International Journal of Scientific Research in Science, Engineering and Technology

Print ISSN - 2395-1990
Online ISSN : 2394-4099

OPEN ACCESS

Available Online at : www.ijsrset.com
doi : https://doi.org/10.32628/IJSRSET2411142

The Synthesis and Application of Reactive Dyes Based on 4,4'-methylene bis-m-nitro aniline on Various Fibres

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ARTICLEINFO

Article History :

Accepted: 08 Feb 2024
Published: 22 Feb 2024

Publication Issue :
Volume 11, Issue 1
January-February-2024
Page Number :
284-290

ABSTRACT

Hot brand bisazo reactive dyes (D_1 to D_{10}) have been synthesized by coupling tetrazotised 4,4'-methylene bis-*m*-nitro aniline with various cyanurated coupling components. They were applied on silk, wool and cotton fibres. Their dyeing performance on silk, wool and cotton has been assessed. The purity of dyes was checked by thin layer chromatography. The IR spectra showed all characteristic band and PMR spectra of representative dye showed all the signals. The percentage dye bath exhaustion on different fibres was reasonably good and acceptable. The dyed fibres showed moderate to very good fastness to light, washing and rubbing.

Keywords: 4,4'-methylene bis-*m*-nitro aniline, Bisazo Reactive Dyes, Cynuric chloride, Application

I. INTRODUCTION

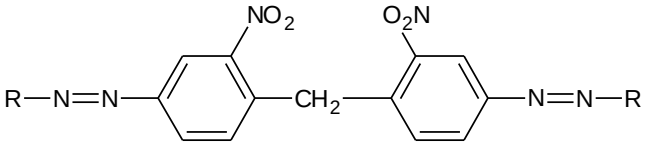
Reactive dyes are extensively used in the textile industry not only to colour mainly cotton, but also wool and silk because of their wide variety of colour shades, high wet fastness properties and easy applications [1]

Reactive dyes are coloured compound which contain one or two groups capable of forming covalent bond between a carbon atom or phosphorous atom of the dye ion or molecule and an oxygen atom, nitrogen or sulphur atom of a hydroxyl, an amino or a mercapto group respectively, of the substrate .
Patel et al [2-5] have reported fibre reactive dyes for silk, wool and cotton.

Mono azo reactive dyes and bis azo reactive dyes have been established as a major group for fixation to cellulose. Bis azo reactive dyes have been widely considered due to their higher fixation yield on various fibres.

The purpose of the present investigation is to obtain reactive dyes with a higher degree of reactivity, we report here the synthesis and study of the dyeing properties of the bis azo dyes based on 4,4'-methylene bis-*m*-nitro aniline.

The general structure of the dyes (D_1–D_{10}) is shown below.



Where R=2,6-Dichloro-4-nitro anilino cyanurated coupling components.

II. METHODS AND MATERIAL

All the melting points (m.p.) were determine in open capillaries and are uncorrected and expressed in ºC. The purity of all the dyes has been checked by TLC [6-7]. The IR spectra were recorded in KBr on a Perkin Elmer Model-881 spectrophotometer and 1H NMR spectra were recorded on a Brucker DRX-300 (300 MHz FTNMR) instrument using TMS as internal standard and DMSO as solvent, where the chemical shift δ are given in ppm. Absorption spectra were recorded on a Beckman DB-GT Grating spectrophotometer. The light fastness was assessed in accordance with BS: 1006–1978 [8]. The rubbing fastness test was carried out with a Crockmeter (Atlas) in accordance with AATCC (1961) and the wash fastness test in accordance with ISO: 765–1979 [9].

Synthesis of 4,4'-methylene bis - (*m*-nitro aniline)

m-nitro aniline **(A)** (6.90 g, 0.05 mole) was dissolved in water (125 ml) and 36.5 % hydrochloric acid (25 ml) at 50°C and then reacted with 3 % aqueous formaldehyde solution **(B)** (35 ml). The temperature was maintained at 60°C and stirred for an hour and neutralized with 10 % sodium hydroxide solution, the white precipitates obtained were filtered, washed with hot water, dried and recrystallized from acetic acid. Yield **(C)** 85 %, m. p. 130°C.

Tetrazotisation of 4,4'-methylene bis-(*m*-Nitro aniline)(D)

4,4'-methylene bis-(*m*-Nitro aniline) **(C)** (1.44 g, 0.005 mole) was suspended in H_2O (60 ml). Hydrochloric acid (0.86 g) 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. A solution of $NaNO_2$ (0.7g, 0.01mole) in water (8ml) previously cooled to 0°C, was then added over a period of 5 minutes with stirring. The stirring was continued for an hour, maintaining the same temperature, with positive test for nitrous acid on starch iodide paper. After destroying excess of nitrous acid with required amount of a solution of sulphamic acid, the clear tetrazo solution-**(D)** at 0-5°C was used for subsequent coupling reaction.

Cyanuration of H-acid

Cyanuric chloride (1.85 g, 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 (3.19 g, 0.01 mole) in aqueous sodium carbonate solution (10% w/v) was then added in small lots in over a period of 1 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 four hours to obtain a clear solution The cyanurated H-acid solution thus formed was used for subsequent condensation reaction.

Condensation with 2,6-dichloro-4-nitro aniline (E) (Formation of 2,6-dichloro-4-nitro anilino cyanurated H-acid)

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 2,6-dichloro-4-nitro aniline (2.07 g, 0.01 mole) was added dropwise at same temperature, over a period of 30 minutes, maintaining the pH neutral by simultaneous addition of sodium bicarbonate (1% w/v). After the addition was completed, stirring was continued for further 3 hours. The 2,6-dichloro-4-niro anilino cyanurated H-acid solution **(E)** thus obtained was subsequently used for further coupling reaction.

Coupling of tetrazo (D) solution with 2,6-dichloro-4-nitro anilino cyanurated H-acid (E) (Formation of dye D_1)

To an ice cold and stirred solution of 2,6-dichloro-4-nitro anilino cyanurated H-acid **(E)** (6.38 g, 0.01 mole), a freshly prepared tetrazo solution-**(D)** (1.92 g, 0.005

mole) was added dropwise over a period of 10-15 minutes. The pH was maintained at 7.5 to 8.5 by simultaneous addition of sodium carbonate solution (10% w/v). During coupling a purple solution is formed. The stirring was continued for 3-4 hours, maintaining the temperature below 5°C. The reaction mixture was then heated up to 60°C and sodium chloride added until the colouring material was precipitated. It was stirred for an hour, filtered and washed with a small amount of sodium chloride solution (5% w/v). The solid was dried at 80-90°C and extracted with DMF. The dye was precipitated by diluting the DMF-extract with excess of chloroform. A violet dye was then filtered, washed with chloroform and dried at 60°C. Yield 85%

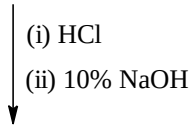
Following the above procedure other reactive dyes D_2 to D_{10} were synthesized using various 2,6-dichloro-4-nitro anilino cyanurated coupling components such as J-acid, Gamma acid, Bronner acid, Tobias acid, Koch acid, Sulpho Tobias acid, Laurant acid, N-methyl-J-acid, Chicago acid

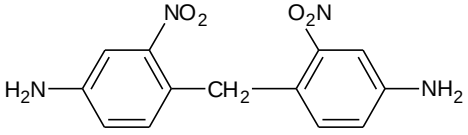
All the synthesized dyes were recorded in **Table - 1**.

Reaction Scheme

(1) SYNTHESIS OF 4,4'-METHYLENE BIS - *m*-NITRO ANILINE (C)

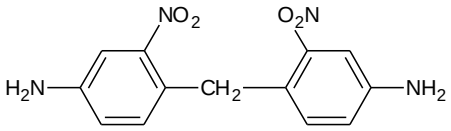
m-Nitro aniline Formaldehyde *m*-Nitro aniline



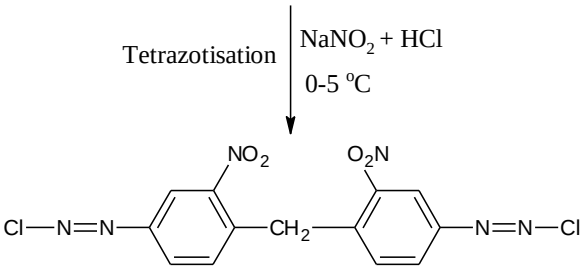


4,4'-Methylene bis-*m*-nitro aniline

(2) TETRAZOTISATION OF 4,4'-METHYLENE BIS-*m*-NITRO ANILINE (D)

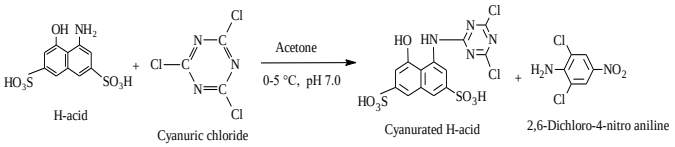


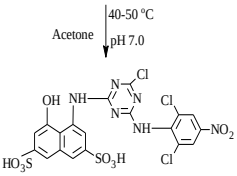
4,4'-Methylene bis-*m*-nitro aniline



Tetrazo solution (D)

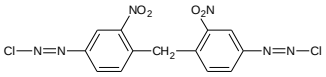
(3) PREPARATION OF 2,6-DICHLORO-4-NITRO ANILINO CYANURATED H-ACID (E)



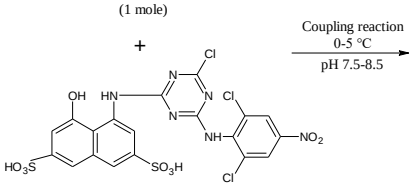


2,6-dichloro-4-nitro anilino cyanurated H-acid

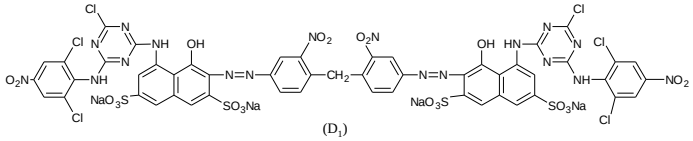
(4) FORMATION OF DYE



Tetrazo solution (D)
(1 mole)



2,6-dichloro-4-nitro anilino cyanurated H-acid (E)
(2 mole)



(D_1)

The characterization data of dyes (Table:1)

No.	2,6-dichloro-4-nitro anilino cyanurated coupling components (R)	Molecular Formula	Mole. Wt. (g)	Yield (%)	% Nitrogen Found / Require	R_f Value
D_1	H-acid	$C_{51}H_{24}O_{22}N_{18}S_4Cl_6Na_4$	1674	85	15.01 / 15.06	0.44
D_2	J-acid	$C_{51}H_{26}O_{16}N_{18}S_2Cl_6Na_2$	1470	75	17.10 / 17.15	0.38
D_3	Gamma acid	$C_{51}H_{26}O_{16}N_{18}S_2Cl_6Na_2$	1470	76	17.06 / 17.15	0.40
D_4	Bronner's acid	$C_{51}H_{26}O_{14}N_{18}S_2Cl_6Na_2$	1438	83	17.48 / 17.54	0.42
D_5	Tobias acid	$C_{51}H_{28}O_8N_{18}Cl_6$	1234	80	20.36 / 20.44	0.35
D_6	Koch acid	$C_{51}H_{22}O_{26}N_{18}S_6Cl_6Na_6$	1846	76	13.62 / 13.66	0.38
D_7	Sulpho Tobias acid	$C_{51}H_{26}O_{14}N_{18}S_2Cl_6Na_2$	1438	78	17.50 / 17.54	0.36
D_8	Laurant acid	$C_{51}H_{26}O_{14}N_{18}S_2Cl_6Na_2$	1438	83	17.46 / 17.54	0.38
D_9	N-methyl-J-acid	$C_{53}H_{30}O_{16}N_{18}S_2Cl_6Na_2$	1498	75	16.75 / 16.83	0.40
D_{10}	Chicago acid	$C_{51}H_{24}O_{22}N_{18}S_4Cl_6Na_4$	1674	80	14.98 / 15.06	0.36

Dyeing Procedure

All the D_1 to D_{10} were applied on silk, wool and cotton fabrics in 2% shade according to the usual procedure[**10**] in the dye-bath containing the materials listed as below.

Dye-Bath

Materials	For silk	For wool	For cotton
Fabric (g)	2.0 g	2.0 g	2.0g
Amount of dye (mg)	40 mg	40 mg	40 mg
Glauber salt (20 %)	1.0 ml	1.5 ml	1.0 ml
Soda ash (10 %)	1.0 ml	1.5 ml	1.0 ml
pH	3.0	3.0	8.0
MLR	1:40	1:40	1:40
Dyeing time (min)	40 min	60 min	90 min
Dyeing temp. (°C)	85°C	100°C	100°C
Total volume	80 ml	80 ml	80 ml

Colour Fastness Tests (Recorded in **Table-2**)

Fastness to Washing

A dyed fabric were stitched between two pieces of undyed fabrics, all of equal length, and then washed at 50 °C for 30 min. The staining on the undyed adjacent fabrics was assessed according to the following gray scale: 1-poor, 2-fair, 3-moderate, 4-good, 5-very good, 6-excellent.

Fastness to Rubbing

The dyed fabrics were placed on the base of the Crockmeter (Atlas), so that it rested flatly on the abrasive cloth with its long dimension in the direction of rubbing. A square of white testing cloth was allowed to slide on the tested fabrics back and forth twenty times by making ten complete turns of crank. For the wet rubbing test, the testing squares were thoroughly immersed in distilled water. The rest of the procedure was the same as in the dry test. The staining on the white testing cloth was assessed according to the gray scale: 1-poor, 2-fair, 3-moderate, 4-good, 5-very good and 6-excellent.

Fastness to Light

Light fastness was determined by exposing the dyed fabric for 40 h. The changes in color were assessed according to the following blue scale: 1-poor, 2-fair, 3-moderate, 4-good, 5-very good and 6-excellent.

Exhaustion and Fixation Study [11]

Table report the percentage exhaustion of 2% dyeing on cotton range from 65-76%, for silk range from 67-78% and wool range from 69-77%. The percentage fixation of 2% dyeing on cotton range from 78-92%, for silk range from 80-91% and wool range from 81-92%.

Dye uptake by the fiber was measured by sampling the dye bath before and after dyeing. The absorbance of the diluted dye solution was measured at λmax of the dye. Recorded in **Table-3**.

$$\% \text{ Exhaustion} = \frac{\text{Initial O.D. - Final O.D.}}{\text{Initial O.D.}} \text{ X } 100$$

III. RESULTS AND DISCUSSION

All the dyes were yellow to brown in colour and obtained in excellent yield (75 to 85 %). The purity of all the dyes has been checked by thin layer chromatography. The absorption spectra of all the dyes were recorded on Beckmann DB-GT Grafting spectrophotometer. **(Figure: 1, 2 & Table: 4)**

IR spectra:

IR spectra **[12]** of all the dyes, in general, showed -N=N stretching vibration at 1621–1625 cm^{-1}, -C-C– stretching vibration at 1491–3100 cm^{-1}, -OH and –NH stretching vibration at 3360–3478cm^{-1}, -C–N stretching vibration at 890–1410 cm^{-1}, -N=O stretching vibration at 1339–1525 cm^{-1}. **(Figure-1)**

PMR spectra :

The PMR spectra **[13-14]** (300 MHz, DMSO) of D_{36} showed signals at 3.50 (4H, -NH), 6.80 – 7.80 (20 H, aromatic proton), 2.55 (2H, $-CH_2-$). **(Table-4, Figure-2)**

Fastness Properties of the Reactive Dyes on Various Fabrics (Table : 2)

Dyes No.	Light fastness			Wash fastness			Rubbing fastness					
							Dry			Wet		
	S	W	C	S	W	C	S	W	C	S	W	C
D_1	5	4-5	4	4-5	5	5	6	3	4	6	4	3
D_2	3	4	5	4	3	5	5	5	4	4-5	5-6	4-5
D_3	6	5	4	5	6	5	3	4	3	5	4	3-4
D_4	6	5	4	4-5	5	5	3	4	3	4	3-4	4
D_5	3	4	4	4	3	5	5	6	3-4	4-5	4-5	4
D_6	4	3	4	4	3	4	4	5	3	3	4	2-3
D_7	6	5	4	6	4	3	4	4	4-5	3	6	5
D_8	3	3	4	6	4	3	3	5	4	5	4-5	3-4
D_9	4	3	4-5	5	4	5	6	4	5	4	5	4
D_{10}	4-5	5-6	6	4	3	4	5	5	4-5	3	4	5

Percentage exhaustion and fixation of reactive dyes (Table: 3)

Dyes No.	Exhaustion (%)			Fixation (%)		
	S	W	C	S	W	C
D_1	71.70	75.45	72.18	85.08	88.80	85.90
D_2	68.88	73.35	71.90	84.94	87.93	89.71
D_3	77.60	69.08	74.13	83.12	81.07	90.39
D_4	75.18	71.50	73.55	79.81	83.92	83.62
D_5	74.18	77.00	71.65	88.92	87.01	80.95
D_6	71.78	75.53	74.63	89.86	83.42	87.10
D_7	67.83	72.10	74.38	89.94	93.62	87.40
D_8	71.30	67.95	69.15	86.96	82.41	90.38
D_9	74.18	72.68	70.43	87.63	90.82	85.20
D_{10}	75.10	74.38	75.78	81.89	82.69	88.42

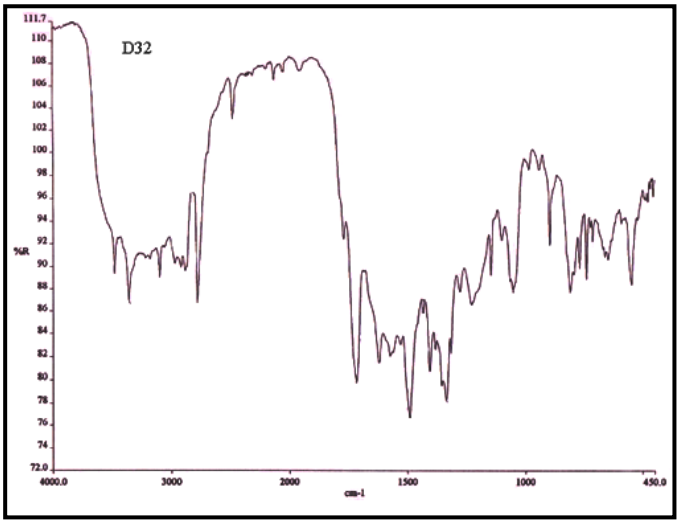
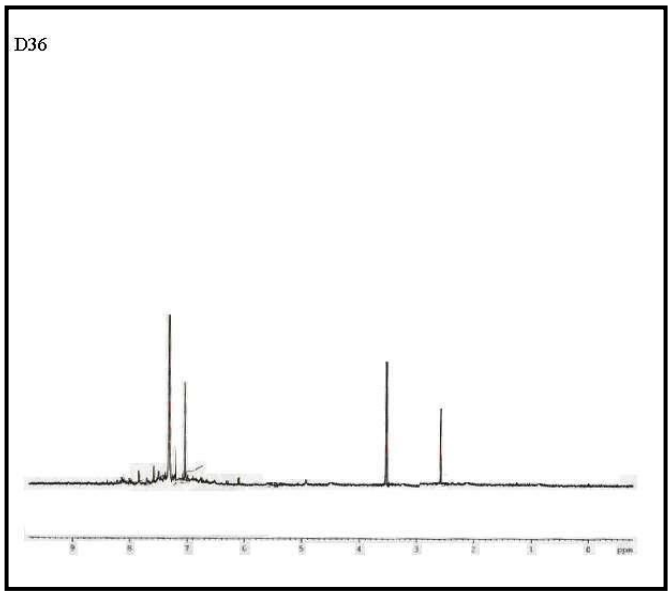


Figure 1: IR spectrum of D_2



Figure–2: PMR Spectrum of D6

Chemical shift δ ppm	Multiplicities	Number of protons	Assignment
2.55	s	2	-CH_2- group
3.50	s	4	-NH- group
6.80-7.80	m	22	Aromatic protons

Table-4: PMR Spectrum of D6

IV. ACKNOWLEDGEMENT

The authors express their sincere gratitude to the Chemistry Department, VNSGU Surat for providing necessary research facility; Principal Dr. S. P. Parekh and Chemistry Department of C. U. Shah Science College, Ahmadabad for providing necessary research facility; SAIF, Chandigarh for NMR and IR spectra; Atul Ltd. (Valsad) for providing dying and fastness tests facilities.

V. CONCLUSION

Dyes based on 4,4'-methylene bis-*m*-nitro aniline were synthesised by using conventional methods. These dyes gave yellow to pink shade on fibres depending upon the coupling component. Dyes exhibit moderate to very good light fastness, good to excellent wash and rubbing fastness.

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Cite this article as :

Lina A. Patel, K. C. Patel, S. A. Patel, " The Synthesis and Application of Reactive Dyes Based on 4,4'-methylene bis-m-nitro aniline on Various Fibres, International Journal of Scientific Research in Science, Engineering and Technology(IJSRSET), Print ISSN : 2395-1990, Online ISSN : 2394-4099, Volume 11, Issue 1, pp.284-290, January-February-2024. Available at doi : https://doi.org/10.32628/IJSRSET2411142