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

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Abstract:
The work presented in this research is aimed at synthesis of new set of Pyrazolone acid reactive dyes based on 3,3'- methylenebis(2-amino-5-bromobenzoic acid). These dyes were synthesized by coupling Tetrazotized compound with different pyrazolone coupling components and their dyeing performance was studied on various fibres such as wool and silk fabrics. Synthesized Dyes were characterized by TLC, IR spectra and NMR Spectra for the study of dye bath exhaustion and fixaton. The dyes were found to exhibit moderate to very good light, wash and rubbing fastness properties.

Keywords: *Acid Reactive dyes, 3,3'- methylenebis (2-amino-5-bromobenzoic acid), Pyrazolone acid reactive dyes, Exhaustion, Fixation, Silk, Wool.*

1. Introduction

The acid dyes were probably originally so named because of the presence of one or more sulphonic acid or other acidic groups in their molecules. Acid dyes are water-soluble anionic dyes that are applied to nitrogenous fibres such as wool, silk, nylon and modified acrylic fibre from acid or neutral-baths. Attachment to the fibre is attributed at least partly to salt formation between anionic groups in the dyes and cationic groups in the fibre. 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 [1]. Reactive dyes constitute the fastest growing class of cellulosic dyestuff and thus have encouraged vast research in this field [2,3]. The structural development of new reactive dyes has been a subject of interest and many novel structures are useful in commercial application to wool, silk and cotton as well as their blends with other fibers has been discovered [4]. This research paper, therefore, is a step in this direction employing 3,3'-methylenebis(2-amino-5-bromobenzoic acid) for synthesis of pyrazolone acid reactive dyes. The research further goes into examining the fastness properties of these dyes with respect to light, wash and rubbing. The general structure of the dyes is as shown below in figure 1:

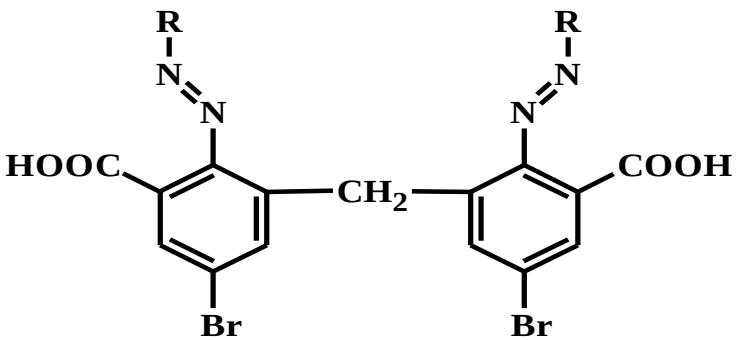

Figure 1: General Structure of Dye

2. Materials and Methods

The chemical compounds which were used as coupling components for synthesis of dyes were procured from M/s ACS Chemicals, Gujarat, India and M/s Atul Limited, Gujarat India. Further solvents used were of spectroscopic grade.

The melting points of synthesized dyes were determined and were expressed in °C. Purity of the dyes were examined by Thin layer chromatography. IR Spectra derivates were registered in KBr pellets by using FT Infrared Spectrophotometer Model. ^{1}H-NMR (400 MHz) was conducted on BRUKER AVANCE II Spectrometer using TMS as internal standard.

The dyes were assessed for light fastness, rubbing fastness and wash fastness in accordance with BS: 1006-1978[5], AATCC -1961[6] and IS: 765-1979[7] respectively.

3. Synthesis of 3,3'-methylenebis (2-amino-5-bromobenzoic acid):

10.85 g, 0.05 mol of 2-amino-5-bromobenzoic acid was dissolved in 125 ml water 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. In the meantime, the Excess acid was neutralized with 10% sodium hydroxide solution, white precipitates obtained was filtered and washed with water. Yield 85 %.

Analysis:
Molecular Formula: $C_{15}H_{12}Br_2N_2O_4$

Tetrazotisation of 3,3'-methylenebis (2-amino-5-bromobenzoic acid):

3,3'-methylenebis (2-amino-5-bromobenzoic 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.

4. 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%

Analysis:
Molecular Formula: $C_{35}H_{22}Br_2Cl_4N_8O_{12}S_2$, Molecular weight: 1112 gm/mol, R_f Value: 0.40%

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.

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

Table 1 – Characterisation of Reactive Dyes

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	$C_{35}H_{22}Br_2Cl_4N_8O_{12}S_2$	1112	85	10.01	10.07	0.40
PA_2	1-Phenyl-3-methyl 5-pyrazolone	$C_{35}H_{26}Br_2N_8O_6$	0814	82	13.71	13.75	0.36
PA_3		$C_{35}H_{24}Br_2Cl_2N_8O_6$	0883	78	12.60	12.68	0.45
PA_4	1-(3-Chlorophenyl)-3-methyl-5-pyrazolone	$C_{37}H_{30}Br_2N_8O_{12}S_2$	1002	80	11.15	11.17	0.43
PA_5	1-(2-Methyl-4-sulphophenyl)-3-methyl-5-pyrazolone	$C_{35}H_{26}Br_2N_8O_{12}S_2$	0974	82	11.40	11.49	0.38
PA_6	1-(3-Sulphophenyl)-3-methyl-5-pyrazolone	$C_{37}H_{30}Br_2N_8O_6$	0842	83	13.24	13.30	0.42
PA_7	1-(4-Tolylphenyl)-3-methyl-5-pyrazolone	$C_{39}H_{34}Br_2N_8O_{18}S_4$	1190	77	9.38	9.41	0.44
PA_8	4-Vinyl sulfone-1-phenyl-3-methyl-5-pyrazolone	$C_{35}H_{26}Br_2N_8O_{12}S_2$	0974	78	11.44	11.49	0.45
PA_9	1-(4-Sulphophenyl)-3-methyl-5-pyrazolone	$C_{35}H_{24}Br_2Cl_2N_8O_6$	0883	80	12.65	12.68	0.38
	1-(2-Chlorophenyl)-3-methyl-5-pyrazolone						

5. Results and discussion

Infrared Spectra:

Infrared Spectra [8] of the PA_1 showed (C-H) Stretching Vibration of Aromatic =CH- group at 3074 cm^{-1}, of $-CH_3$ group at 2936 cm^{-1} , of $-CH_2$ group at 2860 cm^{-1}. (C=O) stretching Vibration of -COOH group at 1682 cm^{-1}, (C=C) stretching Vibration of aromatic ring between 1477 cm^{-1} to 1653 cm^{-1}, (C=N) Stretching Vibration of Tertiary amines at 1582 cm^{-1}, , (N=N) stretching Vibration of Azo group at 1459 cm^{-1}. (C-H) Bending Vibration of $-CH_3$ group at 1382 cm^{-1}, (S=O) stretching Vibration of $–SO_3Na$ group between 1037 cm^{-1} to 1268 cm^{-1} and (C-Cl) stretching Vibration of chloro group at 759 cm^{-1}, C-Br stretching of Bromo group at 575 cm^{-1} .

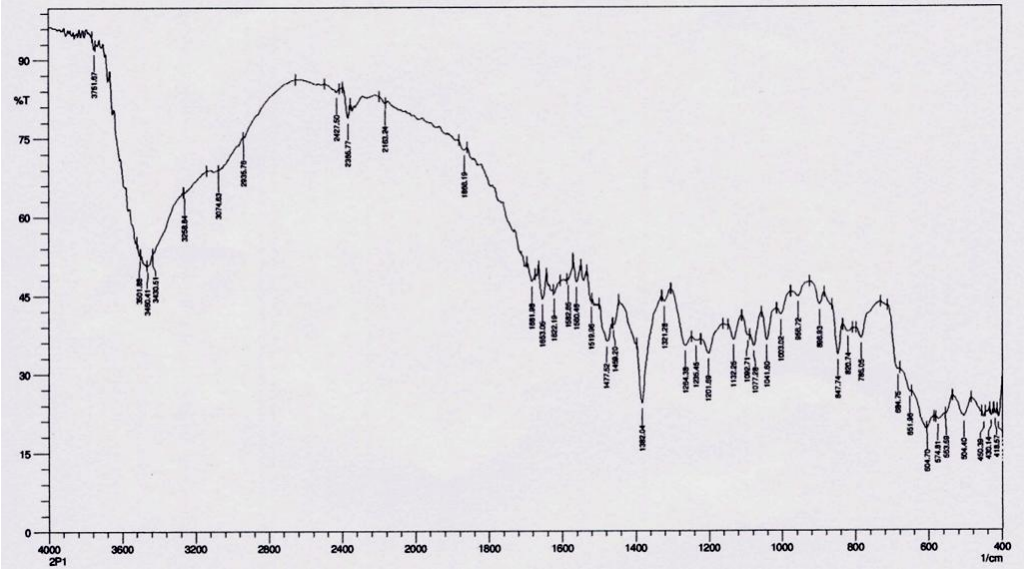

Figure 2. Experimental IR Spectrum of PA_1.

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

Table 2: IR Data for PA_1, PA_2 and PA_3

Position of absorption band wave number cm^{-1}			Bond & its mode of vibration	Functional group
PA_1	PA_2	PA_3		
3074	3072	3070	C-H Stretching	Aromatic =CH- bond
2936	2935	2929	C-H Stretching	$-CH_3$ group
2860	2858	2858	C-H Stretching	$-CH_2$-group
1682	1682	1682	C=O Stretching	-COOH group
1653 1477	1653 1470	1653 1472	C=C Stretching	Aromatic ring
1582	1560	1580	C=N Stretching	Ter. amine
1459	1458	1460	N=N Stretching	Azo group
1382	1383	1382	C-H Bending	$-CH_3$ group
1268 1037	--	--	S=O Stretching	$-SO_3Na$ group
759	---	747	C-Cl Stretching	Chloro group
575	575	572	C-Br Stretching	Bromo group

PMR Spectra:

The PMR Spectra[9,10] of the dye PA_1 showed signals at 1.14 δ ppm (s, 6H, $-CH_3$), 3.04 δ ppm (s, 2H, -CH), 4.19 δ ppm (s, 2H, $-CH_2$), 7.39 δ – 8.30 δ ppm (m, 8H, Ar-H), 10.38 δ ppm (s, 2H, -COOH).

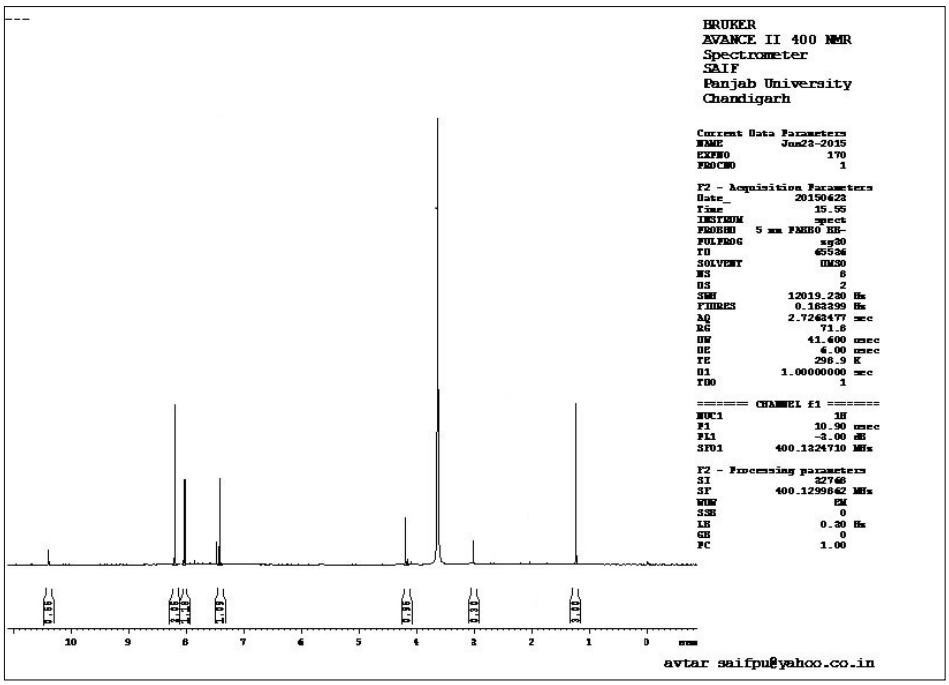

Figure 3: PMR Spectrum of PA_1

Table 3: PMR Spectral Characteristic of Dye PA_1.

Chemical shift (δ in ppm)	Multiplicities	Relative number of protons	Assignment
1.14	s	6	$–CH_3$ protons
3.04	s	2	–CH= protons
4.19	s	2	$–CH_2–$ protons
7.39-8.30	m	8	Aromatic protons
10.38	s	2	Carboxylic group

6. Application

All the synthesized Dyes were applied on Silk and Wool Fabrics as per the standard procedure [11].

The synthesized dyes were studied for their exhaustion and fixation characteristics and the fastness properties of dyed pattern were also studied. The dyes were found to show different shades on the silk and wool fibre due to the coupling with various coupling components. Exhaustion [12] and Fixation [13] studies of these dyes were carried using water and concentrated sulphuric acid as medium of spectral study.

The % Exhaustion of Dyes PA_1 to PA_9 for Wool ranges from 68-74% and for silk ranges from 69-78%. Similarly, the % Fixation of Dyes PA_1 to PA_9 for silk ranges from 77-92% and for Wool ranges from 82-92%.

Synthesised Dyes were studied for their Fastness properties with respect to Light, Wash and Rubbing using standard methods [14]. 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.

Dyes	Wool				Silk			
	Light Fastness	Wash Fastness	Rubbing Fastness		Light Fastness	Wash Fastness	Rubbing Fastness	
			Dry	Wet			Dry	Wet
PA_1	3	3-4	4	4	5	4	4	4
PA_2	5	5	5	3	6	3	3	3
PA_3	4	4	4-5	5	5	3-4	4-5	5
PA_4	5	4-5	5	4	4	5	5	4

PA_5	6	5	5	5	5	5	4	3-4
PA_6	4-5	4	4-5	4	5	3	4	4
PA_7	6	3-4	3	4	4-5	4	3	5
PA_8	3	3	4	4-5	3	3-4	4	5
PA_9	4	4	4	3	5	5	4-5	4

Light fastness: 1-Poor; 2-Slight; 3-Moderate; 4-Fair; 5-Good; 6-Very good; 7-Excellent; 8-maximum
Wash and Rubbing fastness: 1-Poor; 2-Fair; 3-Good; 4-Very good; 5-Excellent

7. Conclusion

Dyes based on 3,3'-methylenebis(**2-amino-5-bromobenzoic acid**) were prepared by using conventional methods. These dyes gave yellow to brown shade on wool and silk fibres. Dyes exhibit moderate to very good light fastness, good to excellent wash and rubbing fastness.

8. 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.

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