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Synthesis and Dyeing Properties of Bifunctional Reactive Dyes of 5(4 bromophenyl) 1, 3 thiazole 2-amine by using Gamma acid and OAVs

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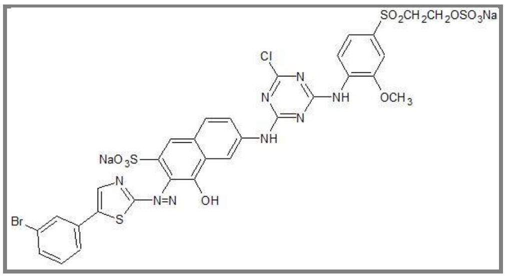
ABSTRACT

Bifunctional reactive dyes are colored compounds that possess more than one reactive moiety per molecule or groups, capable of forming covalent bonds between dye ions or molecules and the substrate. The bifunctional reactive dye was synthesized with s- triazine and vinyl sulphone groups via 5(4 bromophenyl) 1, 3 thiazole 2 - amine. This intermediate was diazotized coupled with gamma acid and other various coupling components to derive such bifunctional reactive dyes by using ortho anisidine vinyl sulphone and λ_{max} *of dyes were measured. % exhaustion, % fixation and % fixation efficiency of dyes was determined by Glauber salt using fixing agent at various temperature condition. Washing and light fastness were determined. The results were confirmed at* λ_{max} *411 nm. The overall result concluded that bromo and methoxy group was introduced in para position of benzene ring induced hypsochromic shift.*

Graphical Abstract



Structure of synthesized bifunctional reactive dye.

Keywords: Bifunctional, Co-valent bond, λ_{max}, Hypsochromic shift.

INTRODUCTION

Reactive dyes are colored organic compounds which contain two or more groups capable of forming covalent bond between the carbon and phosphorous atom of the dye molecule or ion and oxygen, nitrogen and sulphur atom of hydroxyl, amino and mercapto groups respectively of the substrate.

Such covalent bonds are formed with the hydroxyl group of cellulosic fibers, with amino, hydroxyl, and mercapto groups of polyamide fibers, and with amino groups of polyamides [1].

In general, reactive dyes are the only textile colorants that are designed to bond covalently with the substrate on application. They are used for dyeing and printing of cellulosic fibers and to lesser extent of polyamide fibers. They are valued for their brilliance and variety of shade, versatility, and, high wet fastness properties. The possibility of forming covalent bond between the dye and fibers has long been attractive to dye chemists, since attachment by physical adsorption and by mechanical hindrance had disadvantage of either low wash fastness or high cost.[2, 3] The presence of 1,3,5 triazine structure in the dye molecules improves their dyeing ability and possibility for application [4]. The various aspects of s-triazine dyes were published by several workers [5]. S-triazine based chemicals have been widely used in manufacture of polymers, dyes, explosives, pesticides, and commodity chemicals [6].

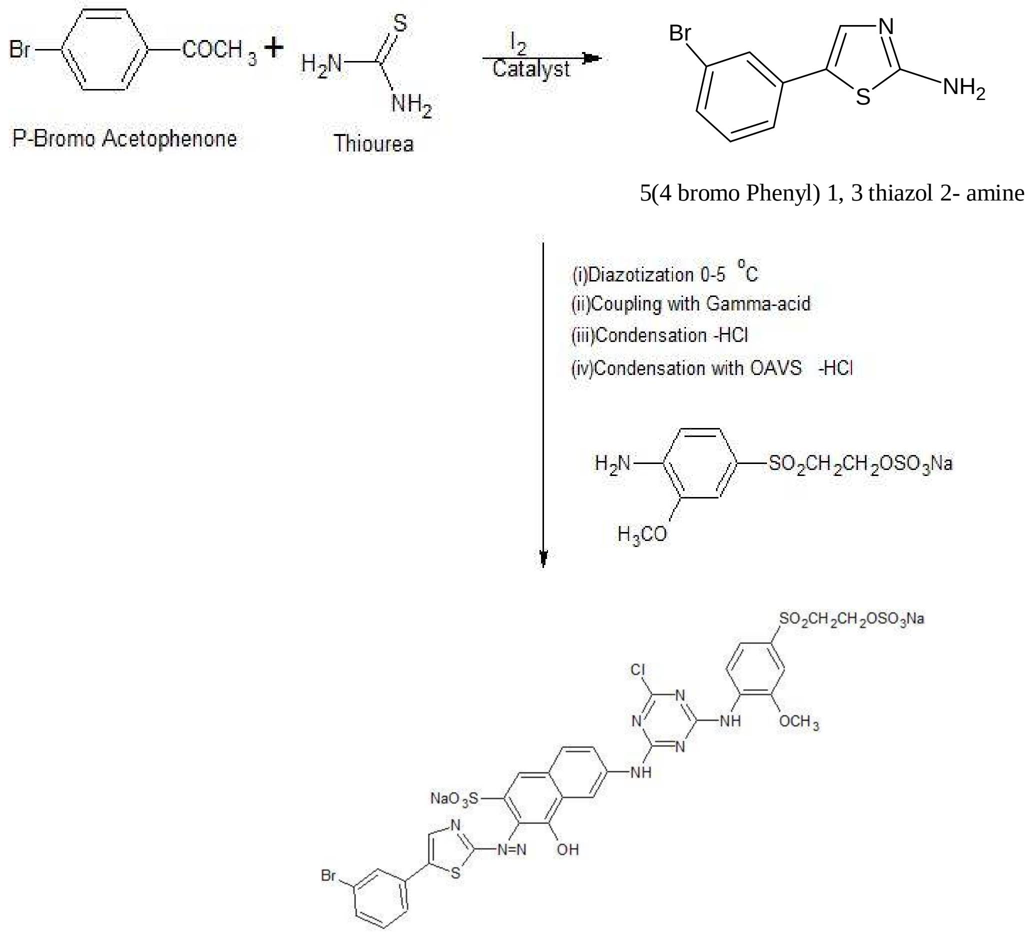
In general, acid dyes have attracted much attention for nylon substrates due to their interactions mechanism and easy method for application.[7] However, to achieve satisfactory levels of wash fastness, choice is required to an after treatment with commercial syntax and other fixing systems. After treatment of dyeing nylon substrates can improve wash fastness, this treatment can impart change in shade of ground color but also it is temporary in nature [8]. Consequent upon this application of reactive dye to nylon substrates has attracted interests to solve those problems [9]. Reactive dye react commercially with amino groups within nylon fiber to form covalent bond. Theoretically by the virtue of covalent nature of dye – fiber bond, reactive dyeing on nylon fiber can display their excellent wash fastness without any choice to an after treatment. Especially, reactive dye containing heterobifunctional groups can provide great opportunity for dye–fiber reaction due to sulphotoethylsulphone and monochlorotriazinyl reactive systems [10]. From the azo chromophore, many dyes can be obtained by varying different couplers, diazo components (Primary amines) and reactive systems. (Most widely used reactive systems are cyanuric chloride (trichloro-triazene), and vinyl sulphone derivatives.) These dyes are known as Azo Reactive Dyes**.** Various Coupling components (Such as, Amidonaphtholsulphonic acid, Naphthyl amine sulphonic acid, etc.) can be used to synthesize the Azo reactive dyes [11-13].

MATERIALS AND METHODS

The bifunctional reactive dye was synthesized in following steps:

Step 1. Synthesis of Intermediate "5(4 bromo phenyl) 1,3 thiazole 2-amine" [14]**:** First 0.062 mol Iodine crystal, 0.100 mol 4-bromo acetophenone and 0.13 mol thiourea were taken in Round bottom flask. Then the reaction mixture was heated in an oil bath at120-130°C for 5-6 h. Then the reaction mixture was cooled and it was diluted with 50-60 mL distilled water and was heated, until dissolve most of solids. Then the reaction mixture was cooled and was treated with 6N NH_4OH (pH 8-10). The precipitates of above intermediate were collected and were purified by crystallization from hot ethanol [14].

Step 2. Preparation of Gamma acid with cyanuric chloride [14]**:** First 0.010 mol cyanuric chloride was taken in Round bottom flask. Then it was dissolved in 40 mL acetone and 10 mL distilled water**.** This solution was kept for 1 h to form fine suspension at low temperature. After 1 h, a solution of gamma acid (0.010-0.020 mol) in 10% w/v NaOH was added in to the solution of cyanuric chloride in acetone and water in such way that the temperature could not rise above 5°C. The reaction mass was stirred up to 2 h. Then, in another beaker, ortho anisidine vinyl sulphone (0.005-0.006 mol) was added in 10 mL distilled water. This OAVs solution was added into above reaction mass with constant stirring. The reaction-mixture was stirred for half an hour at 0-5°C with gradually rising of temperature to 40°C adjusting pH to 7.5. The mixture was stirred for 3-4 h, then filtered it, washed it with cold water and the resultant product was used for subsequent coupling reaction.



Structure of synthesized bifunctional reactive dye.

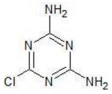
Step 3. Diazotization of Intermediate [14]**:** The diazotization was carried out by direct method. In a 250 mL beaker, 0.010-0.020 mole of 5(4 bromo phenyl) 1,3 thiazol 2- amine, 0.015 mole of Na_2CO_3 and 50 mL of water were taken. The solution was warmed until the clear solution was obtained. The reaction mixture was placed in ice bath to cool at 0-5°C. Now cold the solution of 0.020 mole of $NaNO_2$ into 5 mL of water was added into the cold solution of above 5(4 bromo phenyl) 1, 3 thiazol 2-amine solution slowly with constant stirring. Now, this solution was poured with stirring into 500 mL beaker containing 5 mL concentrated HCl and crushed ice**.** This mixture was stirred well for 10 min and maintaining the temperature below 10°C.

Step 4. General method of Coupling [14]**:** The Coupling compound (0.0050- 0.01 mole) was stirred in water at 0-5°C. The diazonium chloride solution of above intermediate 5(4 bromo phenyl) 1,3 thiazol 2-amine was added over 1 h maintaining the pH at 7.0. The stirring was continued for 4 h at 0-5°C. A solution of Na_2HPO_4 (0.0008-0.0009 mole) and KH_2PO_4 (0.0001-0.0002 mole) in water followed by sufficient amount of NaCl (0.08-0.09 mole) was added to the precipitates of the product. Organic impurities were extracted by washing with small portion of ethyl alcohol/ diethyl ether.

RESULTS AND DISCUSSION

The results of IR analysis (wave number) and UV (%T and ABS) at respective λ_{max} of various functional group of synthesized dye were given in following table 1. The results of IR analysis are compared with standard values [15] and it is matched very well with the standard values. The UV results of %T and Absorbance at λ_{max} is also shown here in table 1 and figure 1.

Table 1. The Results of IR and UV Analysis of Synthesized Dye TP Dye

Functional Groups	**Standard Value Cm^{-1}**	**Observed Value Cm^{-1}**	**%T**	**Abs.**	**λmax**
-Br	600 cm^{-1}	590.24	52%	0.2839	210 nm
C_6H_5- Br	1600 cm^{-1}	1616.40	36%	0.4436	210 nm
Thiazole	840 cm^{-1}	823.63	39%	0.4089	240 nm
	700 - 750 $cm^{-1,}$	750.33	45%	0.3467	200 nm(-NH_2) 230 nm(-Cl) 190 nm(-C=N)
-OCH_3	1200- 1280 cm^{-1}	1276.22	69%	0.1611	190 nm
-$SO_2CH_2CH_2OSO_3Na$	900 -920 cm^{-1}	914.08	51%	0.2924	220 nm(Vinyl sulphone group)
	1345 cm^{-1}	1309.71	75%	0.1249	180 nm(sulphonate)
-SO_3Na	1345 cm^{-1}	1309.71	75%	0.1249	180 nm(sulphonate)
azo	2000 cm-1	2060.04	87%	0.0604	340 nm
-OH	3200-3500 $cm^{-1,}$	3292.90	60%	0.2218	211 nm(-OH)

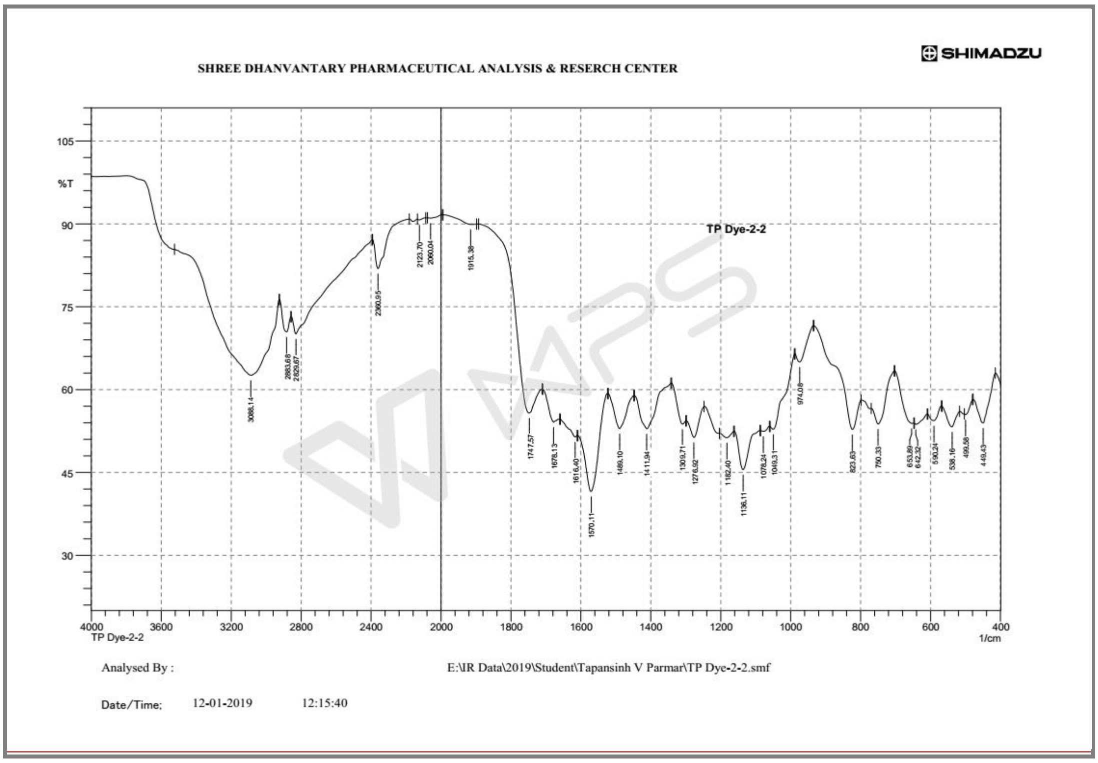


Figure 1. The results of IR analysis.

Dyeing Performance: The dyeing of this synthesized bifunctional reactive dye was done by Glauber salt method. The dye bath was adjusted to pH at 7.0 and 9.0. The dyeing was allowed for 1h at 80°C. Then from the value of initial and final OD of dye solution % Exhaustion was determined. At the end, the tested dyed sample was used for determining fastness properties upon cotton and wool.

$$\% \text{ Exhaustion} = \frac{InitialOD - FinalOD}{InitialOD} \text{ X } 100$$

Where OD = Absorbance/Optical density, Initial OD = Values before dyeing, Final OD = values after dyeing

Shadings of dye upon cotton and wool:

Upon cotton

Upon wool

Result of % Exhaustion of Dyes: The Results of % Exhaustion and % fixation values of synthesized dye is given in following table 2.

Table 2. Results of % Exhaustion and % Fixation values of synthesized Dye

S. No.	TP Dye on Cotton		TP Dye on Wool	
	% Exhaustion	% Fixation	% Exhaustion	% Fixation
1	16.24	83.76	13.75	86.25

From the values of % fixation which is obtained at 84 on cotton we can say that this dye shows excellent dyeing performance on cotton fabric. From the values of % fixation which is obtained between 86 on wool. It can say that this dye shows excellent dyeing performance on wool fabric.

Determination of fastness properties: These are the properties of dyes which indicate tolerance of dyes on the fiber towards the action of various foreign agencies, like, light, washing, heat (sublimation), rubbing, perspiration, etc. The dyed samples are tested by using standard methods.

Color fastness to washing: The dyed sample was stitched between cotton and wool fibers. Then specimen immersed into aqueous solution of soap- nonionic detergent, then samples were removed and rinsed in hot and cold water. Then the results were determined by using gray scale method.

Color fastness to light: The dyed fabric was exposed to light for 24 h. Then the results were determined by using gray scale method.

Fastness of various dyes according to standard method: The fastness properties of synthesized dyes are given in following table 3.

Table 3. The fastness properties of synthesized Dye

Name of Dye	Period of weeks	Wash fastness		Light Fastness	
		Cotton	Wool	Cotton	Wool
TP Dye	1	5	5	4-5	4-5
	2	4	4	4	4
	3	4	4	4	4
	4	4	4	4	4
	5	4	4	4	4

APPLICATION

The synthesis of this bifunctional reactive dye can be used as bright shade dye and has been shown to excellent fastness properties upon cotton and wool.

CONCLUSION

The fastness properties of dye were observed in above table at 4-5 shade at pH 12 and 70°C. The results proved that the fastness on cotton and wool has been good to washing and light. This bi functional reactive dye synthesized from 2-amino thiazole has been synthesized easily and has been shown to have good dyeing performance upon cotton and wool. Exhaustion and fixation were achieved by dye on fibers at pH 12 and 70°C. This new bifunctional reactive dye containing two reactive groups which were synthesized easily and it has been shown to have wide range of bright shades. The elimination of two reactive groups in presence of alkaline and acidic conditions cause formation of vinyl sulphone derivative in combination with s- triazine and so that this dye at various reactivity levels achieved bright shade because bromo and methoxy groups introduced on para position of benzene ring induced hypsochromic shift is confirmed by using Beckmann UV-Visible spectrophotometer.

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