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

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Abstract:
A new set of Pyrazolone reactive dyes were synthesized based on 3,3'-methylenebis (2-amino-5-nitrobenzoic acid). These dyes were synthesized by coupling of tetrazotized solution of 3,3'-methylenebis (2-amino-5-nitrobenzoic acid) with various pyrazolone coupling components. The synthesized dyes were applied to wool and silk fabrics. The dyes were studied for their fastness properties with respect to light, wash and rubbing. TLC, IR Spectra and NMR Spectra confirmed the structure of all the synthesized dyes. Exhaustion and fixation properties of the synthesized dyes were investigated.

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

1. Introduction

In the dye stuff research, reactive dyes are the newest addition and is the center of attention [1,2]. Acid dyes in particular got their name because of the presence of one or more sulphonic acid or or carboxylic acid salt functional groups in their molecules. Only fibers which develop a positive charge in the presence of acid, such as wool and other protein fibers, nylon, and certain modified synthetics, are readily dyed by acid dyes. These are reasonably colorfast to light and laundering, but mordanting (more complete insolubilization of the dye through reaction with a metal salt) will improve the overall fastness properties of the dye [3].

This research paper presents a study of dye pattern of pyrazolone acid reactive dyes based on 3,3'-methylenebis (2-amino-5-nitrobenzoic acid) and characterization of the dyes thus synthesized. The dyes were thereafter applied onto the wool and silk fabrics, where the exhaustion and fixation properties of the dyes were investigated. The general structure of the dyes is as shown below in figure 1:

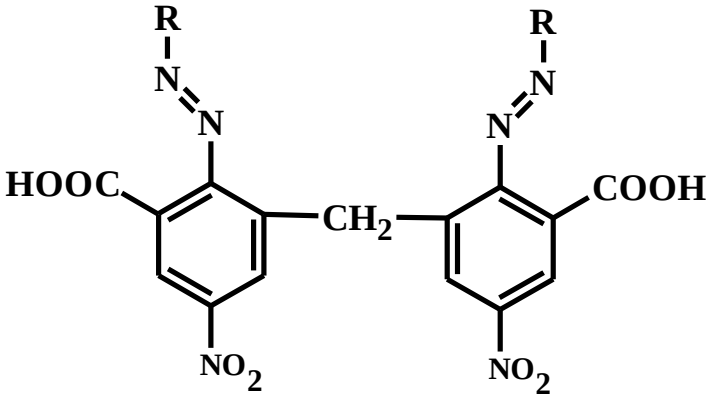


Figure 1: General Structure of Dye

2. Materials and Methods

The raw materials used in the synthesis of the dyes were obtained from M/s ACS Chemicals, Gujarat, India and M/s Atul Limited, Gujarat India. Also the solvents used were of spectroscopic grade. The melting points of synthesized dyes were expressed in °C.

The acid were synthesised under proper experimental conditions and purified. The thin layer chromatography was employed to ascertain purity of the dyes. Each dye is characterized by their nitrogen elemental analysis, IR spectra and some representative PMR spectra.

The dyes were assessed for light fastness, rubbing fastness and wash fastness in accordance with BS: 1006-1978[4], AATCC -1961[5] and IS: 765-1979[6] respectively.

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

10.85 g, 0.05 mol of 2-amino-5-nitrobenzoic 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: $C_{15}H_{12}N_4O_8$

4. Tetrazotisation of 3,3'-methylenebis (2-amino-5-nitrobenzoic acid):

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

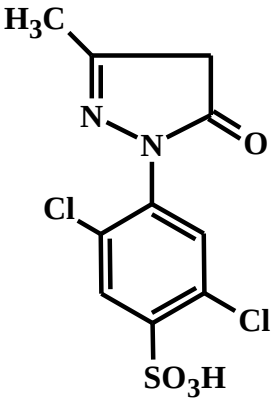
5. Synthesis of Dye: Coupling of Tetrazo solution with 1-(2, 5-dichloro-4-sulpho phenyl)-3-methyl-5-pyrazolone:

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%

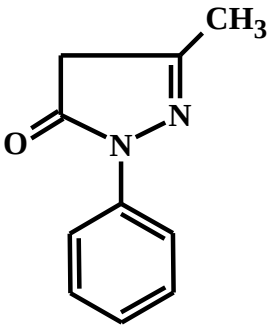
Analysis:

Molecular Formula: $C_{35}H_{22}Cl_4N_{10}O_{16}S_2$, Molecular weight: 1044 gm/mol, R_f Value: 0.45%

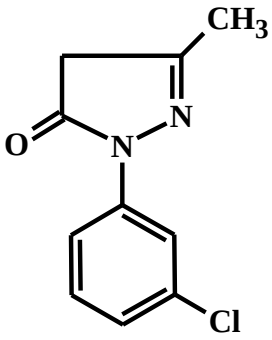
Using the above procedure, remaining dyes of this series were synthesized but with different pyrazolone coupling components such as described below:



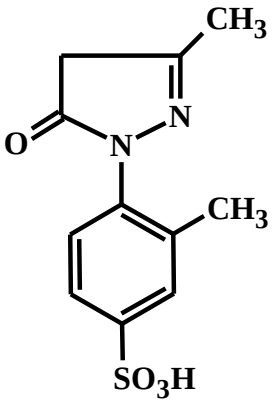
1-(2,5-Dichloro-4-sulphophenyl) -3-methyl-5-pyrazolone



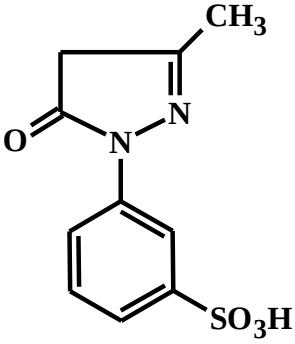
1-Phenyl-3-methyl-5-pyrazolone



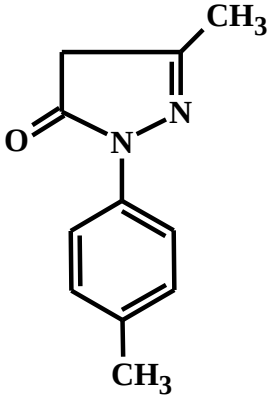
1-(3-Chlorophenyl)-3-methyl-5-pyrazolone



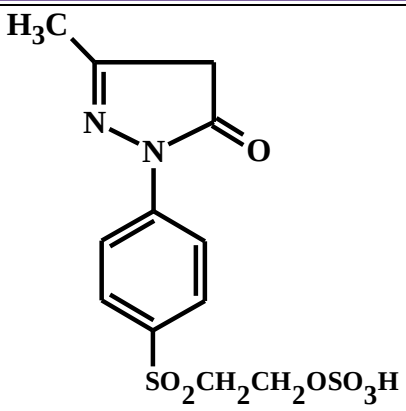
1-(2-Methyl-4-sulphophenyl)-3-methyl-5-pyrazolone



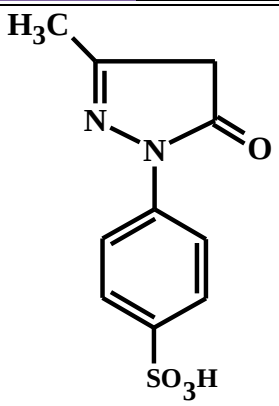
1-(3-Sulphophenyl)-3-methyl-5-pyrazolone



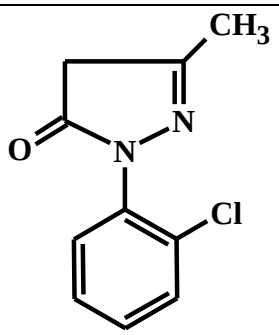
1-(4-Tolylphenyl)-3-methyl-5-pyrazolone



4-Vinylsulphone-1-phenyl-3-methyl-5-pyrazolone



1-(4-Sulphophenyl)-3-methyl-5-pyrazolone



1-(2-Chlorophenyl)-3-methyl-5-pyrazolone

Chart 1: Structure of different Pyrazolone coupling components, used in the synthesis of dyes

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	$C_{35}H_{22}Cl_4N_{10}O_{16}S_2$	1044	85	13.36	13.40	0.45
PA_2	1-Phenyl-3-methyl 5-pyrazolone	$C_{35}H_{26}N_{10}O_{10}$	0746	82	18.74	18.76	0.40
PA_3	1-(3-Chloro) phenyl-3-methyl-5-pyrazolone	$C_{35}H_{24}Cl_2N_{10}O_{10}$	0815	78	17.14	17.17	0.43
PA_4	1-(2-Methyl-4-sulpho)phenyl-3-methyl-5-pyrazolone	$C_{37}H_{30}N_{10}O_{16}S_2$	0934	80	14.94	14.98	0.36
PA_5	1-(3-Sulphophenyl)-3-methyl-5-pyrazolone	$C_{35}H_{26}N_{10}O_{16}S_2$	0906	82	15.41	15.45	0.38
PA_6	1-(4-Tolylphenyl)-3-methyl-5-pyrazolone	$C_{37}H_{30}N_{10}O_{10}$	0774	83	18.02	18.08	0.45
PA_7	4-Vinylsulfone-1-phenyl-3-methyl-5-pyrazolone	$C_{39}H_{34}N_{10}O_{22}S_4$	1123	77	12.41	12.46	0.44
PA_8	1-(4-Sulphophenyl)-3-methyl-5-pyrazolone	$C_{35}H_{26}N_{10}O_{16}S_2$	0906	78	15.40	15.45	0.42
PA_9	1-(2-Chlorophenyl)-3-methyl-5-pyrazolone	$C_{35}H_{24}Cl_2N_{10}O_{10}$	0815	80	17.11	17.17	0.38

6. Results and discussion

Infrared Spectra:

Infrared Spectra [7] of the PA_1 showed (C-H) Stretching Vibration of Aromatic =CH- group at 3072 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 1688 cm^{-1}, (C=C) stretching Vibration of aromatic ring between 1477 cm^{-1} to 1654 cm^{-1}, (C=N) Stretching Vibration of Tertiary amines at 1594 cm^{-1}, (N=O) stretching Vibration of Nitro group between 1340 cm^{-1} to 1525 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 721 cm^{-1}.

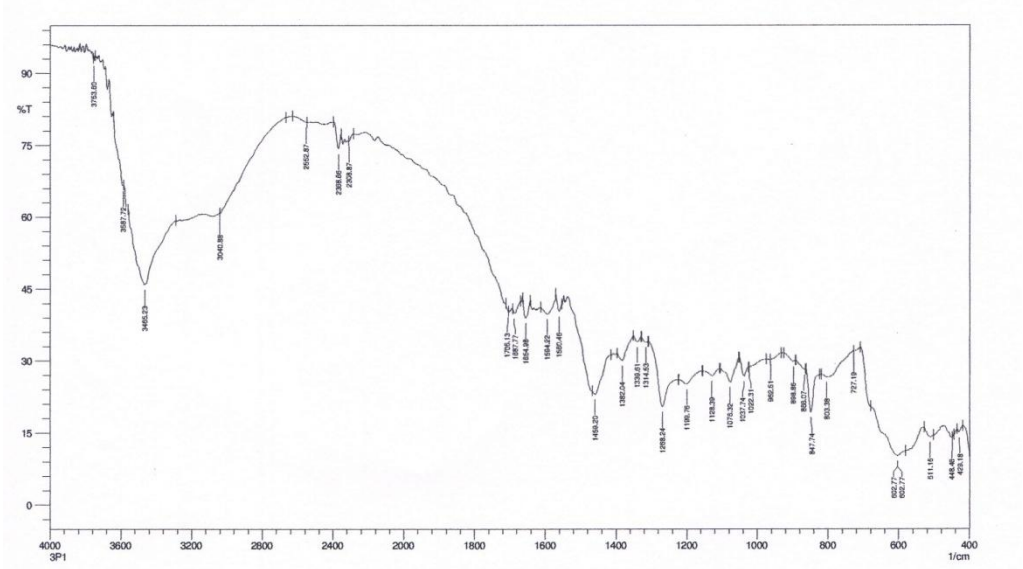


Figure 2. Experimental IR Spectrum of PA_1.

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		
3072	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
1688	1682	1702	C=O Stretching	-COOH group
1654 1477	1653 1470	1653 1472	C=C Stretching	Aromatic ring
1594	1560	1594	C=N Stretching	Ter. amine
1525 1340	1525 1340	1525 1340	N=O Stretching	Nitro group
1459	1458	1459	N=N Stretching	Azo group
1382	1388	1382	C-H Bending	$-CH_3$ group
1268 1037	----	----	S=O Stretching	$-SO_3Na$ group
721	---	740	C-Cl Stretching	Chloro group
3072	3072	3070	C-H Stretching	Aromatic =CH- bond

PMR Spectra:

The PMR Spectra[8,9] of the dye PA_1 showed signals at 1.32 δ ppm (s, 6H, $-CH_3$), 2.66 δ ppm (s, 2H, -CH), 4.44 δ ppm (s, 2H, $-CH_2$), 7.62 δ – 8.10 δ ppm (m, 8H, Ar-H), 10.28 δ ppm (s, 2H, -COOH).

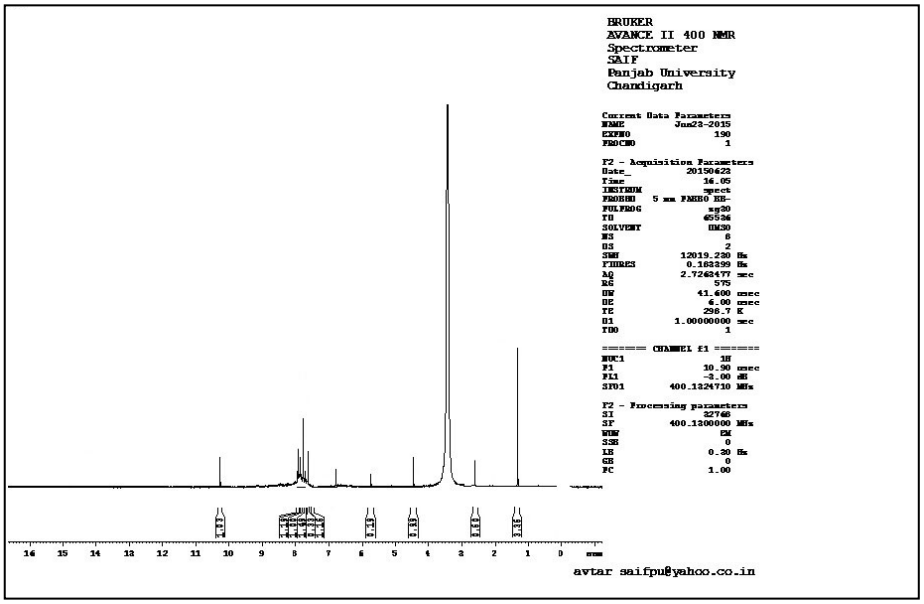


Figure 3: PMR Spectrum of PA_1

Table 3: PMR Spectral Characteristic of Dye PA_1.

Chemical shift (δ in ppm)	Multiplicities	Relative number of protons	Assignment
1.32	s	6	$–CH_3$ protons
2.66	s	2	–CH= protons
4.44	s	2	$–CH_2–$ protons
7.62-8.10	m	8	Aromatic protons
10.28	s	2	Carboxylic group

7. Application

Using the standard dyeing techniques [10], the dyes were applied on Silk and Wool Fabrics.
The synthesized dyes were studied for their exhaustion [11] and fixation [12] characteristics and the fastness properties of dyed pattern were also studied using water and concentrated sulphuric acid as medium of spectral study. The dyes were found to show different shades on the silk and wool fibre as a result of coupling with various pyrazolone coupling components.

The % Exhaustion of Dyes PA_1 to PA_9 for Wool ranges from 68-76% and for silk ranges from 68-79%. Similarly, the % Fixation of Dyes PA_1 to PA_9 for silk ranges from 77-91% and for Wool ranges from 80-91%.

Synthesised Dyes were studied for their Fastness properties with respect to Light, Wash and Rubbing using standard methods [13]. 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	5	4	4-5	5	4	4	5	4-5
PA_2	4	3	4	4	5-6	5	5	5
PA_3	5	4	5	4	4	4	4	3
PA_4	6	5	5	5	5	3	3-4	4
PA_5	3-4	5	4-5	3	4	4-5	5	5
PA_6	4	3	4	5	4	4	4	5
PA_7	5	4-5	4	4	5	3	3	3-4
PA_8	6	4	5	3	6	5	4	5
PA_9	5-6	3	4	4-5	3	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

8. Conclusion

Pyrazolone acid reactive dyes based on 3,3'-methylenebis (2-amino-5-nitrobenzoic acid) were synthesized using conventional methods. These dyes impart yellow to brown shade on wool and silk fibres. Dyes exhibit moderate to very good light fastness, good to excellent wash and rubbing fastness.

9. Acknowledgment

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