Dyeing assessment and antimicrobial activity of tetra azo acid dyes derived from 4,4'-(propane-2,2-diyl)bis(2-methyl-4,1phenylene) bis(3-aminobenzenesulfonate)

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Abstract

4,4'-(Propane-2,2-diyl)bis(2-methyl-4,1-phenylene)bis(3-aminobenzenesulfonate) was synthesized by reduction of condense product of Bisphenol C and *m*-nitrobenzenesulfonyl chloride. The compound was used as a bifunctional middle component in the preparation of tetra azo acid dyes. This di amino compound was tetra azotized and coupled with naphthalene based acid coupling component to give various tetra azo acid dyes. The obtained dyes were characterized by spectroscopic technique (UV-vis., IR, NMR) and the dyeing assessment of all dyes was evaluated on wool, silk and nylon fabrics. These dyes gave brown, violet, yellow, orange and pink shades on each fibers with good to very good fastness properties. The percentage dye bath exhaustion, fixation and biological activity have also been studied.

Keywords: 4,4'-(propane-2,2-diyl)bis(2-methyl-4,1-phenylene)bis(3-aminobenzenesulfonate), Antimicrobial activity, Dyeing, Fastness properties, Tetra azo acid dyes

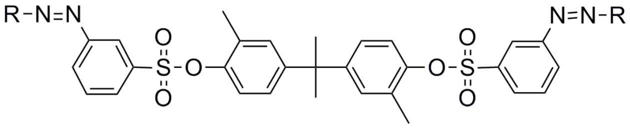
1. Introduction

Acid dyes are highly water soluble and have better light fastness than basic dyes, usually sodium salts of sulfonic acids or less frequently of carboxylic acids and are therefore anionic in aqueous solution. These dyes are completely ionized in the acidic condition used in the dyeing process [1]. Generally acid dyes are applied on nitrogen content fibers such as wool, silk and nylon [2-4]. Acid dyes can be easily applied on wool and polyamide fibres and therefore are largely used on large scale.

Acid dyes are classified based on affinity, dyeing properties and chemical constitution of the dyes. Chemically the acid dyes consist of azo [5,6], anthraquinone [7,8], azine [9], pyrazolone [10], nitro [11] compounds. Out of these azo dyes are the most important class, accounting for over 50% of all commercial dyes, and having been studied more than any other class due to their wide range of color, brightness, dyeing performance and ease of manufacturing [12,13]. Azo dyes contain atleast one azo group (-N=N-) but can contain two, three, or, more rarely four azo groups. A number of monoazo, bisazo, tetraazo dyes have been reported to give good dyeing and fastness properties on fiber [14,15].

Phenol is very use full raw material for the synthesis of dye [16-19], in this work we have synthesize terta azo dyes using Bisphenol C related moiety. Bisphenol C are compounds containing of two phenol nucleus linked by a hydrocarbon chain. Bispenols are used for manufacture of dyes and drugs [20-23], paints [24], printing ink [25], epoxy resins, polymers [26-28], coatings, plasticizers, pesticides, bactericides and in other applications such as home appliances, water bottles, food storage containers, sports safety equipment, medical equipment.

In the present research we have prepare set of fifteen tetra azo acid dyes for this we are using condense moiety of bisphenol C and m-nitro benzene sulphonyle chloride. The various coupling components were selected to get a variety of shades. The dyeing assessment of synthesize dyes was examined on wool, silk and nylon fibers, and also examined fastness properties and exhaustion study of these types of tetra azo acid dyes. The general structure of these tetra azo acid dyes is shown in Figure.



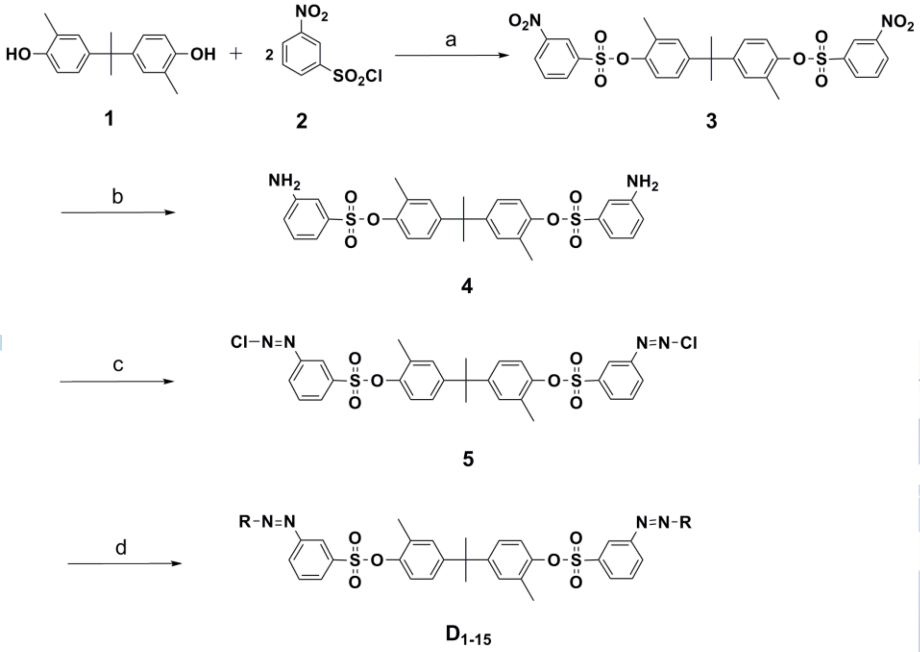
R= various naphthalene based coupling component (D_{1-15}) (Table 1)

Fig.1

2. Materials and Methods

All the used raw materials used for the synthesis of the compounds were obtained from various companies (commercial grade) and were further purified by crystallization before use. Melting points were determined in open capillary tubes and are uncorrected. The Rf values [29,30] of all the dyes have been checked by thin layer chromatography using silica gel G F_{254}-precoated aluminum sheets in the solvent system t-butenol: Ethanol: ammonia: water (4:2:2:2). The IR spectra were recorded on Thermo Scientific Nicolet iS10 FT-IR instrument using KBr pellet method and ^{1}H-NMR spectra on Brucker advance II 400 NMR spectrophotometer using TMS as internal standard and DMSO as solvent. The absorption spectra of all the dyes were recorded on a Shimadzu UV-1700 spectrophotometer at the wavelength of maximum absorption (λmax) using water as solvent. The dyeing was done by using a Laboratory Rota Dyer instrument and exhaustion dying method. The light and perspiration fastnesses test was assessed in accordance with British standard: 1006-1978 [31]. The wash fastness test in accordance with the Indian standard: IS: 765-1979 [32], and the rubbing fastness test was carried out using a Crock meter AATCC-1961[33]. Antibacterial and antifungal activity was performed using broth dilution method [34].

Scheme



Reagent and condition : (a) MDC, TEA, 4 h, RT; (b) MeOH, Fe, HCl; (c) $NaNO_2$, H_2SO_4, 0-5 °C; (d) Na_2CO_3, 0-5 °C, P^H 7-8 (D_{1-6}), P^H 3-5 (D_{7-15}).

R = Napthalene based acid coupling component

Fig.2 Experimental scheme for tetrazo acid dyes.

2.1. Synthesis of 4,4'-(propane-2,2-diyl)bis(2-methyl-4,1-phenylene)bis(3-nitrobenzenesulfonate) (3)

The title compound was synthesized according to a described process. 3-nitrobenzene 1-sulfonyl chloride (6.6 g, 30.0 mmol) was dissolved in dry methylene chloride (40 ml) under a dry nitrogen atmosphere. Then bisphenol C (3.5 g, 14.0 mmol) and triethyl amine (4.0 ml, 28.7

mmol) were added dropwise to the solution. The reaction mixture was stirred for 4 h at room temperature. After complete reaction The solvent was evaporated and the residue dissolved in ethyl acetate. The solution was washed with 1N HCl, 1N NaOH, brine, and dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. Yield 84%; yellowish crystal; mp 157-159 °C; IR (KBr): 1535 (NO_2), 1190 (-S=O), 2970 ($-CH_3$) cm^{-1}.

2.2. Synthesis of 4,4'-(propane-2,2-diyl)bis(2-methyl-4,1-phenylene)bis(3-aminobenzenesulfonate) (4)

The title compound was synthesized according to the reported method [35,36]. 4,4'-(propane-2,2-diyl)bis(2-methyl-4,1-phenylene)bis(3-nitrobenzenesulfonate) (5.0 g, 8.0 mmol) was dissolved in a mixture of MeOH and H_2O (50 ml+5 ml). Powdered iron (2.23 g, 40.0 mmol) and hydrochloric acid (12 M, 10 ml) were added. The mixture was refluxed for 7 h. After the mixture was cooled at room temperature filtere it to remove the iron residue, the solvent was evaporated. HCl (1 N, 100 mL) was added and the mixture was extracted with ethyl acetate (2 x 100 ml). The organic solutions was washed with brine, water, dried over anhydrous Na_2SO_4, and evaporated to dryness. Yield 45%; white solid powder; mp 192-194 °C; IR (KBr): 3387 (NH_2), 1190 (-S=O), 2970 ($-CH_3$) cm^{-1}.

2.3. Tetrazotisation of 4,4'-(propane-2,2-diyl)bis(2-methyl-4,1-phenylene)bis(3-aminobenzenesulfonate) (5)

Tetrazotisation of diamino compound **(4)** was carried out by the reported method [37,38]. 4,4'-(propane-2,2-diyl)bis(2-methyl-4,1-phenylene)bis(3-aminobenzenesulfonate) (1.0 g, 1.8 mmol) was suspended in mixture of sulphuric acid and glacial acetic acid (3 mL+2 mL). The mixture was gradually heated up to 70 °C, till clear solution obtained. It was cooled at 0-5 °C in ice-bath. A solution of sodium nitrite (0.29 g, 4.2 mmol) in dist. water (4 ml) previously cooled to 0-5 ^{o}C was added over a period of 5 min with stirring and maintained the temperature at 0-5 ^{o}C. The Stirring was continued, maintaining the same temperature for an hour, with positive test for nitrous acid on starch iodide paper, excess of nitrous acid was removed by adding required amount of sulfamic acid solution (10%). This clear diazonium salt solution was used immediately for coupling reaction.

2.4. General coupling procedure for Dye ($D_{1\text{-}15}$)

Coupling component was suspended in water (20 ml) and dissolved at neutral P^{H} with sodium carbonate (10 % w/v) to obtain a clear solution. The solution was cooled to below 0-5 °C in an ice bath. To this well stirred solution, above mentioned tetrazotize salt solution **(5)** was added drop wise over a period of 15-20 min maintained the P^{H} 7.0-8.0 ($D_{1\text{-}6}$) and P^{H} 3.0-5.0 ($D_{7\text{-}15}$) by simultaneous addition of sodium carbonate solution (10 %w/v). The reaction was further stirred for 3 hours at 0-5°C. The resulting dye solution was salted out using sodium chloride at 50-60 °C. The precipitated dye was filtered, washed with sodium chloride solution (5 %w/v) and dried in an oven at 50 °C.

3. Results and discussion

3.1. Preparation of dyes

Tetraazo Acid dyes ($D_{1\text{-}15}$) were synthesized by condensation of bisphenol C **(1)** with m-nitrobenzenesufonyl chloride **(2)** in presence of triethyl amine to give 4,4'-(propane-2,2-diyl)bis(2-methyl-4,1-phenylene)bis(3-nitrobenzenesulfonate) **(3)** which on reduction with iron and acid to get 4,4'-(propane-2,2-diyl)bis(2-methyl-4,1-phenylene)bis(3-aminobenzenesulfonate) **(4)** Terazotization of this diamino compound and the resulting diazonium salt **(5)** was coupled with various naphthalene based acid. During coupling reaction we have maintain P^{H} 3.0-5.0 for coupling take place ortho position of amino group of coupler and for ortho position of hydroxyl

Table 1. Characterization data of tetrazo acid dye (D_{1-15}).

Dye no.	Coupling comp.	Molecular formula	Mol. weight (g/mol)	Yield (%)	m.p.(°C)	R_f Value
D_1	J-acid	$C_{49}H_{40}O_{14}N_6S_4Na_2$	1111.11	85	>300 °C	0.46
D_2	H-acid	$C_{49}H_{38}O_{20}N_6S_6Na_4$	1315.20	81	>300 °C	0.47
D_3	G-acid	$C_{49}H_{36}O_{20}N_4S_6Na_4$	1285.17	78	>300 °C	0.44
D_4	*N*-methyl J-acid	$C_{51}H_{44}O_{14}N_6S_4Na_2$	1139.17	81	>300 °C	0.48
D_5	Chromotropic acid	$C_{49}H_{36}O_{22}N_4S_6Na_4$	1317.17	80	>300 °C	0.46
D_6	Gamma acid	$C_{49}H_{40}O_{14}N_6S_4Na_2$	1111.11	77	>300 °C	0.52
D_7	C-acid	$C_{49}H_{38}O_{18}N_6S_6Na_4$	1283.20	78	>300 °C	0.50
D_8	Bronner acid	$C_{49}H_{40}O_{12}N_6S_4Na_2$	1079.11	85	>300 °C	0.49
D_9	Tobias acid	$C_{49}H_{40}O_{12}N_6S_4Na_2$	1079.11	82	>300 °C	0.49
D_{10}	Koch acid	$C_{49}H_{36}O_{24}N_6S_8Na_6$	1487.29	77	>300 °C	0.45
D_{11}	Napthanoic acid	$C_{49}H_{40}O_{12}N_6S_4Na_2$	1079.11	84	>300 °C	0.44
D_{12}	Sulphotobias acid	$C_{49}H_{38}O_{18}N_6S_6Na_4$	1283.20	80	>300 °C	0.42
D_{13}	Peri acid	$C_{49}H_{40}O_{12}N_6S_4Na_2$	1079.11	83	>300 °C	0.48
D_{14}	Laurant acid	$C_{49}H_{40}O_{12}N_6S_4Na_2$	1079.11	78	>300 °C	0.51
D_{15}	Amino G-acid	$C_{49}H_{38}O_{18}N_6S_6Na_4$	1283.20	81	>300 °C	0.50

3.2. IR and ^{1}H NMR spectra

The structures of dyes (D_{1-15}) were confirmed by spectroscopic techniques, including IR [39], ^{1}H-NMR [40] showed in Table 2. The IR spectra of the dyes showed characteristic band at 3380-3605 cm^{-1} for O-H and N-H stretching vibrations, other bands at 2960-2975 cm^{-1} and 2852-2872 cm^{-1} showed asymmetric and symmetric stretching vibration of -CH_3, N=N stretching vibration at 1592-1605 cm^{-1} , S=O of sulfonet ester confirmed by asymmetric and symmetric vibration at 1360-1376 cm^{-1} and 1138-1145 cm^{-1}, while the bands at 1156-1169 cm^{-1} and 1045-1052 cm^{-1} showed the asymmetric and symmetric stretching vibration of S=O of sulfonic acid group. The ^{1}H-NMR of all dyes was recorded in DMSO. Dye (D_{1-15}) showed characteristic singlet signals in the region at 1.52-1.62 ppm due to the six methayl proton and substituted six methayl proton showed at singlet single at 2.06-2.15 ppm. Dye exhibited singlet signals in the region at 3.45-3.50 ppm which can be attributed to the amino proton. Dye (D_{1-6}) showed singlet signals at 5.56-5.61 ppm due to the phenolic proton. The aromatic protons (multiplet) were observed in the range between 6.74-8.25 ppm.

Table 2. IR and ^{1}H NMR Data of tetrazo acid dye (D_{1-15}).

Dye no.	IR data((KBr) ν cm^{-1})	^{1}H NMR data (DMSO) (chemical shift in δppm)
D_1	3587-3398 (-OH & -NH_2), 2970, 2870 (-CH_3 asym. & sym.), 1597 (-N=N-), 1365, 1141 (sulfonate -S=O asym. & sym), 1168, 1045 (-S=O asym. & sym.).	-CH_3 (6H, s, 1.59), -CH_3 (6H, s, 2.09), -NH_2 (4H, s, 3.45), -OH (2H, s, 5.60), Ar-H (22H, m, 6.95-8.60)
D_2	3590-3397 (-OH & -NH_2), 2975, 2870 (-CH_3 asym. & sym.), 1601 (-N=N-), 1361, 1144 (sulfonate -S=O asym. & sym), 1169, 1049 (-S=O asym. & sym.).	-CH_3 (6H, s, 1.60), -CH_3 (6H, s, 2.11), -NH_2 (4H, s, 3.46), -OH (2H, s, 5.59), Ar-H (20H, m, 6.91-8.65)
D_3	3605-3390 (-OH & -NH_2), 2971, 2864 (-CH_3 asym. & sym.), 1595(-N=N-), 1366, 1140 (sulfonate, -S=O asym. & sym), 1158, 1045(-S=O asym. & sym.).	-CH_3 (6H, s, 1.56), -CH_3 (6H, s, 2.08), -OH (2H, s, 5.60), Ar-H (22H, m, 7.01-8.59)
D_4	3594-3401(-OH & -NH_2), 2960, 2854 (-CH_3 asym. & sym.), 1596(-N=N-), 1370, 1138 (sulfonate -S=O asym. & sym), 1156, 1045 (-S=O asym. & sym.).	-CH_3 (6H, s, 1.56), -CH_3 (6H, s, 2.10), -CH_3 (6H, s, 2.56), -NH (2H, s, 4.17), -OH (2H, s, 5.61), Ar-H (22H, m, 6.90-8.65)
D_5	3586-3380 (-OH & -NH_2), 2961, 2855 (-CH_3 asym. & sym.), 1592(-N=N-), 1364, 1140(sulfonate -S=O asym. & sym), 1162, 1050 (-S=O asym. & sym.).	-CH_3 (6H, s, 1.52), -CH_3 (6H, s, 2.15), -OH (4H, s, 5.59), Ar-H (20H, m, 6.95-8.62)
D_6	3590-3384(-OH & -NH_2), 2972, 2865 (-CH_3 asym. & sym.), 1605(-N=N-), 1372, 1142(sulfonate -S=O. & sym), 1161, 1052 (-S=O asym. & sym.).	-CH_3 (6H, s, 1.61), -CH_3 (6H, s, 2.06), -NH_2 (4H, s, 3.48), -OH (2H, s, 5.56), Ar-H (22H, m, 6.89-8.62)
D_7	3406 (-NH_2), 2972, 2857 (-CH_3 asym. & sym.), 1598 (-N=N-), 1371, 1144 (sulfonate -S=O asym. & sym), 1167, 1047 (-S=O asym. & sym.).	-CH_3 (6H, s, 1.59), -CH_3 (6H, s, 2.10), -NH_2 (4H, s, 3.50), Ar-H (22H, m, 6.96-8.61)
D_8	3410 (-NH_2), 2974, 2870 (-CH_3 asym. & sym.),1597 (-N=N-), 1365, 1140 (sulfonate -S=O asym. & sym), 1168, 1051 (-S=O asym. & sym.).	-CH_3 (6H, s, 1.62), -CH_3 (6H, s, 2.10), -NH_2 (4H, s, 3.46), Ar-H (24H, m, 7.05-8.63)
D_9	3401 (-NH_2), 2971, 2855 (-CH_3 asym. & sym.),1600 (-N=N-), 1369, 1145 (sulfonate -S=O asym. & sym), 1165, 1050 (-S=O asym. & sym.).	-CH_3 (6H, s, 1.61), -CH_3 (6H, s, 2.14), -NH_2 (4H, s, 3.50), Ar-H (24H, m, 6.93-8.57)
D_{10}	3405 (-NH_2), 2971, 2856 (-CH_3 asym. & sym.), 1604 (-N=N-), 1360, 1145 (sulfonate -S=O asym. & sym), 1161, 1045 (-S=O asym. & sym.).	-CH_3 (6H, s, 1.58), -CH_3 (6H, s, 2.09), -NH_2 (4H, s, 3.52), Ar-H (20H, m, 6.90-8.59)
D_{11}	3406 (-NH_2), 2960, 2852 (-CH_3 asym. & sym.), 1596 (-N=N-), 1376, 1141 (sulfonate -S=O asym. & sym), 1168, 1046 (-S=O asym. & sym.).	-CH_3 (6H, s, 1.60), -CH_3 (6H, s, 2.09), -NH_2 (4H, s, 3.45), Ar-H (24H, m, 6.99-8.61)
D_{12}	3400 (-NH_2), 2961, 2870 (-CH_3 asym. & sym.),	-CH_3 (6H, s, 1.56), -CH_3 (6H, s, 2.11), -NH_2

	1592 (-N=N-), 1370, 1140 (sulfonate -S=O asym. & sym), 1164, 1046 (-S=O asym. & sym.).	(4H, s, 3.50), Ar-H (22H, m, 7.01-8.57)
D_{13}	3401 (-NH_2), 2966, 2872 (-CH_3 asym. & sym.), 1595 (-N=N-), 1366, 1143 (sulfonate -S=O asym. & sym), 1165, 1045 (-S=O asym. & sym.).	-CH_3 (6H, s, 1.58), -CH_3 (6H, s, 2.13), -NH_2 (4H, s, 3.47), Ar-H (24H, m, 6.91-8.63)
D_{14}	3410 (-NH_2), 2970, 2864 (-CH_3 asym. & sym.), 1597 (-N=N-), 1366, 1139 (sulfonate -S=O asym. & sym), 1160, 1048 (-S=O asym. & sym.).	-CH_3 (6H, s, 1.55), -CH_3 (6H, s, 2.07), -NH_2 (4H, s, 3.46), Ar-H (24H, m, 6.89-8.55)
D_{15}	3406 (-NH_2), 2971, 2858 (-CH_3 asym. & sym.), 1598 (-N=N-), 1365, 1139 (sulfonate -S=O asym. & sym), 1161, 1050 (-S=O asym. & sym.).	-CH_3 (6H, s, 1.60), -CH_3 (6H, s, 2.08), -NH_2 (4H, s, 3.45), Ar-H (22H, m, 6.91-8.59)

3.3. Dyeing properties

Dye ($D_{1\text{-}15}$) were applied on wool, silk and nylon fabrics in 2% shade according to the reported procedure [41,42]. Wool, silk, and nylon were dyed using tetrazo acid dyes in Laboratory Rota Dyer dyeing machine at a material to liquor ratio of 1:20 and P^H 3.0–4.0 by adding (10%) formic acid. Dyeing was sarted at room temperature and raised at a rate of 3 ^{o}C/min to 90 ^{o}C, maintained at this temperature for 60 min, and cooled to room temperature. The dyeing fabrics were rinsed under cold water and allowed to dry in the open air or oven at 50 ^{o}C. These dyes gave broad range of red, brown, violet, pink, yellow and orange shades on each fibers. The variations in hues of the dyed fabric result from the alteration in the coupling components.

3.4. Exhaustion and fixation study

The percentage exhaustion and fixation values of dyes on fabrics were determined according to the reported method [43,44] and are summarized in Table 3. The percentage exhaustion values of dyes ($D_{1\text{-}15}$) for wool ranges from 71% to 80%, in which dye D_5 shows maximum exhaustion value 80.55% while dye D_1 shows minimum exhaustion value 71.16 %; for silk ranges from 70% to 81%, in which dye D_9 shows maximum exhaustion value 81.35% while dye D_1 shows minimum exhaustion value 70.26 %; and for nylon ranges from 69% to

79%, in which dye D_4 shows maximum exhaustion value 79.12 % while dye D_1 shows minimum exhaustion value 69.91 %.

The percentage fixation values of dyes (D_{1-15}) for wool varied from 80% to 91%, in which dye D_6 shows maximum fixation value 91.07 % while dye D_6 shows minimum fixation value 80.51 %; for silk varied from 82% to 92%, in which dye D_9 shows maximum fixation value 92.30 % while dye D_1 shows minimum fixation value 82.41 %; and for nylon varied from 80% to 89%, in which dye D_5 shows maximum fixation value 89.50 % while dye D_1 shows minimum fixation value 80.63 %.

Table 3. Results of Exhaustion and Fixation study of D_{1-15} on wool, silk and nylon.

Dye No.	Shade on dyed fibre	λmax (nm)	%Exhaustion			% Fixation		
			W	S	N	W	S	N
D_1	Dark brown	470	71.16	70.26	69.92	81.51	82.55	80.81
D_2	Light violet	540	78.00	76.18	75.40	88.46	83.36	87.53
D_3	Dark yellow	480	74.28	77.54	73.10	83.47	88.99	88.24
D_4	Light brown	491	75.20	78.62	79.12	87.10	90.31	86.58
D_5	Pink	510	80.56	78.90	76.34	91.24	92.52	89.73
D_6	Maroon	515	72.00	73.20	73.18	80.56	88.11	85.41
D_7	Cream	441	75.86	77.42	73.64	86.34	91.71	83.51
D_8	Dark orange	478	74.26	71.58	72.16	85.51	87.31	81.76
D_9	Light yellow	460	78.00	81.36	76.00	90.38	92.18	88.16
D_{10}	Pale brown	489	72.50	74.08	72.56	82.76	83.69	84.07
D_{11}	Red	503	77.16	82.12	77.32	88.13	90.72	89.24
D_{12}	Pale yellow	450	77.12	74.92	78.20	85.58	86.09	86.32
D_{13}	Red brown	510	78.30	76.54	76.20	89.40	89.50	85.96
D_{14}	Pale mauve	522	75.44	76.28	73.12	83.51	88.49	82.06
D_{15}	orange	475	77.26	78.96	75.08	90.60	91.19	87.24

W= wool, S=silk, N=nylon.

3.5. Fastness properties

Data on fastness properties of light, perspiration, washing and rubbing are shown in Table 4. All the acid azo dyes (D_{1-15}) show fair to good light fastness property and good to very good washing, perspiration, rubbing fastness properties on wool, silk, nylon fibers. Out of this D_3, D_4, D_7, D_8 show good light fastness and very good washing, perspiration, rubbing fastness properties.

Table 4. Fastness properties of D_{1-15} on wool, silk and nylon.

Dye No.	Fastness to Light			Fastness to washing			Fastness to perspiration						Fastness to rubbing					
							Acidic			alkaline			Dry			Wet		
	W	S	N	W	S	N	W	S	N	W	S	N	W	S	N	W	S	N
D_1	4-5	4-5	5	4	3	4	4	3-4	4	4	3-4	4	4-5	4	4-5	4	3-4	4
D_2	4	4-5	4	3-4	4	3-4	3-4	4-5	4	3-4	4-5	4	4	4-5	4	4	4	3-4
D_3	4-5	5	4-5	4-5	4-5	4	4-5	5	4	4-5	5	4	4-5	5	4	4-5	4-5	4
D_4	5	5	5	4-5	5	4-5	5	5	4-5	5	5	4-5	5	5	4-5	5	5	4
D_5	3-4	4	4	3	3-4	3-4	3-4	4	3-4	3-4	4	3-4	4	4	3-4	3-4	3-4	3-4
D_6	4	4-5	4-5	3-4	4	4	3-4	4	4	3-4	4	4	4	4	4	3-4	4	4
D_7	5	4-5	4-5	4-5	4	4	4-5	4	4-5	4-5	4	4-5	5	4	4-5	5	4	4
D_8	4-5	5	4	4-5	4-5	4	4-5	4-5	4	4-5	4-5	4	4-5	4-5	4	4-5	4-5	4
D_9	4	4	4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	4	4	3-4	4	3-4	3-4
D_{10}	4-5	4	3-4	4	4	3-4	4	4	3-4	4	4	3-4	4-5	4	3-4	4-5	3-4	3-4
D_{11}	4-5	4	4	4	3-4	3	4	3-4	3-4	4	3-4	3-4	4	3-4	3-4	4	3-4	3-4
D_{12}	3-4	3-4	3-4	3	3	3	3	3	3	3	3	3	3	3-4	3-4	3	3	3
D_{13}	4	4-5	4-5	3-4	4	4	3-4	4	4	3-4	4	4	3-4	4	4-5	3-4	4	4
D_{14}	3-4	4	4	3	3	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	4	4	3	3	3
D_{15}	4-5	4-5	4-5	3-4	4	4	4	4	4	4	4	4	3-4	4	4-5	4	4	4

W= wool, S=silk, N=nylon.

Light fastness: 1-poor, 2-slight, 3-moderate, 4-fair, 5-good, 6-very good.

Wash, perspiration, rubbing fastness: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent.

Table 5. Antimicrobial activity data of dyes (D_{1-15}).

Dye No.	Minimal bactericidal concentration (µg/ml)				Minimal fungicidal concentration (µg/ml)		
	Gram-negative		Gram-positive				
	E. coli MTCC443	*P. aeruginosa* MTCC 1688	*S. aureus* MTCC 96	*S. pyogenes* MTCC 442	*C. albicans* MTCC 227	*A. niger* MTCC 282	*A. clavatus* MTCC 1323
D_1	500	500	500	250	>1000	1000	1000
D_2	500	500	250	500	>1000	1000	1000
D_3	250	250	250	200	500	500	500
D_4	200	250	200	250	500	500	500
D_5	500	500	1000	500	>1000	1000	1000
D_6	500	500	100	500	>1000	100	100
D_7	500	250	200	200	1000	250	250
D_8	62.5	200	500	500	1000	250	250
D_9	500	500	50	200	500	>1000	>1000
D_{10}	250	500	500	500	250	>1000	>1000
D_{11}	250	250	250	500	1000	500	500
D_{12}	100	200	250	500	1000	>1000	>1000
D_{13}	500	250	200	100	1000	>1000	>1000
D_{14}	500	250	200	200	500	>1000	>1000
D_{15}	125	100	500	250	250	>1000	>1000
Ampicillin	100	100	250	100	-	-	-
Chloramphenicol	50	50	50	50	-	-	-
Nystatin	-	-	-	-	100	100	100
Greseofulvin	-	-	-	-	500	100	100

3.6. Antimicrobial activity:

All the synthesized acid azo dyes (D_{1-15}) were tested for their antibacterial and antifungal activity (MIC) in vitro by broth dilution method. Antimicrobial data of all the dyes are summarized in Table 5.

3.7. Antibacterial Activity

Dye D_8 showed excellent activity and D_{12} showed equipotential activity against *E. coli* with respect to standard drug Ampicillin. Dye D_{15} showed equipotential activity against *P.aeruginosa* with respect to standard drug Ampicillin. Dye D_9 showed excellent activity against *S. aureus* with respect to standard drug Chloramphenicol. Dye D_4, D_6, D_7, D_{13}, D_{14} showed excellent activity and D_2, D_3, D_{11}, D_{12} showed equipotential activity against *S. aureus* with respect to standard drug Ampicillin. Dye D_{13} showed equipotential activity against *S. pyogenes* with respect to standard drug Ampicillin.

3.8. Antifungal Activity

Dye D_{10}, D_{15} showed excellent activity and D_3, D_4, D_9, D_{14} dye showed equipotential activity against *C. albicans* with respect to standard drug Greseofulvin. Dye D_6 showed equipotential activity against *A. niger* and *A. clavatus* with respect to both standard drug nystatin and greseofulvin.

4. Conclusion

Tetra azo acid dyes based on 4,4'-(propane-2,2-diyl)bis(2-methyl-4,1-phenylene)bis(3-aminobenzenesulfonate) were synthesized. These dyes give mostly orange, brown, violet, pink, yellow and orange shades on each fibers having good to very 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 synthesized dyes showed significant antibacterial and antifungal activity. The exhaustion and fixation of these dyes are very good this indicates that the dyes have good solubility and affinity 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 tetrazo structure results in very good colour strength.

Acknowledgements

The authors wish to thank the Professor and Head, Department of Chemistry, Veer Narmad South Gujarat University, Surat for providing research facilities. D. Rajani, Micro-care laboratory, Surat for antimicrobial activity, They are also thankful to the S.A.I.F, Chandigarh for spectral data and Atul Ltd., Valsad for dyeing facility and fastness test.

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