-5	5	4	5	4	4-5	4	3-4	4-5	5

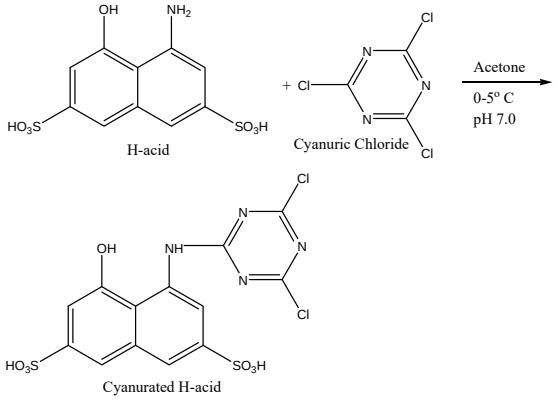
S=Silk, W=Wool, C=Cotton

Reaction Scheme

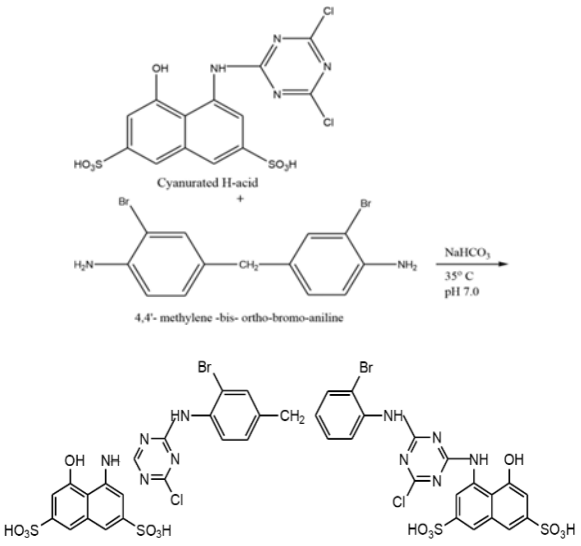
Synthesis of 4, 4'-methylene-bis-ortho-bromo aniline



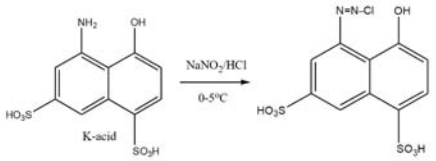
Cyanuration of H-acid



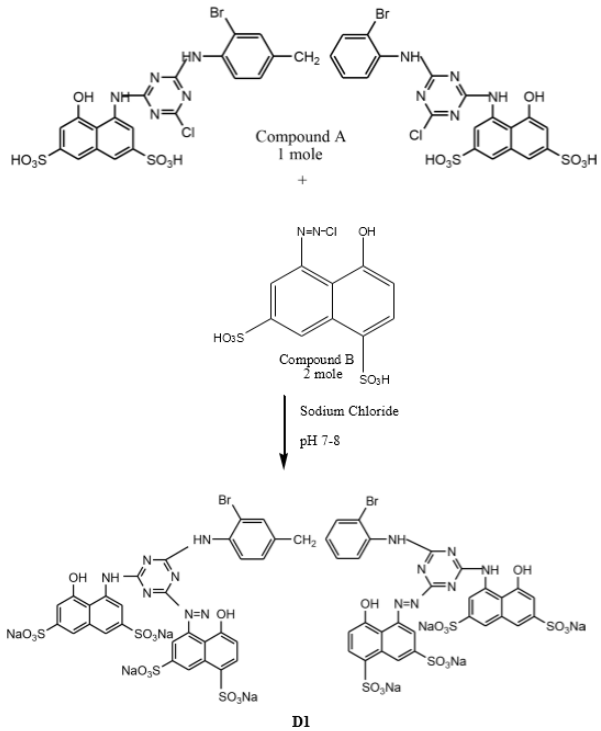
Condensation of 4, 4'-methylene-bis-ortho-bromo aniline with cyanurated H-acid (Compound A):



Diazotization of K-acid (B)



Coupling of A and B (Formation Dyes)



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