



# **Synthesis and Structural-reactivity Studies of Bifunctional MCT/SES (Monochlorotriazine/Sulphatoethylsulphone) Azo Reactive Disperse Dyes Applied to Wool and Polyester Fabric**

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## **Authors' contributions**

*This work was carried out in collaboration among all authors. Author IJE designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Author BKA managed the analyses of the study. Authors NPO and AAK managed the literature searches. All authors read and approved the final manuscript.*

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## **ABSTRACT**

Reactive disperse dyes containing monochlorotriazine/sulphatoethylsulphone reactive moieties were synthesized by condensing aniline with cyanuric chloride and further reacting it with a series of monoazo dyes obtained by diazotising 1-aminobenzene-4- $\beta$ -sulphatoethylsulphone and coupling with various substituted 2-amino-4-phenylthiazole derivatives. The dyeing performance of the dyes was evaluated on polyester and wool fabrics. The dyes obtained gave various shades ranging from reddish to bright red colours. They had good depth and good levelling properties. They dyed fabrics showed moderate to good light fastness properties and very good to excellent fastness to washing and perspiration. The dye bath exhaustion on the polyester and wool fabrics were found to be very good and their fixation values were moderate.

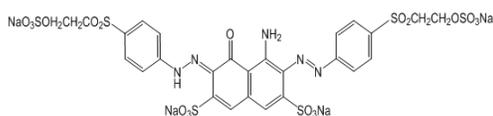
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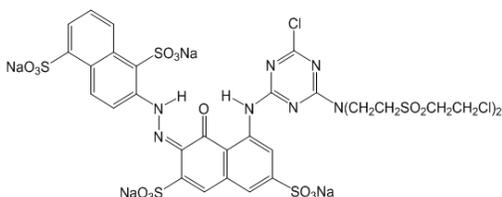
## 1. INTRODUCTION

Bifunctional reactive dyes are coloured compounds that possess more than two reactive moieties per molecule or groups, capable of forming covalent bonds between dye ions or molecules and the substrate [1]. The four characteristic feature of a typical reactive dye molecule are a reactive group, a chromophoric group, a bridging group and a solubilizing group.

Reactive dyes owe their covalent bond forming ability to the presence of the reactive groups in their structure. Bifunctional reactive dyes contain two separate reactive centres for reaction with suitable groups in the fibre. They also have the potential to combine with more than one group in the fibre chain molecule. Bifunctional reactive dyes can be homofunctional and heterofunctional [2].



**Remazol Black B (CI Reactive Black 5)**



**Remazol Red SBB (CI Reactive Red 181)**

Attempts have been made to produce different types of reactive disperse dyes, for example, reactive disperse dyes carrying monochlorotriazine [3,4], vinylsulphone[5,6] and disulphide bis (methyl sulphone) [5] reactive groups.

Disperse reactive dye containing both temporarily anionic sulphatoethylsulphone and nonionic disulphide bis (methyl sulphone) reactive groups have been applied to the cotton polyester fabric by exhaust dyeing. The optimum exhaustion and fixation were achieved at pH 6 and at the dyeing temperature of 1,300°C. This dye exhibited a good build-up even at the

conventional dyeing temperature of 90-100 because of its high substantivity resulted from the temporarily anionic sulphatoethylsulphone groups. The B-elimination of both, temporarily anionic sulphatoethylsulphone and nonionic Disulphide bis (methyl sulphone) group, result in the formation of bis (methyl sulphone) derivatives which increase the dye-fibre fixation [7].

The dyeing performance of such a sulphatoethylsulphone disulphide bis (methyl sulphone) reactive disperse dye on cotton polyester fibre should lead to the design of novel reactive disperse dye with good application properties.

In this paper, we report a series of bifunctional azo reactive disperse dyes containing monochlorotriazine / sulphatoethylsulphone reactive moieties which were synthesized by condensing aniline with cyanuric chloride and further reacting it with a series of monoazo dyes obtained by diazotising 1-aminobenzene-4-β-sulphatoethylsulphone and coupling with various substituted 2-amino-4-phenylthiazole derivatives.

## 2. EXPERIMENTAL

### 2.1 Materials and Apparatus

All the chemicals used in the synthesis of the dyes were of analytical grade. They were used without further purification. The melting points of the synthesized compounds were determined in open capillary tubes using melting point apparatus expressed in °C and are uncorrected.

The purity of the compound was checked by TLC on silica gel plates using diethyl ether: ethanol (75%: 25%) solvent mixture. The Visible absorption spectra were measured using CARY 630 UV-visible spectrophotometer. model: Agilent technology. The infra-red spectra were measured and recorded on FTIR Nexus 670 spectrometer in KBr disc (thermo Nicolet) and absorption bands are expressed in cm<sup>-1</sup>. GC-MS and NMR was carried out using Agilent technologies 7890 B GC system- 5977A Mass spectrometer and Neutron Magnetic Resonance spectrometer.

The light fastness was carried out using Microcell light fastness tester model no 225 and Blue wool standards.

### 2.1.1 Synthesis of 2-Amino-4-phenylthiazole derivatives

Resublimed iodine (7.6 g, 0.03 mol) was added to the slurry of the acetophenone (3.6 ml, 0.03 mol) and thiourea (4.5 g, 0.06 mol) in toluene and the mixture was heated in an oil bath at 130°C-140°C overnight. After cooling, the reaction mixture was diluted with distilled water (50ml) and heated to dissolve most of the solid, again cooled to ambient temperature. The aqueous solution was treated with 25% aqueous ammonium hydroxide (to pH 9-10). The precipitated thiazole was filtered, washed successively with water, collected and dried. The yellow crystals obtained were purified by crystallization from hot ethanol [8]. It was then taken for melting point determination.

The purity was checked by spotting on a TLC Plate coated with silica gel. The process was repeated by replacing acetophenone with its para substituent. e.g, chloroacetophenone, aminoacetophenone, 2,4-chloroacetophenone, bromoacetophenone and 2,4-bromoacetophenone to obtain other aminothiazole derivatives.

#### 2.1.1.1 Diazotization of 1-aminobenzene-4-β-sulphatoethylsulphone

A well-stirred solution of 1-aminobenzene-4-β-sulphatoethylsulphone (10.2 g, 0.05mol) in 2 N HCl (15 mL) was cooled at 0°C -5°C in an ice bath and diazotized with 1 N NaNO<sub>2</sub> solution (3.5 g, 0.05 mol; in 20 mL water). The sodium nitrite was added drop wisely over 30 minutes while stirring. The reaction mixture was stirred for another 2 hours. The mixture was then tested for complete diazotization using starch iodide paper which gave a weak blue test. When the mixture did not give the test, more sodium nitrite was added drop wisely until a positive test was obtained and the colour was stable for few minutes. A small amount of urea was also added to destroy excess nitrous acid [9].

### 2.2 Coupling of the Diazotized 1-Aminobenzene-4-β-Sulphatoethylsulphone with the 4-ARYL-2-Aminothiazole Derivatives

A solution of diazotised 1-aminobenzene-4-β-sulphatoethylsulphone (14.8 g at 95% purity, 0.05mol), was reacted with a solution of each of the 4-aryl-2-aminothiopyne intermediates (Al<sub>1</sub>-Al<sub>6</sub>) (4.9 g, 0.05 mol) respectively in distilled

water (25 ml) and hydrochloric acid (6 ml, 36%) over 30 min at 0-5°C. The mixture was stirred for 3 hours, maintaining the temperature below 5°C and the pH at 3.5 - 4. The six mono azo reactive disperse dyes (II<sub>1</sub>-II<sub>6</sub>) obtained was filtered off and dried at room temperature and weighed [10].

### 2.2.1 Synthesis of hetero bifunctional AZO reactive disperse dyes based on 4-ARYL-2-aminothiazole intermediates (II<sub>7</sub>-II<sub>12</sub>)

This was obtained by condensation of cyanuric chloride with aniline. the product was prepared from equimolar amounts of analogous starting materials in toluene solution at a temperature of -10°C to 50°C. cyanuric chloride (9.22 g, 0.05 moles) was reacted with aniline (27 g, 0.3 moles) at a molar ratio of 1: 6. the compound (2-aniline-4, 6-dichloro-1, 3, 5-triazine (0.05moles) was further reacted in ratio of 1:1 with the mono azo reactive disperse dyes (ii<sub>1</sub>-ii<sub>6</sub>) earlier obtained respectively, at a temperature of 0-5°C for 3 hours to get six heteros bifunctional azo reactive disperse dyes.

#### 2.2.1.1 Dyeing of wool

The stock solution of each dye was prepared by weighing 0.3 g dye powder and adding it to a beaker containing 20ml distilled water and the dispersing agent 0.75 g/l. the dispersion was further diluted to the final volume required using a liquor ratio of 50: 1. 2% shade on weight of fabric (O.W.F) was used on 1g of wool fabric .the dyeing was carried out at a pH of 4 at 80°C for 60 minutes after which sodium carbonate for fixation of the dyes into the fabric.

#### 2.2.1.2 Dyeing of polyester

The dye baths were prepared from the dye (2% o.w.f) with a dispersal -levelling agent (1 g/l) and 5% toluene as a carrier to a final liquor ratio of 50: 1, w/w. The pH value of the baths was adjusted to 4-5 with acetic acid (10%). The polyester fabrics, previously wetted were placed into the liquor ratio at 25°C - 30°C. The temperature was raised to 100°C at the rate of 2°C/min and dyeing continued for 60 minutes. After cooling, the dyed fabrics were reduction cleared in NaOH (2 g/l), a dispersing agent (1.5 g/l) and sodium dithionite (2 g/l) at 60°C for 30 minutes and then washed and dried. Percentage exhaustion was calculated to determine the dye absorption unto the fabric.

## 2.3 Determination of Percentage Exhaustion

The uptakes of the azo reactive disperse dyes by nylon 6.6 and wool fabrics was measured by sampling the dye bath before and after dyeing. The dye concentration (g/L) of the dye bath, diluted with 25 ml acetone, was measured spectrophotometrically at the  $\lambda_{max}$  value. The percentage of dyebath exhaustion (%E) was calculated using Equation 1 [11].

$$\%E = \left[ 1 - \left( \frac{A_2}{A_1} \right) \right] \times 100 \quad (1)$$

$A_1$  and  $A_2$  are the dye absorbance in the dye bath before and after dyeing respectively.

### 2.3.1 Dye fixation

The dye fixation (%F), the percentage of the exhausted dye chemically bound on the fibre, was measured by stripping and refluxing the dyed samples in 50% aqueous DMF (20:1 LR) or 25% (w/w) pyridine in water solution (LR 10:1) for 2 min at 100°C to extract the unfixed dye.

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

Where  $C_3$  is the concentration of extracted dye.

#### 2.3.1.1 Fastness test

The dyed samples were tested by the standard ISO methods (Methods of the test, 1990). The tests are as follows: Colour fastness to washing, ISO 105-C02 (1989); ISO 105-X12 (1987); fastness to perspiration, ISO 105-E04 (1989); and fastness to light using microsal tester xenon lamp.

## 3. RESULTS AND DISCUSSION

### 3.1 Synthesis of Intermediates and Dyes

2-amino-4-phenylthiazole was synthesized following the reaction steps in scheme 1. In this scheme, Resublime iodine (7.6 g, 0.03 mol) was added to the slurry of thiourea (4.5 g, 0.06 mol) and para-aminoacetophenone in toluene and the mixture was heated in an oil bath at 140°C overnight. After cooling, the reaction mixture was diluted with distilled water (50 ml) and heated to dissolve most of the solid, again cooled to room

temperature. The aqueous solution was treated with 25% aqueous ammonium hydroxide (to pH 9-10). The deep yellow precipitated thiazole was filtered, washed successively with water, collected and dried. The yellow crystals obtained were purified by recrystallization from hot ethanol and the melting point was taken.

Substituted 2-amino-4-phenylthiazole derivatives (All<sub>1</sub>-All<sub>6</sub>) were prepared from the condensation of the corresponding ketone; acetophenone (1), p-chloroacetophenone (2), p-aminoacetophenone (3), 2,4-dichloroacetophenone (4), p-bromoacetophenone (5) and 2,4-dibromoacetophenone (6) respectively.

1-aminobenzene-4-β-sulphatoethylsulphone was diazotized using Hydrochloric acid and sodium nitrite at 0°C to 50°C and the diazonium salts coupled with the aminothiazole derivatives at 0°C to 5°C and the mixture was stirred for 3 hours maintaining the temperature below 5°C and the pH at 3.5 – 4 [12]. The six azo reactive disperse dyes (II<sub>1</sub>-II<sub>6</sub>) were filtered, dried and weighed as shown in scheme 2.

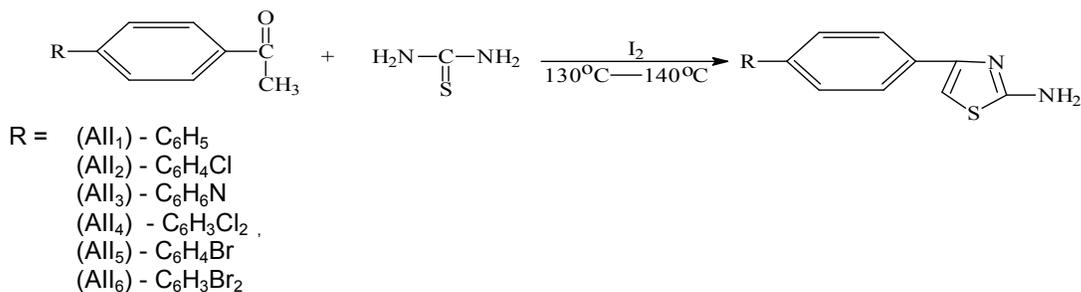
The heterobifunctional azo reactive dyes were obtained by following the reaction steps in scheme 3. This was obtained by condensation of cyanuric chloride with aniline. The product was prepared from equimolar amounts of analogous starting materials in toluene solution at a temperature of -10°C to 50°C. Cyanuric chloride (9.22 g, 0.05 moles) was reacted with aniline (27 g, 0.3 moles) at a molar ratio of 1: 6 [13]. The compound (2-aniline-4, 6-dichloro-1, 3, 5-triazine (0.05 moles) was further reacted in a ratio of 1:1 with the mono azo reactive disperse dyes (II<sub>1</sub>-II<sub>6</sub>) earlier obtained respectively, at a temperature of 0-5°C for 3 hours to get six heteros bifunctional azo reactive disperse dyes.

The structures of the intermediates and dyes were confirmed by NMR, Mass and infra-red spectrometry. The physical characteristics of the intermediates and dyes are summarized in Table 1.

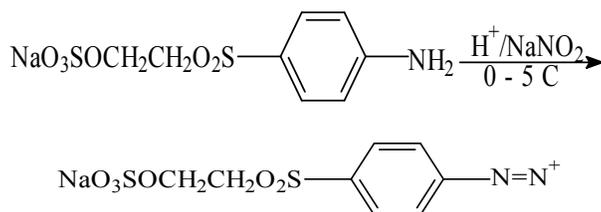
From the results shown in Table 1, 2 and 3, the percentage yield of the coupling components and dyes were of good yield ranging from 52% to 87% for the intermediates and 45% to 91% for the dyes. This is not too far from the range of results from previous and similar works [14]. One of the methods mentioned as a way of overcoming low yield is a prolonged reaction time. The basic condition that was pointed out,

was also very critical to the cyclization step using iodine crystals as shown in scheme 1. The R<sub>f</sub> values of the coupling component in diethyl ether: ethanol (75%: 25%) gave the highest value at 0.9 and the lowest value at 0.82. All the purified

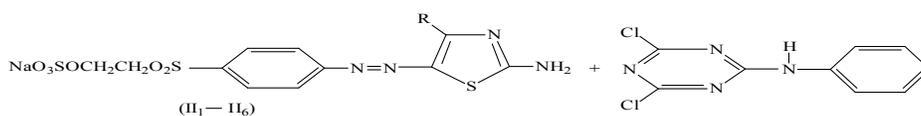
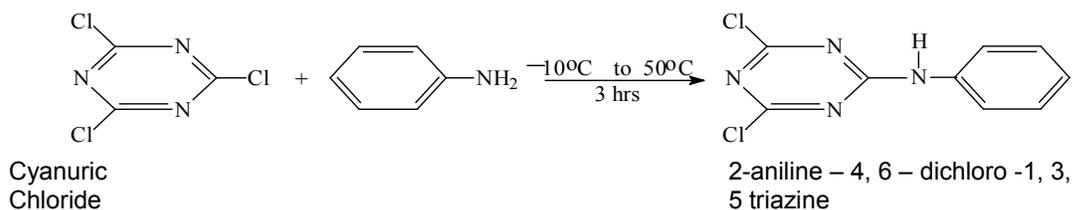
intermediates and dyes exhibited well-defined melting points characteristics of the pure compound. The intermediates gave different shades of yellow colours while the dyes had shades ranging from red, orange and reddish brown.



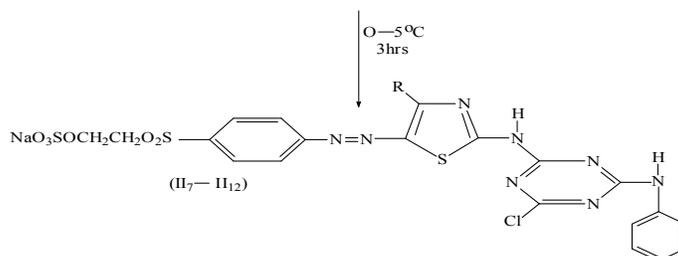
**Scheme 1. Synthesis of 2-amino-4-phenylthiazole intermediates**



**Scheme 2. Diazotization of 1-aminobenzene-4-β-sulphatoethylsulphone**



Monofunctional dye



**Scheme 3. Synthesis of heterobifunctional dye from thiazole derivatives**

**Table 1. Physical characteristics of the intermediates**

Intermediate code	Empirical formula	Molecular mass (gmol <sup>-1</sup> )	Melting point (°C)	% Yield	Colour of crystals	Rf
All <sub>1</sub>	C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> S	176	144-147	74	yellow	0.9
All <sub>2</sub>	C <sub>9</sub> H <sub>7</sub> N <sub>2</sub> SCl <sub>2</sub>	210.5	166-168	87	Off white	0.65
All <sub>3</sub>	C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> S	191	187-188	52	Dark yellow	0.73
All <sub>4</sub>	C <sub>9</sub> H <sub>6</sub> Cl <sub>2</sub> N <sub>2</sub> S	245	190-192	69	Brownish yellow	0.79
All <sub>5</sub>	C <sub>9</sub> H <sub>7</sub> N <sub>2</sub> SBr	254.9	190-192	69	Brownish yellow	0.82
All <sub>6</sub>	C <sub>9</sub> H <sub>6</sub> N <sub>2</sub> SB <sub>2</sub>	329.8	199-202	67	Greenish yellow	0.85

**Table 2. Physical characteristics of the monofunctional reactive disperse dyes**

Dye code	Empirical formula	Molecular mass (gmol <sup>-1</sup> )	Melting point (°C)	% Yield	Colour of crystal
II <sub>1</sub>	C <sub>17</sub> H <sub>16</sub> O <sub>6</sub> N <sub>4</sub> S <sub>3</sub>	468	139-141	81	Reddish brown
II <sub>2</sub>	C <sub>17</sub> H <sub>15</sub> O <sub>6</sub> N <sub>4</sub> S <sub>3</sub> Cl	502.5	158-159	54	Orange
II <sub>3</sub>	C <sub>17</sub> H <sub>17</sub> O <sub>6</sub> N <sub>5</sub> S <sub>3</sub>	483	123-125	58	Brownish orange
II <sub>4</sub>	C <sub>17</sub> H <sub>14</sub> O <sub>6</sub> N <sub>4</sub> S <sub>3</sub> Cl <sub>2</sub>	537	118-121	91	Grey
II <sub>5</sub>	C <sub>17</sub> H <sub>15</sub> O <sub>6</sub> N <sub>4</sub> S <sub>3</sub> Br	546.9	131-133	83	Red
II <sub>6</sub>	C <sub>17</sub> H <sub>14</sub> O <sub>6</sub> N <sub>4</sub> S <sub>3</sub> Br <sub>2</sub>	625.8	136-138	80	Orange

**Table 3. Physical characteristics of the heterobifunctional reactive disperse dyes**

Dye code	Empirical formula	Molecular mass (gmol <sup>-1</sup> )	Melting point (C)	% Yield	Colour of crystal
II <sub>7</sub>	C <sub>26</sub> H <sub>21</sub> O <sub>6</sub> N <sub>8</sub> S <sub>3</sub> Cl	672.5	159-161	52	Orange
II <sub>8</sub>	C <sub>26</sub> H <sub>20</sub> O <sub>6</sub> N <sub>8</sub> S <sub>3</sub> Cl <sub>2</sub>	731	148-149	45	Red
II <sub>9</sub>	C <sub>26</sub> H <sub>22</sub> O <sub>6</sub> N <sub>9</sub> S <sub>3</sub> Cl	707	186-188	60	Reddish brown
II <sub>10</sub>	C <sub>26</sub> H <sub>19</sub> O <sub>6</sub> N <sub>8</sub> S <sub>3</sub> Cl <sub>3</sub>	687.5	143-145	63	Red
II <sub>11</sub>	C <sub>26</sub> H <sub>20</sub> O <sub>6</sub> N <sub>8</sub> S <sub>3</sub> ClBr	741.5	128-131	53	Red
II <sub>12</sub>	C <sub>26</sub> H <sub>19</sub> O <sub>6</sub> N <sub>8</sub> S <sub>3</sub> ClBr <sub>2</sub>	751.5	140-143	78	Red

The results obtained from the infra-red spectra analysis shows that all the synthesized aminothiazole based coupling component gave absorption peaks due to aromatic C=C stretching vibration at 1602-1630-cm<sup>-1</sup>, aromatic C-H bending vibration at 771-847 cm<sup>-1</sup>, C-N stretching vibration at 1039-1110 cm<sup>-1</sup> as supported by literature [15]. The amino group absorption peak showed at 3391-3451 cm<sup>-1</sup>, C=C bending vibration at 1625-1654 cm<sup>-1</sup>. C-S (in-plane bend) showed a peak at 674-741 cm<sup>-1</sup> as interpreted by literature [16].

It can also be seen that the dyes gave absorption peaks due to azo group stretching vibration at 1397-1772 cm<sup>-1</sup>, aliphatic C-C stretch at 1039-1285 cm<sup>-1</sup>, aromatic C-H bending vibration at 734-890 cm<sup>-1</sup>, N-H stretch at 3298-3551 cm<sup>-1</sup>, N-H bend at 1580-1662 cm<sup>-1</sup>, an aromatic stretch of phenyl ring at 3049-3138 cm<sup>-1</sup> as also interpreted by related previous studies[17].

### 3.1.1 Visible absorption spectra of the dyes

The visible absorption spectra of the dyes were measured in different solvents and extinction

coefficient calculated in ethanol. The results obtained are shown in Table 5.

The visible absorption properties were measured in ethanol, acetone, chloroform, ethanol +HCl. The wavelengths of maximum absorption of the dyes range from 421 to 510 nm in ethanol, 421 to 471 nm in acetone, 418 to 457 nm in chloroform and 417 to 493 nm in ethanol + HCl. Bathochromic shifts of the visible absorption band were observed on increasing the solvent polarity, where the difference in λ<sub>max</sub> was noticed upon measuring the dyes in ethanol, acetone and chloroform. This is of course expected for a system in which the excited state is more polar than the ground state [18,19,20]. The effect of few drops of acids on ethanolic solution of the dyes was also observed and the results shows that dyes II<sub>7</sub>, II<sub>8</sub>, II<sub>9</sub>, II<sub>10</sub> and II<sub>11</sub> have positive halochromism as they absorbed maximally at 510, 437,415,505 and 483 respectively in a neutral solution of ethanol and absorb maximally at 471, 417, 412, 482 and 422 respectively in acidic of ethanol, indicating a bathochromic shift of +39, +20, +3, +23 and +61 respectively. Only Dye II<sub>12</sub> showed negative

Table 4. Infra-red data of the intermediates

Functional group	C=C	C-H	N-H	N-H	C-S	C-N	C-C	C=C	C-H	C-Cl	C-Br	C- H
Type of vibration/ Code	Bending aliphatic	Bending Aromatic	Bending all	Str	In-plane bend	Stretch aliphatic	Stretch aliphatic	Stretch aromatic	In-plane bend Ar-H			Stretching aliphatic
All1	1624	847	1577	3435	691 715	1039	1340	1483 1532	1191			2283
All2	1621	827 741	1569	3391	741	1088 1036		1494	1196	827		2847 2948
All3	1610	738	1539	3410	685	1043	1267	1490 1427	1125			2776
All4	1630	764 827	1580	3306	674	1028	1632	1461	961	723		2922
All5	1602	771 849		3432	693	1086	1028 1326	1159			693	
All6	1621	823	1565	3384	741	1069	1319		1189		741	2847 2948

Table 5. Infra-red data of the dyes

Functional group	C=C	C-H	N-H	N-H	C-S	C-N	C-C	N=N	C-H	C-Cl	C-Br	Ar- H
Type of vibration/ Code	Bending aliphatic	Bending Aromatic	Bending	Str	In-plane bend	stretch	Stretch aliphatic	Stretch	In-plane bend Ar-H			Stretching aromatic
II1	1654	839	1595	3313	741	1110	1285 1039	1498	1133 1002			3108
II2	1640	890	1587	3406	734	1043	1226	1397		834		3138
II3	1640	805 730	1662	3298 3406	689	1066	1222	1772	998			3108
II6	1640	734	1584	3298	700	1047	1386	1498	1084			
II7	1628	745	1584	3511	685	1043	1248	1662 1517		835		3049
II8	1625	745	1580	3004	685	1088	1043 1133	1446	1224	827		3194
II11	1628	868	1584		685	1039	1088	1446 1517			738	3093

**Table 6. Visible absorption spectra of the dyes**

Dyes	$\epsilon_{\max} 10^5 \text{ Lmol}^{-1} \text{ cm}^{-1}$ in EtOH	Ethanol $\lambda_{\max}$	Acetone $\lambda_{\max}$	Ethanol + HCl $\lambda_{\max}$	Chloroform $\lambda_{\max}$	Change in $\lambda_{\max}$
II <sub>7</sub>	1.25	510	471	471	418	+39
II <sub>8</sub>	0.84	437	427	417	420	+20
II <sub>9</sub>	0.7	415	413	412	402	+3
II <sub>10</sub>	1.3	505	448	482	457	+23
II <sub>11</sub>	1.2	483	431	422	426	+61
II <sub>12</sub>	1.21	421	421	493	356	-72

**Table 7. Mass spectra data of the intermediates and dyes**

Code	Molecular formula	Calculated molecular Mass (m/z)	Experimental Mass (m/z)
All4	C <sub>9</sub> H <sub>6</sub> Cl <sub>2</sub> N <sub>2</sub> S	(M+H) <sup>+</sup> 245 (M+Na) <sup>+</sup> 268	244 267
All1	C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> S	(M+H) <sup>+</sup> 176 (M+Na) <sup>+</sup> 199	173 196
All6	C <sub>9</sub> H <sub>6</sub> Br <sub>2</sub> N <sub>2</sub> S	(M+H) <sup>+</sup> 329.8 (M+Na) <sup>+</sup> 352	329
II10	C <sub>26</sub> H <sub>19</sub> Cl <sub>3</sub> N <sub>8</sub> S <sub>3</sub> O <sub>6</sub>	(M+H) <sup>+</sup> 741 (M+Na) <sup>+</sup> 764	733

halochromism as it absorbed at 421 in a neutral solution of ethanol and absorb maximally at 493nm in acidic of ethanol, indicating a bathochromic shift of -8,-26 and -27 nm respectively. None of the dyes exhibited zero halochromism. The shift may be attributed to the electron withdrawing strength of the substituent (21). If the electron withdrawing strength of the substituent is sufficiently high, zero or negative halochromism can be observed.

The mass spectra as shown in the table above showed relevant protonated peaks and sodiated

peaks which corresponds to the various molecular mass of the intermediates and dyes as seen in the calculated peaks and the experimental peak.

### 3.1.1.1 Dyeing and fastness properties

The synthesized dyes were applied on polyester and wool and the results are summarized in Table 8.

The results indicate a higher percentage exhaustion on wool than on polyester, though

**Table 8. Percentage exhaustion and fixation on substrates**

Dye code	% exhaustion polyester	%exhaustion wool	% fixation polyester	%fixation wool
II <sub>7</sub>	46	80	43	64
II <sub>8</sub>	57	80	40	62
II <sub>9</sub>	46	76	43	46
II <sub>10</sub>	67	79	38	50
II <sub>11</sub>	43	92	50	59
II <sub>12</sub>	55	74	52	68

**Table 9. Wash fastness properties of the dyes**

Dye code	Change in colour polyester	Staining on cotton	Staining on polyester	Change in colour wool	Staining on wool	Staining on cotton
II <sub>7</sub>	4-5	4	4-5	4-5	4	4
II <sub>8</sub>	4-5	4	4-5	4	3-4	4
II <sub>9</sub>	3-4	4-5	4	4	4	4
II <sub>10</sub>	4	4	4	4	4	4
II <sub>11</sub>	4	4	4-5	4	4	4
II <sub>12</sub>	4-5	4	4	4	3-4	3-4

**Table 10. Light fastness properties of the dyes**

Dye code	Polyester	Wool
II7	3	3
II8	5	5
II9	4	3
II10	5	5
II11	4	3
II12	4	4

**Table 11. Perspiration fastness properties for polyester**

Dye code	Colour change	Acidic		Alkaline		
		Staining on polyester	Staining on wool	Colour change	Staining on polyester	Staining on wool
II7	4-5	4	4-5	4	4-5	4-5
II8	4	4	4	4	5	5
II9	4-5	4-5	4-5	4	4	4
II10	4	4	4	4	4-5	4
II11	4	4	4	4	4	4-5
II12	4	4-5	4-5	4	4	4

**Table 12. Perspiration fastness properties of wool**

Dye code	Colour change	Acidic		Alkaline		
		Staining on cotton	Staining on wool	Colour change	Staining on cotton	Staining on wool
II7	4-5	4-5	4	4	4	4-5
II8	4	4	4	5	5	5
II9	4-5	4-5	4-5	4	4	4
II10	4	4-5	4-5	4	4	4-5
II11	4-5	4	4	5	5	4-5
II12	4-5	4	4	4	4	4-5

they both possessed good to moderate exhaustion values. The dyes gave very good levelness and fibre penetration on all the fabrics used. The exhaustion was between 46% to 67% on polyester and 74% to 92% on wool. The higher percent exhaustion may be attributed to the presence of electrolytes/dye bath assistants used during the dyeing process. The percentage fixation values were slightly higher in wool compared to polyester. The fixation values are moderate, this is due to the problem of hydrolysis when dyeing with reactive dyes and also due to the crystalline nature of polyester hindering dye uptake. The dyes gave excellent to very good wash fastness, moderate to good light fastness, excellent fastness to perspiration on polyester and wool similar to results reported in literature [22].

#### 4. CONCLUSION

The heterobifunctional dyes produced from coupling 2-amino-4-phenylthiazole derivatives with sulphatoethylsulphone diazo component showed reactive disperse dyes properties. They

possess wide shade of red and orange colours. The dyes fixed effectively to both wool and polyester with improved application properties being accounted to its highly non-ionic reactive sulphatoethylsulphone system, good dye structure-reactivity, excellent levelling and fastness properties were also obtained. The dyes showed good exhaustion and fixation values indicating that the dyes have good affinity for the wool fabric than the polyester fabric. They exhibited excellent fastness to washing and perspiration and good to moderate fastness to light for both wool and polyester.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

#### REFERENCES

1. Ezeribe AI, Bello KA, Adamu H, Boryo DE, Omar PG. Synthesis And Dyeing Properties Of Novel Bifunctional Reactive Dyes Via 4-(4-Nitrophenyl)-1, 3-Thiazole-2-

- Amine,4-(4-Methylphenyl)-1, 3-Thiazol-2-Amine And H-Acid On Nylon Fabrics. The International Journal of Engineering and Science (IJES). 2013;2(8):28-36.
2. Broadbent Authur D. Basic principles of textile colouration. Bradford: Society of Dyers and Colourists. 2001;268.
  3. Egli R, Peter I, Freeman HS. The design and synthesis of organic dyes and pigment. Elsevier London. 1999;28-32.
  4. Suwanruji P, Freeman H. The design, synthesis and application of easy wash off reactive dyes. 2011;51:13-33,38,48.
  5. Stapleton IW, Waters PJ. Dyeing of wool-polyester blends with reactive disperse dyes: Variation of dye distribution and Reactivity for Wool. JSDC. 1981;56:97.
  6. Mousa AA, Youssef YA. Dyeing of nylon 6 and silk fabrics with a model disulphide bis(ethylsulphone) reactive disperse dye. Coloration Technology. 2003;225:119.
  7. Meena CR, Girenda, Adivarekar RV, Sekar N. Synthesis and application of vinylsulphone disperse reactive dyes for polyester. International Journal of Chem Tech Research. 2013;585-591.
  8. Lewis DM, Renfrew AH, Siddique AA. The synthesis and application of a new reactive dye based on disulfide-bis-ethylsulfone. Dyes and Pigments. 2000;47:151-167.
  9. Mohammed FA, Farouk R, Youssef YA, Mousa AA. Dyeing of nylon 6 and silk fabrics with novel polyfunctional disazo reactive disperse dye. Journal of American Science; 2013;9(1):34-39. (ISSN:1545-1003).
  10. Gewald K. Chemistry of heterocyclic compounds. 1976;12:1077.
  11. Isha Tomer, Raghav Mishra, Priymanka, Sharma NK, Jha KK. Synthesis and antimicrobial evaluation of some novel thiazole derivatives. 2012;3(3):361-366.
  12. Lee JJ, Lee WJ, et al. Synthesis and application of temporarily solubilised azo disperse dyes containing  $\beta$ -sulphatoethylsulphonyl group. Dyes and Pigments. 2005;65-75.
  13. Lee WJ, Kim JP. After treatment of polyester fabric dyed with temporarily solubilised disperse dyes. JSDC. 2000; 116:345.
  14. Lee WJ, Choi WH, Kim JP. Dyeing of wool with temporarily solubilized disperse dyes. Coloration Technology, 2001;117-212.
  15. Arun Bahl, Bahl BS. Advance organic chemistry, 2005;1308-1309,1312-1313.
  16. Infrared Spectroscopy, Fundamentals and Applications by Barbara Atuart, John Wiley&Sons, Ltd; 2004.
  17. Interpretation of Infrared Spectra. A Practical Approach by John Coates in Encyclopedia of Analytical Chemistry. 2000;10815-10837.
  18. Mohammed FA, Farouk R, Youssef YA, Mousa AA. Dyeing of nylon 6 and silk fabrics with novel polyfunctional disazo reactive disperse dye. Journal of American Science. 2013;9(1):34-39. (ISSN: 1545-1003).
  19. Mousa AA, Youssef YA, Farouk R, El-Kharadly EA. Dyeing of nylon 6 fabric with a new bifunctional vinyl sulphone reactive disperse dye. Coloration Technology. 2006;122:338-344.
  20. Nishida K, Ando Y, et al. Dyeing properties of reactive azo disperse dyes from N-Ethyl- N -  $\beta$  - vinylsulphonylethyl-m-toluidine as coupling component and substituted 3-Aminobenzothiophenes as Diazo Components. JSDC. 1981;97:469.
  21. Reichardt C, Welton T. Solvents and Solvents Effect in Organic Chemistry. 2<sup>nd</sup> Rev and Enl. Ed. Weinham; VCH. 2010; 360.
  22. SDC. Standard methods for the determination of the colour fastness of textiles and Leather. 5<sup>th</sup> Edition. Bradford 1991.

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