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Synthesis of Azo Reactive Dyes Containing Aldehyde Group

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A new series of reactive dyes containing formyl group were prepared by diazotizing 2-amino-4-chloro-5-formylthiazole and coupling with γ-acid *i.e.*, naphthionic acid. Bisazo dyes based on H-acid were prepared. The dyes were applied on wool, silk and nylon and their fastness properties were measured.

Key Words: Synthesis, Azo reactive dyes, Aldehyde.

INTRODUCTION

A black colour is the result of uniform complete extinction of the incoming visible light. Single molecule black dyes like green dyes are relatively rare and it is generally more common to use mixture of dyes to produce black shades. In mixture of dyes however, selection of dyes is very critical to avoid problems associated with compatibility of dyes, therefore it is always advantageous to have a single molecule black dyes. The general approach for obtaining single molecules black is summarized by Griffiths and Reipl[1].

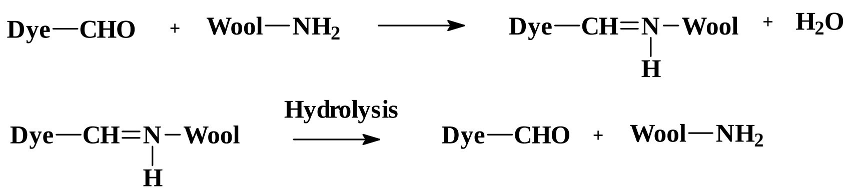
It is widely known that presence of an aldehyde group in a dye molecule renders the dye capable of reacting with the free functional groups of the wool keratin, or with the hydroxyl group of the cellulose[2,3]. Azo dyes containing aldehyde group can thus be considered as reactive dyes[4]. It is further known that the reaction of the formyl group with the amino function as well as with active methylene compound lead to bathochromic shift[1]. There are some anionic dyes with aldehyde group reported in the literature[5,6]. It is also mentioned in one of the reports that the polymeric substrates dyed with aldehyde group containing anionic dyes change their shade on heating with dilute alkaline soap solution[5].

In this paper we report a series of azo dyes containing an aldehyde group which are capable of reacting with polyamide substrate giving black shades and their comparison with commercial reactive dye (C.I. Reactive Black 5).

Reaction between the dye containing formyl group and wool fiber

Azo dyes containing formyl functional group on aryl rings have not attained commercial importance for dyeing of textile substrates. However anionic dyes containing formyl group have been examined as potential reactive dyes for polyamide fibers[2,3,5-13]. The reaction between the aldehyde function and the fiber is considered to be the formation of Schiffs base kind of reaction involving the free amino group contained in the wool keratin[2,3,8,9]. It is further mentioned that various types of functional groups in keratin including amino, thio, guanidine, thiol, carboxylic acid and phenolic groups are capable of participatation in reaction with aldehyde[10]. If an aldehyde group reacts with the free amino group in two neighbouring like side chain in wool keratin, it is possible for new crosslinks to be formed. Thus the dye is not held on the fiber by electrostatic interactions between the ionic centers of the polyamide and the dye, but also by a strong covalent bond between the dye and the fiber as well as possible crosslinks.

The observation that the polyamide dyed with dyes synthesized showed no loss of dye when treated with warm dilute sodium bicarbonate, warm pyridine and also with (1:1) DMF-water. This observation is in strongly in favour of formation of covalent bond between the dye and the polypeptide chain wool keratin[4]. The dye fiber reaction and the hydrolysis is shown in the **Scheme-I**[3].



$$\text{Dye—CHO} + \text{Wool—NH}_2 \longrightarrow \text{Dye—CH}{=}\underset{\substack{|\\ \text{H}}}{\text{N}}\text{—Wool} + \text{H}_2\text{O}$$

$$\text{Dye—CH}{=}\underset{\substack{|\\ \text{H}}}{\text{N}}\text{—Wool} \xrightarrow{\text{Hydrolysis}} \text{Dye—CHO} + \text{Wool—NH}_2$$

Scheme-I

EXPERIMENTAL

Naphthionic acid (1-aminonaphthalene-4-sulfonic acid), γ-acid (2-amino-8-hydroxynaphthalene-6-sulfonic acid.) and H-acid (1-amino-8-hydroxynaphthalene-3,6-disulfonic acid) were of commercial grade obtained from Atul (India) Ltd. 2-Amino-4-chloro-5-formylthiazole was prepared as per literature[14]. Elemental analysis was carried out in Microanalytical Laboratories of University of Mumbai Institute of chemical technology. Nitrogen, carbon, hydrogen and chlorine were analyzed on Heraeus analyzer. Nitrogen by Dumas method, Hydrogen by Preql catalytic combustion method and chlorine by Schoniger flask combustion method. IR Spectra (KBr) were measured on FTIR/5300 spectrophotometer. Ultraviolet spectra were recorded on Perkin Elmer Lambda 3B

UV-Vis spectrophotometer. A Datacolor spectraflash SF 300 spectrophotometer (Data colour International, NJ, USA) linked to a personal computer with She Lyn SLIFORM N/G software (She Lyn Inc.,Greensboro, NC,USA) was used to measure reflectance spectra of the dyed samples and calculate CIELAB colorimetric data and AATCC grey scale colour difference ratings for light exposed fabric samples. Colorimetric data were obtained using specular included, illuminant D65 and CIE 1964 10^0 supplemental standard observer. Each fabric sample was measured three times and data averaged. Wool hanks ready for dyeing were obtained from Piyush syndicate, Mumbai and the hanks were used as such without any pretreatment as specified by the supplier.

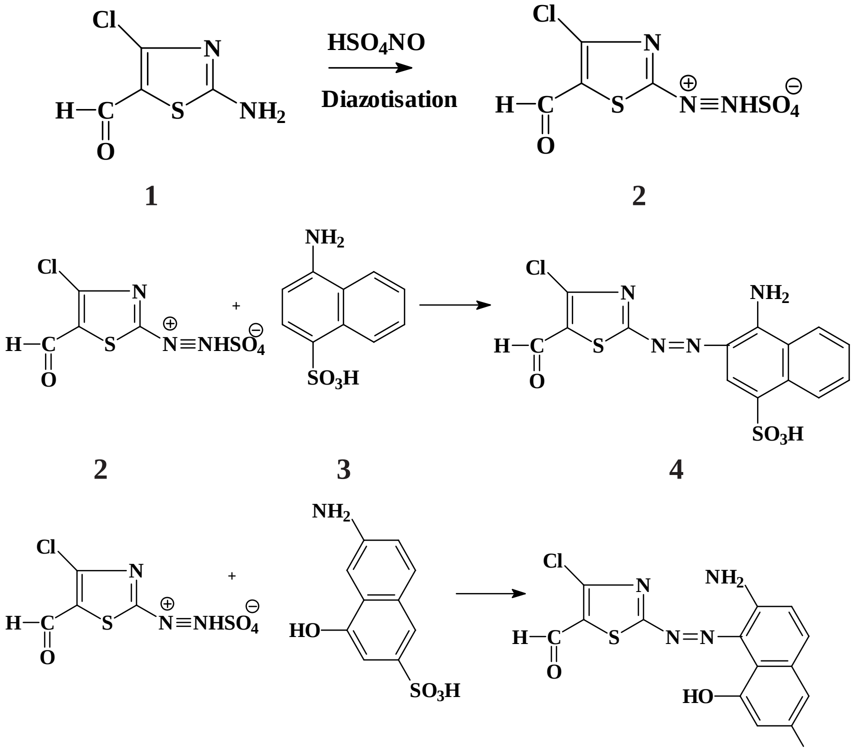
Synthesis

The diazotization of 2-amino-4-chloro-5-formylthiazole (**1**) was carried out in a non aqueous medium as reported[15]. The diazotized **1** was then reacted with naphthionic acid and γ-acid to give dyes **4** and **6**, respectively as shown in **Scheme-II**. The diazotized (**1**) was reacted with H-acid at acidic pH to give a monoazo dye which on coupling with aniline and *p*-chloroaniline gave bisazodyes **9** and **10**, respectively as shown in **Scheme-III**. Diazotization and coupling were carried out in one pot as reported in the literature[15]. Yield and microanalytical data of the dyes are shown in Table-1. The IR spectral data of the representative dyes are shown in Table-2.

Diazotization of 2-amino-4-chloro-5-formylthiazole (amine + nitrosylsulphuric acid mixture): 2-Amino-4-chloro-5-formylthiazole (12.2 g, 0.075 mol) was added to sulphuric acid (38 mL, 98 %) gradually in 1.5 h at a temperature of 25ºC. Then to above mixture nitrosyl sulphuric acid (60 mL, 1.53 M) was added slowly within 1 h. The resulting solution was stirred for 1 h and used to prepare dyes (**4**, **6**, **9**, **10**).

Synthesis of 4-amino-3-(4-chloro-5-formyl-2-thiazolylazo)-naphthalene sulfonic acid (4): Sufficient quantity of ice (500 g) was added to naphthionic acid (1-aminonaphthalene-4-sulfonic acid) (**3**) (18.37 g, 0.075 mol) in order to bring the temperature to 5°C. (amine + nitrosylsulphuric acid mixture) as prepared above was added to naphthionic acid solution slowly so that there should be no formation of brown fumes. During coupling the pH was adjusted to 4 by using 10 % sodium hydroxide solution. Next day dye was filtered and dried in an oven at 100ºC.

Synthesis of 8-(4-chloro-5-formyl-2-thiazolylazo)-7-amino-1-hydroxy-3-naphthalenesulfonic acid (6): Sufficient quantity of ice (500 g) was added to γ-acid (2-aminonaphthalene-6,8-disulfonic acid) (**5**) (17.92 g, 0.075 mol) in order to bring the temperature to 5ºC. (amine + nitrosylsulphuric acid mixture) as prepared above was added to γ-acid solution slowly so that there should be no formation of brown fumes. During coupling pH was adjusted to 4 by using 10 % sodium hydroxide solution. Next day dye was filtered and dried in an oven at 100ºC.

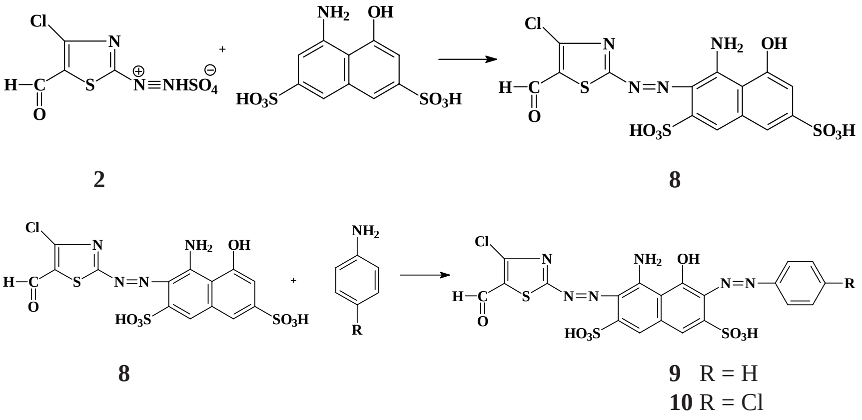


1 2

2 3 4

2 5 6

Scheme-II



2 8

8 9 R = H
10 R = Cl

Scheme-III

TABLE-1
YIELDS AND ELEMENTAL ANALYSIS[a] DATA FOR THE DYES **4, 6, 9, 10**

Dye no.	Yield (%)	m.f.	Found (%)				Required (%)			
			C	H	N	Cl	C	H	N	Cl
4	39	$C_{12}H_{11}N_4OSCl$	42.8	2.3	14.0	8.2	42.3	2.26	14.2	8.9
6	42	$C_{14}H_{15}N_4OSCl$	41.0	2.2	13.2	8.5	40.7	2.18	13.5	8.1
9	40	$C_{16}H_{18}N_5O_2SCl$	37.6	2.1	13.5	5.6	37.4	1.71	13.1	5.5
10	48	$C_{17}H_{20}N_5O_3SCl$	35.5	1.5	12.6	11.1	35.5	1.48	12.4	10.5

[a] A small amount of sample was separately salted out carefully to give a sample showing single TLC spot. This sample was carefully made acidic using acetic acid to give dye in the free sulfonic acid form, which was dried and subjected to elemental analysis.

TABLE-2
IR ABSORPTION BAND (cm^{-1}) OF THE REPRESENTATIVE DYES

Dye No.	$\nu(–NH_2)$	$\nu(–N=N–)$
4	3370	1635
9	3420	1616

Synthesis of bisazoformyl dye (9): H-acid (0.075 mol, 23.92 g) was dissolved in water (300 mL) and its pH was adjusted to neutral by using dilute sodium carbonate solution and sufficient quantity of ice pieces were added in order to bring the temperature between 0-5ºC. (Amine+ nitrosylsulphuric acid) solution was added slowly to H-acid solution so that there should be no formation of brown fumes.During coupling, pH was maintained at 4 by using 10 % sodium hydroxide solution. After 6 h, pH of the reaction mixture was brought to neutral. Aniline (0.075 mol, 6.47 g) was taken in a beaker and ice (100 g) was added to bring temperature 5ºC, hydrochloric acid (20 mL, 33 %) was added and then 20 % solution of sodium nitrite (0.07 mol, 5.75 g) was added, completion of diazotization was checked by using starch iodide paper and then aniline diazo solution was added to above monoazo dye solution slowly within 1.5 h and during coupling pH was maintained between 7-7.5 and temperature was maintained between 0-5ºC. Next day dye was filtered and dried in an oven at 100ºC.

Synthesis of bisazoformyl dye (10): H-acid (1-amino-8-hydroxynaphthalene-3,6-disulfonic acid) (0.075 mol, 23.92 g) was dissolved in water (300 mL) and its pH was adjusted to neutral by using dilute sodium carbonate solution and sufficient quantity of ice pieces were added in order to bring the temperature between 0-5ºC. (Amine + nitrosylsulphuric acid) solution was added slowly to H-acid solution so that there are no formation of brown fumes.During coupling pH was maintained at 4 by using 10 % sodium hydroxide solution. After 6 h, pH of the reaction mixture was brought to neutral. *p*-Chloroaniline (0.075 mol, 9.56 g) was taken in a beaker and ice (100 g) was added to bring temperature 5ºC, hydrochloric acid (20 mL, 33 %) was added and then 20 % solution of sodium nitrite (0.07 mol, 5.75 g) was added, completion of diazotization was checked by using starch iodide paper and then aniline diazo solution was added to above monoazo dye solution slowly within 1.5 h and during coupling pH was maintained between 7-7.5 and temperature was maintained between 0-5ºC. Next day dye was filtered and dried in an oven at 1000ºC.

Dyeing procedure

The synthesized reactive dyes were applied on wool silk and nylon 6.6 using standard dyeing methods[16-19].

Colour and fastness measurements

Light fastness and wash fastness tests were carried out using standard methods and assessed according to international blue scale (1-8) and grey scale (1-5), respectively[20,21].

Assessment of light fastness: A xenon arc lamp weathering tester model 60 X-H machine was used to assess light fastness of dyed samples by comparison with relative blue scale standards of ATTC (16E-1964R). The xenon arc lamp employed in this apparatus was of water cooled variety.

The specimens were exposed in a well-ventilated exposure chamber. The air temperature in the chamber was maintained at 30ºC. The variation of the light intensity over area covered by specimen and standard should not exceed 20 %. The samples and the standard were exposed simultaneously under the same conditions for the same time (100 h).

Assessment of wash fastness: The Launder-Ometer (Atlas Electric type) was used to assess the wash fastness of the dyed samples. A composite specimen was made from dyed sample (10 × 4 cm) as a layer between two undyed cloths (5 × 4 cm), one cotton and one wool. The weight of the two undyed cloths was approximately the same as that of dyed sample.

The composite specimen was placed in the container of the mechanical washing machine. The washing solution and conditions of testing were as follows: soap solution 5 g/L non-ionic detergent (Deter fix D3) and sodium bicarbonate to adjust the pH, 8.5-9.5. Following washing, the composite specimen was rinsed twice in cold water for 10 min and dried in air. The change in colour of the uncovered portion of the specimen and the staining of both undyed samples were assessed with grey scale.

Dye uptake: The dye uptake values were evaluated by measuring the concentration of the dye in the dye bath before and after dyeing. The dye concentration in the dye bath was determined by titrating the solution with $TiCl_3$ as well as by measurement of absorption values. The titration was carried out as described in the literature[22].

RESULTS AND DISCUSSION

Visible absorption properties of the dyes: The visible absorption properties of the dyes were measured in water and the results are summarized in Table-3. A comparison of the visible absorption properties of the dyes **4** and **6** shows that dye **6** in which γ-acid is used as a coupling component has a bathochromicity of 45 nm as compared to dye **4** in which naphthoic acid is used as a coupling component. The high bathochromicity of dye **6** is because in dye **6** azo group is flanked between amino and hydroxyl groups by strong hydrogen bonding which accounts for the rigidity of the azo group and hence bathochromic effect as compared to dye **4**. Wool dyed with the synthesized dyes showed no loss of dye when treated with warm pyridine and also with DMF-H_2O (1:1) mixture. This confirms the formation of the covalent bond between the dye and the polypeptide chain of the wool keratin[4].

TABLE-3
VISIBLE ABSORPTION DATA[a] AND FASTNESS PROPERTIES OF THE DYES ON WOOL SILK AND NYLON 6.6 AT 2 % DEPTH OF SHADE

Dye No.	Fibers	Light fastness	Wash fastness	Uptake (%)	Absorption maxima λ_{max} (nm)	log ε
4	Wool	6	3	93	490	4.37
	Silk	6	3	91		
	Nylon	5	3	90		
6	Wool	7	5	92	535	4.46
	Silk	7	4	89		
	Nylon	6	5	88		
9	Wool	6	5	93	628	4.43
	Silk	6	4	90		
	Nylon	5	4	88		
10	Wool	5	4	94	628	4.04
	Silk	6	4	90		
	Nylon	5	5	85		

[a] A small amount of the dye in each case was carefully and repeatedly salted out to give a sample showing a single spot on TLC. This sample was carefully made acidic with acetic acid to give dye in its free sulphonic acid form. The purity of the latter was close to 100% as indicated by the reduction titration using titanium chloride solution. Thus it was possible to calculate the molar extinction of the dyes.

Colour fastness and dye uptake: All the synthesized dyes were applied on wool silk and nylon 6.6 fabrics, the colours obtained ranged between violet to bluish black. The light fastness properties of the dyed material were assessed according to international blue scale (1-8), while wash fastness were assessed according to international grey scale (1-5), with scales 8 and 5, respectively ranked the best, while 1 is the most inferior. The light fastness of the dyes ranged between 5-7, while wash fastness results ranged between 3-5. This indicates that colour is stable to both light and washing. Dye uptake ranging between 85-94 %. The results are summarized in Table-3.

Colour properties of the dyes on wool silk and nylon: The dyes were applied on wool silk and nylon. To derive the colorimetric data dyeings at 1/1 standard depth were used[23]. The dyeings were evaluated using CIELAB[24,25] system in terms of L*,a*,b*,C*and H*. Results are summarized in Table-4. Dye **9** is darker than dye **10** and among all the synthesized dyes, dye **4** was redder in shade. The colour difference between the C.I. Reactive Black 5 (standard) and the synthesized dyes *i.e.* dye No. **9** and **10** are shown in Table-5. The Dye No. **9** in which aniline is used as a diazo component is darker that the standard and the Dye No. **10** in which *p*-chloroaniline is used as a diazo component is lighter than the standard.

TABLE-4
COLOUR COORDINATES^a OF THE DYES **4, 6, 9, 10**^{b}
ON WOOL, SILK AND NYLON

	Dye No.	**4**	**6**	**9**	**10**	C.I. Reactive Black **5**
Wool	L*	34.69	47.44	17.08	21.21	18.18
	a*	17.54	12.69	-0.73	1.61	-1.97
	b*	7.74	1.18	-5.95	-3.31	-7.50
	C*	19.17	12.74	6.00	3.68	7.75
	H*	23.81	5.31	262.98	296.02	255.30
Silk	L*	38.85	26.79	25.11	28.66	–
	a*	12.57	12.24	0.23	3.37	–
	b*	-1.36	0.07	-4.95	-1.40	–
	C*	5.04	12.24	4.96	3.65	–
	H*	344.40	344.02	272.64	337.44	–
Nylon	L*	27.86	28.69	22.50	24.32	–
	a*	13.50	5.17	-1.47	-1.22	–
	b*	-13.87	-7.17	-4.29	-3.08	–
	C*	13.88	8.84	4.53	3.52	–
	H*	272.07	305.80	251.07	248.48	–

a1/1 standard depth; b Light source = D65/10^0 observer

TABLE-5
COLOUR DIFFERENCE BETWEEN C.I.REACTIVE BLACK **5**
(STANDARD) AND DYE **9** AND **10**

Dye No.	dE*	dL*	Da*	Db*	DC*	DH*
9	2.26	-1.10	1.23	1.55	-1.76	0.91
10	6.29	3.03	3.58	4.19	-4.07	40.72

a 1/1 standard depth; b Light source = D65/10^0 observer

Conclusion

Wool dyed with the synthesized dyes showed no loss of dye when treated with warm pyridine and also with DMF-H_2O (1:1) mixture. This interprets the formation of the covalent bond between the dye and the polypeptide chain of the wool keratin[4]. This leads to a new series of reactive dyes for wool having high fastness properties. Generally black shades are obtained only by a mixture of two or more dyes. Here we observed that as single dye giving black shades can be obtained.

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