Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 6, Issue, 01, pp.4528-4531, January, 2014

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

SYNTHESIS, CHARACTERIZATION AND APPLICATION OF REACTIVE DYES BASED ON 4,4'-DIAMINO DIPHENYL SULPHONAMIDE ON VARIOUS FIBRES

[1,*]Lina A. Patel and [2]Patel, K. C.

[1]Department of Chemistry, C. U. Shah Science College, Ahmadabad (Gujarat), India
[2]Department of Chemistry, VNSG University, Surat (Gujarat), India

ARTICLE INFO

Article History:
Received 13th September, 2013
Received in revised form
07th October, 2013
Accepted 22nd December, 2013
Published online 26th January, 2014

Key words:
4, 4'-diamino diphenyl sulphonamide,
Bisazo reactive dyes,
Dyeing, Silk,
Wool & cotton.

ABSTRACT

Ten hot brand reactive dyes have been prepared by coupling tetrazotised 4, 4'-diaminodiphenyl sulphonamide with 2-chloro-4-nitro anilino cyanurated coupling components and their dyeing performance on silk, wool, cotton fibres has been assessed. All the dyes give well to very good light fastness on each fibre. Purity of all the dyes was checked by Thin Layer Chromatography (TLC). The structures of all the dyes have been confirmed by Nitrogen Elemental Analysis, FTIR, ^{1}H-NMR spectra and UV visible spectra. The percentage dye-bath exhaustion on different fibres are reasonable good and acceptable. The dyed fibres showed moderate to very good fastness to light, washing and rubbing.

INTRODUCTION

It is well known that benzidine based dye manufacture is prohibited due to the carcinogenicity of the precursor. Thus extensive research has been conducted to find alternative dyes. All previous research work can be involves the use of benzidine homologs that are less toxic than benzidine (Zhang *et al*., 1999). 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 (Suwanruji and Freeman, 2006; Shah, K.M, "Hand Book of Synthetic Dyes and Pigments"1994). (Patel *et al.,* 2001; Patel *et al*., 2004; Mehta *et al*., 2004; Patel *et al*., 2004) 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 (Patel *et al*., 2004; Mehta *et al*., 2004; Patel *et al*., 2004). 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'-diaminodiphenylsulphonamide.

MATERIALS AND METHODS

All the chemicals were purchased from local market and purified according to established method. Melting points were recorded using VEEGO digital melting point apparatus. The homogeneity and purity of synthesized compounds was established by Thin Layer Chromatography (TLC).

Synthesis of 4,4'diaminodiphenylsulphonamide(A) [4]

Synthesis of *p*-acetamidobenzenesulphonyl chloride

Chlorosulphonic acid (29.0 g, 0.249 mole) was added to a 250 ml three necked flask equipped with a stirrer, thermometer and a reflux condenser. The reagent was cooled to 5°C in an ice bath, and acetanilide (6.76 g, 0.05 mole) was added slowly at 5°C. The mixture was heated to 60°C and kept for 2 hours. Then 100 g of ice was added with continuous stirring, the precipitates of p-acetamidobenzenesulphonyl chloride were collected by filtration. It was washed with cold water, neutralized and dried. Yield 80 %, m.p. 148-149°C.

Synthesis of 4,4'-diacetamidodiphenylsulphonamide

p-Aminoacetanilide (5.0 g, 0.033 mole) in acetone (20 ml) was stirred at room temperature. After some time a solution of p-acetamido- benzenesulphonyl chloride (8.5 g, 0.036 mole) in acetone (15 ml) was added and stirring was continued at room temperature. Pyridine (1 ml) was added after 1 hour and 2 hours respectively. Reaction progress was assessed after 5 hours. When reaction was completed, acetone was decanted and water (20 ml) was added with stirring and heating. The product mixture was filtered, washed, dried and recrystallized from benzene. Yield 84 %.

**Corresponding author: Lina A. Patel*, *Department of Chemistry, C. U. Shah Science College, Ahmadabad (Gujarat), India*

Synthesis of 4,4'-diaminodiphenylsulphonamide

4,4'-diacetamidodiphenylsulphonamide was added to water (20 ml). Sodium hydroxide (15 ml, 20%) was added slowly with stirring. The mixture was reflux for 2 hour and cooled. The precipitates collected by filtration to give 4,4'-diaminodiphenylsulphonamide. Recrystallization from alcohol and water. Yield 72%, m.p. 136-138°C.

Tetrazotisation of 4,4'-diaminodiphenylsulphonamide (B)

4,4'-diaminodiphenylsulphonamide (2.63 g, 0.01 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 $NaNO_2$ (1.2 g, 0.02 mole) in water (8 ml) 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-B at 0-5°C was used for subsequent coupling reaction.

Formation of 2-chloro-4-nitro anilino cyanurated H-acid

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 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 when a clear solution was obtained. The cyanurated H-acid solution thus formed was used for subsequent condensation reaction.

Condensation with 2-chloro-4-nitro aniline

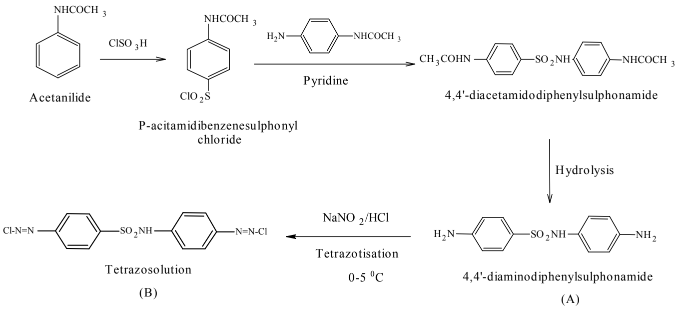
The temperature of ice-cooled well stirred solution of cyanurated H-acid (4.67 g, 0.01 mole) was gradually raised to 45°C for half an hour. To this cyanurated H-acid the 2-chloro-4-nitro aniline (1.72 g, 0.01 mole) was added dropwise at same temperature, over a period of 30 minutes, maintaining the pH neutral by simultaneous addition of sodium bicarbonate (1% w/v). After the addition was completed, stirring was continued for further 3 hours. The 2-chloro-4-nitro anilino cyanurated H-acid solution thus obtained was subsequently used for further coupling reaction.

Coupling of tetrazo (B) solution with 2-chloro-4-nitro anilino cyanurated H-acid (Formation of dye D_1)

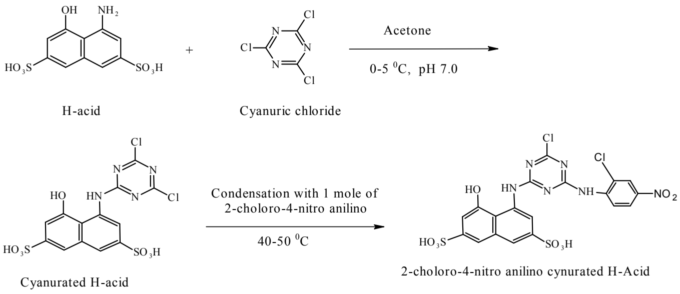
To an ice cold and stirred solution of 2-chloro-4-nitro anilino cyanurated H-acid (6.03 g, 0.01 mole), a freshly prepared tetrazo solution-B (1.79 g, 0.005 mole) was added dropwise over a period of 10-15 minutes. The pH was maintained at 7.5 to 8.5 by simultaneous addition of sodium carbonate solution (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 was added till 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-chloro-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.

Scheme:

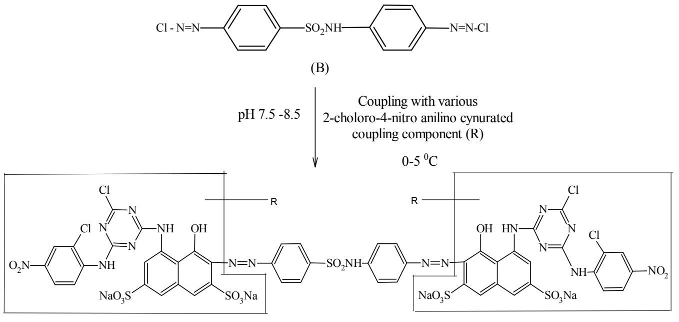
Synthesis of 4, 4'- diaminodiphenylsulphonamide (Patel *et al.*, 2006)



Synthesis of 2-choloro-4-nitro anilino cynurated H-Acid:



Formation of Dyes (D_1 to D_{10}):



D_1

RESULTS AND DISCUSSION

All the dyes were yellow to brown in colour and obtained in excellent yield (73 to 84 %). 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. The characterization data of dyes are given in Table 2.

IR spectra: IR spectra (Bassler *et al.,* 1991) of all the dyes, in general, showed –N=N stretching vibration at 1624 –1628 cm^{-1}, -C=C– stretching vibration at 1490–1590 cm^{-1}, -N=O stretching vibration at 1300-1550 cm^{-1}, -OH and –NH stretching vibration at 3300–3510 cm^{-1}, - C – N stretching vibration at 1200–1500 cm^{-1}, -S=O stretching vibration at 1020–1200 cm^{-1}, -C-Cl stretching vibration at 740 – 760 cm^{-1}.

Table 1. Dye-Bath materials

Materials	For silk	For wool	For cotton
Fabric (g)	2.0 g	2.0 g	2.0 g
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	----	1.0 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

Table 2.

Dye No	2-choloro-4-nitro anilino Cyanurated coupling Components (R)	Molecular Formula	Mol. Weight	Yield (%)	%Nitrogen		R_f Value
					Found	Required	
D_1	H-acid	$C_{50}H_{27}O_{20}N_{17}Cl_4S_5Na_4$	1580	80	15.02	15.07	0.40
D_2	J-acid	$C_{50}H_{29}O_{14}N_{17}Cl_4S_3Na_2$	1376	82	17.25	17.31	0.36
D_3	Gamma acid	$C_{50}H_{29}O_{14}N_{17}Cl_4S_3Na_2$	1376	75	17.27	17.31	0.38
D_4	Bronner acid	$C_{50}H_{29}O_{12}N_{17}Cl_4S_3Na_2$	1344	73	17.68	17.72	0.42
D_5	Tobias acid	$C_{50}H_{31}O_6N_{17}Cl_4S$	1140	78	20.82	20.89	0.42
D_6	Koch acid	$C_{50}H_{25}O_{24}N_{17}Cl_4S_7Na_6$	1552	74	13.52	13.59	0.36
D_7	Sulphotobias acid	$C_{50}H_{29}O_{12}N_{17}Cl_4S_3Na_2$	1344	80	17.64	17.72	0.34
D_8	Laurant acid	$C_{50}H_{29}O_{12}N_{17}Cl_4S_3Na_2$	1344	82	17.66	17.72	0.38
D_9	N-methyl j-acid	$C_{52}H_{33}O_{14}N_{17}Cl_4S_3Na_2$	1404	76	16.92	16.96	0.42
D_{10}	Chicago acid	$C_{50}H_{27}O_{20}N_{17}Cl_4S_5Na_4$	1580	80	15.02	15.07	0.40

Table 3. Percentage exhaustion and fixation of reactive dyes on silk, wool and cotton

Dye No.	Exhaustion (%)			Fixation (%)		
	S	W	C	S	W	C
D_1	70.80	75.15	69.6	80.51	88.49	90.52
D_2	71.90	77.48	71.4	87.62	89.06	81.23
D_3	69.00	71.28	69	89.86	86.29	87.68
D_4	72.00	68.75	74	80.56	85.09	87.84
D_5	75.73	70.88	75.83	85.18	83.25	81.77
D_6	75.43	76.55	71.88	78.22	82.95	78.61
D_7	73.80	73.35	67.55	88.08	81.8	88.08
D_8	68.73	74.5	70.18	85.85	89.93	81.94
D_9	72.30	68.93	75.15	91.98	88.5	79.84
D_{10}	75.35	72.05	74.1	85.60	82.58	90.42

PMR spectra: The PMR spectra (Dean 1968) (300 MHz, DMSO) of D_4 showed signals at 3.70 (4H, -NH), 6.85 – 7.91 (24H, aromatic proton), 8.40 (1H, -SO_2NH).

Dying of fibres: All the D_1 to D_{10} were applied on silk, wool and cotton fabrics in 2% shade according to the usual procedure (Bassler *et al.,* 1991) in the dye-bath containing the materials listed in Table 1.

Exhaustion and fixation study

Table report the percentage exhaustion of 2% dyeing on cotton range from 68-76%, for silk range from 67-76% and wool range from 67-78%. The percentage fixation of 2% dyeing on cotton range from 77-91%, for silk range from 77-92% and wool range from 80-90% (Table 3). Dye uptake by the fiber was measured by sampling the dye bath before and after

Table 4.

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

S= Silk, W= Wool, C= Cotton

dyeing. The absorbance of the diluted dye solution was measured at λ_{max} of the dye. Percentage dye bath exhaustion was calculated using the relationship.

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

Fastness properties: (Table – 4)

(a) 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– moderate, 3– fair, 4–good and 5–excellent.

(b) Fastness to rubbing: The dyed fabrics were placed on the base of the Crock meter (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 grey scale 1–poor, 2– moderate, 3– fair, 4–good and 5–excellent.

(c) 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-slight, 3–moderate, 4- fair, 5–good and 6–very good

Conclusion

A series of reactive dyes have been synthesized and their colour properties have been examined both in solution and on application to silk, wool and cotton fibres. The dyes give yellow to pink shades on fibres depending upon the coupling component.

Acknowledgement

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

REFERENCES

Zhang, S., X. Cheng., J. Yang; Dyes and Pigments 43 1999. 167-172.

Suwanruji, P., H. S. Freeman; Colourage, Vol. L 111-No. 4, April 2006.

Shah, K.M, "Hand Book of Synthetic Dyes and Pigments", Multi- Tech. Publishing Co., Vol. 1,184 1994.

Patel, M. S., S. K. Patel, K. C. Patel; *Proc. Nat. Acad. Sci.* India 71(A), 5-12 2001.

Patel, Y. S., Rutesh Shah, K. C. Patel; *Acta Ciencia Indica*, XXX c(1). 001 2004.

Mehta, J. R., K. C. Patel, S. K. Patel, R. R. Shah; *Acta Ciencia Indica*, XXX c(1) 009 2004.

Patel, R. S., K. C. Patel, S. K. Patel, P. S. Patel; *Acta Ciencia Indica*, XXX c(2) 113 2004.

Patel, K. C., N. B. Patel, B. M. Patel; CAIJ, 3(1) 35-40 2006.

Bassler, G. C., R. M. Silverstein, J. C. Morrill, Spectrophotometric Identification of organic compounds. 5th Ed. Wiley New York 1991.

Dean, J. A. *Chim. Chem.* 14, 324 1968.

****