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RESEARCH ARTICLE

SYNTHESIS OF MONOAZO REACTIVE DYES AND THEIR DYEING PERFORMANCE ON VARIOUS FIBRES

Patel Pratixa K[1], Patel Sandip K[2], *Patel Paresh S[1] and Patel Keshav C[3]

[1]Department of Chemistry, Narmada College of Science and Commerce, Zadeshwar, Bharuch Gujarat, India
[2]Department of Chemistry, Navyug Science College, Surat, Gujarat, India
[3]Department of Chemistry, Veer Narmad South Gujarat University, Surat, Gujarat, India

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ABSTRACT

Various monoazo reactive dyes have been synthesized by coupling diazotized 2-amino-5-(3-carboxy-4-(4-oxo-2-phenylquinazolin-3(4H)-yl) benzyl) benzoic acid with various 2-(4-aminophenylsulphonyl) ethyl hydrogen sulphato cyanurated coupling components such as H-acid, gamma acid, J-acid, N-Methyl J-acid, N-Phenyl J-acid, S-acid, Naphthionic acid, Peri acid, Bronner acid, Tobias acid, K-acid and Koch acid. They are characterised by elemental analysis, IR and PMR spectra. Their dyeing performance has been assessed on cotton, wool, and silk fibres.

INTRODUCTION

Reactive dyes are a coloured compound which has a suitable group capable of forming a covalent bond between a carbon atom of the dye ion or molecule and oxygen, nitrogen or sulphur atom of a hydroxyl an amido or a mercapto group respectively of a substrate [Zollinger, *et al.*, 1991]. A great number of monochloro triazinyl reactive dyes have been synthesized for inartificial and synthetic fibres [Klier *et al.*, 1996 and Patel *et al.*, 2001]. Reactive dyes became very popular for dyeing cellulosic fibre promptly after marketing in 1956 due to above reasons and then use in dyeing cellulosic fibre has important evolved in the last four decennium [Zhan *et al.*, 1996].Reactive dyes can deduced also that dyes with two reactive groups give a higher fixation yield than dyes with one reactive group for it one of the two dye-fibre bonds is hydrolyzed, one is still left for fixation [Patel *et al.*, 2004 2011, Bredereck *et al.*, 1993]. Improvement in the structure of reactive chromogens, selection and large number of reactive groups led to an increased use of reactive dyes [Zheng *et al.*, 2004]. The presence of *s*-triazine structure in the dye molecule improves their dyeing ability and possibility for application [Konstantinova *et al.*, 2002 and Patel *et al.*, 2010]. These dyes are commonlly used on higher value clothes, which are normally mercerized [Shah *et al.*, 1994]. Pasha Khalid and Taylor A. John have synthesized two hetero bi-functional reactive dyes and their dyeing properties including exhaustion, colour strength on fabric, fixation and wash fastness were compared with leading products [Pasha *et al.*, 2013].

MATERIALS AND METHODS

The melting points of the compounds were determined using open capillary and are uncorrected. The purity of dyes was determined by thin-layer chromatography using silica gel-G coated Al-plates. IR were spectra recorded on FTIR spectrophotometer Perkin Elmer using KBr pellets. ^{1}H NMR were spectra obtained on Bruker Avance-II 400 NMR spectrometer using DMSO solvent and TMS as internal reference (chemical shifts in δ, ppm).

Synthesis of 4-oxo-2-phenyl -4H-3,1-benzoxazine (I)

Benzoyl chloride (14.05 g, 0.1 mol) was added dropwise to anthranilic acid (13.7 g, 0.1 mol) in ethanol (50 ml), with constant stirring at 8-10 ˚C over the period of one hour. After the completion of addition, the reaction mixture was stirred for half an hour at room temperature. At the end of the reaction solid mass was obtained, it was filtered, washed with sodium bicarbonate solution to remove completely unreacted acid and then with water, dried and recrystallized from rectified spirit.
Yield: 85 %, m.p.158-160 ˚C

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*Corresponding author: **Patel Paresh S**
Department of Chemistry, Narmada College of Science and Commerce, Zadeshwar, Bharuch Gujarat, India

Synthesis of 4,4′-methylene-bis anthranilic acid (II)

Anthranilic acid (13.7 g, 0.1 mol) was dissolved in water and 36.5% hydrochloric acid (25 ml) at 50°C and then treated with 3% aqueous formaldehyde solution (35ml). The temperature was maintained 60°C and stirred for an hour and neutralized with 10% sodium hydroxide to give yellow precipitates of 4,4'-methylene-bis anthranilic acid. It was filtered, washed with hot water, dried and recrystallized from ethanol. Yield: 82 %, m.p. 200-205°C

Synthesis of 2-amino-5-(3-carboxy-4-(4-oxo-2-phenylquinazoline-3(4H)-yl) benzyl) benzoic acid (III) (Alagarsamy et al 2013)

The mixture of 4-oxo-2-phenyl-4H-3,1-benzoxazine (I) (22.3 g, 0.1 mol), 4,4'-methylene bis-anthranilic acid (II) (28.6 g, 0.1 mol) and K_2CO_3 (6.9 g, 0.05 mol) was refluxed in dry ethanol (50 ml) for 8 hours. The reaction mixture was allowed to cool at 15-20°C to give 2-amino-5-(3-carboxy-4-(4-oxo-2-phenylquinazoline-3(4H)-yl) benzyl) benzoic acid (III). It was filtered, dried and recrystallized from ethanol.Yield 87 %, m.p.170-175 °C

Diazotization of 2-amino-5-(3-carboxy-4-(4-oxo-2-phenylquinazolin-3(4H)-yl) benzyl) benzoic acid (IV)

2-Amino-5-(3-carboxy-4-(4-oxo-2-henylquinazoline-3(4H)-yl) benzyl) benzoic acid (4.91 g, 0.01 mol) was suspended in H_2O (30ml). Conc. hydrochloric acid (10 ml) was added dropwise to this well stirred suspension. The mixture was gradually heated up to 70°C, till clear solution was obtained. The solution was cooled to 0-5°C in an ice bath. To this solution of $NaNO_2$ (1.38 g, 0.02 mol) in water (5ml) was added to 0°C, over a period of five minutes with continuous stirring. The stirring was continued for an hour, maintaining the same temperature, with

Table 1 Characterization of reactive dyes

Dye no.	Coupling component (R)	Molecular Formula	Mol. Weight g	Yield (%)	λ_{max} nm	Nitrogen %	
						Found	Req.
PS_1	H-acid	$C_{50}H_{33}ClN_9O_{18}S_4Na_3$	1280.5	86	520	9.76	9.84
PS_2	Gamma acid	$C_{50}H_{34}ClN_9O_{15}S_3Na_2$	1178.5	80	414	10.78	10.70
PS_3	J-acid	$C_{50}H_{34}ClN_9O_{15}S_3Na_2$	1178.5	86	480	10.62	10.70
PS_4	N-Methyl J-acid	$C_{51}H_{36}ClN_9O_{15}S_3Na_2$	1192.5	82	485	10.50	10.57
PS_5	N-Phenyl J-acid	$C_{56}H_{38}ClN_9O_{15}S_3Na_2$	1254.6	78	495	10.14	10.05
PS_6	S-acid	$C_{50}H_{34}ClN_9O_{15}S_3Na_2$	1178.5	80	377	10.60	10.70
PS_7	Naphthionic acid	$C_{50}H_{34}ClN_9O_{14}S_3Na_2$	1162.4	75	470	10.96	10.84
PS_8	Peri acid	$C_{50}H_{34}ClN_9O_{14}S_3Na_2$	1162.48	78	402	10.93	10.84
PS_9	Bronner acid	$C_{50}H_{34}ClN_9O_{14}S_3Na_2$	1162.4	81	520	10.72	10.84
PS_{10}	Tobias acid	$C_{50}H_{35}ClN_9O_{11}S_2Na$	1060.44	79	440	11.80	11.89
PS_{11}	K-acid	$C_{50}H_{32}ClN_9O_{20}S_5Na_4$	1366.5	82	450	9.30	9.22
PS_{12}	Koch acid	$C_{50}H_{32}ClN_9O_{20}S_5Na_4$	1366.5	83	460	9.16	9.22

Table 2 IR (PS_1-PS_{12}) and ^1H NMR (PS_3) data of reactive dyes

Dye No.	IR (KBr) (cm^{-1})
PS_1	3580 (O-H), 3410 (N-H), 3281 (C-H), 1630 (C=O), 1624 (N=N), 1540 (C-N), 1162 1056 (S=O, asy & sym), 807 (C-S), 718 (C-Cl).
PS_2	3582 (O-H), 3400 (N-H), 3278 (C-H), 1625 (C=O), 1620 (N=N), 1538 (C-N), 1158 1054 (S=O, asy & sym), 800 (C-S), 710 (C-Cl).
PS_3	3585 (O-H), 3412 (N-H), 3280 (C-H), 1628 (C=O), 1628 (N=N), 1535 (C-N), 1155 1050 (S=O, asy & sym, 810 (C-S), 715 (C-Cl).
PS_4	3587 (O-H), 3414 (N-H), 3288 (C-H), 3112 (CH_3), 1634 (C=O), 1620 (N=N), 1537 (C-N), 1159 1051 (S=O, asy & sym), 802 (C-S), 712 (C-Cl).
PS_5	3575 (O-H), 3405 (N-H), 3275 (C-H), 1628 (C=O), 1620 (N=N), 1530 (C-N), 1160 1060 (S=O, asy & sym), 805 (C-S), 720 (C-Cl).
PS_6	3570 (O-H), 3400 (N-H), 3270 (C-H), 1630 (C=O), 1622 (N=N), 1535 (C-N), 1155 1052 (S=O, asy & sym), 810 (C-S), 722 (C-Cl).
PS_7	3412 (N-H), 3285 (C-H), 1635 (C=O), 1624 (N=N), 1536 (C-N), 1160 1058 (S=O, asy & sym), 808 (C-S), 714 (C-Cl).
PS_8	3407 (N-H), 3275 (C-H), 1635 (C=O), 1628 (N=N), 1532 (C-N), 1158 1050 (S=O, asy & sym), 810 (C-S), 715 (C-Cl).
PS_9	3405 (N-H), 3278 (C-H), 1637 (C=O), 1621(N=N), 1530 (C-N), 1165 1032 (S=O, asy & sym), 802 (C-S), 712 (C-Cl).
PS_{10}	3412 (N-H), 3270 (C-H), 1640 (C=O), 1628 (N=N) , 1535 (C-N), 1150 1045 (S=O, asy & sym), 800 (C-S), 714 (C-Cl).
PS_{11}	3405 (N-H), 3275 (C-H), 1632 (C=O), 1620 (N=N), 1538 (C-N), 1160 1061 (S=O, asy & sym), 802 (C-S), 713 (C-Cl).
PS_{12}	3412 (N-H), 3283 (C-H), 1635 (C=O), 1627 (N=N), 1535 (C-N), 1165 1063 (S=O, asy & sym), 812 (C-S), 720 (C-Cl).
Dye No.	1H NMR(DMSO-d6) (Chemical shift in δ ppm)
PS_3	3.65-3.67 (t, 2H, $–CH_2–$), 3.85 (s, 2H, $–CH_2–$), 4.00 (s, 2H, –NH–), 4.25-4.27 (t, 2H, $–CH_2–$), 5.40 (s, 1H, –OH), 11.19 (s, 2H, –COOH, 7.09-8.72 (m, 23H, Ar–H)

Abbreviations in ^1H NMR data: s, singlet, d, doublet, t, triplet, m, multiplet.

Table 3 Result of Exhaustion and Fixation study of reactive dyes on silk, wool, cotton and shade on fabrics

Dye No.	Shade on silk fabrics	Shade on wool fabrics	Shade on cotton fabrics	Exhaustion (%)			Fixation (%)		
				S	W	C	S	W	C
PS_1	Light pink	Pink	Pink	70.20	70.10	67.25	85.25	89.20	87.35
PS_2	Light orange	Red	Khakhi	76.35	71.24	68.48	90.25	91.56	90.45
PS_3	Golden yellow	Cream	Red	80.45	73.10	71.45	93.20	86.25	85.26
PS_4	Brown	Yellow	Coffee	68.67	68.25	67.22	82.34	81.36	80.10
PS_5	Light cream	Yellowish brown	Khakhi	75.47	67.22	65.24	85.46	86.62	84.23
PS_6	Golden brown	Light cream	Turmeric yellow	79.20	70.27	69.40	87.60	88.24	87.60
PS_7	Light yellow	Orange	Yellow	73.27	66.47	70.20	89.89	90.26	89.21
PS_8	Dark cream	Light orange	Pale yellow	68.20	69.38\	67.45	92.78	91.24	88.24
PS_9	Light cream	Yellow	Yellow	72.35	70.45	70.68	87.68	85.61	84.32
PS_{10}	Yellow	Cream	Yellow	67.28	66.78	66.97	89.10	88.23	86.58
PS_{11}	Dark yellow	Dark cream	Dark yellow	78.46	72.20	72.61	91.22	90.87	89.78
PS_{12}	Yellowish brown	Orange	yellow	75.29	69.35	68.54	86.45	85.68	84.92

Determined in water at 28 °C at 2×10^{-3} M dye concentrations. S = Silk, W = Wool, C = Cotton.

Table 4 Fastness properties of reactive dyes on wool silk and cotton

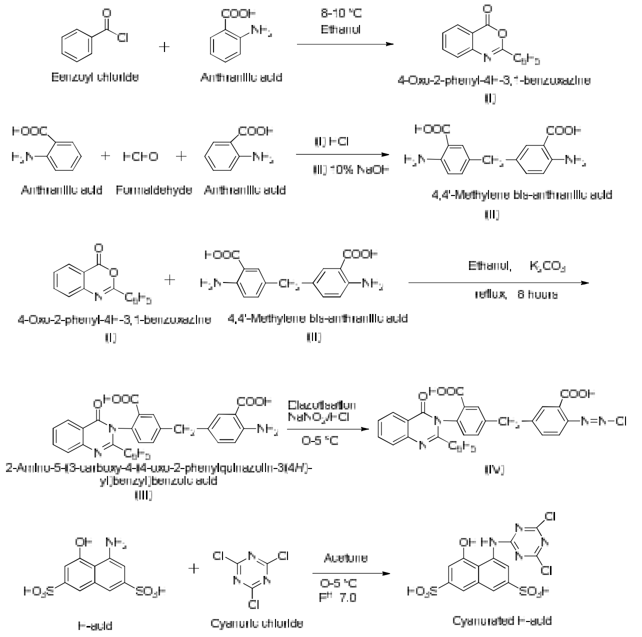
Dye No.	Light fastness			Wash fastness			Rubbing fastness					
							Dry			Wet		
	S	W	C	S	W	C	S	W	C	S	W	C
PS_1	5	5	4	4-5	4	3-4	4	5	4	4	4-5	4
PS_2	5-6	4-5	3-4	4-5	5	4	4-5	4	4-5	4-5	5	5
PS_3	4	5	4	3-4	4-5	3-4	5	5	4	5	4-5	5
PS_4	6	4-5	5	4-5	5	5	3-4	4	4-5	4-5	4	5
PS_5	5	4	4-5	4	4-5	4-5	4-5	4	5	3-4	4	4-5
PS_6	5	4-5	4	4-5	5	4	3-4	4-5	4-5	4	4	4
PS_7	5	4-5	4	5	4-5	5	4-5	4	5	3-4	4-5	5
PS_8	4-5	5	4-5	4	4-5	5	4	4-5	3-4	4	5	4-5
PS_9	3-4	4	4	4	3-4	4	4-5	4	4	3-4	4-5	4
PS_{10}	5	4-5	4-5	5	5	4-5	5	4-5	5	4-5	4	5
PS_{11}	4	4-5	5	5	4-5	5	4	5	4-5	3-4	4-5	4-5
PS_{12}	5	5	4-5	4-5	4	4-5	4	4	4-5	4	3-4	4

S = Silk, W = Wool, C = Cotton.

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

Wash & Rubbing fastness: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent

Reaction Scheme



The excess of nitrous acid was destroyed with required amount of sulphamic acid solution in water. The clear diazotized solution (IV) at 0-5°C was obtained and used for subsequent coupling reaction.

Synthesis of 2-((4-aminophenyl)sulfonyl)ethyl hydrogen sulfato cyanurated H-acid (V) (patel et al *2011)*

Cyanuration of H-acid

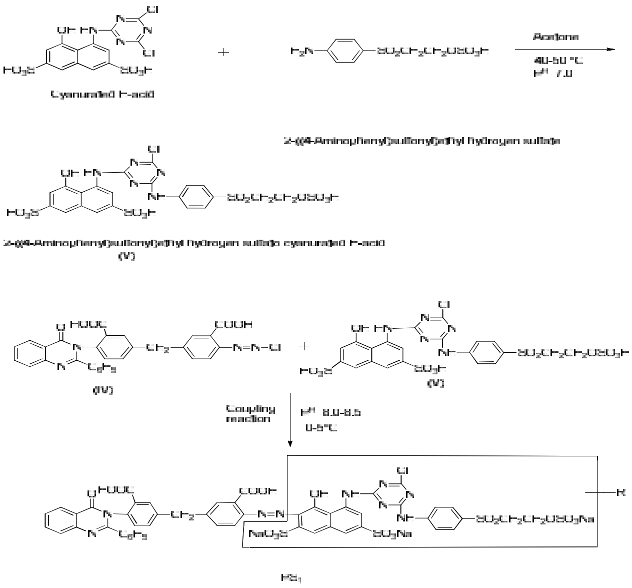
Cyanuric chloride (1.84 g, 0.01 mol) was stirred in acetone (25ml) at a temperature below 5°C for a period of an hour. A neutral solution of H-acid (3.19 g, 0.01mol) in aqueous sodium carbonate solution (10% w/v) was then added in small lots about an hour. The pH was maintained neutral by simultaneous addition of sodium carbonate solution (1% w/v). The reaction mass was then stirred at 0-5°C for further 4 hours. The cyanurated H-acid solution was used for subsequent coupling reaction.

Condensation with 2-((4-aminophenyl)sulfonyl)ethyl hydrogen sulfate

The ice-cooled well stirred solution of cyanurated H-acid, (4.67 g, 0.01 mol) was gradually raised to 45°C for half an hour. To this cyanurated H-acid the 2-((4 aminophenyl)sulfonyl)ethyl hydrogen sulfate (2.81 g, 0.01 mol) was added slowly at same temperature, during a period of 30 minutes, maintaining the pH neutral by simultaneous addition of sodium bicarbonate solution (1%w/v). After the addition was completed, stirring was continued for further 3 hours. The 2-((4-aminophenyl)sulfonyl)ethyl hydrogen sulfato cyanurated H-acid solution (V) thus obtained was subsequently used for further coupling reaction.

Coupling of diazotized solution (IV) with 2-((4-aminophenyl)sulfonyl)ethyl hydrogen sulfato cyanurated H-acid coupling component (V): synthesis of dyes (PS_1-PS_{12})

To an ice cold and well stirred solution of 2-((4-aminophenyl)sulfonyl)ethyl hydrogen sulfato cyanurated H-acid (V), the above mentioned freshly prepared diazotized solution (IV) was added dropwise over a period of 10-15 minutes. The pH was maintained at 8.0 to 8.5 by simultaneous addition of sodium carbonate solution (10% w/v) and stirring was continued for 4 hours. Sodium chloride (15 g) was then added and the mixture was stirred for an hour. The solid dye separated out was filtered, washed with minimum amount of acetone and dried.



Where, R= various 2-((4-aminophenyl)sulfonyl)ethyl hydrogen sulfato cyanurated coupling components to synthesized PS_1 to PS_{12} (Table-1)

RESULTS AND DISCUSSION

Dyeing of fibres

All the synthesized dyes (PS_1-PS_{12}) were applied on silk, wool and cotton fabrics in 2% shade according to usual procedure [Shenai *et al*., 1973]. The variation colour of the dyed fabric results from both the nature and position of the substituent present on the coupler ring.

Spectral properties

It is clear that the value of λ_{max} depends on the coupling component used. Visible absorption spectroscopic properties of dye were recorded in water (Table-1).The colour change observed for each dye is due to the oscillation of electrons and the presence of additional substituents.

IR and ^{1}H NMR spectral study

IR spectra of all the dyes, in general showed in the region O-H stretching at 3570-3587 cm^{-1}, N-H stretching vibration at 3400-3414 cm^{-1}, C-H stretching vibration at 3270-3281 cm^{-1}, N=N stretching vibration at 1620-1628 cm^{-1}, C-N stretching vibration at 1530-1540 cm^{-1}, S=O stretching vibration at 1032-1165 cm^{-1}, C-S stretching vibration at 800-812 cm^{-1}, C-Cl stretching vibration at 710-722 cm^{-1} (Table-2). The ^{1}H NMR spectra of selected dye showed all the signals (Table-2).

Exhaustion and fixation study

The percentage exhaustion of 2% dyeing on silk fabric showed from 67.28 to 80.45%, for wool fabric showed from 66.47 to 73.10% and for cotton fabric showed from 65.24 to 72.61%.The percentage fixation of 2% dyeing on silk fabric showed from 82.34 to 93.2%, for wool fabric showed from 81.36 to 91.56% and for cotton fabric showed from 80.10 to 90.45%, (Table-3).

Fastness properties

The light fastness was study according to BS: 1006-1978 [Standard Test Method, 1994]. The rubbing fastness test was carried out with a Crock meter (Atlas) in accordance with AATCC-1961 [AATCC Test, 1961] and the wash fastness test in accordance with IS: 765-1979 [Indian Standard, 1979]. The light fastness of all the dyes showed moderate to good on cotton, silk and wool. The wash fastness of all the dyes showed good to excellent on silk, wool ,cotton and the rubbing fastness (dry and wet) of all the dyes showed very good order on wool, silk and cotton fabrics(Table-4).

CONCLUSIONS

2-Amino-5-(3-carboxy-4-(4-oxo-2-phenylquinazolin-3(4H)-yl) benzyl) benzoic acid was diazotized and coupled with various 2-((4-aminophenyl)sulfonyl)ethyl hydrogen sulfato cyanurated coupling components to give the corresponding monoazo reactive dyes (PS_1 to PS_{12}). These dyes gave pink, orange, brown and yellow shade on wool, silk and cotton having very good fastness properties. Exhaustion and fixation of these dyes are very good in order. These dyes PS_1 PS_2 PS_4 PS_5 PS_6 PS_7 PS_{10} and PS_{12} gave better light fastness. The introduction of a triazine group to the dye molecule improves the degree of exhaustion and fixation of the dyes. The remarkable degree of levelness after washing indicates the good penetration and affinity of these dyes to the fabric.

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