

Synthesis of Monoazo Reactive Dyes based on 4,4'-Methylene bis-(2-nitro aniline) and their Dyeing Performance on Various Fibres

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Abstract: Various monoazo reactive dyes have been synthesized by diazotized 3-(4-(4-amino-3-nitrobenzyl)-2-nitrophenyl)-2-phenylquinazolin-4(3H)-one and coupling with various 2-(4-aminophenylsulphonyl) ethyl hydrogen sulfato 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. Dyeing properties of these dyes on silk, wool and cotton have been assessed. The dyed fibres showed moderate to very good fastness properties.

Keywords: 3-(4-(4-amino-3-nitrobenzyl)-2-nitrophenyl)-2-phenylquinazolin-4(3H)-one, dyeing, silk, wool, cotton, IR and PMR spectra.

1. Introduction

Dyeing using reactive dyes have recently led to increased demands on the quality of the dyeing and profitability of the dyeing process. There is compliant still a demand for novel reactive dyes which have improved properties, especially in respect of application [1]. Reactive dyes have a sufficient substantivity and at the same time a good ease of washing out of the non fixed portions are required for dyeing. They should furthermore have a good tinctorial yield and high reactivity and dyeing having high degrees of fixing in particular should be produced [2]. Reactive dyes are now a major group of dyes, though a late entry into the family of synthetic dyes, very soon attained a commercial status. There is no slackening of activity in this field as seen from the large number of patent specification and several ranges which continue to appear in the market [3, 4].

It can also be easily understood 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 [5, 6]. The possibility of forming covalent bond between dyes and fibres had long been attractive to dye chemists, since attachment by physical adsorption and by mechanical obstruction had the disadvantage of either low wash fastness or high cost [7, 8]. It was anticipated that the covalent attachment of the dye molecules to the fibre would produce very high fastness because covalent bonds were the strongest known binding forces between molecules [9, 10]. s-Triazine based chemicals have been applied variously in the manufacture of polymers, dyes, drugs, explosives, pesticides and commodity chemicals [11] as a consequence, theoretical and experimental studies on these chemicals have been widely carried out [12, 13] with the result that the s-triazine ring is known as an important conjugated heterocycle whose electronics properties are expected to show suitable differences from those of benzene due to the alternate replacement of -CH- group by nitrogen atoms [14]. Hot-

Brand reactive dyes have been widely considered due to their fixation yield on various fibres [15]. Patel et al. have also synthesized bisazo reactive dyes by diazotization of 4,4'-diaminobenzanilide with various cyanurated coupling components. Their dyeing performance on silk, wool and cotton fibres has been assessed. The dyed fibre showed fair to very good light fastness and very good to excellent washing and rubbing fastness [16-19].

2. Materials and Methods

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

Benzoyl chloride (14.05 g, 0.1 mole) was added dropwise to anthranilic acid (13.7 g, 0.1 mole) 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 washed with water, dried and recrystallized from rectified spirit.

Yield: 85 %, m.p. 158-160 °C

2.2 Synthesis of 4, 4'-methylene-bis (2-nitro aniline) (II)

2-Nitro aniline (13.8 g, 0.1 mole) was dissolved in water and 36.5% hydrochloric acid (25 ml) at 50°C and then treated with 3% aqueous formaldehyde solution (35 ml) at 60°C with stirring. The temperature was maintained at 60°C with stirring for an hour and then neutralized with 10% sodium hydroxide to give yellow precipitates of 4, 4'-methylene-bis (2-nitro aniline). It was filtered, washed with hot water, dried and recrystallized from rectified spirit.

Yield: 85 %, m.p. 170-175°C

2.3 Synthesis of 3-(4-(4-amino-3-nitrobenzyl)-2-nitrophenyl)-2-phenylquinazolin-4(3H)-one (III)

The mixture of 4-oxo-2-phenyl-4H-3, 1-benzoxazine (I) (22.3 g, 0.1 mole), 4, 4'-methylene bis-(2-nitro aniline) (II) (28.8 g, 0.1 mole) and K_2CO_3 (6.9 g, 0.05 mole) was refluxed in dry ethanol (50.0 ml) for 8 hours. The reaction mixture was allowed to cool at 15-20°C to give 3-(4-(4-amino-3-nitrobenzyl)-2-nitrophenyl)-2-phenylquinazolin-4(3H)-one (III). It was filtered, dried and recrystallized from ethanol.

Yield 85 %, m.p.190-195 °C

2.4 Diazotization of 3-(4-(4-amino-3-nitrobenzyl)-2-nitrophenyl)-2-phenylquinazolin-4(3H)-one (IV)

3-(4-(4-Amino-3-nitrobenzyl)-2-nitrophenyl)-2-phenylquinazolin-4(3H)-one (4.93 g, 0.01 mole) was suspended in H_2O (30 ml). 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 mole) in water (5 ml) 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 positive test for nitrous acid on starch iodide paper. 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) Cyanuration of H-acid

Cyanuric chloride (1.84g, 0.01 mole) was stirred in acetone (25 ml) at a temperature below 5°C for a period of an hour. A neutral solution of H-acid (3.19g, 0.01mole) 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.

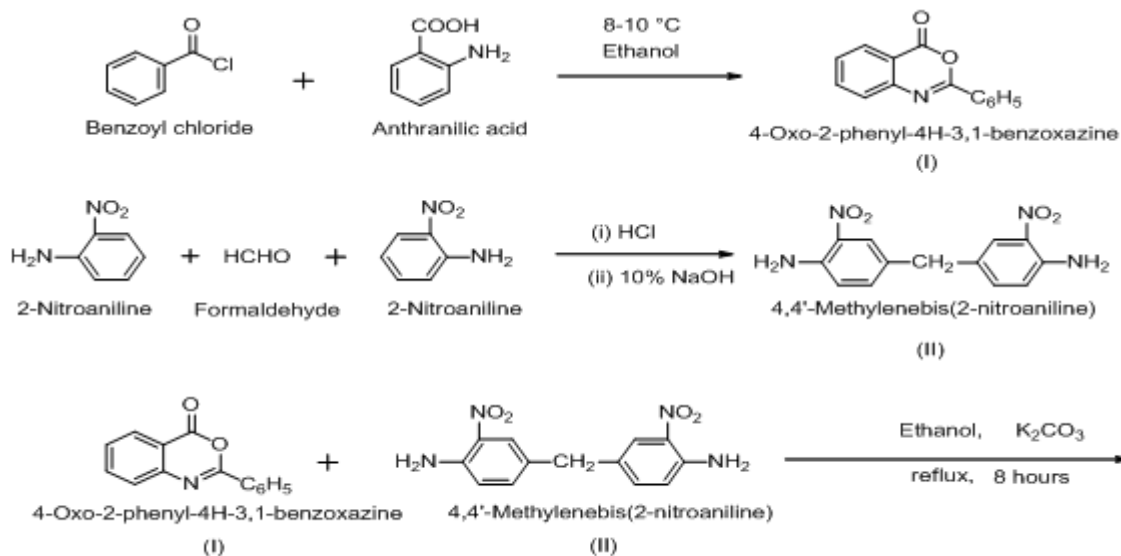
Condensation with 2-((4-aminophenyl)sulfonyl)ethyl hydrogen sulfate

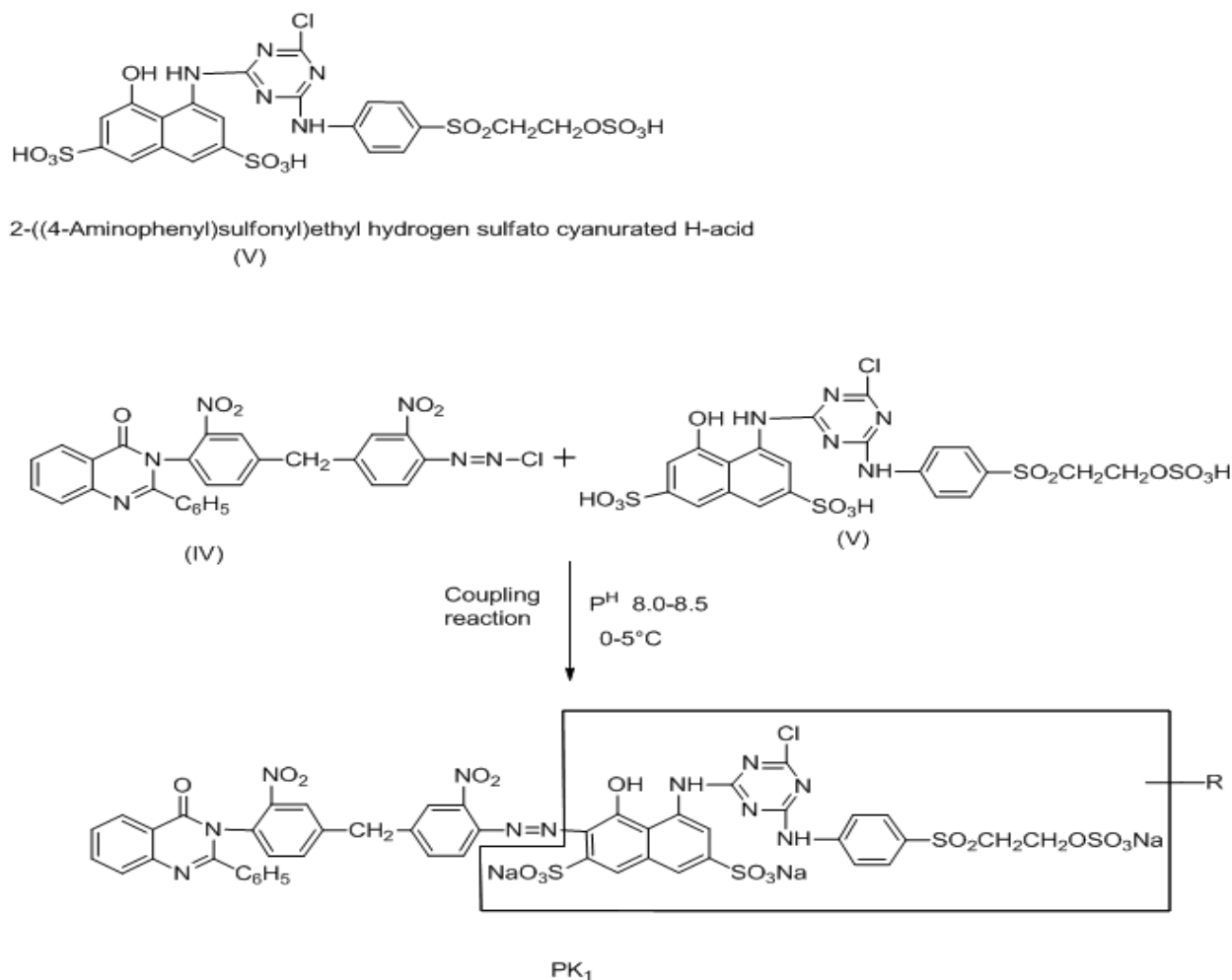
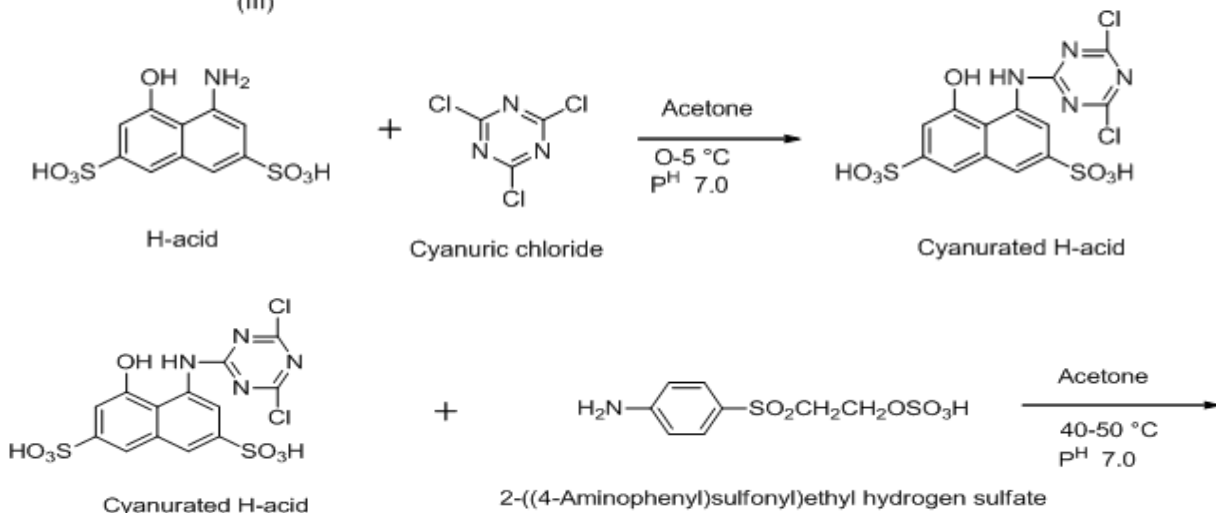
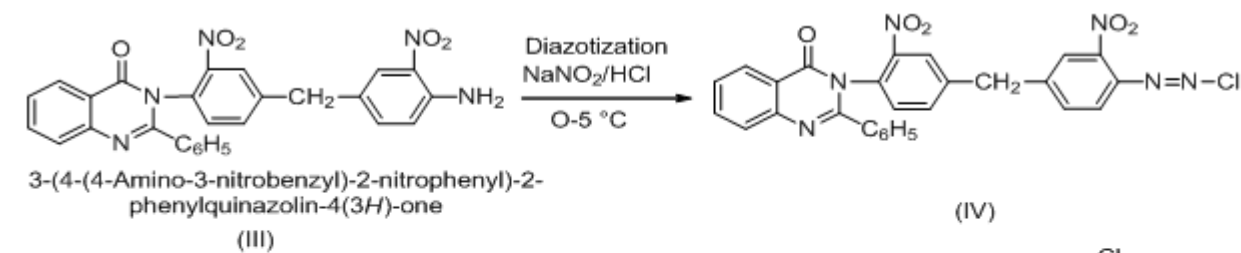
The temperature of ice-cooled well stirred solution of cyanurated H-acid, (4.67 g, 0.01 mole) was gradually raised to 45°C for half an hour. To this cyanurated H-acid, the 2-((4-aminophenyl)sulfonyl)ethyl hydrogen sulfate (2.81 g, 0.01 mole) was added slowly at same temperature, during a period of 30 min, 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): Formation of dyes (PK₁-PK₁₂)

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 min. 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.

3. Reaction Scheme





Where, R = various 2-((4-aminophenyl)sulfonyl)ethyl hydrogen sulfato cyanurated coupling components to synthesized PK₁ to PK₁₂ (Table-1)

4. Results and Discussion

Dyeing of fibres

All the dyes were applied on silk, wool and cotton fabrics in 2% shade according to usual procedure [20]. The variation in the hues of the dyed fabric results from both the nature and position of the substituent present on the coupler ring. The remarkable degree of levelness after washing indicates good penetration and affinity of these dyes to the fabric.

A series of reactive dyes were synthesized in order to evaluate their stability for dyeing cotton, wool and silk fabrics. The yield of these dyes ranges from 78 to 88 %. The structures were identified by analytical and spectral evidences.

IR and ¹H NMR spectral study

IR spectra of all the dyes, in general showed O-H and N-H stretching vibrations in the region 3570-3588 cm⁻¹, 3401-3418 cm⁻¹ respectively, C-H stretching vibration at 3270-3288 cm⁻¹, N=N stretching vibration at 1610-1629 cm⁻¹, C-N stretching vibration at 1507-1548 cm⁻¹, S=O stretching vibration at 1033-1168 cm⁻¹, C-Cl stretching vibration at 709-724 cm⁻¹, NO₂ stretching vibration at 1521-1529 cm⁻¹ (Table-2). The ¹H NMR spectra of representative dyes showed all the signals (Table-2).

Exhaustion and fixation study

The percentage exhaustion of 2% dyeing on silk fabric showed from 65.67% to 78.99%, for wool fabric showed from 65.41% to 76.46% and for cotton fabric showed from 66.02% to 75.98%. The percentage fixation of 2% dyeing on silk fabric showed from 70.39% to 93.78 %, for wool fabric showed from 75.97% to 92.90% and for cotton fabric showed from 73.39% to 95.31 %, (Table-3).

Spectral properties

Electronic spectra: From the data reported in Table-3, it is apparent that the value of λ_{max} depends on the coupling components used. The colour change observed for each dye is due to the oscillation of electrons and the presence of additional substituents.

Visible Absorption Spectroscopic Properties of Dye: The visible absorption spectroscopic properties of dyes were recorded in water (Table-3). The colour of the dye is affected by substituents in the coupling constituent.

Fastness properties

The light fastness was study according to BS: 1006-1978 [21]. The rubbing fastness test was carried out with a Crock meter (Atlas) in accordance with AATCC-1961 [22] and the wash fastness test in accordance with IS: 765-1979 [23]. The light fastness of all the dyes showed moderate to good on silk, wool and cotton. The wash fastness of all the dyes showed good to excellent on silk, wool and cotton and the rubbing fastness (dry and wet) of all the dyes showed good to excellent rubbing fastness on wool, silk and cotton fabrics (Table-4).

5. Conclusions

3-(4-(4-Amino-3-nitrobenzyl)-2-nitrophenyl)-2-phenylquinazolin-4(3H)-one was diazotized and coupled with various 2-((4-aminophenyl)sulfonyl)ethyl hydrogen sulfato cyanurated coupling components to give the corresponding monoazo reactive dyes (PK₁ to PK₁₂). These dyes gave pink, orange, cream, maroon and yellow shade on wool, silk and cotton and showed very good fastness properties. Exhaustion and fixation of these dyes are very good in order. These dyes PK₁ PK₃ PK₄ PK₅ PK₇ and PK₁₁ 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.

6. Acknowledgement

The authors thankful to Department of Chemistry, Narmada College of Science and Commerce Zadeshwar, Bharuch and Newreka green synth technologies pvt. Ltd for providing necessary research facility, SAIF Chandigarh for spectral data and Atul Ltd, Valsad for dyeing and fastness tests.

Table 1: Physical properties of dyes PK₁-PK₁₂

Dye No.	R	Molecular Formula	Molecular Weight (g.)	Yield %	M.P °C	λ_{max} nm	Nitrogen %	
							Found	Calcd.
PK1	H-acid	C ₄₈ H ₃₁ CIN ₁₁ Na ₃ O ₁₈ S ₄	1282	80	260	535	12.11	12.01
PK2	Gamma acid	C ₄₈ H ₃₂ CIN ₁₁ Na ₂ O ₁₅ S ₃	1180	81	220	509	13.15	13.05
PK3	J-acid	C ₄₈ H ₃₂ CIN ₁₁ Na ₂ O ₁₅ S ₃	1180	80	240	413	13.18	13.05
PK4	N-Methyl J-acid	C ₄₉ H ₃₄ CIN ₁₁ Na ₂ O ₁₅ S ₃	1194	85	280	495	12.97	12.90
PK5	N-Phenyl J-acid	C ₅₄ H ₃₆ CIN ₁₁ Na ₂ O ₁₅ S ₃	1256	84	220	490	12.36	12.26
PK6	S-acid	C ₄₈ H ₃₂ CIN ₁₁ Na ₂ O ₁₅ S ₃	1180	80	240	420	13.21	13.05
PK7	Naphthionic acid	C ₄₈ H ₃₂ CIN ₁₁ Na ₂ O ₁₄ S ₃	1164	87	205	412	13.32	13.23
PK8	Peri acid	C ₄₈ H ₃₂ CIN ₁₁ Na ₂ O ₁₄ S ₃	1164	79	170	410	13.15	13.23
PK9	Bronner acid	C ₄₈ H ₃₂ CIN ₁₁ Na ₂ O ₁₄ S ₃	1164	83	140	419	13.28	13.23
PK10	Tobias acid	C ₄₈ H ₃₃ CIN ₁₁ NaO ₁₁ S ₂	1062	79	230	397	14.62	14.50
PK11	K-acid	C ₄₈ H ₃₀ CIN ₁₁ Na ₄ O ₂₀ S ₅	1368	88	150	379	11.18	11.26
PK12	Koch acid	C ₄₈ H ₃₀ CIN ₁₁ Na ₄ O ₂₀ S ₅	1368	78	170	512	11.40	11.26

Table 2: IR and ¹H NMR data of dyes PK₁-PK₁₂

Dye No.	IR (KBr) cm ⁻¹
PK ₁	3584 (O-H), 3416 (N-H), 3287 (C-H), 1635 (C=O), 1627 (N=N), 1548 (C-N), 1163, 1057 (S=O, asy & sym), 803 (C-S), 714 (C-Cl), 1524 (NO ₂).
PK ₂	3586 (O-H), 3407 (N-H), 3279 (C-H), 1626 (C=O), 1624 (N=N), 1539 (C-N), 1153, 1050 (S=O, asy & sym), 803 (C-S), 714 (C-Cl), 1525 (NO ₂).
PK ₃	3581 (O-H), 3411 (N-H), 3282 (C-H), 1629 (C=O), 1629 (N=N), 1537 (C-N), 1154, 1057 (S=O, asy & sym), 817 (C-S), 713 (C-Cl), 1522 (NO ₂).
PK ₄	3570 (O-H), 3401 (N-H), 3275 (C-H), 1620 (C=O), 1610 (N=N), 1507 (C-N), 1152, 1052 (S=O, asy & sym), 818 (C-S), 709 (C-Cl), 1529 (NO ₂).
PK ₅	3578 (O-H), 3408 (N-H), 3270 (C-H), 1621 (C=O), 1624 (N=N), 1533 (C-N), 1166, 1065 (S=O, asy & sym), 807 (C-S), 724 (C-Cl), 1523 (NO ₂).
PK ₆	3571 (O-H), 3409 (N-H), 3271 (C-H), 1636 (C=O), 1627 (N=N), 1538 (C-N), 1153, 1054 (S=O, asy & sym), 811 (C-S), 720 (C-Cl), 1526 (NO ₂).
PK ₇	3583 (O-H), 3418 (N-H), 3288 (C-H), 1630 (C=O), 1620 (N=N), 1531 (C-N), 1168, 1060 (S=O, asy & sym), 809 (C-S), 710 (C-Cl), 1522 (NO ₂).
PK ₈	3580 (O-H), 3406 (N-H), 3270 (C-H), 1634 (C=O), 1627 (N=N), 1530 (C-N), 1154, 1056 (S=O, asy & sym), 811 (C-S), 714 (C-Cl), 1524 (NO ₂).
PK ₉	3587 (O-H), 3406 (N-H), 3277 (C-H), 1635 (C=O), 1620(N=N), 1529 (C-N), 1165, 1050 (S=O, asy & sym), 812 (C-S), 716 (C-Cl), 1529 (NO ₂).
PK ₁₀	3580 (O-H), 3412 (N-H), 3270 (C-H), 1640 (C=O), 1628 (N=N), 1535 (C-N), 1150, 1058 (S=O, asy & sym), 800 (C-S), 714 (C-Cl), 1525 (NO ₂).
PK ₁₁	3573 (O-H), 3409 (N-H), 3272 (C-H), 1637 (C=O), 1626 (N=N), 1539 (C-N), 1165, 1069 (S=O, asy & sym), 808 (C-S), 710 (C-Cl), 1521 (NO ₂).
PK ₁₂	3588 (O-H), 3411 (N-H), 3286 (C-H), 1639 (C=O), 1621 (N=N), 1538 (C-N), 1164, 1065 (S=O, asy & sym), 811 (C-S), 724 (C-Cl), 1522 (NO ₂).

Dye No.	¹ H NMR (DMSO) Chemical shift in δ ppm
PK ₁	3.62-3.64 (t, 2H, -CH ₂ -), 3.81 (s, 2H, -CH ₂ -), 3.98 (s, 2H, 2, -NH), 4.22 (t, 2H, -CH ₂ -), 5.36 (s, 1H, -OH), 6.96-8.67 (m, 22H, 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
PK ₁	Pink	Dark maroon	Pink	73.76	74.53	70.56	85.45	92.08	92.73
PK ₂	Light maroon	Light maroon	Yellowish pink	68.97	71.78	70.90	77.90	90.92	86.84
PK ₃	Light orange	Light Orange	Light orange	72.56	65.64	66.87	92.95	88.51	76.23
PK ₄	Orange	Orange	Orange	73.87	72.28	75.76	93.78	89.06	90.73
PK ₅	Dark orange	Dark orange	Dark orange	68.97	76.46	73.90	74.67	88.40	95.31
PK ₆	Golden	Cream	Cream	65.98	67.75	64.78	72.76	87.89	78.95
PK ₇	Yellow	Dark Yellow	Yellow	74.97	76.97	72.87	92.74	91.24	93.73
PK ₈	Cream	Yellow	Light cream	69.97	69.99	67.97	75.98	75.98	74.44
PK ₉	Yellow	Pale yellow	Pale yellow	76.98	65.41	66.02	91.54	77.77	76.87
PK ₁₀	Dark yellow	Dark orange	Dark cream	78.99	70.54	75.98	93.63	92.90	75.89
PK ₁₁	Yellow	Light Yellow	Light cream	78.97	68.62	71.09	87.52	90.56	73.39
PK ₁₂	Dark cream	Dark yellow	Pale yellow	65.67	77.77	69.87	70.39	78.54	94.87

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

Table 4: Fastness properties of dyes PK₁-PK₁₂

Dye No.	Light fastness			Wash fastness			Rubbing fastness					
	S	W	C	S	W	C	Dry			Wet		
							S	W	C	S	W	C
PK ₁	5-6	5	5	4-5	4	5	5-6	5	5	5	5	4-5
PK ₂	4-5	4	5	5	5	4	5	4-5	5	4	4-5	4
PK ₃	5-6	6	4	5	5	5	5-6	5	4	4-5	3-4	3
PK ₄	5	5	4-5	4	5	5	4	4-5	4	5	5	3
PK ₅	5	5	5	3-4	5	4	4	4-5	4	4	4	4
PK ₆	3-4	3	4	3-4	3	4	3	3-4	4	3	4	3
PK ₇	5	5	4-5	4	4	4	4-5	5	5	4	5	3-4
PK ₈	3-4	4	5	3	4	3	3	4-5	3-4	5	5	3
PK ₉	4	5	5	3-4	4	4	4	4	4-5	3-4	3	3-4
PK ₁₀	5	4	3-4	4-5	5	4	4-5	3-4	5	5	4	4
PK ₁₁	5	5	4-5	4	4	4	5	5	4	4	4	4
PK ₁₂	3-4	5	4	2-3	4	3	3-4	4-5	5	3-4	4	3

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

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