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Original Research Article

Synthesis and application of novel bifunctional pyrazolo [1,5-a] pyrimidine reactive dyes

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ABSTRACT

Keywords

Synthesis;
Pyrazoloprymidine dyes;
Bifunctional reactive dyes;
properties.

New bifunctional bis-sulphatoethylsulphone and bis-monochlorotriazine reactive dyes of pyrazolo[1,5-a]pyrimidine derivatives were synthesized and their dyeing behaviour on cotton, wool and silk fabrics were investigated. The results assessed for the exhaust dyeing methods on the different fabrics indicate that reactive dyes having this molecular structure give a high level of exhaustion and fixation values. The dyed fabrics also showed very good light fastness and good to excellent washing, rubbing and perspiration fastness.

Introduction

Reactive dyes are known for their excellent dyeing efficiency and overall wet fastness properties. (Taylor, 2000; Berger, 2005; Omura, 1994; Philips *et al.*, 1982 and Collishaw *et al.*, 1993) Of these dyes, the synthesis and applications of bifunctional dyes containing two reactive groups stand as an ever-expanding area of research activities. These interesting activities have stimulated dyers and chemists to develop new dyestuffs by careful selection of reactive systems and chromogens (Carr, 1995). Further interesting researches resulted in the eventual introduction of newly heterocyclic derivatives as dye precursors. The aminopyrazole derivatives are important intermediates in the synthesis of heterocyclic dyestuffs. Their fused pyrimidine derivatives have recently reported as disperse dyes (Elgemeie *et al.*, 2003; Tsai *et al.*, 2005; Al-Etaibi *et al.*, 2011; Ahmed Z. Sayed et al., 2012 and Youssef *et al.*, 2006) .

As a part of our ongoing interest on the design of novel heterocyclic azopyrazole reactive dyes (Shams *et al.*, 2009 and Youssef *et al.*, 2014), an attempt made to identify the structural features associated with the dyeing performance of pyrazolo[1,2-a]pyrazole reactive dyes. The effects of changes in the dye chromophore, number and type of reactive groups were evaluated. Also, we have recently reported the synthesis and application of monofunctional pyrazolo[1,5-a]pyrimidine reactive dyes (Lewis *et al.*, 2000). The dyes exhibited relatively low substantivity and fixation yield, probably due to the presence of a single reactive group in the dye structure.

As no report seems to be available in the literature on the introduction of bifunctional reactive system into the heterocyclic pyrazolopyrimidine, herein, two models of homobifunctional bis (sulphatoethyl sulphone) 1 and bis(monochlorotriazine) 2 reactive dyes based on pyrazolo[1,5-a]pyrimidine derivatives were synthesized and their dyeing properties on cotton, wool and silk fabrics were investigated. The influence factors on the dyeability of these dyes were thoroughly investigated.

Materials and Methods

Mill-scoured and bleached cotton fabric (130 g/m^2; Misr El- Mahalla Co., Egypt), wool fabric (310 g/m^2; Golden Tex Co., Cairo, Egypt) and degummed and bleached silk fabric (90 g/m^2; El-Khateib Co., Cairo, Egypt) were used throughout this work.

Sera®wash (DyStar, Cairo, Egypt) was used as a nonionic detergent. AlbegalA (amphoteric levelling agent; Ciba) was used as an auxiliary for dyeing wool. 1-Aminobenzene-4-β-sulphatoethylsulphone (PABSES) was obtained from Amar Impex, Mumbai, India. Aminobenzene-2-sulphonic acid and 2,4-diaminobenzene sulphonic acid were provided by Isma Dyestuff and Chemical Co., Egypt. Cyanuric chloride was supplied by Merck. All other chemicals and auxiliaries used in this study were of laboratory reagent grade and applied without further purification.

Synthesis of dyes

The procedures used for the synthesis of bifunctional reactive dyes, shown in structures 1 and 2, are represented by the initial preparation of dye intermediates (IV and V) below.

[Bis(5-Amino-3-hydroxy-1H-pyrazolo)]disazostilbene-2,2'-disulphonic acid disodium salt intermediate IV (Scheme 1)

A neutral solution of 4,4'-diaminostilbene-2,2'-disulphonic acid **I** (0.05 mol) was bis-diazotized using sodium nitrite in a concentrated hydrochloric acid at 0°C; the pH was maintained at 5-6 by simultaneous addition of 2M sodium carbonate solution while cooling at 0-5°C. The resulting solution of *bis*-diazonium salt was then added with continuous stirring to cyanoethylacetate II (0.1 mol) to produce 4,4'-(*bis*-ethylcyanoacetate) dihydrazonostilbene-2, 2'-disulphonic acid disodium salt solution III. The precipitated product, formed upon the addition of 10% w/v sodium chloride, was filtered off, washed with 10% brine solution and dried in an oven at 50°C. Hydrazine hydrate (0.05mol) was added to a neutral solution of III (0.025 Mol). The reaction mixture was heated under reflux for 3-4 h, then cooled to room temperature and the precipitated dye intermediate that isolated by the addition of sodium chloride (5% w/v) was filtered off, and dried in a vacuum oven at 50°C to give dye intermediate IV (86% yield, $\lambda_{max.}H_2O$ = 427.60 nm).

To a neutral solution of dye intermediate (IV, 0.025 mol), ethylacetoacetate II (0.05 mol) was added. The reaction mixture was stirred under reflux for 4 h, then cooled to room temperature and the product was precipitated using sodium chloride (10% w/v), filtered off and dried in an oven at 50°C to give the dye intermediate **V** (83% yield, $\lambda_{max.}H_2O$ = 431 nm).

Synthesis of bis-sulphatoethylsulphone pyrazolo[1,5-a]pyrimidine bifunctional reactive dye 1 (Scheme 2)

A solution of PABSES diazonium chloride D1 (0.05 mol), prepared using a previously described method (Youssef *et al.*, 2003), was added slowly to a stirred solution of the dye intermediate **V** (0.025 mol) at pH 5-6 and at 0-5°C. The reaction mixtures were stirred for further 4 h, then the resulting solutions of reactive dyes were precipitated using sodium chloride (10% w/v), filtered and dried in a vacuum oven at 40°C to give the desired bis-sulphatoethylsulphone bifunctional reactive dye **1** (81 % yield, $\lambda_{max.}H_2O$ = 433.20 nm and ε_{max} = 45530 M.L cm^{-1}).

Synthesis of bis-monochlorotriazine pyrazolo[1,5-a]pyrimidine bifunctional reactive dye 2 (Scheme 3)

A solution of diazonium chloride D2 (0.05mol), prepared using a previously described method (Guo *et al.*, 1993), was added slowly to a stirred solution of the dye intermediate **V** (0.025 mol) at pH 5-6 and at 0-5°C. The reaction mixtures were stirred for further 4 h, then the resulting solutions of reactive dyes were precipitated using sodium chloride (15% w/v), filtered and dried in a vacuum oven at 40°C to give the desired bis-monochlorotriazine bifunctional reactive dye **2** (80 % yield, $\lambda_{max.}H_2O$ =439.6 nm and ε_{max} = 31923 M.L cm^{-1}).

Dye purification

Dye purity was assessed by thin layer chromatography (TLC) using an ethylacetate: n-propanol (2:1, v/v) eluent on silica gel plates. Infrared (IR) spectra were recorded on a Nexus 670 FTIR Spectrometer (KBr; Thermo Nicolet). ^{1}H-NMR spectra were recorded on a JEOL JNM-EX 270 MHz spectrometer in deuterated dimethylsulphoxide (DMSO-D_6) using tetramethylsilane (TMS) as the internal reference and the chemical shifts (δ) given in ppm. Absorbance of dyes, in aqueous solution, were recorded using a Shimadzu UV-2401PC UV/Vis spectrophotometer and maximum absorption wavelength (λ_{max}) and molar extinction coefficient (ε_{max}) were determined. UltraScan PRO spectrophotometer (Hunter Lab) with a D65 illuminant and 10° standard observer was used for the assessment of the optical strength of the dyed fabrics in terms of color yield (K/S) values.

For convenient dyeing and chemical investigations, it was necessary to purify the dye intermediates IV and V as well as bifunctional reactive dyes 1 and 2 from impurities (Guo *et al.*, 1993). This was done by dissolving the dyes in DMSO at 40-45°C. Inorganic impurities were eliminated by filtration and the dye solutions were re-precipitated in n-butanol at room temperature. The dyes were filtered, washed with acetone and diethyl ether then dried in a vacuum oven at 40°C.

Dye 1: $C_{42}H_{32}N_{16}S_6O_{22}Na_4$ (MW 1397) was confirmed by IR (ν/cm^{-1}): 3434.6 (pyrazolone-OH), 3232.1(NH_2), 2122.2(C≡N), 1634.0(C=O), 1596.0 (-N=N), 1882.0 (-SO_2-) and 1399 cm^{-1} (-OSO_3H).

^{1}H-NMR: δH (ppm) in [$^2H_6$]DMSO: 3.25-3.57(2H,t,2CH_2), 3.91-3.98 (2H,t,2CH_2), 5.77 (2H,s,NH_2), 7.59-7.30 (6H,t,6CH), 7.81-7. 7.91 (8H, d, 8CH) 7.97-8.03 (2H, s, CH) and 10.57 (2H, s, -OH)

Dye 2: $C_{56}H_{34}N_{26}S_6O_{22}Na_6Cl_2$ (MW 1824) was confirmed by IR (ν/cm^{-1}): 3520.00 (pyrazolone-OH), 3470.28 (NH), 3414.35(NH_2), 2083.71 (C=N), 1619.91(C=O), 1486.85 (-N=N-), 1142 (-SO_2-) and 1412.60 cm-1 (-OSO_3H).

^{1}H-NMR: δH (ppm) in [$^2H_6$]DMSO: 5.79 (2H,s,NH_2), 7.50-7.59 (2H,t,2CH), 7.59-7.7.91 (16H,d,16CH) 7.99-8.02 (2H,s,2CH) 10.44 (H,s,4NH), 10.58 (H,s,2OH).

Dyeing procedures

Applications of the synthesized dyes **1** and **2** were conducted in distilled water using 2 g pieces of fabric, at a liquor ratio of 40:1. Several depths of shade were employed using dye concentrations 1-5% (owf). The dyes were applied to cotton using 20, 40 and 60 g/l sodium sulphate at 40°C for 30 minutes, then 5, 10, 15 and 20 g/l sodium carbonate was added portion-wise while the temperature was raised to 60 °C (dye **1**) and 80°C (dye **2**) over 15 minutes. Dyeing was then continued for a further 60 minutes. The dyed samples were thoroughly rinsed with water and dried. The dyes were applied to wool fabric at pH 3-7, 5 % owf ammonium sulphate and 1 g/l Albegal A, while dyeing of silk was conducted at pH 4, 7, 8, 9 and 10 in the presence of 40 g/l sodium sulphate. Dyeing was started at 40°C and the dye bath was raised to the dyeing temperature (wool, 100°C; silk, 90°C) over 30 minutes. The dyeing was continued for a further 60 minutes and the dyed samples were thoroughly rinsed with water and dried.

Measurements and testing

Dye exhaustion

For all dyeings, the dye exhaustion was measured by sampling the dye bath before and after dyeing. The dye concentration (g/l) of the dye bath was measured spectrophotometrically at λ_{max} of each dye. The percentage of dye exhaustion (% E) was calculated using equation (1):

$$\%E = \left[1 - \left(C_2 / C_1 \right)\right] \times 100 \tag{1}$$

where C_1 and C_2 are the concentrations of dye in the dye bath before and after dyeing, respectively.

Dye fixation

Dye fixation (%F) (percentage of the exhausted dye that chemically bound on the fiber) was measured by refluxing the dyed samples in 50% aqueous DMF (liquor ratio 20:1) for 15 min to extract the unfixed dye (Gordon and Gregory, 1983). This procedure was repeated until the extract was colorless. The concentration of the extract was then measured spectrophotometrically at λ_{max} of each dye and the dye fixation ratio calculated using equation 2:

$$\%F = \frac{(C_1 - C_2 - C_3)}{(C_1 - C_2)} \times 100 \tag{2}$$

Where, C_3 is the concentration of extracted dye.

From the dye bath exhaustion (E) and dye fixation (F), the total dye fixation (T), which is the percentage of dye chemically bound relative to the total amount of dye used, was calculated for all dyeings using equation 3:

$$\%T = \frac{(\%E \times \%F)}{100} \tag{3}$$

Color strength

The reflectance values of each dyed fabric were measured at the λ_{max} and the corresponding color strength (K/S) values were calculated using Kubelka-Munk equation (4):

$$\boldsymbol{K} / \boldsymbol{S} = \frac{(1 - \boldsymbol{R})^2}{2\boldsymbol{R}} \tag{4}$$

Where:

R = A decimal fraction of the reflection of the dyed fabric; K = the absorption coefficient; and S = the scattering coefficient.

Fastness testing

The dyed samples were washed-off using 2 g/l nonionic detergent at 80°C for 30 minutes, and tested according to ISO standard methods (Gordon and Gregory 1983). The specific tests were ISO 105-X12 (1987), ISO 105-C02 (1989), ISO 105-E04 (1989), and ISO 105-B02 (1988) corresponding to color fastness to rubbing, washing, perspiration and light, respectively.

Results and Discussion

Synthetic Strategies and Structure Characterization

The synthetic strategies of bifunctional reactive dyes 1 and 2 and dye intermediates IV and V are outlined in schemes 1-3. The key step of the reaction mechanism involves the condensation of the 5-NH_2 group of the pyrazole ring with ester group of II to yield the intermediate V. The C-4 of the pyrazole nucleus is blocked by the arylazo moiety, acting as 1,5-dineucleophiles when subjected to reaction with 1,3-bielectrophilic reagent II leading, in turn, to produce a fused pyrazolo[1,5-a]pyrimidine disazodye intermediate V with active C-6 coupling site. Thus, the coupling of aryl diazonium salt D1 and D2, bearing a sulphatoethylsulphone (SES) and monochlorotriazine (MCT) reactive groups, onto the chromophoric intermediate V afforded the respective pyrazolopyrimidine bis(SES) and bis(MCT) bifunctional reactive dyes 1 and 2, respectively.

The visible absorption spectrophotometeric properties of the reactive dyes and the corresponding intermediates were recorded in water and are mentioned in the experimental part. The values of ε_{max} for both dyes depend on the number of sulphonic groups present in the dye structure. Dye **2** exhibited a lower extinction coefficient (ε_{max}) than dye **1**, possibly due to the electronic effect of the additional sulphonic groups in the dye molecule (Biolchi *et al.*, 2006).

IR spectra of 1 and 2 revealed NH_2 stretching modes around 3232.1 and 3414.35cm^{-1} respectively, as well as two bis 2 C=O absorption modes at 1634.0 and 1619.91cm^{-1}due to bis pyrazolopyrimidine . ^{1}HNMR of 1 revealed δ-1H singlet (2H) at about 3.25-3.37ppm integrating for two bis α CH2, 3.57- 3.82 and for two bis β CH_2 (SES), while ^{1}HNMR of 2 exhibited, triplet (2H) at about 7.50-7.59 ppm integrating for two bis CH and two singlet (2H each) at δ 10.44 ppm resonating for each pair of NH flanking the bismonochlorotriazine cores .

Dyeing of fibers

Both of the reactive dyes **1** and **2** are derived from the same chromophore and each possesses a homobifunctional bis-SES and bis-MCT reactive system, respectively. Consideration of the molecular structure of the dyes shows that there is also a difference in the level of dye sulphonation. In order to evaluate the dyeing performance of these novel dyes, it was necessary to determine the percentage exhaustion and total fixation yield as well as the build up properties of each dye on cotton, wool and silk fabrics.

Application to cotton

From the results displayed in Figure 1, it can be seen that the levels of primary exhaustion are extremely higher for dye 1 compared to those achieved using dye 2. It also indicates that the high values achieved using dye 1 being less pronounced by increasing the salt concentration. This presumably reflects high dye-fiber interaction; the presence of salt allows overcoming the electrostatic repulsion between the negative charge on the fibre surface and the dye sulphonate groups, thereby increasing its substantivity towards cotton and low salt dyeing. In other words, this may suggest that in the case of neutral or primary exhaustion, a lower degree of sulphonation, hence lower net negative charge leads to lower repulsion with the negatively charged fibre, even at low salt concentration. Thus, the tetra-sulphonated bis-SES dye 1 was more substantive than the hexa-sulphonated bis-MCT dye 2. In terms of final exhaustion and total fixation yield, the inclusion of sulphonate groups seems to be essential in order to prevent aggregation of the large dye molecules and provide sufficient solubility, which in turn offering the beneficial effect of the dye fixation via chemical reaction between cellulose hydroxyl groups and the bifunctional reactive system of the exhausted dye. Examination of the exhaustion and fixation values of the novel dyes show that dye 2 exhibits better levels than dye 1 at the end of the dyeing, which may attributed to its lower aggregation in the bath. It is also interesting to note that the bis-SES dye 1, compared to bis-MCT dye 2, showed very little variation in the primary and secondary exhaustion values, at any level of sodium carbonate concentration within the range 5-20 g/l. In the case of bis-SES dye, the addition of alkali brings about β-elimination of the SES groups to generate highly reactive bis-vinylsulphone dye. The relatively high amount of bis-SES dye present in the fiber owing to its high substantivity at the neutral stage as well as the generated bis-VS reactive molecules after the addition of alkali would increase the probability of dye-fiber covalent bonding. Additionally, as more dye fixes, more reactive sites on the cotton are occupied and thus less are available for further dye uptake. The probability of dye aggregation in the bath is increased due to the reduction in the dye solubility of being converted into the disulphonated bis-VS form relative to the hexasulphonated bis-MCT molecules in the case of dye 2.

The exhaustion and total fixation values of dyes 1 and 2 were also investigated at different dye concentrations (1-5% owf). Figure 2 clearly shows that the lower dye concentration exhibited a higher extent of exhaustion and total fixation than the higher depth of shade. This is believed to be due to the fact that increasing dye concentration would led to an increase in dye aggregation, which in turn reduces the dye penetration in the fiber. Additionally, at high dye concentration the number of available dye sites on the fiber decrease, resulting in a lower extent of exhaustion and fixation yield on cotton fabric.

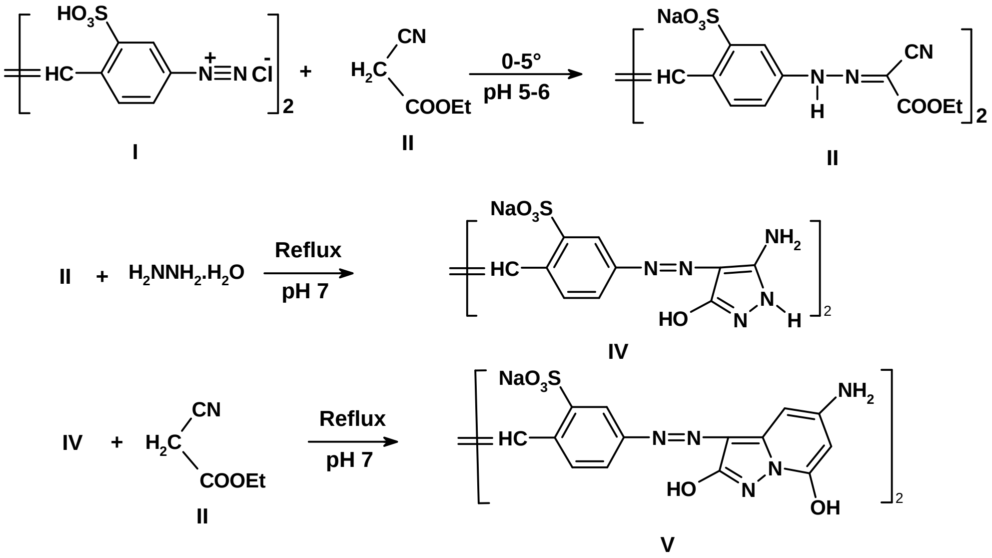
Application to wool and silk

The influence of pH on the dyeability of wool and silk with the bifunctional bis-SES dye **1** and bis-MCT dye **2** was investigated. From the results displayed in Figures 3 and 4, the pH range of dyeing wool and silk fabrics indicate that the reactive dyes exhibited high substantivity for the wool fiber at low pH values 3-4 and at pH values 4-6 for the silk fiber. The bis-MCT dye **2** shows remarkably higher exhaustion than the bis-SES dye 1. However, as the pH increased a reduction in percentages exhaustion and total fixation yield is observed with both dyes. Under acidic dyeing conditions used, as the number of sulphonic groups increases, the opportunity for greater attraction between the dye anionic sulphonate groups and cationic protonated amino groups in the fiber increases. Additionally, this might help in positioning the bifunctional reactive groups within the proximity of deprtonated amino groups thus facilitating covalent bond formation and dye fixation.

Having established that the optimum application pH was 3 on wool and pH 6 on silk, the extent of exhaustion and fixation values of both dyes **1** and **2** were further evaluated at different depth of shade (1-5% owf). Figures 5 and 6 show the data obtained on wool and silk fabrics, respectively. The results indicated that the lower dye concentration exhibited higher extent of exhaustion and total fixation than the higher depth of shade. It is believed that the proportion of available dye sites on the fiber would be decreased at higher dye concentration. In addition, because of the large molecular size of both reactive dyes, the extent of exhaustion and fixation efficiency is also likely to be reduced by steric hindrance and/or electrostatic repulsion where fixed dye impedes approach of more dye molecules.

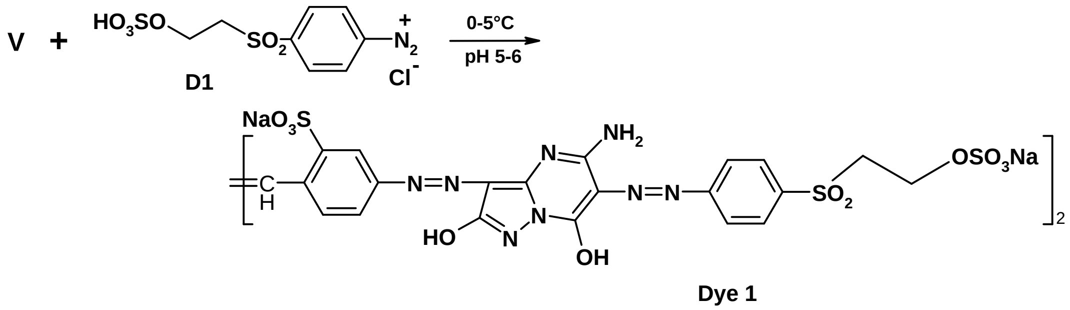
Fastness Properties

The fastness properties and color yields of the investigated dyes 1 and 2 on the test fabrics are given (Table 1). The dyes revealed approximately similar results of fastness properties for all fabrics. The high ratings of fastness properties could be referred to the covalent binding linkages between the dye and the fiber. Both dyes revealed higher color yields due to their increased substantivity to the fiber. The molecular design of the dyes comprising a heterocyclic chromophoric moiety leads to good light fastness.

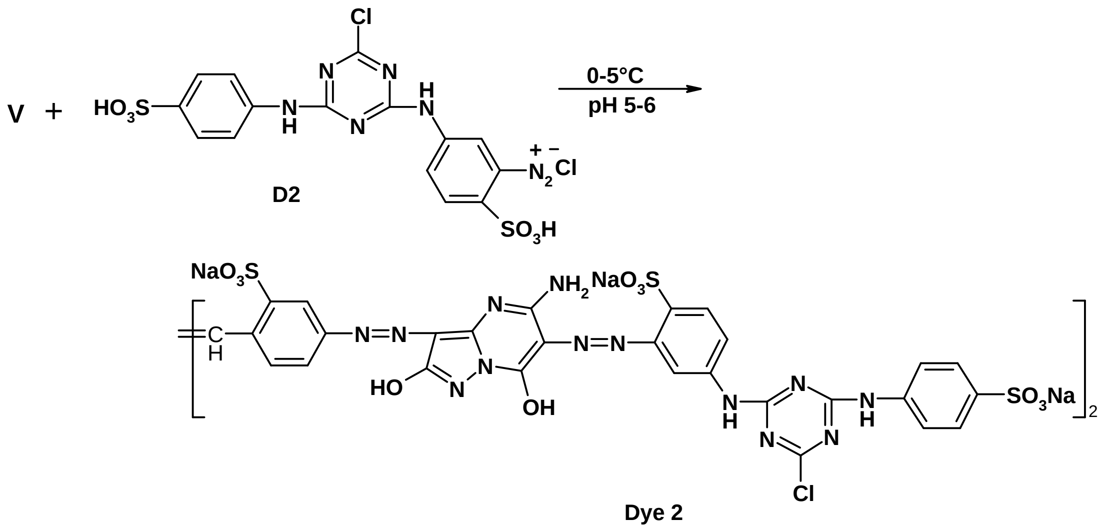


Scheme 1

4,4'-(bis(2,7-dihydroxy-5-aminopyazolo[1,5-a]pyrimidine)disazostilbene-2,2'-disulphonic acid disodium sat ***V*** (Scheme 1)



Scheme 2



Scheme 3

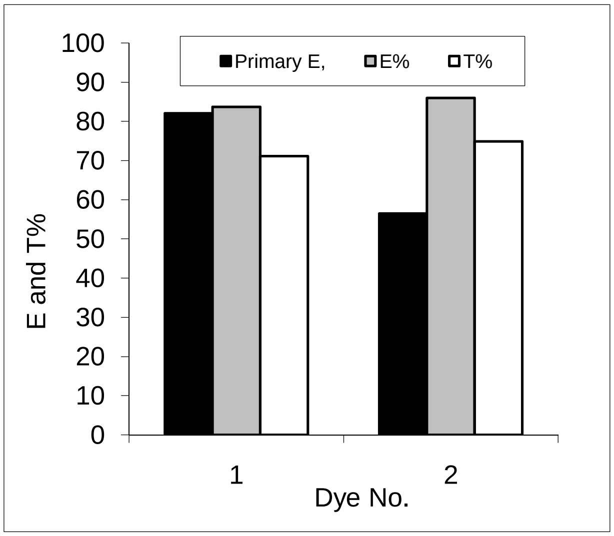


Figure.1 Exhaustion and fixation values of homobifunctional (bis-SES) dye 1 and homobifunctional (bis-MCT) dye 2 on cotton

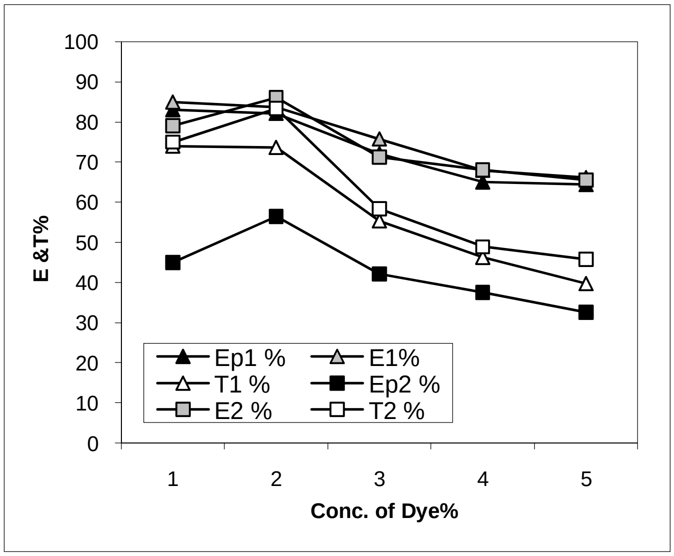


Figure.2 Effect of conc.of dye on exhaustion (E) and total fixation (F) on dyes 1,2 on cotton

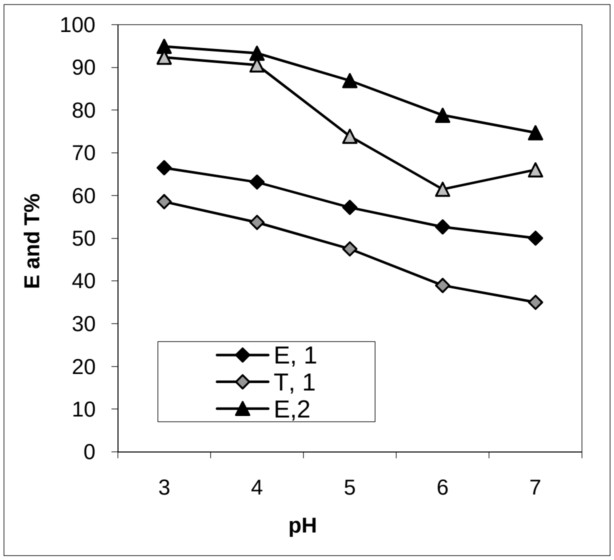


Figure.3 Exhaustion and total fixation yield of dyes 1,2 on wool at different pH values

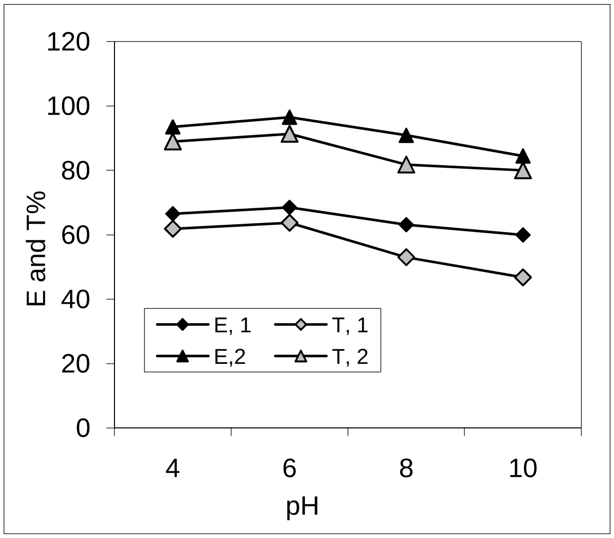


Figure.4 Exhaustion and total fixation yield of dyes **1** and **2** on silk at different pH values

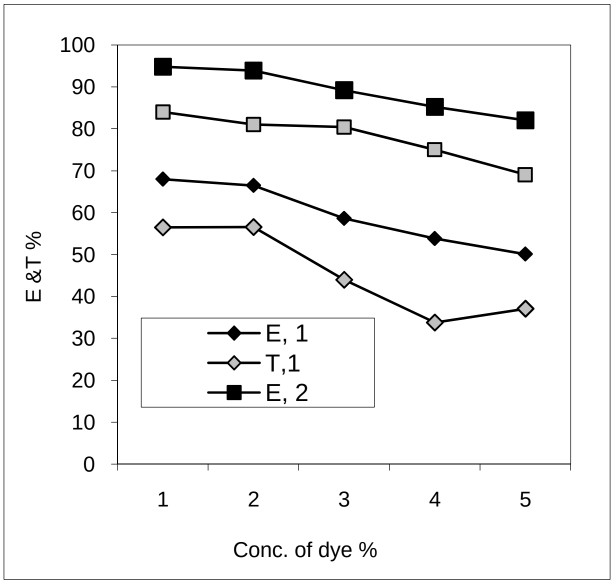


Figure.5 Exhaustion and total fixation yield of dyes 1,2 on wool at different conc. of dye

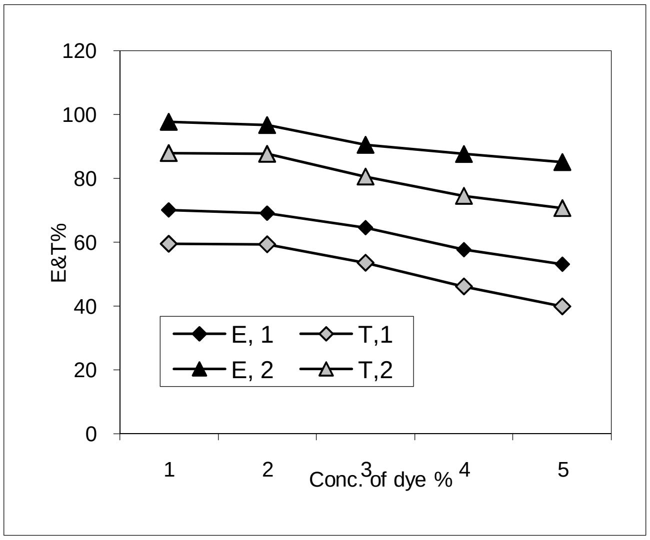


Figure.6 Exhaustion and total fixation yield of dyes 1,2 on silk at different conc.of dye

Table.1 The fastness properties and color yields of the investigated dyes 1,2 on the test fabrics are given

Dye	**shade**	**Dyed samples**	**K/S**	**Fastness to rubbing**		**Wash fastness**			**Fastness to perspiration**						**light**
				Wet	**Dry**	**Alt.**	**Sc**	**Sw**	**Alkaline**			**Acidic**			
									Alt	**Sc**	**Sw**	**Alt**	**Sc**	**Sw**	
1	**2%**	**C**	10.75	3	4-5	3-4	3	4	3-4	4	3	3-4	5	4	3-4
		W	18.60	4	4	4	4	4	4	4	4-5	4	4-5	4-5	4-5
		S	12.44	4-5	4	4	4-5	4-5	4-5	4-5	5	5	4-5	4-5	4-5
	4%	**C**	12.51	4-5	5	5	4-5	4-5	5	4-5	4-5	5	4-5	5	4-5
		W	20.45	5	4-5	4-5	5	4-5	5	4-5	5	5	5	5	5-6
		S	15.95	5	5	5	5	5	4-5	5	5	4-5	5	4-5	4-5
2	**2%**	**C**	12.75	4-5	4-5	4-5	4-5	4-5	5	4-5	5	4-5	5	4-5	4
		W	25.60	5	4-5	4-5	5	5	4-5	5	4-5	4-5	4-5	5	6
		S	14.44	5	5	5	5	5	4-5	5	4-5	5	4-5	5	6
	4%	**C**	14.71	5	5	5	5	5	4-5	5	4-5	4-5	5	4-5	6
		W	26.85	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5	4-5	4-5	5-6
		S	16.35	4-5	4-5	4-5	4-5	4-5	5	4-5	5	5	4-5	5	6

C,Cotton;W,Wool;S,Silk
Alt= alteration; Sc= Staining on cotton; Sw =Staining on wool.

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