Synthesis, Characterization and Application of some new 3,3'-Methylene bis (2-amino-5-sulphobenzoic acid) based Reactive Dyes

PARIKSHIT I. VASHI, PARESH S. PATEL, KESHAV C. PATEL
Department of Chemistry, Veer Narmad South Gujarat University, Surat, Gujarat, India

Abstract:
This research work was carried out for synthesis of new Pyrazolone acid reactive dyes based on 3,3'-Methylene bis (2-amino-5-sulphobenzoic acid). Tetrazotized compound was coupled with different pyrazolone coupling components and dye performance was studied subject to its application on wool and silk fabrics. The dyes were analysed for percentage dye bath exhaustion and fixation and were characterised by TLC, IR spectra and NMR Spectra. The dyes showed moderate to very good fastness to light, wash and rubbing.

Keywords: *Pyrazolone acid reactive dyes, 3,3'- Methylene bis (2-amino-5-sulphobenzoic acid), Exhaustion, Fixation, Silk, Wool*

1. Introduction

Acid Dyes constitutes an important class of Reactive dyes. Acid Reactive Dyes owing to the presence of one or more sulphonic acid or other acidic group easily binds to wool, silk and other polyamide fibres using an acidic or neutral dye bath[1,2], but they have to meet certain conditions for their application on different fibres[3]. Although these dyes are not substantive to cellulosic fibres, they can be applied directly by printing on protein fibres and nylon. Few selected dyes can be impressed on viscose from a paste containing Urea [4].

This dyeing behaviour has incited eagerness in respect of acid reactive dyes, in this context the present research paper deal with synthesis of pyrazolone acid reactive dyes based on 3,3'- Methylene bis (2-amino-5-sulphobenzoic acid) and further examines dyeing properties, fastness properties. The general structure of the dye is as given below in Figure 1:

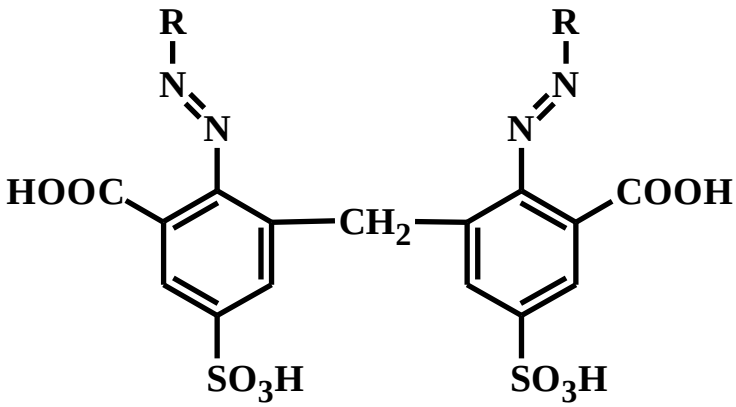

Figure 1: General Structure of Dye

2. Materials and Methods

The coupling components used for synthesis of dyes were obtained from M/s ACS Chemicals, Gujarat, India and M/s Atul Limited, Gujarat India. The solvents used were of spectroscopic grade.

The determined melting points of synthesized dyes were uncorrected and were expressed in °C. Thin layer chromatography [5] was applied to ensure the purity of dyes, using Benzoyl alcohol, DMF and water (3:2:3) as solvent composition and DMF as solvent of spotting at 30-32°C, maintaining chamber saturation for 6 hours. The IR spectra of synthesised derivates were registered in KBr pellets by using FT Infrared Spectrophotometer Model RZX (Perkin Elmer Spectrum 400) instrument in mid infrared region i.e. 4000cm^{-1} to 400cm-, using highly purified and desiccated 0.1g KBr and 4 to 5 mg of dye sample, at Shri Dhanvantary Pharmaceutical Analysis and Research Centre (Kim). Proton Magnetic Resonance of dyes was observed on BRUKER AVANCE II 400 MHz NMR Spectrometer in DMSO-d6 solvent using TMS as internal standard at SAIF Punjab University Chandigarh. The dyes were assessed for light fastness, rubbing fastness and wash fastness in accordance with BS: 1006-1978[6], AATCC - 1961[7] and IS: 765-1979[8] respectively.

3. Synthesis of 3,3'- Methylene bis (2-amino-5-sulphobenzoic acid):

2-Amino-5-sulpho benzoic acid (10.85 g, 0.05 mol) was dissolved in water (125 ml) and 36.5 % hydrochloric acid (25 ml) at 50°C. This mixture was treated with 3 % aqueous formaldehyde solution (35 ml). During reaction, the temperature was maintained at 60°C with continuous stirring for an hour. The Excess acid was neutralized with 10% sodium hydroxide solution, white precipitates obtained was filtered and washed with water. Yield 85 %.

Analysis:

Molecular Formula: $C_{15}H_{14}N_2O_{10}S_2$

4. Tetrazotisation of 3, 3'-methylene bis (2-amino-5-sulpho benzoic acid):

3,3'-Methylene bis (2-amino-5-sulpho benzoic acid) (2.23 g, 0.005 mol) was suspended in H_2O (60 ml). To this well stirred suspension, 1 ml Hydrochloric acid was added drop wise. Thereafter the reaction mixture was cooled to 0-5^{0}C in an ice-bath. To this mixture, a cooled solution of $NaNO_2$ (1.4 g) in water (8 ml) at 0^{0}C, was then included over a period of 5 minutes with steady stirring. Keep on stirring the solution for an hour, at the constant Temperature. The solution was checked for the presence of Nitrous Acid, by using Starch Iodide Paper and its excess was nullified with the required amount of sulphamic acid solution. A clear Tetrazo solution thus obtained at 0-5°C was used for subsequent coupling reaction.

5. Synthesis of Dye: Coupling of Tetrazo solution with 1-(2, 5-dichloro-4-sulpho phenyl)-3-methyl-5-pyrazolone:

An ice cooled solution of 1-(2,5-dichloro-4-sulphophenyl)-3-methyl-5-pyrazolone (3.23 g, 0.01 mol) in sodium carbonate solution (10 % w/v) was produced. In this solution, fresh Tetrazo solution that was prepared earlier was added drop wise over a period of 10-15 minutes at 0-5°C temperature. During the reaction process, the pH was maintained at 7.5 – 8.5 by parallel addition of Sodium Carbonate Solution. Steady stirring was continued for another one hour. 12 g of Sodium Chloride was added and the mixture was further stirred for one hour. Solid dye PA_1 was then collected. Yield: 85%

6. Analysis

Molecular Formula: $C_{35}H_{24}Cl_4N_8O_{18}S_4$, Molecular weight: 1114 gm/mol, R_f Value: 0.43%

Similar procedure was adopted for synthesis of other reactive dyes ie. PA_2 to PA_9 employing different pyrazolone coupling components such as 1-Phenyl-3-methyl 5-pyrazolone, 1-(3-Chlorophenyl)-3-methyl-5-pyrazolone, 1-(2-Methyl-4-sulphophenyl)-3-methyl-5-pyrazolone, 1-(3-Sulphophenyl)-3-methyl-5-pyrazolone, 1-(4-Tolylphenyl)-3-methyl-5-pyrazolone, 4-Vinyl sulfone-1-phenyl-3-methyl-5-

pyrazolone, 1-(4-Sulphophenyl)-3-methyl-5-pyrazolone, 1-(2-Chlorophenyl)-3-methyl-5-pyrazolone respectively. The structure of these pyrazolone coupling components are summarised in Chart 1.

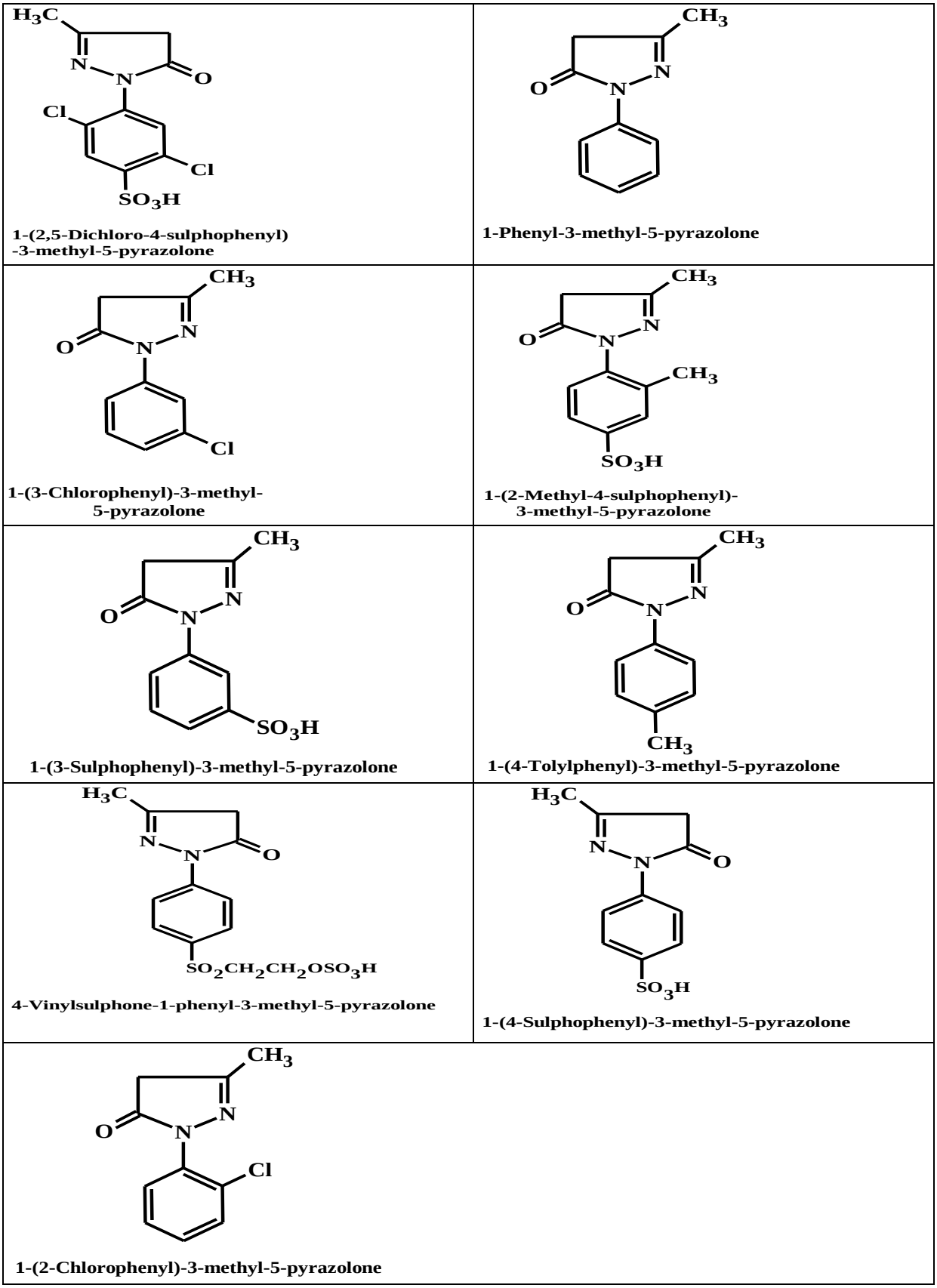

Chart 1: Structure of different Coupling components

Characterisation of all the reactive dyes is given in Table 1.

Dye **No.**	*Coupling component*	**Molecular Formula**	**Mol.** Weight**g.**	**Yield (%)**	**% Nitrogen**		**R_f Value**
					Found	**Required**	
PA_1	1-(2,5-Dichloro-4-sulphophenyl)-3-methyl-5-pyrazolone	$C_{35}H_{24}Cl_4N_8O_{18}S_4$	1114	85	10.01	10.05	0.43
PA_2	1-Phenyl-3-methyl 5-pyrazolone	$C_{35}H_{28}N_8O_{12}S_2$	0816	82	13.63	13.72	0.45
PA_3	1-(3-Chlorophenyl)-3-methyl-5-pyrazolone	$C_{35}H_{26}Cl_2N_8O_{12}S_2$	0885	78	12.50	12.65	0.38
PA_4	1-(2-Methyl-4-sulphophenyl)-3-methyl-5-pyrazolone	$C_{37}H_{32}N_8O_{18}S_4$	1004	80	11.00	11.15	0.36
PA_5	1-(3-Sulphophenyl)-3-methyl-5-pyrazolone	$C_{35}H_{28}N_8O_{18}S_4$	0976	82	11.44	11.47	0.45
PA_6	1-(4-Tolylphenyl)-3-methyl-5-pyrazolone	$C_{37}H_{32}N_8O_{12}S_2$	0844	83	13.20	13.27	0.41
PA_7	4-Vinyl sulfone-1-phenyl-3-methyl-5-pyrazolone	$C_{39}H_{36}N_8O_{24}S_6$	1193	77	9.29	9.38	0.40
PA_8	1-(4-Sulphophenyl)-3-methyl-5-pyrazolone	$C_{35}H_{28}N_8O_{18}S_4$	0976	78	11.43	11.47	0.42
PA_9	1-(2-Chlorophenyl)-3-methyl-5-pyrazolone	$C_{35}H_{26}Cl_2N_8O_{12}S_2$	0885	80	12.60	12.65	0.45

Table 1 – Characterisation of Reactive Dyes

7. Results and discussion

7.1 Infrared Spectra

Infrared Spectra[9] of the PA_1 showed (C-H) Stretching Vibration in the range 2860 cm^{-1} to 3094 cm^{-1}, (C=O) stretching Vibration at 1679 cm^{-1}, (C=C) Stretching Vibration between 1474 cm^{-1} - 1653 cm^{-1}, (C=N) Stretching Vibration at 1582 cm^{-1}, (N=N) stretching Vibration at 1442 cm^{-1}, (C-H) Bending Vibration at 1383 cm^{-1}, (S=O) stretching Vibration at 1040 cm^{-1} to 1268 cm^{-1} and (C-Cl) stretching Vibration at 759 cm^{-1}.

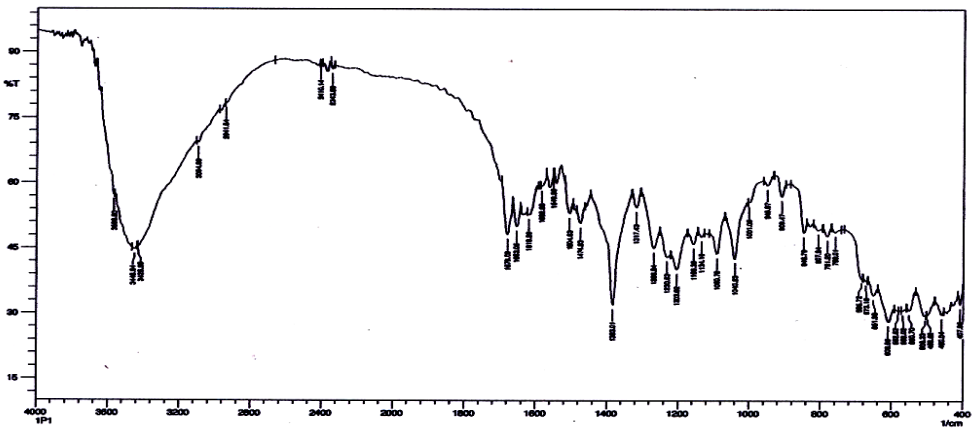

Figure 2. Experimental IR Spectrum of PA_1

The IR data for dyes PA_1, PA_2 and PA_3 were summarised in Table 2.

Position of absorption band wave number cm^{-1}			Bond & its mode of vibration	Functional group
PA_1	PA_2	PA_3		
3094	3099	3099	C-H Stretching	Aromatic =CH-bond
2941	2941	2920	C-H Stretching	$-CH_3$ group
2860	2860	2860	C-H Stretching	$-CH_2$-group
1679	1682	1682	C=O Stretching	-COOH group
1653 1474	1652 1469	1651 1472	C=C Stretching	Aromatic ring
1582	1580	1580	C=N Stretching	Ter. amine
1442	1442	1446	N=N Stretching	Azo group
1383	1385	1383	C-H Bending	$-CH_3$ group
1268 1040	1269 1163 1037	1228 1051 1092	S=O Stretching	$-SO_3Na$ group
759	---	747	C-Cl Stretching	Chloro group

Table 2: IR Data for PA_1, PA_2 and PA_3

7.2 PMR Spectra

The PMR Spectra[10,11] of the dye PA_1 showed signals at 1.26 δ ppm (s, 6H, $-CH_3$), 3.02 δ ppm (s, 2H, -CH), 4.22 δ ppm (s, 2H, $-CH_2$), 7.42 δ – 8.40 δ ppm (m, 8H, Ar-H), 10.44 δ ppm (s, 2H, -COOH).

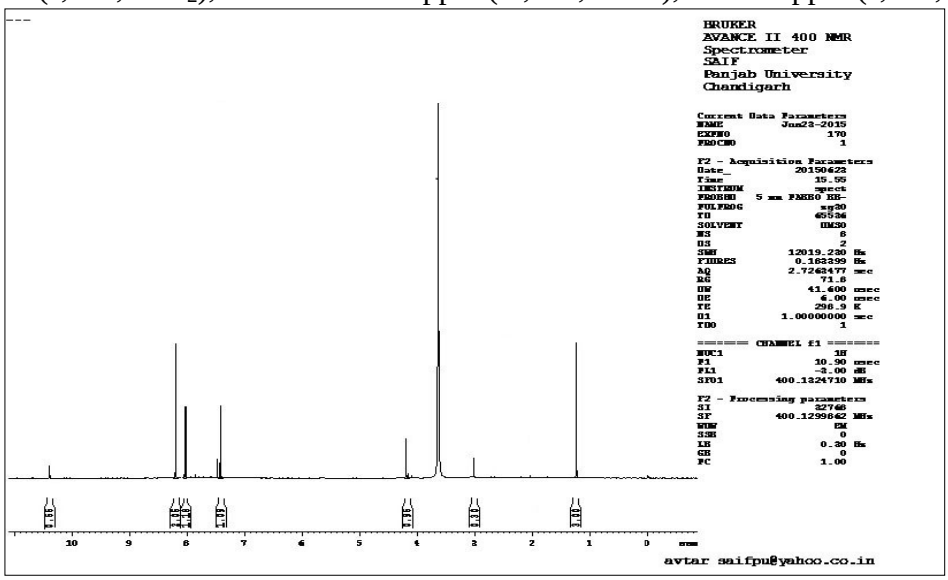

Figure 3: PMR Spectrum of PA_1

Chemical shift (δ in ppm)	Multiplicities	Relative number of protons	Assignment
1.26	S	6	$-CH_3$ protons
3.02	S	2	–CH= protons
4.22	S	2	$-CH_2-$ protons
7.42-8.40	M	8	Aromatic protons
10.44	S	2	Carboxylic group

Table 3: PMR Spectral Characteristic of Dye PA_1.

8. Application

All the synthesized Dyes were applied on Silk and Wool Fabrics as per the standard procedure [12]. The exhaustion and fixation study of synthesized dyes have been carried out, the fastness properties of dyed pattern have also been studied. On account of coupling with various coupling components, the dyes have shown different shades on the Silk and Wool Fibre. Exhaustion [13] and Fixation [14] studies of these dyes were carried for Silk and Wool Fibres using Water and Concentrated Sulphuric Acid as medium of Spectral Study. The % Exhaustion of Dyes PA_1 to PA_9 for Silk and Wool ranges from 69-77%. Similarly, the % Fixation of Dyes PA_1 to PA_9 for silk ranges from 78-92% and for Wool ranges from 77-91%. Synthesised Dyes were studied for their Fastness properties with respect to Light, Wash and Rubbing using standard methods [15]. The dyes demonstrated Moderate to Very good Light Fastness, Moderate to Good Wash Fastness and Moderate to Good Rubbing Fastness properties on Silk and Wool Fibre.

9. Conclusion

A Pyrazolone acid reactive dyes based on 3,3'- Methylene bis (2-amino-5-sulphobenzoic acid) were prepared using conventional techniques. Their spectral properties were examined in solution and application on fibres was studied. The dyes demonstrated level dyeing and very good dyeing ability. The exhaustion and fixation of these dyes were good indicating good affinity towards the silk and woolen fibre.

10. Acknowledgment

The authors express their gratitude to the Professors and the Head of Chemistry Department at V N S G University for their kind co-operation in executing this research work and for research facilities. Atul Ltd and ACS Chemicals, Gujarat for furnishing required chemicals. Shri Dhanvantary Pharmaceutical Analysis and Research Centre (Kim) and S A I F for helping with Spectral data.

References

1. AATCC Test Method, p. 8; 1961
2. Blus K, Dyes Pigm., 41(1,2),149–157 (1995).
3. Bovey F.A., “Nuclear Magnetic Resonance Spectroscopy”, Academic Press, New York (1969).
4. Color Index, Society of Dyers and Colorists, Bardford, 3rd edition, Vol.1 (1971).
5. Fried B, Sherma J. Thin layer chromatography, Revised and Expanded. 4th ed. New York and Basel: Marcel – Dekker Inc; 1999
6. Indian Standard ISO:765 (1979).
7. Jackman L.M., Sternhell S., “Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry”, Pergamon, Oxford (1969).
8. K Venkatraman, The Analytical Chemistry of Synthetic Dyes, p. 524 (1977)
9. Lewis D.M., Wool dyeing, Society of Dyers and Colourists, Leeds, pp 283–295 (1992).
10. Rao C. N. R., Chemical application of Infrared spectroscopy, Academic press, New York, (1963).
11. Standard Test Method BS 1006, (1978) (UK): ISO India, 105 (1994).
12. The Society of Dyers and Colourists. Standard method for the determination of the colour fastness of Textiles and leather. 4th ed. England: Society of Dyers and Colourists; 1981
13. V Iyer, A M Gurjar, K S Bhyrappa, Indian J. Fiber Text. Res. 18, 120 (1993).
14. V. A. Shenai, Chemistry of Dyes and Principles of Dyeing, Sevak Publication, Bombay (1973).
15. Venkataraman K., The chemistry of synthetic dyes, vol 3, Academic press, New York, pp 249–301(1970).