

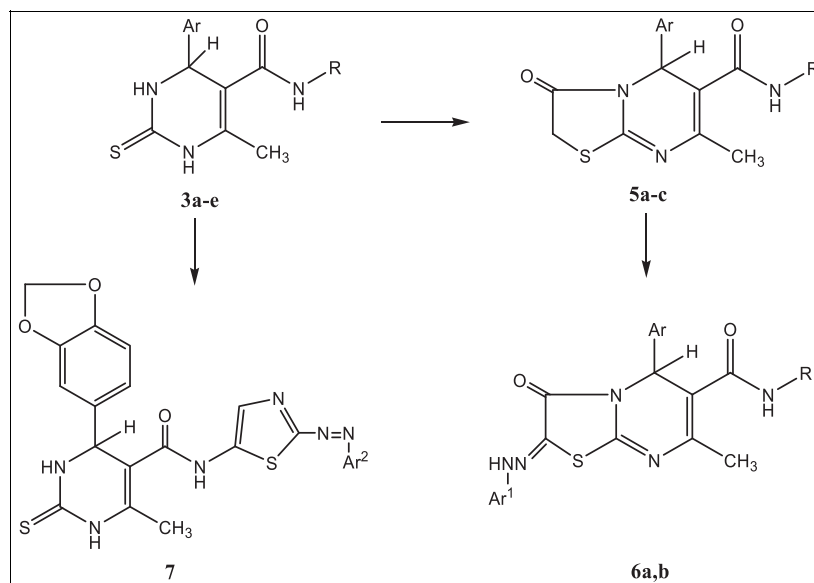
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A series of novel thiazolo[3,2-*a*]pyrimidine derivatives were synthesized by using  $\beta$ -ketoanilides **1a–c** as starting materials and as key intermediates for preparation of new pyrimidine compounds **3a–e** and fused heterocyclic pyrimidine derivatives **5a–c**. The new compounds were transformed to disperse dyes **6a,b** and **7**. The chemical structures were elucidated by spectroscopic and elemental analyses and found to be in good agreement with the proposed structures. The versatility of compounds **6a,b** and **7** for textile dyeing as disperse dyes was reported. The synthesized dyes were applied to polyester fabrics by using high temperature dyeing method at 120°C. The dye uptake expressed as color strength (*k/s*) of the dyed samples has been measured. Moreover, the color strength was examined in detail. In addition, the position of color in CIELAB coordinates (*L\**, *a\**, *b\**, *h*, and *C\**) was assessed. The color fastness of the dyed samples gave excellent results for washing and rubbing; however, the light fastness was moderate. Raman spectra of dyed samples unequivocally excluded ring dyeing and found to match with the proposed structures.

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## INTRODUCTION

$\beta$ -Ketoanilides are versatile reagents that have been extensively utilized in heterocyclic synthesis [1–16]. In this work, the prepared heterocycles are proved to be interesting for their potentiality as biodegradable agrochemicals [7], pharmaceuticals [3,7], as non-peptide HIV [6], protease inhibitors, anti-schistosomal agents [3,4], and intermediates for the manufacture of dyestuffs. In the past few years, we have been involved in a program aiming to develop new simple routes for the synthesis of different heterocyclic compounds of interest to be evaluated as disperse dyestuff [17–24]. Several synthetic approaches have been reported for the synthesis

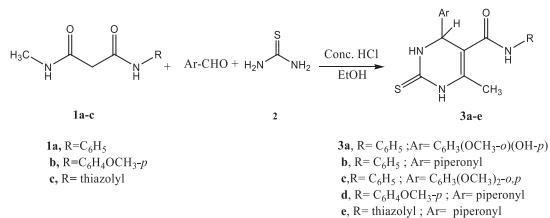
of fused heterocyclic pyrimidine derivatives [25–30]. Aryl-azo and hetaryl-azo coloring matters have been in use since prehistoric times [31]. The interest in such coloring materials is due to the fact that many derivatives were found useful in the field of material science and applied chemistry [32]. For example, many such azo dyes have been extensively used as dyes in various fields such as dyeing of textile fibers, colored plastics, biological-medical studies, and advanced applications in organic synthesis [33]. Recently, arylazo derivatives of various heterocyclic systems have been receiving more research attention by organic chemists [34] and dye manufacturers [35]. It is worth mentioning that azo-hydrazone tautomerism is of importance not only to dyestuff

manufacture but also to other areas of chemistry. Also, azo-hydrazone tautomers have different tinctorial strengths (and economics) and different properties, e.g., rubbing and washing fastness [36]. From the above and from the conjunction to previous interest in developing synthesis of poly functionally substituted hetero aromatics utilizing readily obtainable and inexpensive starting components [37–41], we report here on synthesis of thiazolo[3,2-*a*]pyrimidine derivatives using  $\beta$ -ketoanilides **1a–c**, aromatic amines, and thiourea **2** as starting materials and as key intermediates for application as disperse dyes for dyeing polyester fabrics.

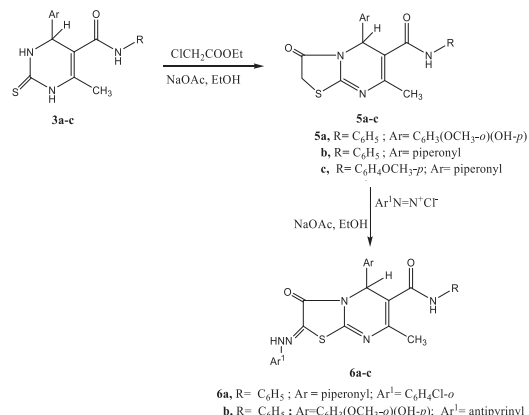
## RESULTS AND DISCUSSION

**Synthesis and reactions.** A mixture of  $\beta$ -ketoanilides **1a–c**, aromatic aldehydes, and thiourea **2** was heated under reflux in ethanol containing a few drops hydrochloric acid as a catalyst to afford 4-aryl-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxamides **3a–e** (Scheme 1). Structure **3a–e** was supported by its analytical and spectral data. As an example, the infrared spectrum of **3a** exhibited bands at 3398 and 3284  $\text{cm}^{-1}$  (NH), 1674  $\text{cm}^{-1}$  (C=O), and 1236  $\text{cm}^{-1}$  (C=S). The  $^1\text{H-NMR}$  spectrum of **3a** showed the singlet signal at  $\delta = 2.04$  ppm due to the methyl group protons, a singlet signal at  $\delta = 3.68$  ppm attributed to the methoxy group protons, a singlet signal at  $\delta = 5.30$  ppm for the H-4 pyrimidine ring proton, multiple signals in the range  $\delta = 6.67$ – $7.53$  ppm for the aromatic protons, a singlet signal at  $\delta = 8.99$  ppm due to the hydroxyl group proton, and three singlet signals at  $\delta = 9.32$ , 9.68, and 9.90 ppm due to three NH protons. The mass spectrometric measurements of compound **3a** gave an additional confirmation for the proposed structure that showed the molecular ion peak at  $m/z$  369 corresponding to ( $\text{M}^+$ , 29.0%). Cyclo-condensation of 4-aryl-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxamides **3a–e** with ethyl chloroacetate in refluxing ethanol catalyzed by sodium acetate gave thiazolo[3,2-*a*]pyrimidine derivatives **5a–c** (Scheme 2). Compounds **5a–c** were confirmed on the basis of the correct analytical and spectral data of the

**Scheme 1.** Synthesis of 4-aryl-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxamides **3a–e**.



**Scheme 2.** Synthesis of thiazolo[3,2-*a*]pyrimidine **5a–c** and arylazothiazolo[3,2-*a*]pyrimidines derivatives **6a–b**.



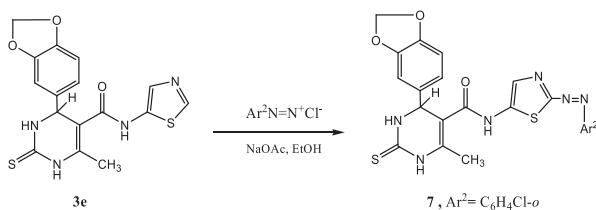
products. Indication of structure **5b** is based on the correct values of elemental analysis and appropriate spectral data (IR,  $^1\text{H-NMR}$ , and mass spectrum). As an example, the IR spectrum of **5b** exhibited the bands at 3373  $\text{cm}^{-1}$  (NH) and 1730 and 1649  $\text{cm}^{-1}$  (C=O). The  $^1\text{H-NMR}$  spectrum of **5b** revealed a singlet signal at  $\delta = 2.05$  ppm due to the methyl group protons, doublet doublet signals in the range  $\delta = 4.05$ – $4.15$  ppm for  $\text{CH}_2$  protons at  $J = 18$  Hz, a singlet signal at  $\delta = 5.30$  for the H-4 pyrimidine ring proton, a single singlet at  $\delta = 5.97$  ppm for (O– $\text{CH}_2$ O–) protons, multiple signals in the range  $\delta = 6.71$ – $7.54$  ppm due to the aromatic protons, and a singlet signal at  $\delta = 9.70$  ppm for NH proton. The mass spectrometric measurements of compound **5b** gave an additional confirmation for its structure that showed the molecular ion peak at  $m/z$  407 corresponding to ( $\text{M}^+$ , 12.09%).

Compounds **5a–c** were coupled readily with aryl diazonium chlorides to yield the arylazothiazolo[3,2-*a*]pyrimidines **6a,b** in excellent yields (Scheme 2). Elucidation of structure **6a** was based on the correct values of elemental analysis and appropriate spectral data (IR,  $^1\text{H-NMR}$ , and mass spectrum). The IR spectrum of **6a** gave the bands at 3467  $\text{cm}^{-1}$  (NH) and 1712 and 1651  $\text{cm}^{-1}$  (C=O). The  $^1\text{H-NMR}$  spectrum of **6a** showed a singlet signal at  $\delta = 2.12$  ppm due to the methyl group protons, a singlet signal at  $\delta = 5.96$  ppm for the H-4 pyrimidine ring proton, a singlet signal at  $\delta = 5.99$  ppm for (O– $\text{CH}_2$ O–) protons, multiple signals in the range  $\delta = 6.72$ – $7.72$  ppm due to the aromatic protons, and two singlet signals at  $\delta = 9.97$  and 12.25 ppm for two NH protons. The mass spectrometric measurements of compound **6a** gave an additional confirmation for its structure that showed the molecular ion peak at  $m/z$  545 corresponding to ( $\text{M}^+$ , 14.17%). Also, 4-benzo[1,3]dioxol-5-yl-6-methyl-2-thioxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid thiazol-2-ylamide

**3e** was reacted with *o*-chlorobenzene diazonium chloride to afford 4-benzo[1,3]dioxol-5-yl-6-methyl-2-thioxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid [5-(2-chloro-phenylazo)-thiazol-2-yl]-amide **7** (Scheme 3). The formed product was found in a full agreement with assigned structure based on elemental analysis and spectral data that confirmed the formation of structure **7**. The IR spectrum of **7** gave 3240 and 3174  $\text{cm}^{-1}$  (NH) and 1658  $\text{cm}^{-1}$  (C=O). The  $^1\text{H-NMR}$  spectrum of **7** showed a singlet signal at  $\delta = 2.13$  ppm for the methyl group protons, a singlet signal at  $\delta = 5.45$  ppm due to the H-4 pyrimidine ring proton, a single singlet at  $\delta = 5.97$  ppm for (O—CH<sub>2</sub>O—) protons, multiple signals in the range  $\delta = 6.70$ – $7.44$  ppm for the aromatic protons, a singlet signal at  $\delta = 7.93$  for the C-4 thiazole ring proton, and three singlet signals at  $\delta = 9.51$ , 10.13, and 11.90 ppm for three NH protons.

**Dyeing and fastness properties.** For dyeing polyester fabrics, in practical terms, only disperse dyes are suitable. Through their hydrophobic properties, these dyes are capable of penetrating into the similarly hydrophobic polyester fiber. The dyes on polyester fabrics were evaluated in terms of their fastness properties and given in Table 1 using standard method. Fastness to washing and rubbing were tested according to the reported methods [42]. The dyes obtained (**6a,b**; **7**) gave good leveling, uniformity of coloration, and exhaustion of dye liquor. The good results of the dyestuff under study on polyester fabrics might be attributed to the fact that these disperse dyes are mainly dispersed within the pores in the polyester fabrics and are held in their places by different

**Scheme 3.** Synthesis of 4-benzo[1,3]dioxol-5-yl-6-methyl-2-thioxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid [5-(2-chloro-phenylazo)-thiazol-2-yl]-amide (**7**).



**Table 1**

Fastness properties of the synthesized dyes **6a**, **6b**, and **7** on 100% polyester fabrics.

| Dye color | Fastness properties |      |         |     |   | Light (100 h) |
|-----------|---------------------|------|---------|-----|---|---------------|
|           | Washing             |      | Rubbing |     |   |               |
|           | St.                 | Alt. | Wet     | Dry |   |               |
| <b>6a</b> | Yellow              | 5    | 5       | 5   | 5 | 1/2           |
| <b>6b</b> | Orange              | 5    | 5       | 5   | 5 | 3             |
| <b>7</b>  | Yellow              | 5    | 5       | 5   | 5 | 2/3           |

forces including Van der Waals forces. Electron-attracting groups enable stronger Van der Waals forces and hydrogen bonding with the dyed fabrics that increases their stability to washing. As shown in Table 1, the results showed that the dyed fabrics have excellent fastness to rubbing (wet, dry) especially wet rubbing fastness. As for the light fastness of the synthesized dyes on polyester, it is significantly affected by the nature of substituent in the diazo component. Al-Etaibi *et al.* [43] suggested that fading of azo dyes is mainly a consequence of decomposition of the —N=N— moiety by oxidation, reduction, or photolysis. The rates of these processes should be sensitive to the chemical structure of the dye, the type of substrate, and treatment conditions. Because the dyed substrate employed in this study is polyester fabrics (i.e., non-proteinic), the fading process likely occurs by oxidation [44]. The ease of oxidation of azo linkages should be a function of electron density. Therefore, electron-donating substituent on this moiety should increase the fading rate. This proposal is in agreement with the observed results (Table 1) that demonstrated the decrease of light fastness to 1–3 caused by the presence of a methyl group in dyestuff under study.

**Color assessment.** The colors of dyestuff under study on polyester fabrics were expressed in terms of CIELAB values (Table 2), and the following CIELAB coordinates were measured by the reflectance spectrometer, where (L\*) values represent color lightness. Chroma (C\*) values represent color purity, hue angle (h) values, which varies from 0° to 360°, to specify the color related to the principle colors, (a\*) values represent the degree of redness (positive) and greenness (negative), and (b\*) values represent the degree of yellowness (positive) and blueness (negative) [45]. As shown in Table 2, dyes **6a,b** and **7** showed good affinity to polyester fabrics through the satisfactory color yields and accepted values of K/S. The dyes **6b** and **7** were found to be lighter than the other derivative **6a** according to the color lightness values L\*. These results were in line with the previously reported by Muller on the effect of substituent in the dye structure and hue [46].

**Effect of dye concentration.** Figure 1 showed that, for all dyes under study **6a**, **6b**, and **7**, increasing in concentration of dyestuff from 2% to 6% of the weight of

**Table 2**

Optical measurements of dyes **6a**, **6b**, and **7**.

| Dye       | L*    | a*    | b*    | C*    | h     | K/S  |
|-----------|-------|-------|-------|-------|-------|------|
| <b>6a</b> | 86.56 | −5.42 | 48.46 | 48.76 | 96.39 | 3.45 |
| <b>6b</b> | 72.49 | 26.03 | 48.81 | 55.31 | 61.93 | 3.12 |
| <b>7</b>  | 81.04 | 5.43  | 49.27 | 49.57 | 83.71 | 5.19 |

the fabric was accompanied by an increase in the dye uptake expressed as color strength (K/S) values reaching a maximum at 4% for dyes **6a,b** and then went down by further increase in concentration. This is probably due to the fact that dye **6a,b** has strong saturation in water at low concentration. In the case of dyeing with dye **7**, the maximum color strength K/S value was obtained at a 6% concentration of the dye. This may be attributed to the fact that more amount of dyes were diffused into fabrics with increasing dye concentration [47]. It can be concluded from Figure 1 and the results in Table 2 that

the dispersed dye **7** has good affinity to fabric than others and the K/S value was increased by increasing the dye concentration to 6%.

**Raman spectra for the dyed samples.** Raman spectroscopy allows for the detection of dyes used in the coloration of such samples. Its potential was also demonstrated for the analysis of textile fibers. For the fiber dye analysis, Raman spectroscopy plays a complementary role that allows for identifying the main dye used for the impregnation of the fiber. The Raman technique presents advantages such as its nondestructive

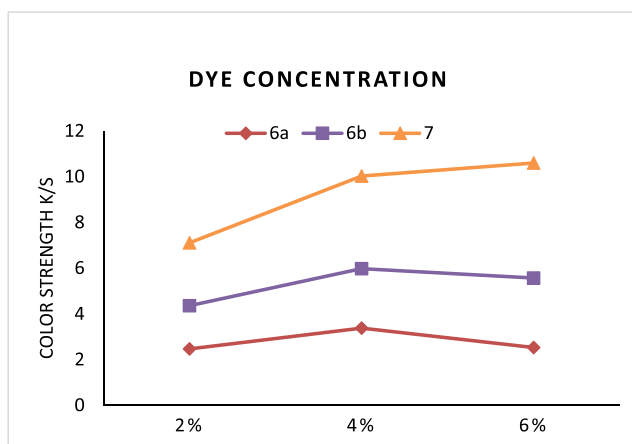


Figure 1. Color strength of synthesized disperse dyes with different concentrations. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

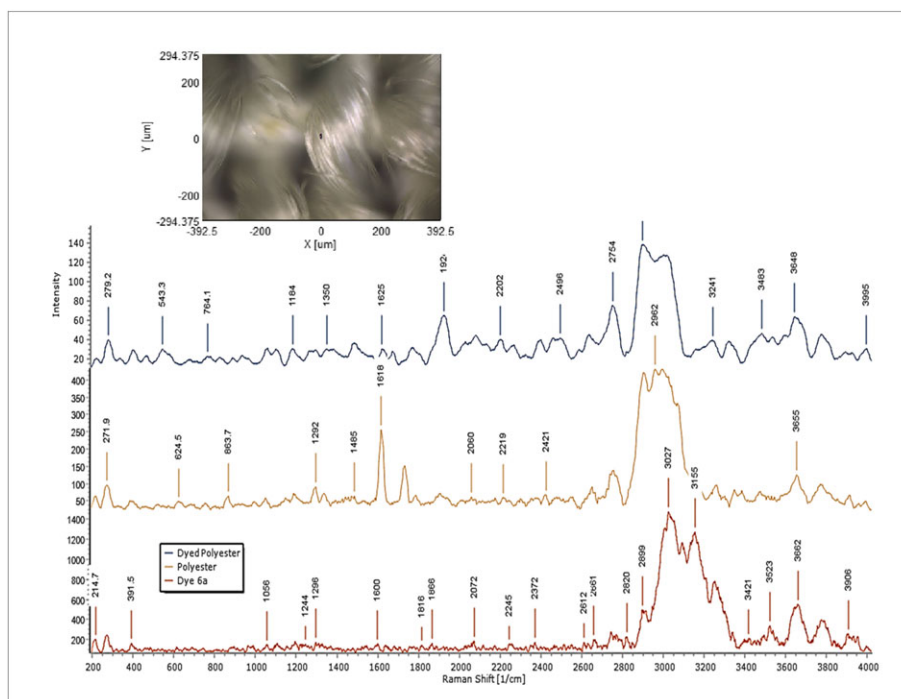


Figure 2. Raman spectrum of dyed polyester **6a**. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

nature, its fast analysis time, and the possibility of performing microscopic *in situ* analyses. Here, spectra were collected in the range of 0 to 4000  $\text{cm}^{-1}$ . They were acquired using scan time settings of 50 s for fiber analysis. Raman data acquisition and data processing

were achieved using Lab Spec 6 spectroscopy suit software. It can be seen from Figures 2–4 that the polyester dyed with dye **6a** showed signals at  $\delta = 1795$ , 1626 ( $\text{C}=\text{O}$ ), and 3241 and 3403  $\text{cm}^{-1}$  (NH), polyester dyed with dye **6b** showed signals at  $\delta = 1787$ , 1616

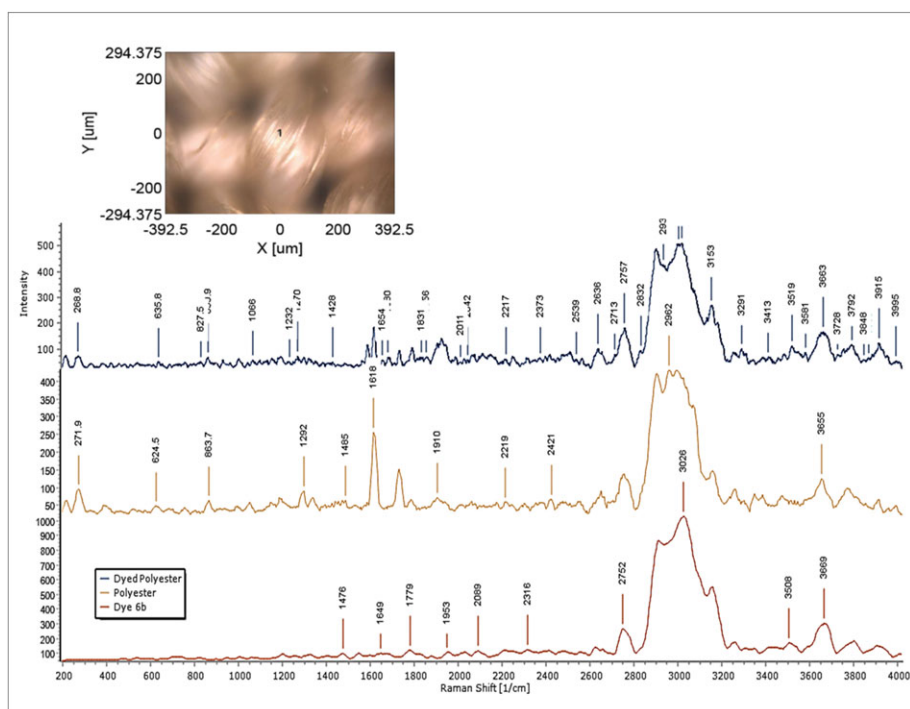


Figure 3. Raman spectrum of dyed polyester **6b**. [Color figure can be viewed at wileyonlinelibrary.com]

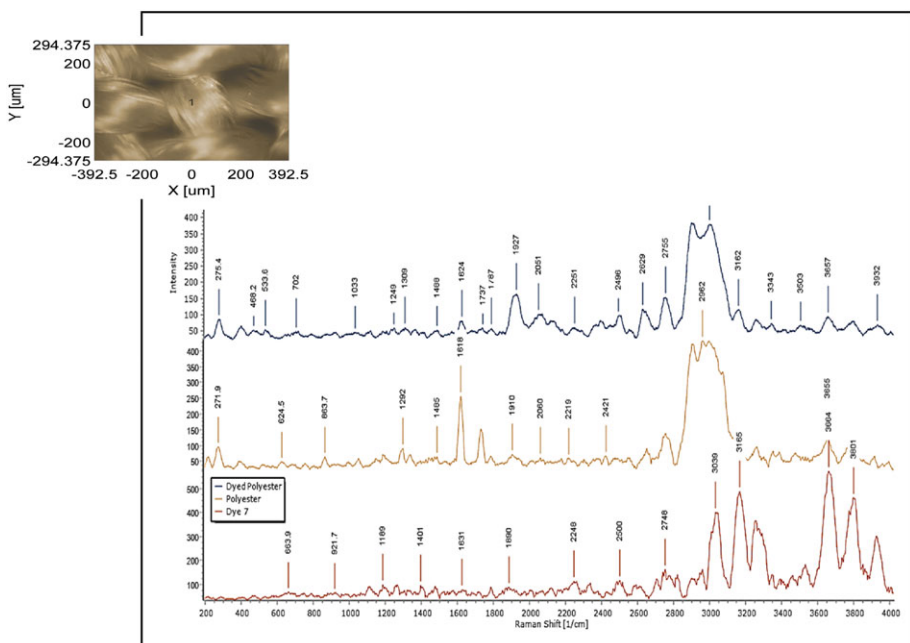


Figure 4. Raman spectrum of dyed polyester **7**. [Color figure can be viewed at wileyonlinelibrary.com]



(C=O), 3291 (NH), and 3663  $\text{cm}^{-1}$  (OH), and polyester dyed with dye **7** showed signals at  $\delta = 1249$  (C=S), 1737 (C=O), and 3162 and 3343  $\text{cm}^{-1}$  (NH).

## CONCLUSION

A series of novel thiazolo[3,2-*a*]pyrimidine derivatives were synthesized by using  $\beta$ -ketoanilides **3a–c** as starting materials. The synthesized dyes were applied for dyeing 100% polyester fabrics using high temperature dyeing method at 120°C. The dyed polyester fabrics, displayed redness to yellowness hues, exhibited excellent fastness to washing and rubbing fastness properties and moderate light fastness depending on the amount of dye fixed. Finally, the synthesized dye 4-benzo[1,3]dioxol-5-yl-6-methyl-2-thioxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid [5-(2-chloro-phenylazo)-thiazol-2-yl]-amide **7** gave the best results with the fastness for washing, rubbing, and light. It gave a good affinity to fabric than others, and its dye uptake expressed as color strength (K/S) value was increased by increasing the dye concentration.

## EXPERIMENTAL

Melting points were measured on Griffin & George MBF 010T (London) apparatus with model R 134301 and are uncorrected. Recorded yield corresponds to the pure products. The infrared spectra were recorded for (KBr) disk on a Perkin Elmer SP-880 spectrophotometer at Faculty of Science, Damietta University, New Damietta, Egypt. The  $^1\text{H-NMR}$  spectra were recorded on Delta 2  $^1\text{H-NMR}$  spectrometer (500 MHz) in dimethyl sulfoxide (DMSO- $d_6$ ) as solvent, using tetramethylsilane as an internal standard, and chemical shifts are expressed as  $\delta$  ppm at Mansoura University, Mansoura, Egypt. Mass spectra were determined on Finnigan in COS (70 eV) on DSQ instrument model. The Raman spectra were collected using laser Raman spectrometer with NRS-4500 model at Faculty of Applied Arts, Damietta University, Egypt. Elemental analyses (C, H, and N) were carried out at the Micro-analytical Center of Cairo University, Giza, Egypt; the results were found to be in good agreement with the calculated values.

**Synthesis of 4-aryl-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxamides (3a–e).** A mixture of  $\beta$ -ketoanilides **1a–c** (0.01 mol), aromatic aldehydes (0.01 mol), and (1.28 g, 0.01 mol) of thiourea **2** in ethanol (50 mL) containing few drops of concentrated HCl was heated under reflux for 5–6 h until the precipitates were formed. The reaction mixtures were left to cool at room temperature, and the precipitates formed were collected by filtration and recrystallized from suitable solvents to give compounds **3a–e**.

### 4-(4-Hydroxy-3-methoxy-phenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid phenylamide (3a).

Colorless crystals (EtOH); yield 76%; mp 194–196°C; IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 3398, 3284 (NH), 1674 (C=O), 1236 (C=S). MS:  $m/z$  369 ( $\text{M}^+$ , 29.0%).  $^1\text{H-NMR}$  (DMSO- $d_6$ ) ( $\delta$ , ppm): 2.04 (s, 3H,  $\text{CH}_3$ ), 3.68 (s, 3H,  $\text{OCH}_3$ ), 5.30 (s, 1H, pyrim H-4), 6.67–7.53 (m, 8H, Ar–H), 8.99 (s, 1H, OH), 9.32, 9.68, 9.90 (3s, 3H, 3NH); *Anal.* Calcd for  $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$  (MW: 369.44): C, 61.77; H, 5.18; N, 11.37%. Found: C, 61.54; H, 4.95; N, 11.13%.

### 4-Benzo[1,3]dioxol-5-yl-6-methyl-2-thioxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid phenylamide (3b).

Colorless crystals (EtOH); yield 79%; mp 160–162°C; IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 3259, 3005 (NH), 1682 (C=O), 1239 (C=S); MS:  $m/z$  367 ( $\text{M}^+$ , 18.60%);  $^1\text{H-NMR}$  (DMSO- $d_6$ ) ( $\delta$ , ppm): 2.06 (s, 3H,  $\text{CH}_3$ ), 5.30 (s, 1H, pyrim H-4), 5.98 (s, 2H,  $-\text{O}-\text{CH}_2\text{O}-$ ), 6.71–7.54 (m, 8 H, Ar–H), 9.38, 9.70, 9.98 (3s, 3H, 3NH); *Anal.* Calcd for  $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_3\text{S}$  (MW: 367.42): C, 62.11; H, 4.66; N, 11.44%. Found: C, 61.90; H, 4.44; N, 11.21%.

### 4-(3,4-Dimethoxy-phenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid phenylamide (3c).

Yellow crystals (EtOH); yield 76%; mp 171–176°C; IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 3197 (NH), 1649 (C=O), 1263 (C=S); MS:  $m/z$  383 ( $\text{M}^+$ , 21.99%);  $^1\text{H-NMR}$  (DMSO- $d_6$ ) ( $\delta$ , ppm): 2.05 (s, 3H,  $\text{CH}_3$ ), 3.65, 3.69 (2s, 6H,  $2\text{OCH}_3$ ), 5.34 (s, 1H, pyrim H-4), 6.76–7.54 (m, 8H, Ar–H), 9.37, 9.71, 9.95 (3s, 3H, 3NH); *Anal.* Calcd for  $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_3\text{S}$  (MW: 383.46): C, 62.64; H, 5.52; N, 10.96%. Found: C, 62.45; H, 5.35; N, 10.77%.

### 4-Benzo[1,3]dioxol-5-yl-6-methyl-2-thioxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid (4-methoxy-phenyl)-amide (3d).

Colorless crystals (EtOH/ $\text{H}_2\text{O}$ ); yield 77%; mp 239–240°C; IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 3259 (NH), 1685 (C=O), 1230 (C=S);  $^1\text{H-NMR}$  (DMSO- $d_6$ ) ( $\delta$ , ppm): 2.05 (s, 3H,  $\text{CH}_3$ ), 3.68 (s, 3H,  $\text{OCH}_3$ ), 5.28 (s, 1H, pyrim H-4), 5.98 (s, 2H,  $\text{O}-\text{CH}_2\text{O}-$ ), 6.70–7.45 (m, 7 H, Ar–H), 9.35, 9.56, 9.94 (3s, 3H, 3NH); *Anal.* Calcd for  $\text{C}_{20}\text{H}_{19}\text{N}_3\text{O}_4\text{S}$  (MW: 397.45): C, 60.44; H, 4.82; N, 10.57%. Found: C, 60.16; H, 4.61; N, 10.36%.

### 4-Benzo[1,3]dioxol-5-yl-6-methyl-2-thioxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid thiazol-2-ylamide (3e).

Colorless crystals (EtOH/DMF); yield 75%; mp 264–266°C; IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 3163 (NH), 1662 (C=O), 1238 (C=S);  $^1\text{H-NMR}$  (DMSO- $d_6$ ) ( $\delta$ , ppm): 2.13 (s, 3H,  $\text{CH}_3$ ), 5.45 (s, 1H, pyrim H-4), 5.97 (s, 2H,  $\text{O}-\text{CH}_2\text{O}-$ ), 6.70–6.80 (m, 3H, Ar–H), 7.44 (s, 1H, thiazole H-5), 7.93 (s, 1H, thiazole H-4), 9.51, 10.13, 11.90 (3s, 3H, 3NH); *Anal.* Calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_3\text{S}_2$  (MW: 374.44): C, 51.32; H, 3.77; N, 14.96%. Found: C, 51.16; H, 3.69; N, 14.89%.

### Synthesis of thiazolo[3,2-*a*]pyrimidine derivatives 5a–c.

A mixture of pyrimidinethiones **3a–c** (0.01 mol) and ethyl chloroacetate **4** (0.69 g, 0.01 mol) in the presence of ethanol and sodium acetate anhydrous was heated under

reflux for 5–6 h, and then, the reaction mixture was left to cool at room temperature. The solid products formed after pouring onto ice/water were filtered off and crystallized from the proper solvents to give the pure products as **5a–c**.

**5-(4-Hydroxy-3-methoxy-phenyl)-7-methyl-3-oxo-2,3-dihydro-5H-thiazolo[3,2-*a*]pyrimidine-6-carboxylic acid phenylamide (5a).** Pale yellow crystals (EtOH); yield 74%; mp 258–259°C; IR (KBr)  $\nu_{\max}$   $\text{cm}^{-1}$ : 3305 (NH), 1734, 1647 (C=O);  $^1\text{H-NMR}$  (DMSO- $d_6$ ) ( $\delta$ , ppm): 2.05 (s, 3H, CH<sub>3</sub>), 3.64 (s, 3H, OCH<sub>3</sub>), 4.07–4.16 (dd, 2H, CH<sub>2</sub>,  $J = 17$  Hz), 5.95 (s, 1H, pyrim H-4), 6.60–7.54 (m, 8H, Ar–H), 9.11 (s, 1H, OH), 9.90 (s, 1H, NH); *Anal.* Calcd for C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>S (MW: 409.4): C, 61.60; H, 4.68; N, 10.26%. Found: C, 61.53; H, 4.55; N, 9.99%.

**5-Benzo[1,3]dioxol-5-yl-7-methyl-3-oxo-2,3-dihydro-5H-thiazolo[3,2-*a*]pyrimidine-6-carboxylic acid phenylamide (5b).** Yellow crystals (xylene); yield 68%, mp 140–143°C; IR (KBr)  $\nu_{\max}$   $\text{cm}^{-1}$ : 3373 (NH), 1730, 1649 (C=O); MS:  $m/z$  407 (M<sup>+</sup>, 12.09%);  $^1\text{H-NMR}$  (DMSO- $d_6$ ) ( $\delta$ , ppm): 2.05 (s, 3H, CH<sub>3</sub>), 4.05–4.15 (dd, 2H, CH<sub>2</sub>,  $J = 18$  Hz), 5.30 (s, 1H, pyrim H-4), 5.97 (s, 2H, O–CH<sub>2</sub>O–), 6.71–7.54 (m, 8H, Ar–H), 9.70 (s, 1H, NH); *Anal.* Calcd for C<sub>21</sub>H<sub>17</sub>N<sub>3</sub>O<sub>4</sub>S (MW: 407.44): C, 61.90; H, 4.21; N, 10.31%. Found: C, 61.68; H, 4.11; N, 10.12%.

**5-Benzo[1,3]dioxol-5-yl-7-methyl-3-oxo-2,3-dihydro-5H-thiazolo[3,2-*a*]pyrimidine-6-carboxylic acid (4-methoxy-phenyl)-amide (5c).** Pale yellow crystals (EtOH); yield 76%; mp 198–200°C; IR (KBr)  $\nu_{\max}$   $\text{cm}^{-1}$ : 3290 (NH), 1736, 1640 (C=O);  $^1\text{H-NMR}$  (DMSO- $d_6$ ) ( $\delta$ , ppm): 2.05 (s, 3H, CH<sub>3</sub>), 3.68 (s, 3H, OCH<sub>3</sub>), 4.05–4.15 (dd, 2H, CH<sub>2</sub>,  $J = 17.5$  Hz), 5.92 (s, 1H, pyrim H-4), 6.71–7.44 (m, 7H, Ar–H), 9.77 (s, 1H, NH); *Anal.* Calcd for C<sub>22</sub>H<sub>19</sub>N<sub>3</sub>O<sub>5</sub>S (MW: 437.47): C, 60.40; H, 4.38; N, 9.61%. Found: C, 60.21; H, 4.29; N, 9.42%.

**General procedure for synthesis of arylazothiazolo[3,2-*a*]pyrimidines 6a,b.** A solution of thiazolo[3,2-*a*]pyrimidines **5a–c** (0.01 mol) in ethanol/water mixture (1:1) containing sodium acetate anhydrous (2 g) was treated with (0.01 mol) aromatic diazonium chloride at 0–5°C with continuous stirring. The reaction mixture was left overnight in the refrigerator. The precipitates formed were collected by filtration and recrystallized from suitable solvents to give crystals of **6a–b**.

**5-Benzo[1,3]dioxol-5-yl-2-(2-chloro-phenylazo)-7-methyl-3-oxo-2,3-dihydro-5H-thiazolo[3,2-*a*]pyrimidine-6-carboxylic acid phenylamide (6a).** Yellow crystals (EtOH/H<sub>2</sub>O); yield 81%; mp 173–177°C; IR (KBr)  $\nu_{\max}$   $\text{cm}^{-1}$ : 3467 (NH), 1712, 1651 (C=O); MS:  $m/z$  545 (M<sup>+</sup>, 14.17%);  $^1\text{H-NMR}$  (DMSO- $d_6$ ) ( $\delta$ , ppm): 2.12 (s, 3H, CH<sub>3</sub>), 5.96 (s, 1H, pyrim H-4), 5.99 (s, 2H, O–CH<sub>2</sub>O–), 6.72–7.72 (m, 7 H, Ar–H), 9.97, 12.25 (2s, 2H, 2NH); *Anal.* Calcd for C<sub>27</sub>H<sub>20</sub>ClN<sub>5</sub>O<sub>4</sub>S (MW: 545.5): C, 59.39; H, 3.69; N, 12.83%. Found: C, 59.28; H, 3.51; N, 12.74%.

**2-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylazo)-5-(4-hydroxy-3-methoxy-phenyl)-7-methyl-3-oxo-2,3-dihydro-5H-thiazolo[3,2-*a*]pyrimidine-6-carboxylic acid phenylamide (6b).** Orange crystals (xylene); yield 82%; mp 190–192°C; IR (KBr)  $\nu_{\max}$   $\text{cm}^{-1}$ : 3390 (NH), 1730, 1657 (C=O);  $^1\text{H-NMR}$  (DMSO- $d_6$ ) ( $\delta$ , ppm): 2.04 (s, 3H, CH<sub>3</sub>), 2.23 (s, 3 H, CH<sub>3</sub>), 3.35 (s, 3H, N–CH<sub>3</sub>), 3.63 (s, 3H, OCH<sub>3</sub>), 5.94 (s, 1H, pyrim H-4), 6.69–7.54 (m, 8H, Ar–H), 8.09 (s, 1H, OH), 9.10, 9.89 (2s, 2H, 2NH); *Anal.* Calcd for C<sub>32</sub>H<sub>29</sub>N<sub>7</sub>O<sub>5</sub>S (MW: 623.68): C, 61.62; H, 4.69; N, 15.72%. Found: C, 61.40; H, 4.45; N, 15.44%.

**Synthesis of 4-benzo[1,3]dioxol-5-yl-6-methyl-2-thioxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid [5-(2-chloro-phenylazo)-thiazol-2-yl]-amide (7).** A solution of 4-benzo[1,3]dioxol-5-yl-6-methyl-2-thioxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid thiazol-2-ylamide **3e** (0.8 g, 0.01 mol) in ethanol/DMF containing sodium acetate anhydrous (2 g) was treated with (0.27 g, 0.01 mol) 2-chlorobenzene diazonium chloride at 0–5°C with continuous stirring. The reaction mixture was left overnight in the refrigerator. The precipitate formed was collected by filtration and recrystallized from EtOH/DMF to give yellow crystals of **7**; yield (80%); mp 252–254°C; IR (KBr)  $\nu_{\max}$   $\text{cm}^{-1}$ : 3240, 3174 (NH), 1658 (C=O);  $^1\text{H-NMR}$  (DMSO- $d_6$ ) ( $\delta$ , ppm): 2.13 (s, 3H, CH<sub>3</sub>), 5.45 (s, 1H, pyrim H-4), 5.97 (s, 2H, O–CH<sub>2</sub>O–), 6.70–7.44 (m, 6H, Ar–H), 7.93 (s, 1H, thiazole H-4), 9.51, 10.13, 11.90 (3s, 3H, 3NH); *Anal.* Calcd for C<sub>22</sub>H<sub>17</sub>ClN<sub>6</sub>O<sub>3</sub>S<sub>2</sub> (MW: 512.9): C, 51.51; H, 3.34; N, 16.38%. Found: C, 51.44; H, 3.12; N, 16.24%.

**Dyeing of polyester fabrics procedure using conventional method.** Polyester fabric samples (0.3 g) were dyed with the disperse dyestuff (**6a,b–7**) at liquor ratio 1:20. Dyeing was carried out at different concentrations of dye (2%, 4%, and 6%, respectively). The dye was dissolved in ethanol and added dropwise with stirring to a solution of an anionic dispersing agent (0.012 g/dm<sup>3</sup>), and then, the dye precipitated in a fine dispersion was ready for use in dyeing. The dyebath, containing 0.03 g/dm<sup>3</sup> carrier, 4% acetic acid at pH = 5.5, brought to 60°C. The polyester fabric was entered and run for 15 min, and then, the fine dispersion of the dye was added, and the temperature raised to boiling within 45 min. Dyeing was continued at boiling temperature (120°C) for about 1 h, and then the dyed material was rinsed and soaped with 2% nonionic detergent [48].

**Color fastness tests.** Fastness properties to washing, rubbing, and light of the dyed polyester fabrics were determined according to JIS L 0844, JIS L 0849, and JIS L 0842:2004 test methods, respectively.

**Fastness to washing.** A specimen of dyed polyester fabric was stitched between two pieces of undyed cotton fabric (all fabric pieces had the same diameter) and then washed at 50°C for 30 min. The staining of the undyed

adjacent fabric was assessed using gray scale (1, poor; 2, fair; 3, moderate; 4, good; 5, excellent).

**Fastness to rubbing.** The dyed polyester fabric was placed on the base of a Crockmeter so that it was rested flat on the abrasive cloth with its long dimension in the direction of rubbing. A square of white testing cloth was forced to slide on the tested fabric back and forth 20 times by turning the crank 10 complete turns. For the wet rubbing test, the test square was thoroughly wetted in distilled water. The rest of the procedure was the same as the dry test. The staining on the white testing cloth was assessed using gray scale (1, poor; 2, fair; 3, moderate; 4, good; 5, excellent).

**Fastness to light.** Light fastness was determined by exposing the dyed polyester on a Xenotest 150 [Original Hanau, chamber temperature 25–30°C, black panel temperature 60°C, relative humidity 50–60%, and dark glass (UV) filter system] for 100 h. The evaluation was performed using standard gray scale (1, totally faded; 3, moderately faded; 5, no change) (Table 1).

**Color assessment.** The color parameters of the dyed polyester fabric were measured using the (Konica Minolta CM-3600 d) spectrophotometer. The following CIELAB coordinates were measured: lightness ( $L^*$ ), chroma ( $C^*$ ), hue ( $h$ ), the degree of redness (+ve) and greenness (–ve) ( $a^*$ ), and the degree of yellowness (+ve) and blueness (–ve) ( $b^*$ ). The color strength (K/S) values were obtained using the (Konica Minolta CM-3600 d) spectrophotometer (Table 2). The Raman spectra were collected using laser Raman spectrometer.

#### REFERENCES AND NOTES

- [1] Abdelrazek, F. M.; Bahbouh, M. S.; Earth, J. J. *Environ Sci* 2012, 4, 47.
- [2] Hussein, A. M.; Harb, A. A.; Mousa, I. A. *J Heterocyclic Chem* 2008, 45, 1819.
- [3] Mohareb, R. M.; Abbas, N. S.; Ibrahim, R. A. *Acta Chim Slov* 2013, 60, 583.
- [4] Abdelrazek, F. M.; Sharaf, M. F.; Metz, P.; Jaeger, A. *J Heterocyclic Chem* 2010, 47, 528.
- [5] Sofan, M. A.; El-Taweel, F. M.; Abu Elmaati, T. M.; El-Agamey, A. A. *Pharmazie* 1994, 49, 482.
- [6] El-Taweel, F. M.; Abou Elmaati, T. M. *J Chin Chem Soc* 2002, 49, 1051.
- [7] Abou Elmaati, T. M.; El-Taweel, F. M. *J Chin Chem Soc* 2002, 49, 1045.
- [8] Osman, A. I.; El-Taweel, F. M.; El-Awaad, S. M.; El-Agamey, A. A. *Indian J Chem* 1998, 37B, 399.
- [9] Han, M.; Nam, K. D.; Hanh, H. G.; Shin, D. *Tetrahedron Lett* 2008, 49, 5217.
- [10] Abou El-Maati, T. M.; Said, S.; El-Enein, N. A.; Sofan, M.; Khodeir, N. *Polish J Chem* 2002, 76, 945.
- [11] Bondock, S.; El-Azab, H.; Kandeel, E. M.; Metwally, M. A. *Synth Commun* 2013, 43, 59.
- [12] Abou Elmaaty, T.; Ma, J.; El-Taweel, F.; Abd El-Aziz, E.; Okubayashi, S. *Ind & Eng Chem Res* 2014, 53, 15566.
- [13] Harikrishnan, U.; Menon, S. K. *Dyes Pigm* 2008, 77, 462.
- [14] Huang, L.; Hsieh, M.; Teng, C.; Lee, K.; Kuo, S. *Bioorg Med Chem* 1998, 6, 1657.
- [15] El-Sharkawy, K. A.; Ibrahim, R. A. *Eur Chem Bull* 2013, 2, 530.
- [16] Svobodova, M.; Barta, J.; Simunek, P.; Bertolasi, V.; Machacek, V. *J Org Chem* 2009, 694, 63.
- [17] Salem, M. A.; Marzouk, M. I.; Mashaly, H. M. *Soc Dyers Color Technol* 2015, 131, 288.
- [18] Otutu, J. O. *IJRRAS* 2013, 15, 292.
- [19] Zhi-Hua, C.; Xiao-Hong, C.; Xin, L.; Hong-Hui, L.; Xi-Dong, W.; Wei-Guo, C. *Chin Chem Lett* 2014, 25, 1121.
- [20] Hye-jin, K.; Jae-ho, K.; Dong-uk, K.; Seung-pyo, H.; Sang-jin, K.; Hee-dong, K.; Hyun-ah, K.; Man-woo, H. *J Korean Soc Finish* 2014, 26, 290.
- [21] Gouda, M. A.; Fakhr Eldien, H.; Girges, M. M.; Berghot, M. A. *J Saudi Chem Soc* 2016, 20, 151.
- [22] Al-Mousawi, S. M.; El-Asasery, M. A. *Molecules* 2013, 18, 8837.
- [23] Patel, D. R.; Patel, N. B.; Patel, B. M.; Patel, K. J. *Saudi Chem Soc* 2014, 18, 902.
- [24] Al-Etaibi, A.; Kamel, M.; El-Asasery, M. A. *Int J Curr Microbiol App Sci* 2014, 3, 826.
- [25] Behalo, M. S. *J Heterocyclic Chem* 2018, 55, 1391.
- [26] Cai, D.; Zhang, Z.; Chen, Y.; Yan, X.; Zhang, S.; Zou, L.; Meng, L.; Li, F.; Fu, B. *Med Chem Res* 2016, 25, 292.
- [27] Bhoi, M. N.; Borad, M. A.; Pithawala, E. A.; Patel, H. D. *Arab J Chem* 2016, 1.
- [28] Cai, D.; Zhang, Z.; Chen, Y.; Yan, X.; Zou, L.; Wang, Y.; Liu, X. *Molecules* 2015, 20, 16419.
- [29] Bhalgat, C. M.; Ramesh, B. *Bulletin of Faculty of Pharmacy, Cairo University* 2014, 52, 259.
- [30] Fadda, A. A.; Bondok, S. B.; Khalil, A. M.; Tawfik, E. H. *J Heterocyclic Chem* 2013, 50, 838.
- [31] Shawali, A. S.; Mosselhi, M. A. N. *J Heterocyclic Chem* 2003, 40, 725.
- [32] Shawali, A. S.; Abdelkader, M. H.; Eltalbawy, F. M. A. *Tetrahedron* 2002, 58, 2875.
- [33] Se Ner, I.; Karci, F.; Ertan, N.; Kilic, E. *Dyes Pigm* 2006, 70, 143.
- [34] Takagi, K.; Mizuno, A.; Iwamoto, H.; Kawashima, S.; Nishida, S.; Hashikawa, T. *Dyes Pigm* 1994, 26, 51.
- [35] ElKholy, Y. M.; Abd El-Hafiz, S. A. *Pigm Resin Technol* 1994, 23, 3.
- [36] Abou El-maaty, T. M.; Abd El-Aziz, E.; Ma, J.; El-Taweel, F.; Okubayashi, S. *Fibers* 2015, 3, 309.
- [37] El-Taweel, F. M.; Abou El-Maati, T. M.; Mofeed, M. *Int J Sci Eng Res* 2014, 5, 838.
- [38] El-Taweel, F. M.; El-Agamey, A. A.; Khalil, M. H. *Am Chem Soc J* 2013, 3, 532.
- [39] Ayyad, S. N.; El-Taweel, F. M.; El-Agamey, A. A.; El-Mashad, T. M. *Int J Org Chem* 2012, 2, 135.
- [40] El-Taweel, F. M. *Phosphorous Sulfur Silicon* 2004, 179, 1267.
- [41] Abou El-Maati, T. M.; El-Taweel, F. M. *J Chin Chem Soc* 2003, 50, 413.
- [42] Sayed, A. Z.; Aboul-Fetouh, M. S.; Nassar, H. S. *J Mol Struct* 2012, 1010, 146.
- [43] Al-Etaibi, A. M.; El-Asasery, M. A.; Ibrahim, M. R.; Al-Awadi, N. A. *Molecules* 2012, 17, 13891.
- [44] Chipalkatti, H. R.; Desai, N. F.; Giles, C. H.; Macaulay, N. J. *Soc Dyers Colour* 1954, 70, 487.
- [45] Khalifa, M. E.; Abdel-latif, E.; Gobouri, A. A. *J Heterocyclic Chem* 2015, 52, 674.
- [46] Muller, C. *Am Dyest Rep* 1970, 59, 37.
- [47] Abou Elmaaty, T. A.; El-Taweel, F.; Elsisy, H.; Okubayashi, S. *J Supercrit Fluids* 2018, 139, 114.
- [48] Abou Elmaaty, T. M.; Elnagar, K.; Hassan, S.; Gamal, H. *Int J Sci Eng Res* 2014, 5, 1156.