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SCIENTIFIC PAPER

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DYEING OF POLYESTER FIBERS WITH SULFUR- AND NITROGEN-CONTAINING ANTHRAQUINONE DERIVATIVES*

Article Highlights

- A series of disperse dyes, 9,10-anthraquinone were prepared
- Dyes containing dithiocarbamate, thiourea and triazole fragments
- The compounds were applied to polyester fibers and dyeing properties were investigated
- The color changes and staining fastnesses of the dyeings were found to be to “4-5” to “5”

Abstract

A series of disperse dyes, 9,10-anthraquinone containing dithiocarbamate, thiourea and triazole fragments, were prepared via consecutive refunctionalization of aminoanthraquinones in our previous studies and their structures were confirmed by the ^{1}H-, ^{13}C-NMR, IR spectra, LC-MS and elemental analysis data. The obtained compounds were applied on polyester fabrics by the exhaustion method at 130 °C at pH 4.0-5.0, and their dyeing properties were evaluated by color measurements, the washing fastness test and the light fastness test. Many of these dyes gave solid and level dyeings on polyester fabric with low % concentration of dye. The dyed samples displayed very good color fastnesses. The color change and staining test results were quite good with ratings of “4-5” or above. The light fastness test results were also satisfactory for the most of the dyed samples.

Keywords: anthraquinone dyes, application, dyeing of polyester, textile, fastness.

Anthraquinone is used for the manufacture of a wide range of acid, vat and disperse dyes [1] and these dyes very important in dye chemistry and provide an number of dyes, from bright red to greenish-blue, depending on the nature of the substitution structure. The commercially useful dyes are produced by introducing strong electron donating groups, such as amino or hydroxyl, at positions 1, 4, 5 or 8 in the anthraquinone molecule [2-5]. They are mainly in the shade range of violet, blue and green hue sectors [3,4].

Moreover, several heterocyclic anthraquinone analogues are important in disperse dye chemistry. However, an interesting exception is provided by the series of dyes derived by annellation of heterocyclic rings in the 2,3-position of the anthraquinone nucleus which are beautiful bright greenish-blues hitherto unmatched by any azo dye structure [6]. Azo anthraquinone disperse dyes with high light fastness on polylactide fibers were obtained [7].

Anthraquinone derivatives can be found in natural or synthetic dyes. Anthraquinone dyestuffs are also represented in disperse dyes. Synthetic quinone derivatives have been synthesized and studied also for their remarkable staining properties. They are characterized by very good light fastness [8]. There are numerous patents and studies in the literature about anthraquinone dyes. For example, dyeing properties of anilino- and aryl-mercapto anthraquinone series have been studied for bulk-dyeing linear polyesters [9]. 1-Hydroxy-4-*N*-*p*-(2'-pyrrolidon-1-yl)phenylamino anthraquinones were used to dye polyester

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textile material [10]. Some anthraquinone compounds are isolated from citrus trees.

Anthraquinone dyes are surpassed in importance only by azo dyes. The more complicated syntheses and lower tinctorial strengths of the anthraquinone dyes make production costs higher than for azo dyes [11-13]. Therefore, anthraquinone dyes tend to be used only when the required properties and color fastness are extreme or when the colors desired are not obtained easily with azo dyes (especially bright blue to turquoise shades). The use of a dye in vat dyeing requires the presence of special structural features (quinoid or indigoid). Therefore, most vat dyes are derived from anthraquinone [12]. The synthesis of an anthraquinone dye generally involves a large number of steps. For example, the preparation of a vat dye may require as many as eight steps and may necessitate the preparation of seven different anthraquinone intermediates. Aminoanthraquinones, especially 1-amino- and 1,5-diaminoanthraquinone, are key products for essentially all classes of anthraquinone dyes. Modifications of the amino function have industrial importance [12]. In recent years, efforts have been made to synthesize anthraquinone dyes under green chemistry conditions. Dye series of 1,8-dihydroxy-4,5-dinitroanthracene-9,10-dione and 1,4-dihydroxyanthracene-9,10-dione analogs were synthesized using supercritical carbon dioxide dying conditions [14].

In this study, the dyeing properties of a series of derivatives of 9,10-anthraquinone containing dithiocarbamate, thiourea and triazole fragments **8-18**, which were prepared *via* effective consecutive refunctionalization of 1(2)-aminoanthraquinones **1-7**, have been investigated for their potential as novel dyes for polyester fiber (Figure 1). The synthesis and the spectral properties of these compounds were reported in our previous studies [15-18].

EXPERIMENTAL

Materials and methods

Melting points were measured using a Büchi B-540 melting point apparatus. Elemental analyses were performed on a Thermo Finnigan Flash EA 1112 elemental analyzer, and their results were found to be in good agreement with the calculated values. IR spectra were recorded in KBr pellets on a Specord M-80 spectrometer. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were recorded in DMSO-d_6 on a Varian Mercury-400 spectrometer with TMS as the internal standard. Thin-layer chromatography (TLC) was performed on Merck silica gel plates (60G F254), and detection was carried out with ultraviolet light

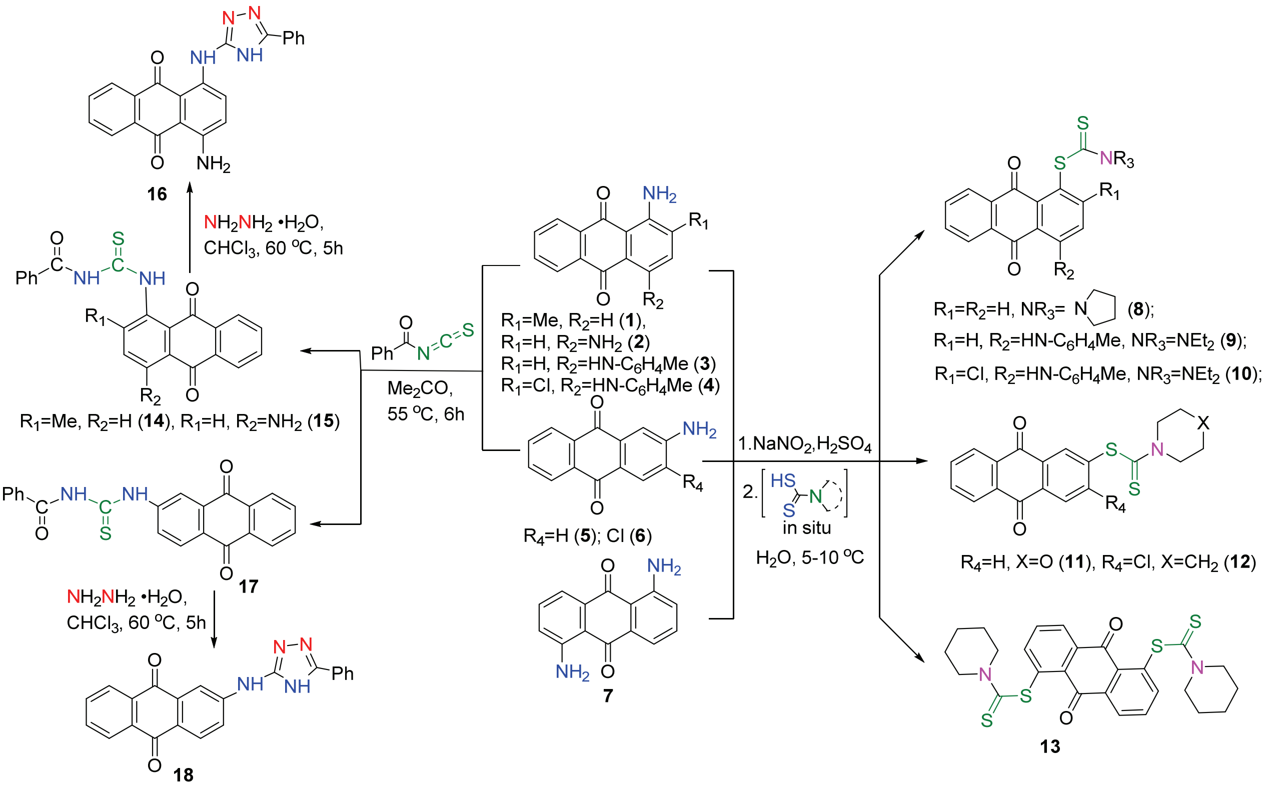


*Figure 1. Synthesis of sulfur- and nitrogen-containing substituted anthraquinone dyes **8-18**.*

(254 nm). All chemicals were of reagent grade and used without further purification. Aminoanthraquinones **1-7** were purchased from Sigma-Aldrich. *N,N*-benzoyl thioureas **15** and **17** were obtained using the method [15].

Preparation of dithiocarbamates of 9,10-anthraquinone [16-17]

To 13.44 mmol of carbon disulfide in 15 ml of water at constant stirring and cooling at 0-5 °C, 6.72 mmol of diethylamine/morpholine/piperidine/pyrrolidine was added. The reaction mixture was kept at stirring for 15 min. The solution of dithiocarbamic acid was ready for the synthesis of dithiocarbamates **8-13**. Diazonium salt was obtained without isolation from 2.24 mmol of appropriate aminoanthraquinone **1-6** and 0.201 g of sodium nitrite (2.91 mmol) (or 0.402 g, 5.81 mmol in case of diamine **7**) in 20 ml of concentrated sulfuric acid. The obtained solution was neutralized with 10% aqueous solution of sodium carbonate (up to pH 7). To the neutralized solution of diazonium sulfate at constant stirring and temperature 5-10 °C, the solution of previously *in situ* generated dithiocarbamic acid of diethylamine/morpholine/piperidine or pyrrolidine was added. The reaction mixture was stirred for 30 min. The precipitate was filtered, washed with water (2×40 ml), and dried on air.

9,10-Dihydro-9,10-dioxoanthracen-1-yl pyrrolidin-1-carbodithioate (8)

Yield: 91%, m.p. = 110 °C (decomp.). ^{1}H-NMR, ppm: δ = 1.91-2.11 (m, 4H, CH_2), 3.76-3.91 (m, 4H, CH_2), 7.84-7.97 (m, 3H, CH_{Ar}), 8.03-8.24 (m, 4H, CH_{Ar}). ^{13}C-NMR, ppm: δ = 24.15, 26.46, 51.27, 57.28 (CH_2), 126.92, 127.24, 127.35, 128.02, 132.63, 133.39, 133.53, 133.89, 134.73, 135.05, 135.34, 141.39 (C_{Ar}), 181.26, 182.89 (C=O), 191.73 (C=S). IR (KBr): ν = 1681, 1635 (C=O), 1268, 1210 (-S-C(S)-) cm^{-1}. Found, %: C, 64.63; H, 4.24; N, 3.99; S, 18.11 $C_{19}H_{15}NO_2S_2$. Calculated, %: C, 64.57; H, 4.28; N, 3.96; S, 18.14.

9,10-Dihydro-9,10-dioxo-4-(p-tolylamino)anthracen-1-yl diethylcarbamodithioate (9)

Yield: 69%, m.p. = 110 °C (decomp.). ^{1}H-NMR, ppm: δ = 1.17 (t, *J* = 6.8 *Hz*, 3H, CH_3), 1.37 (t, *J* = 7.2 *Hz*, 3H, CH_3), 2.33 (s, 3H, CH_3), 3.95 (m, 4H, CH_2), 7.37 (m, 2H, CH_{Ar}), 7.56-7.77 (m, 3H, CH_{Ar}), 7.91-8.07 (m, 3H, CH_{Ar}), 8.21-8.24 (m, 2H, CH_{Ar}), 13.07 (s, 1H, NH). ^{13}C-NMR, ppm: δ = 11.51, 13.73, 21.29 (CH_3), 47.57, 52.09 (CH_2), 124.39, 126.71, 128.24, 129.86, 130.82, 133.97, 134.39, 135.21, 136.02 (C_{Ar}), 181.78, 182.45 (C=O), 191.63 (C=S). IR (KBr): ν = 1680, 1642 (C=O), 1261, 1205 (-S-C(S)-) cm^{-1}. Found, %: C, 67.85; H, 5.21; N, 6.10; S, 13.99. $C_{26}H_{24}N_2O_2S_2$. Calculated, %: C, 67.80; H, 5.25; N, 6.08; S, 13.92.

2-Chloro-9,10-dihydro-9,10-dioxo-4-(*p*-tolylamino)-anthracen-1-yl diethylcarbamodithioate (10)

Yield: 59%, m.p. = 110 °C (decomp.). ^{1}H-NMR, ppm: δ = 1.16 (t, *J* = 6.8 *Hz*, 3H, CH_3), 1.37 (t, *J* = 7.2 *Hz*, 3H, CH_3), 2.32 (s, 3H, CH_3), 3.95 (m, 4H, CH_2), 7.56-7.71 (m, 2H, CH_{Ar}), 7.91-7.98 (m, 2H, CH_{Ar}), 8.14-8.24 (d, *J* = 7.5 *Hz*, 1H, CH_{Ar}), 12.01 (s, 1H, NH). ^{13}C-NMR, ppm: δ = 11.26, 13.66, 21.27 (CH_3), 47.63, 52.25 (CH_2), 112.75, 116.76, 118.16, 124.87, 126.97, 130.88, 132.28, 134.59, 135.39, 135.89, 135.98, 141.09, 150.42 (C_{Ar}), 182.07, 184.56 (C=O), 191.69 (C=S) ppm; and IR (KBr): ν = 1673, 1638(C=O), 1266, 1210 (-S-C(S)-) cm^{-1}. Found, %: C, 63.12; H, 4.61; N, 5.71; S, 13.00. $C_{26}H_{23}ClN_2O_2S_2$, Calculated, %: C, 63.08; H, 4.68; N, 5.66; S, 12.95.

9,10-Dihydro-9,10-dioxoanthracen-2-yl morpholin-4-carbodithioate (11)

Yield: 91%, m.p. > 110 °C (decomp.). ^{1}H-NMR, ppm: δ = 3.33 (m, 2H, CH_2), 3.66-3.74 (m, 4H, CH_2), 4.07-4.41 (m, 2H, CH_2), 7.89-7.91 (m, 3H, CH_{Ar}), 8.11-8.20 (m, 4H, CH_{Ar}). ^{13}C-NMR, ppm: δ = 51.79, 66.09 (CH_2), 127.16, 127.25, 127.82, 133.25, 133.39, 133.57, 133.77, 134.79, 134.96, 135.13, 138.52, 142.33 (C_{Ar}), 182.16, 183.37 (C=O), 191.66 (C=S). IR (KBr), cm^{-1}: ν = 1676, 1637 (C=O), 1262, 1202 (-S-C(S)-). Found, %: C, 61.81; H, 4.05; N, 3.76; S, 17.41. $C_{19}H_{15}NO_3S_2$, Calculated, %: C, 61.77; H, 4.09; N, 3.79; S, 17.36.

3-Chloro-9,10-dihydro-9,10-dioxoanthracen-2-yl piperidin-1-carbodithioate (12)

Yield: 67%, m.p. = 120 °C (decomp.). ^{1}H-NMR, ppm: δ = 1.56-1.67 (m, 6H, CH_2), 3.31-3.39 (m, 2H, CH_2), 4.12-4.26 (m, 2H, CH_2), 7.86-7.89 (m, 3H, CH_{Ar}), 8.11-8.17 (m, 3H, CH_{Ar}). ^{13}C-NMR, ppm: δ = 24.10, 25.54, 26.68, 52.74, 53.54 (CH2), 127.01, 127.33, 127.43, 127.51, 132.21, 132.66, 134.11, 134.27, 134.78, 135.26, 136.75, 139.86 (C_{Ar}), 182.70, 183.021 (C=O), 191.45 (C=S). IR (KBr), cm^{-1}: ν = 1680, 1643 (C=O), 1269, 1211 (-S-C(S)-). Found, %: C, 59.74; H, 4.00; N, 3.46; S, 15.99. $C_{20}H_{16}ClNO_2S_2$, Calculated, %: C, 59.77; H, 4.01; N, 3.48; S, 15.95.

9,10-Dihydro-9,10-dioxoanthracen-1,5-diyl bis(piperidin-1-carbodithioate) (13)

Yield: 95%, m.p. = 160 °C (decomp.). ^{1}H-NMR, ppm: δ = 1.67 (m, 12H, CH_2), 4.05-4.23 (m, 8H, CH_2), 7.80-7.84 (m, 4H, CH_{Ar}), 8.08-8.11 (m, 2H, CH_{Ar}). ^{13}C-NMR, ppm: δ = 24.09, 25.98, 27.09, 53.01, 53.97 (CH_2), 127.52, 127.69, 131.84, 134.24, 135.91, 139.87 (C_{Ar}), 182.35, 182.46 (C=O), 191.41 (C=S). IR (KBr), cm^{-1}: ν = 1672, 1639 (C=O), 1264, 1202 (-S-C(S)-). Found, %: C, 59.26; H, 5.01; N, 5.30; S, 24.39. $C_{26}H_{26}N_2O_2S_4$. Calculated, %: C, 59.29; H, 4.98; N, 5.32; S, 24.35.

Preparation of *N*-((2-Methyl-9,10-dioxo-9,10-dihydroanthracen-1-yl)carbamoyl) benzamide (14) [15]

Aminoanthraquinone (0.009 mol) was added to a solution of benzoyl isothiocyanate in 50 ml of acetone, obtained from the reaction of 0.87 g (0.009 mol) of potassium thiocyanate and 1.25 g (0.009 mol) of benzoyl chloride. The reaction mixture was stirred at room temperature for 1 h and then boiled for 6 h. The reaction mixture was cooled, the precipitate was filtered, washed with a small amount of acetone and then with water. The residue was dried in air and recrystallized from toluene. Yield: 75%, m.p. = 208-209 °C. ^{1}H-NMR, ppm: δ = 2.44 (s, 3H, CH_3); 7.57-7.61 (m, 2H, CH_{Ar}); 7.69-7.73 (m, 1H, CH_{Ar}); 7.86-7.91 (m, 3H, CH_{Ar}); 8.08-8.19 (m, 5H, CH_{Ar}); 11.79 (s, 1H, NH); 12.57 (s, 1H, NH). LC-MS, *m*/*z* (I_{rel}, %): 401 [M+1] (100). Found, %: C 68.81; H 3.85; N 6.83; S 7.90. $C_{23}H_{16}N_2O_3S$. Calculated, %: C 68.98; H 4.03; N 7.00; S 8.01.

Preparation of 1,2,4-triazoles of 9,10-anthaquinone [18]

To a stirred suspension of 0.0518 mmol of *N*-benzoyl thiourea **15** or **17** [15] in 30 ml of chloroform, 0.013 g (0.259 mmol) of hydrazine hydrate was added. The reaction mixture was heated under reflux for 5 h and cooled to room temperature. The precipitate formed was filtered, washed with water, and dried.

1-Amino-4-[(5-phenyl-4H-1,2,4-triazol-3-yl)-amino]-anthracene-9,10-dione (16)

Yield: 74%, m.p. = 273 °C. ^{1}H-NMR, δ, ppm (*J*, Hz): 7.12-7.28 (4H, m, CH_{Ar}, NH_2); 7.58-7.92 (8H, m, CH_{Ar}); 8.40 (1H, d, J = 7.48 Hz, CH_{Ar}); 10.43 (1H, s, NH); 14.43 (1H, s, NH). IR (KBr), ν, cm^{-1}: 3361, 3315 (NH_2), 3304 ($NH_{triazole\ ring}$), 1679, 1620 ($C{=}O_{quinone\ ring}$). Found, %: C 69.11; H 3.84; N 18.27. $C_{22}H_{15}N_5O_2$. Calculated, %: C 69.28; H 3.96; N 18.36.

2-((5-Phenyl-4H-1,2,4-triazol-3-yl)amino)anthracene-9,10-dione (18)

Yield: 84%, m.p. = 255 °C. ^{1}H-NMR, δ, ppm (*J*, Hz): 7.56-7.53 (3H, m, CH_{Ar}); 8.01-7.88 (4H, m, CH_{Ar}); 8.21-8.12 (4H, m, CH_{Ar}); 8.52 (1H, d, 8.7, CH_{Ar}); 10.41 (1H, s, NH); 14.15 (1H, s, NH). IR (KBr), ν, cm^{-1}: 3281 ($NH_{triazole\ ring}$), 1675, 1625 ($C{=}O_{quinone\ ring}$). LC-MS, m/z (I_{rel}, %): 367 $[M+H]^+$ (100). Found, %: C 72.05; H 3.75; N 15.41. $C_{22}H_{14}N_4O_2$. Calculated, %: C 72.12; H 3.85; N 15.29.

Dyeing process

The polyester fabric used in the dyeings was woven, pretreated and ready to be dyed. The fabric weight was 120 g/m^2. The CIE Whiteness Index of the fabric was 65.8.

5 g of fabric samples were dyed with 0.5% o.m.f. (% on mass of fiber) of each dye. The exhaust dyeing process was carried out in a laboratory-scale HT dyeing machine (Roaches) using a liquor ratio of 20:1. 0.5 g/L dispersing agent (Dispersogen P) was added to each dyebath. The dyeing was initiated with pH 4.0-5.0 at 40 °C. Acetic acid was used to adjust the pH of the dyebath. After 10 min, the temperature was raised to 130 °C at a heating rate of 3 °C/min and the dyeing was carried out at 130 °C for 30 min. The dyebath was then cooled down at a cooling rate of 2 °C/min. Having taken the samples out from the dyeing tubes, the samples were given a reductive washing with 2 g/L sodium dithionite, 2 g/L NaOH (38 °Bé) and 2 g/L dispersing agent at 75 °C for 25 min. Then, the samples were washed in hot water and rinsed with cold water.

Color measurement of the dyed samples

The reflectance values of the undyed fabric, dyed and reduction cleared fabric samples were measured using a Datacolor SF 600$^+$ spectrophotometer. The CIELab values were calculated using Illuminant D65 and 10° Standard Observer values by Datamatch 3.2 software. The specular component included mode and USAV (Ultra Small Area View) 6.6 mm diameter measurement plate was used in the measurements. The color strength values of the reduction cleared samples were calculated at the wavelengths of maximum absorption in the visible spectrum in accordance with the Kubelka-Munk equation which is given by Eq. (1):

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

where *K* and *S* are the absorption and scattering coefficients at the wavelength of maximum absorbance of the dyed material, and *R*, is the reflectance value of the dyed material at the wavelength of maximum absorption in a decimal way.

RESULTS AND DISCUSSIONS

Continuing our research on the search for new substances with practically valuable properties among the functionalized derivatives of 9,10-anthraquinone [19-23], in this work presented herein we report a series of 9,10-anthraquinone derivatives containing dithiocarbamate, thiourea and triazole fragments applied as dyes for the polyester fibers. The sulfur- and nitrogen-containing derivatives **8-18** were prepared *via* consecutive refunctionalization of aminoanthraquinones **1-7** using methods published in the previous works [15-18]. The spectral curves of the dyed and the undyed PES fabric samples are shown in Figure 2. The *K*/*S* graphs of the dyed samples are also given in Figure 3. *K*/*S* (absorption coefficient (*K*) and scattering coefficient (*S*)) is a value used to represent the relative depth of shade of a dyeing. It is calculated by the Kubelka-Munk equation from the reflectance value at the wavelength of maximum adsorption, λ_{max}, of the dyeing. It is directly proportional to the amount of dye present on the dyed fabric and, therefore, to the depth of shade. The higher the *K*/*S* value, the greater is the color strength (depth of shade) of the dyeing [24]. It should be stated that the yields of our starting materials and the product compounds were very high (59-95%). The dyes were obtained on milligram (mg) scale after the purification process. For this reason, the fabrics were dyed with a dye concentration of 0.5% o.m.f. and the dyes were used as pure without adding any auxiliaries to them. *K*/*S* values of these dyes are quite high even at very low concentration of 0.5%. The fabrics dyed with the limited amount of dye were just enough to be used for the wash fastness and the light fastness tests.

Since % on mass of fiber of each dye is the same in this study, the difference of *K*/*S* values among fabrics dyed with dyes **8-18** can be explained by structures of dye, effect of the substituent and the auxochrome groups. The *K*/*S* values of the synthesized dyes **8-18** were found in the range of 0.949--10.158. (Figure 3 and Table 1) The *K*/*S* values of dyes **8** and **11-13** were in the range of 1.463-4.688. As the structures of these dyes are considered, they are substituted with non-aromatic cyclic amines such as pyrrolidine, piperidine and morpholino at auxochrome parts (Figure 1). Relatively low *K*/*S* values were obtained as compared to the aromatic analogues (dyes **9** and **10**). At the same time, these derivatives exhibited poor light fastness and the results of non-aromatic cyclic amine derivatives (dyes **8**, **11** and **13**) were lower than those for the aromatic derivatives (dyes **9** and **10**). The light fastness results for our compounds are consistent with the literature [25]. This may be due to the conjugation sequences of the dyes that were broken down with non-aromatic substituents.

Dyes **14**, **16** and **18** have fully aromatic and continuous conjugated systems as seen in the molecular formulas in Figure 1. The structures of dye **16** and **18** are exactly the same, except that dye **16** has bearing NH_2 as the auxochrome group at the anthraquinone ring. Although the structures of these two dyes are similar, their *K*/*S* values are surprisingly different. The *K*/*S* values of dyes **16** and **18** are 0.949 and 10.107,

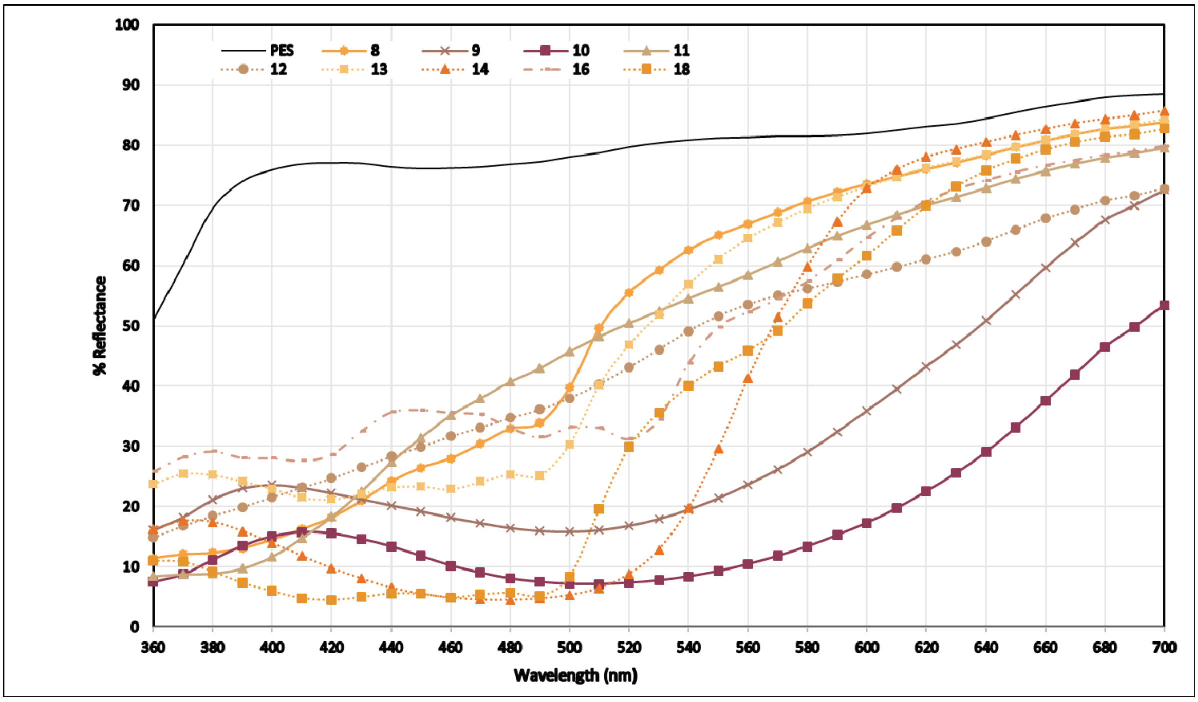
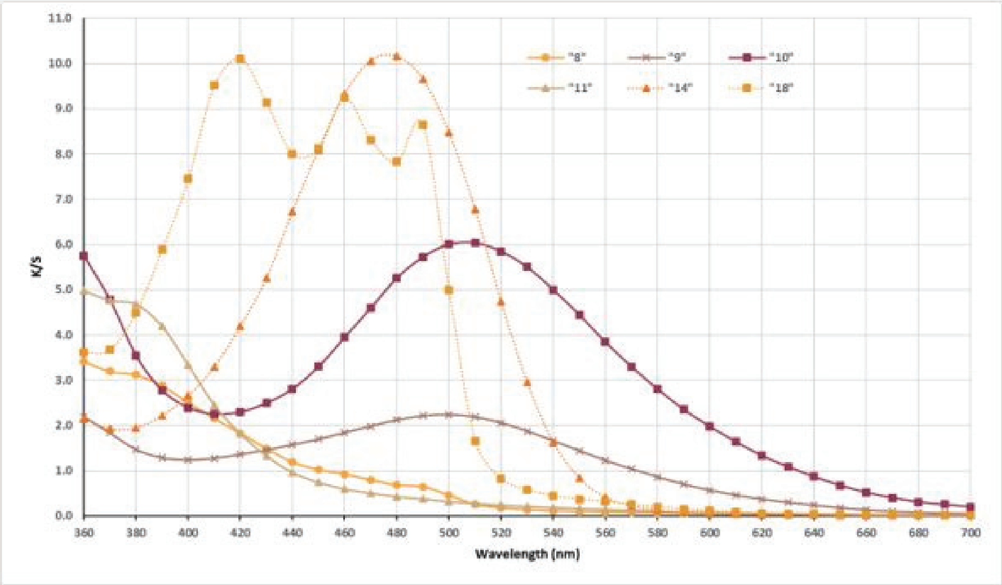
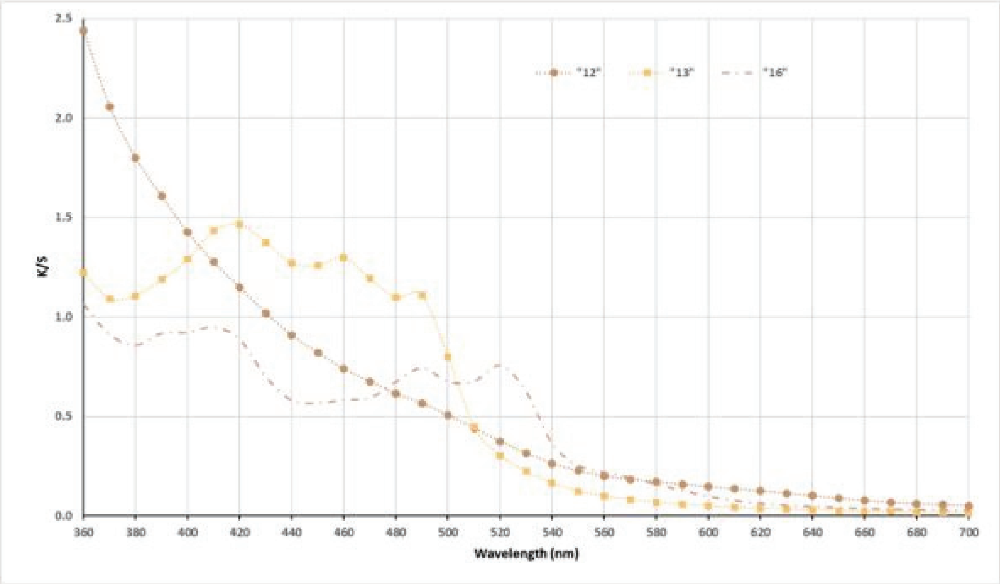


Figure 2. The spectral curves of the dyed fabrics and the undyed PES fabric.



(a) K/S values of the dyed fabrics of **8**, **9**, **10**, **11**, **14** and **18**.



(b) *K/S* values of the dyed fabrics of **12**, **13** and **16**.

Figure 3. K/S values of the dyed fabrics.

respectively. Likewise, dye **14**, which does not contain an NH_2 group in the anthraquinone ring, has the highest *K/S* value (10.158) among all dyes. It was obvious that the auxochromic effect of NH_2 is directly responsible for these results.

Tables 2 and Table 3 summarize the CIELab values and the color coordinates of the undyed, dyed and the reduction cleared fabric samples, respectively. An increase in (+a*) means the color is getting reddish and an increase in (-a*) means the color is getting greenish. Also, an increase in (+b*) means the color is getting yellowish, and an increase in (-b*) the color is getting blueish. Most of the substituted anthraquinone dyes gave very good level dyeings and solid dyeings on polyester. The dyes **9** and **10** gave unlevel dyeings only, probably due to their poor dispersion in the dyeing bath.

The wash fastness test of the dyed fabrics was carried out in James Heal GyroWash equipment in accordance with BS EN ISO 105-C06 standard [26]. The washing fastness test results were given in Table 4, which are quite good. The color changes were found to be “4-5” to “5” for most of the dyed samples. The dyed sample **10** was an exception, for which the color change was “4” in accordance with the Gray Scale rating. The staining test results on the multifiber fabrics were also quite good with rating “5” for the majority of the samples, except the dyed samples **14** and **16**. The Gray Scale ratings for staining on acetate and polyamide fabrics for **14**, and on wool fabric for **16** were found to be “4-5”, respectively. The colors and K/S values at λ_{max} of the dyed samples are given in Table 1. Among the dyed samples, two groups appear at two different ranges of λ_{max}, namely 380-420 nm and 480-510 nm. The samples, coded as **8**, **11**- **13**, **16** and **18** have the maximum absorbance wavelength range at 380-420 nm. The samples of **9**, **10** and **14** have the maximum wavelength range at 480-510 nm.

Table 1. Colors and K/S values at λ_{max} of the dyed samples

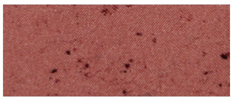
Material	Color / image of the dyed fabric	λ (nm)	*K/S* at λ
Dyed Fabric ID # 8		380	3.122
Dyed Fabric ID # 9		500	2.239
Dyed Fabric ID # 10		510	6.038
Dyed Fabric ID # 11		380	4.688
Dyed Fabric ID # 12		380	1.799
Dyed Fabric ID # 13		420	1.463
Dyed Fabric ID # 14		480	10.158
Dyed Fabric ID # 16		410	0.949
Dyed Fabric ID # 18		420	10.107

Table 3. CIELab and the tristimulus values of the dyed fabrics

Dye ID	CIELAB values					Tristimulus values		
	L*	a*	b*	C*	h°	X	Y	Z
8	82.45	3.57	40.84	41.00	85.01	59.43	61.12	28.73
9	57.15	23.74	10.91	26.12	24.67	29.56	25.08	20.52
10	41.11	25.50	1.04	25.52	2.34	15.21	11.94	12.41
11	79.80	3.60	29.31	29.53	83.01	54.81	56.33	33.64
12	75.99	5.32	24.27	24.84	77.64	49.21	49.87	32.52
13	80.17	9.73	41.94	43.05	76.94	57.91	56.98	25.49
14	66.62	41.06	63.20	75.37	56.99	47.53	36.14	6.68
16	75.10	18.23	17.29	25.13	43.48	52.63	48.44	36.64
18	70.20	19.38	71.68	74.26	74.87	45.32	41.04	6.11

Table 4. Washing fastness test results of the reduction cleared samples; Ac: cellulose acetate; Co: cotton; PA: polyamide; PES: polyester; PAN: acrylic; Wo: wool

Dye ID	Washing Fastness (ISO 105 - C06 A1S)						
	Color change	Staining					
		Ac	Co	PA	PES	PAN	Wo
8	4-5	5	5	5	5	5	5
9	4-5	5	5	5	5	5	5
10	4	5	5	5	5	5	5
11	4-5	5	5	5	5	5	5
12	4-5	5	5	5	5	5	5
13	4-5	5	5	5	5	5	5
14	5	4-5	5	4-5	5	5	5
16	4-5	5	5	5	5	5	4-5
18	4-5	5	5	5	5	5	5

The light fastness test of the dyed samples was carried out in accordance with ISO 105-B02 in James H. Heal Microsol Light Fastness Tester [27]. The Blue Wool Scale (1-8) was used for the assessment of the light fastness. Most of the dyed samples displayed good light fastness, except the dyed fabrics **8**, **11** and **13**. It is known from the literature that the light fastnesses were found to be moderate for the piperidine derivatives of 1,4-anthraquinone analogous. Also, the light fastness of 1,8-naphthalic derivatives is condensed with non-aromatic cyclic amines, such as pyrrolidine, piperidine and piperazine which showed moderate-to-good light fastness for piperidine derivatives, poor-to-moderate light fastness for pyrrolidine dyestuffs, while the piperazine derivatives exhibited poor light fastness [25]. The light fastness results for our compounds are consistent with the literature and

Table 2. CIELab and tristimulus values of the untreated fabric

Undyed PES Fabric	CIELAB values					Tristimulus values		
	L*	a*	b*	C*	h°	X	Y	Z
Polyester (PES)	91.95	0.86	3.18	3.29	74.90	76.83	80.59	82.14

the results for non-aromatic cyclic amine derivatives of pyrrolidine, piperidine and morpholine at auxochrome part dyes **8**, **11** and **13**) were lower than those for the aromatic derivatives (dyes **9** and **10**). The light fastness results are given in Table 5.

Table 5. Light fastness test results and the CIELab values of the light fastness tested samples

Dye ID	CIELAB values					Tristimulus values			Light Fastness
	L*	a*	b*	C*	h°	X	Y	Z	
8	84.40	7.71	39.88	40.62	79.06	64.82	64.84	31.72	2
9	56.06	26.92	9.53	28.55	19.50	29.19	24.00	20.27	3
10	42.23	26.56	2.80	26.71	6.01	16.22	12.65	12.47	4
11	82.24	9.33	38.91	40.01	76.52	61.49	60.75	29.80	2
12	84.21	4.38	25.20	25.58	80.13	63.00	64.46	43.11	3
13	83.29	6.86	21.95	22.99	72.65	62.36	62.71	44.59	2
14	67.41	44.86	64.47	78.55	55.17	50.15	37.17	6.70	4
16	82.37	17.96	18.55	25.83	45.92	65.48	60.98	46.23	4
18	76.15	22.92	75.03	78.45	73.01	56.25	50.14	7.91	4

CONCLUSIONS

The aim of this study was to synthesize a series of dyes of 9,10-anthraquinone containing dithiocarbamate, thiourea and triazole fragments by consecutive refunctionalization of aminoanthraquinones and eventually to use these dyes in the dyeing of polyester fabric samples at 130 °C by the exhaustion method. The structures of the synthesized dyes were confirmed by the ^{1}H-, ^{13}C-NMR, FTIR, LC-MS and the elemental analysis data. The synthesized dyes gave very good dyeings on the polyester fiber under high temperature dyeing conditions at 130 °C, and the wash fastness performances were quite good. Only the dyes **9** and **10** showed poor dispersion properties under dyeing conditions in this study and they gave unlevel dyeings. The results showed that 9,10-anthraquinone containing dithiocarbamate, thiourea and triazole fragments can be used as dye in polyester dyeing at pH 4.0-5.0 at high temperature. Future works have been planned to investigate their dyeing, color, fastness and other functional properties on other textile fibers.

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NAUČNI RAD

BOJANJE POLIESTERSKIH VLAKANA DERIVATIMA ANTRAHINONA KOJI SADRŽE SUMPOR I AZOT

Konsekutivnom refunkcionalizacijom aminoantrahinona pripremljena je serija disperznih boja 9,10-antrahinona koji sadrži fragmente ditiokarbamata, tiouree i triazola, a njihove strukture su potvrđene ^{1}H-, ^{13}C-NMR i IR spektrima, kao i LC-MS i podacima o elementalnoj analizi. Dobijena jedinjenja su primenjena na poliesterske tkanine metodom iscrpljivanja na 130 °C pri pH 4,0-5,0, a njihova svojstva bojenja su procenjena merenjem boje, testom postojanosti na pranje i testom postojanosti na svetlost. Mnoge od ovih boja dale su čvrste i ravne boje na poliesterskoj tkanini sa niskom koncentracijom boje. Obojeni uzorci su pokazali veoma dobru postojanost boja. Promena boje i rezultati testa bojenja bili su prilično dobri sa ocenama „4-5“ ili više. Rezultati ispitivanja otpornosti na svetlost bili su, takođe, zadovoljavajući za većinu obojenih uzoraka..

Ključne reči: antrahinonske boje, primena, bojenje poliestera, tekstil, postojanost.