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Synthesis of some 4-arylazo-3-hydroxythiophene disperse dyes for dyeing polyester fabrics

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Abstract A series of novel 4-arylazo-3-hydroxythiophene disperse dyes was synthesized by heterocyclization of ethyl 2-arylhydrazono-2-phenylthiocarbamoyl acetates with a variety of α-halogenated reagents. The structures of the synthesized dyes were confirmed by UV-Vis, IR, ^{1}H NMR, and MS spectroscopic techniques and elemental analysis. The dyes were applied to conventional polyester fabric by high temperature exhaust dyeing. These dyes were found to give orange to reddish-violet shades with very good depth, levelness, and brightness on polyester fabric. The dyed fabric showed moderate to good light fastness and very good fastness to washing and perspiration. Also the position of color in CIELAB coordinates (L^*, a^*, b^*, H^*, and C^*) was assessed.

Keywords Thiocarbamoyl; Thiophene; Disperse dyes; Polyester fabrics; Fastness properties.

Introduction

Azo compounds are the most widely used class of dyes due to their versatile application in various fields, such as the dyeing of textile fiber, the coloring of different materials, colored plastics, biological-medical studies, and advanced applications in organic synthesis. A number of azo disperse dyes have been reported in literature [1], offering a clear-cut advantage due to their ease of synthesis, structural variability, and higher chromophoric strength in comparison to anthraquinone based dyes [2, 3]. Especially, thiophene-based azo dyes have been developed, and the resultant dyes have many advantages including a color deepening effect and small molecular structure leading to better dyeability.

The highly bathochromic disperse dyes derived from 2-aminothiophenes as diazo components are not only technically important [4–9]; they have been used industrially in polyester coloration for a quarter of a century now. Although thiophene derivatives have rarely been reported as coupling components, some examples of disperse dyes obtained from the coupling moieties of electron rich thiophenes were described as having red-violet and greenish-blue colors [10–12].

In this paper, efforts were made to synthesize the first reported moiety of 4-arylazo-3-hydroxythiophene dyes **4**–**7** from ethyl 2-arylhydrazono-2-phenylthiocarbamoylacetates **2**. The synthesized disperse dyestuffs containing a thienyl coupling moiety were subsequently applied as disperse dyes on polyester fabric, the dyeing characteristics and fastness properties of the resultant dyeings were also evaluated.

Results and discussion

Synthesis of 5-anilino-4-arylazo-3-hydroxythiophene dyes

Treatment of ethyl α-phenylthiocarbamoylacetoacetate (**1**) [13] with the appropriate aromatic diazonium salt in ethanol containing sodium acetate effected acetyl group cleavage (*Japp-Klingmann* reaction)

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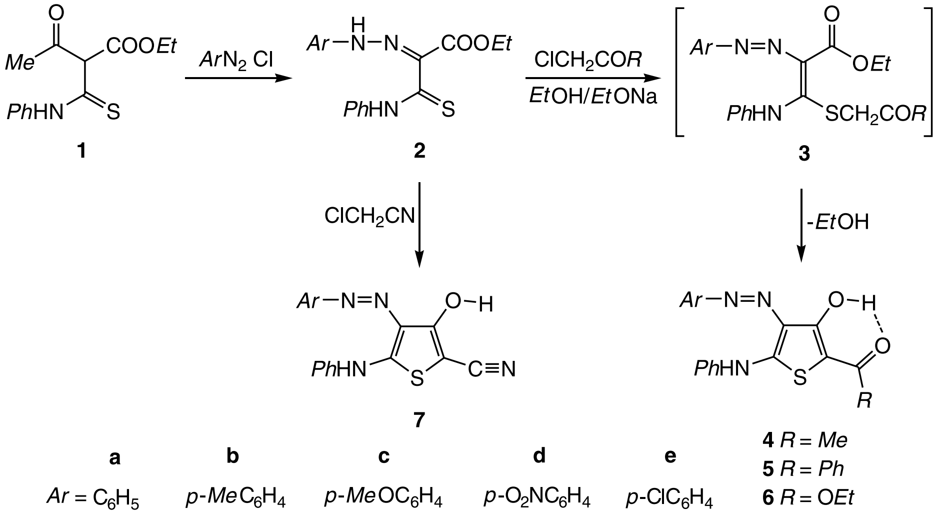

Scheme 1

with the formation of the corresponding thiocarbamoyl intermediates **2** [14]. The versatile ethyl 2-arylhydrazono-2-phenylthiocarbamoylacetate derivatives **2** underwent heterocyclization with several α-halocarbonyl reagents, *e.g.* chloroacetone, phenacyl chloride, and ethyl chloroacetate in the presence of sodium ethoxide to furnish the corresponding 4-arylazo-3-hydroxythiophene dyes **4**–**6**.

The formation of thiophene derivatives **4**–**6** from the reaction of **2** with appropriate alkylating agent, such as chloroacetone, phenacyl chloride, and ethyl chloroacetate seems to follow the sequence outlined in Scheme 1. It is suggested that the reaction starts through nucleophilic attack of the thiolate group to form intermediate **3** which *via* nucleophilic substitution and intramolecular cyclocondensation by ethanol elimination gave the corresponding polyfunctionally substituted thiophenes **4**–**6**.

The structures of the highly functionalized thiophene dyes **4**–**6** were elucidated on the basis of their elemental analyses and spectral data. The stretching frequency values of the carbonyl and hydroxyl groups in the IR spectra have received special attention. The IR of the dyes **4** and **5** showed absorption peaks in the range 1573–1598 and 3112–3162 cm^{-1} due to the presence of conjugated carbonyl and hydroxyl group. The strong decrease in the carbonyl and hydroxyl absorption frequencies is attributed to the intramolecular H-bond structure. The absorption frequencies for the carbonyl and hydroxyl groups in the structure of dyes **6** appear at a considerably higher frequency 1638–1652 and 3215–3259 cm^{-1} as compared with the frequencies of those groups in dyes **4** and **5**.

The ^{1}H NMR spectrum of **4b** (as an example) showed a singlet at 2.20 ppm due to methyl protons ($COCH_3$), a singlet at 2.40 ppm due to methyl protons on the phenyl ring, in addition to a multiplet in the region 7.20–7.60 corresponding to the aromatic protons. The broad singlet at 13.95 ppm was attributed to the presence of NH group, while the hydrogen bonded OH group is downfield shifted to 15.20 ppm.

The ^{1}H NMR spectra showed that the chemical shifts for hydroxylic protons in the structures of dyes **4** and **5** (2-acetyl- and 2-benzoyl-3-hydroxythiophene dyes) appear at lower field ($\delta_{\mathrm{OH}} = 14.60$–15.25 ppm), as compared with the chemical shifts in the 2-ethoxycarbonyl-3-hydroxythiophene dyes **6** ($\delta_{\mathrm{OH}} = 10.60$–11.10 ppm).

In a similar manner, a series of 4-arylazo-2-cyanothiophene dyes **7** was prepared by reaction of **2** with chloroacetonitrile in ethanolic sodium ethoxide solution; the structure of these dyes was verified by elemental analysis and by spectroscopic methods (IR, mass, and ^{1}H NMR). The IR spectra of the dyes **7a**–**7e** exhibited, in all cases, the presence of cyano and hydroxy stretching bands near 2194–2204 and 3170–3214 cm^{-1}. The ^{1}H NMR spectrum of **7c** (for example) revealed a singlet at 3.80 ppm due to the methoxy protons, a multiplet at 6.80–7.70 ppm due to the aromatic protons, a broad singlet at 12.20 ppm assigned to the OH group, and a singlet at 13.60 ppm assigned to the NH group.

Absorption spectroscopic characteristics

Absorption maxima of the dyes **4**–**7** were measured in CH_2Cl_2 solutions and are listed in Table 2. The substituent at the 2-position in the thiophene ring affects the absorption characteristics of the dyes. As can be seen from the data in Table 2, large bathochromic shift can be obtained by the 2-ethoxycarbonylthiophene dyes **6**, which absorb maximally at longer wavelengths (464–497 nm) than the other corresponding dyes. The hypsochromic shifts observed for most of the dyes **4** and **5** compared with their 2-cyano analogues **7** emphasize the dramatic effect caused by intramolecular hydrogen bonding. The absorption maxima of the dyes **4a**–**4e** and **5a**–**5e** ranged from 443 to 497 nm and from 425 to 485 nm. All the 2-acetyl dyes **4** absorb bathochromically compared with their 2-benzoyl analogues **5**. This bathochromic shift results from the fact that the σ-electrons of the methyl group (dyes **4**) are mobile enough to interact with the chromophoric groups, while the lower wavelengths accompanying dyes **5** may be attributed to disruption of planarity necessary for conjugation of the carbonyl and phenyl group by steric hindrance [15]. In conclusion, the bathochromic shift by the substituents at the 2-positon of the thiophene ring was in the order CO*Ph*→CO*Me*→CN→COO*Et*.

A closer inspection of the visible spectral data for the *para*-substituents at the aromatic diazo component shows that only the 4-nitro group produces a more bathochromic shifted $\lambda_{\max}$, whereas the other substituents did not affect significantly the absorption maxima.

Dyeing and fastness properties

The highly functionalized thiophene dyes **4**–**7** were applied to polyester fabric at 2% shade by high-temperature pressure technique and gave generally deep and bright hues ranging from orange to reddish-violet. The dyeings on polyester fabric were evaluated in terms of their fastness properties. The overall fastness properties (Table 1) are generally satisfactory. The results for washing fastness (at 50°C) show that the dyed polyester samples have generally very good washing fastness.

The results obtained show that the fastness to acid and alkaline perspiration could be generally considered to be very good; such results indicate the relative stability of the dyes in acid and alkaline medium. Most of the dyes have a moderate (3) to good (4) rubbing fastness; only a few of these dyes have fair rubbing fastness (dry and wet), *e.g.* dye **4c**.

Table 1 Fastness properties of the dyes **4**–**7** on polyester fabrics

Dye	Washing	Perspiration		Rubbing		Sublimation fastness		Light (40 h)
		Acid	Alkali	Dry	Wet	Staining at 180°C	Staining at 210°C	
4a	4–5	4–5	4–5	3	3–4	2–3	2	3–4
4b	4–5	4–5	4–5	2–3	3	2–3	2	3
4c	4–5	4	4–5	2	2–3	2–3	2	2–3
4d	4–5	4–5	4–5	3–4	4	4	2–3	5–6
4e	4–5	4–5	4–5	2–3	3	3–4	2	5
5a	4–5	4–5	4–5	3	3–4	4	4	4
5b	4–5	4–5	4–5	3	3–4	4	4	3–4
5c	4–5	4–5	4–5	4	4	2	2	3–4
5d	4–5	4–5	4–5	4	4–5	4–5	4–5	5–6
5e	4–5	4–5	4–5	4	4–5	4	3–4	5–6
6a	4–5	4	4–5	3	3	2–3	2	4
6b	4–5	4–5	4–5	3	3–4	2–3	2–3	3–4
6c	4–5	4–5	4–5	3–4	4	2–3	2–3	4
6d	4–5	4–5	4–5	4	4	4	3	5–6
6e	4–5	4–5	4–5	4	4	4	2–3	4–5
7a	4–5	4–5	4–5	3	3–4	2–3	1–2	2–3
7b	4–5	4–5	4–5	3	3–4	4–5	3	3–4
7c	4–5	4	4–5	2–3	3–4	4–5	3	3
7d	4–5	4–5	4–5	4	4–5	4–5	4	5–6
7e	4–5	4–5	4–5	2–3	3–4	4	3–4	4–5

Table 2 UV-Vis spectroscopic data and color coordinates of the dyes **4–7** (light source = D65/10° observer)

Dye	Absorption λ_{max}/nm (ε/l mol^{-1} cm^{-1})	Color coordinates				
		L*	C*	H*	a*	b*
4a	443 (19870)	57.93	62.07	51.58	38.57	48.63
4b	448 (22792)	54.67	65.34	51.41	40.75	51.08
4c	452 (22955)	52.63	64.75	53.14	38.84	51.81
4d	497 (19978)	55.58	52.01	51.38	32.46	40.64
4e	456 (23980)	62.45	59.63	60.48	29.38	51.89
5a	425 (23875)	69.90	33.17	59.70	16.73	28.64
5b	431 (26885)	65.64	45.47	60.95	22.08	39.75
5c	442 (28180)	74.15	53.71	68.06	20.06	49.82
5d	485 (25125)	70.67	21.48	28.54	18.87	10.26
5e	446 (26915)	74.91	37.72	73.79	10.53	36.22
6a	464 (17782)	56.01	63.87	50.93	40.25	49.59
6b	467 (19050)	62.41	67.51	52.04	41.51	53.23
6c	469 (19498)	57.03	64.44	54.76	37.18	52.63
6d	497 (17378)	57.01	47.21	35.98	38.20	27.74
6e	470 (19508)	63.99	68.18	51.53	42.41	53.39
7a	458 (23386)	51.09	72.46	48.02	48.46	53.87
7b	464 (23420)	62.24	54.86	55.68	30.92	45.31
7c	467 (24542)	61.99	63.07	54.94	36.22	51.63
7d	482 (25085)	53.30	50.50	30.71	43.42	25.79
7e	464 (23980)	67.22	47.76	52.17	29.28	37.72

Sublimation fastness properties of dyes **4**–**7** expressed as color staining on the undyed polyester piece ranged from moderate to good. In most cases, the best sublimation fastness was obtained in the dyes containing a nitro group into the diazonium component and/or a nitrile group in the 2-position of the thiophene (*e.g.* dyes **4d**, **5d**, **6d**, and **7b**–**7e**). Light fastness of the arylazothiophene dyes **4**–**7** on polyester was moderate to good (according to the blue scale) and is significantly affected by the nature of the substituents in the diazonium component. In most cases, the best light fastness (good, 5–6 of the blue wool standard scale 1–8) was obtained by incorporation of a nitrogroup into the diazonium component (*cf.* dyes **4d**, **5d**, **6d**, and **7d**). This agrees with the notion that the azo compounds appended with electron-withdrawing substituents on the diazo components are less prone to photofading [16].

Color assessment

The color of a dyeing on polyester fabric is referenced to the CIELAB values L*, a*, and b* (Table 2). The color values tend to give the following results: (i) Dyes **5** containing the bulkiest 2-substituent (benzoyl), could be expected to build-up the least, hence giving dyeings with the highest L* and lowest C* values. In general, dyeings with dyes **5** were lighter (as shown by the higher L* values) and duller (as shown by the lower C* values) than the other dyeings with dyes **4**, **6**, and **7**, which are substituted with acetyl, ethoxycarbonyl, and nitrile groups. (ii) The positive values of a* (red–green axis) and b* (yellow–blue axis) indicate that the color hues of the thiophene dyes **4**–**7** on polyester fabric are shifted to the reddish and yellowish directions.

Conclusion

A set of twenty 4-arylazothiophene disperse dyes **4**–**7** were synthesized by heterocyclization of ethyl 2-arylhydrazono-2-phenylthiocarbamoylacetates **2** with a variety of α-halogenated reagents. All of them were investigated for their dyeing characteristics on polyester fabric. The electronic absorption spectra cover a λ_{max} range of 425–497 nm and give bright intense hues from orange to reddish-violet on polyester fabric. The dyed fabrics exhibit very good washing and perspiration fastness properties, with little variations in the moderate to good rubbing fastness. The light fastness is moderate although the incorporation of a nitro group in the diazonium components results in an improvement in light fastness to good.

Experimental

All melting points were measured on an electrothermal Gallenkamp melting apparatus. Elemental analyses were carried out at the Microanalytical Unit, Faculty of Science, University of Mansoura, Egypt; the results were in satisfactory agreement with the calculated values. UV-Vis spectra were recorded with a Perkin-Elmer Lambda 551 S spectrometer, using dichloromethane as the solvent. IR spectra (KBr) were determined on a Mattson 5000 FTIR spectrometer (not all frequencies are reported). The ^{1}H NMR spectra were acquired using a Bruker WP 300 spectrometer at 300 MHz using *TMS* as an internal standard. Mass spectra were obtained at a Finnigan MAT 212 instrument. The starting thiocarbamoyl derivatives **2** were prepared according to Ref. [14].

Synthesis of 5-anilino-4-arylazo-3-hydroxythiophene dyes ***4–7***

To a solution of 5 mmol **2** in ethanolic sodium ethoxide (prepared by dissolving 0.23 g sodium metal in 30 cm^3 absolute ethanol), 5 mmol of the appropriate α-halogenated reagent, *e.g.* chloroacetone, phenacyl chloride, ethyl chloroacetate, or chloroacetonitrile were added. The reaction mixture was heated under reflux for 2 h. The reaction mixture was poured into cold H_2O, neutralized with dilute HCl, the solid product that formed was filtered off, and recrystallized from ethanol or an ethanol:*DMF* (2:1) mixture to afford the corresponding thiophene dyes **4–7**.

2-Acetyl-3-hydroxy-4-phenylazo-5-anilinothiophene (**4a**, $C_{18}H_{15}N_3O_2S$)

Yield 74%; red crystals, mp 180–182°C (*Et*OH); IR (KBr): $\bar{\nu} = 3128$ (OH), 1575 (broad, C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.20$ (s, $COCH_3$), 7.15–7.70 (m, *Ar*′H), 14.10 (s, NH), 15.20 (s, OH) ppm; MS ($M^+ + H$, CI *iso*-butane): m/z (%) = 338 (100).

2-Acetyl-3-hydroxy-4-(p-tolylazo)-5-anilinothiophene (**4b**, $C_{19}H_{17}N_3O_2S$)

Yield 86%; red crystals, mp 177–178°C (*Et*OH); IR (KBr): $\bar{\nu} = 3112$ (OH), 1587 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.20$ (s, $COCH_3$), 2.40 (s, CH_3), 7.20–7.60 (m, *Ar*′H), 13.95 (s, NH), 15.20 (s, OH) ppm; MS (M^+, EI): m/z (%) = 351 (100).

2-Acetyl-3-hydroxy-4-(p-anisylazo)-5-anilinothiophene (**4c**, $C_{19}H_{17}N_3O_3S$)

Yield 82%; red crystals, mp 155–156°C (*Et*OH); IR (KBr): $\bar{\nu} = 3131$ (OH), 1594 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.25$ (s, $COCH_3$), 3.90 (s, OCH_3), 6.90–7.75 (m, *Ar*′H), 13.45 (s, NH), 14.90 (s, OH) ppm; MS ($M^+ + H$, CI *iso*-butane): m/z (%) = 368 (100).

2-Acetyl-3-hydroxy-4-(p-nitrophenylazo)-5-anilinothiophene (**4d**, $C_{18}H_{14}N_4O_4S$)

Yield 90%; reddish-violet crystals, mp 251–253°C (*Et*OH: DMF = 2:1); IR (KBr): $\bar{\nu} = 3147$ (OH), 1575 (broad, C=O) cm^{-1}; ^{1}H NMR ($CDCl_3/CF_3COOD$): $\delta = 2.30$ (s, $COCH_3$), 7.35–8.25 (m, *Ar*′H) ppm.

2-Acetyl-3-hydroxy-4-(p-chlorophenylazo)-5-anilinothiophene (**4e**, $C_{18}H_{14}ClN_3O_2S$)

Yield 82%; red crystals, mp 207–208°C (*Et*OH); IR (KBr): $\bar{\nu} = 3130$ (OH), 1573 (broad, C=O) cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): $\delta = 2.20$ (s, $COCH_3$), 7.20–7.70 (m, *Ar*′H), 12.85 (s, NH), 14.60 (s, OH) ppm.

2-Benzoyl-3-hydroxy-4-phenylazo-5-anilinothiophene (**5a**, $C_{23}H_{17}N_3O_2S$)

Yield 78%; red crystals, mp 210–211°C (*Et*OH); IR (KBr): $\bar{\nu} = 3137$ (OH), 1594 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.30$–7.75 (m, *Ar*′H), 13.90 (s, NH), 14.80 (s, OH) ppm.

2-Benzoyl-3-hydroxy-4-(p-tolylazo)-5-anilinothiophene (**5b**, $C_{24}H_{19}N_3O_2S$)

Yield 84%; red crystals, mp 198–200°C (*Et*OH); IR (KBr): $\bar{\nu} = 3144$ (OH), 1593 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.40$ (s, CH_3), 7.15–7.85 (14H, m, *Ar*′H), 14.10 (s, NH), 15.25 (s, OH) ppm; MS (M^+, EI): m/z (%) = 413 (100) ppm.

2-Benzoyl-3-hydroxy-4-(p-anisylazo)-5-anilinothiophene (**5c**, $C_{24}H_{19}N_3O_3S$)

Yield 91%; red crystals, mp 203–204°C (*Et*OH); IR (KBr): $\bar{\nu} = 3154$ (OH), 1596 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta =$ 3.90 (s, OCH_3), 6.90–7.65 (m, *Ar*′H), 13.80 (s, NH), 14.70 (s, OH) ppm.

2-Benzoyl-3-hydroxy-4-(p-nitrophenylazo)-5-anilinothiophene (**5d**, $C_{23}H_{16}N_4O_4S$)

Yield 82%; violet crystals, mp 251–252°C (*Et*OH: DMF = 2:1); IR (KBr): $\bar{\nu} = 3162$ (OH), 1598 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3/CF_3COOD$): $\delta = 7.35$–8.20 (m, *Ar*′H) ppm.

2-Benzoyl-3-hydroxy-4-(p-chlorophenylazo)-5-anilinothiophene (**5e**, $C_{23}H_{16}ClN_3O_2S$)

Yield 76%; brown crystals, mp >300°C (*Et*OH:DMF = 2:1); IR (KBr): $\bar{\nu} = 3141$ (OH), 1594 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3/CF_3COOD$): $\delta = 7.30$–7.85 (m, *Ar*′H) ppm.

2-Ethoxycarbonyl-3-hydroxy-4-phenylazo-5-anilinothiophene (**6a**, $C_{19}H_{17}N_3O_3S$)

Yield 74%; red crystals, mp 136–138°C (*Et*OH); IR (KBr): $\bar{\nu} = 3226$ (OH), 1643 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.30$ (t, CH_3), 4.25 (q, OCH_2), 7.25–7.70 (m, *Ar*′H), 10.60 (s, OH), 13.60 (s, NH) ppm.

2-Ethoxycarbonyl-3-hydroxy-4-(p-tolylazo)-5-anilinothiophene (**6b**, $C_{20}H_{19}N_3O_3S$)

Yield 89%; red crystals, mp 172–173°C (*Et*OH); IR (KBr): $\bar{\nu} = 3222$ (OH), 1638 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.35$ (t, CH_3), 2.40 (s, CH_3), 4.30 (q, OCH_2), 7.10–7.60

(m, *Ar*′H), 10.60 (s, OH), 14.10 (s, NH) ppm; MS ($M^+ + H$, CI *iso*-butane): m/z (%) = 382 (100).

2-Ethoxycarbonyl-3-hydroxy-4-(p-anisylazo)-5-anilinothiophene (**6c**, $C_{20}H_{19}N_3O_4S$)

Yield 92%; orange crystals, mp 274–275°C (*Et*OH); IR (KBr): $\bar{\nu} = 3215$ (OH), 1641 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.30$ (t, CH_3), 3.90 (s, OCH_3), 4.30 (q, OCH_2), 6.90–7.70 (m, *Ar*′H), 10.80 (s, OH), 14.00 (s, NH) ppm.

2-Ethoxycarbonyl-3-hydroxy-4-(p-nitrophenylazo)-5-anilinothiophene (**6d**, $C_{19}H_{16}N_4O_5S$)

Yield 81%; reddish-violet crystals, mp 229–230°C (*Et*OH); IR (KBr): $\bar{\nu} = 3259$ (OH), 1652 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3/CF_3COOD$): $\delta = 1.40$ (t, CH_3), 4.40 (q, OCH_2), 7.10–8.20 (m, *Ar*′H) ppm.

2-Ethoxycarbonyl-3-hydroxy-4-(p-chlorophenylazo)-5-anilinothiophene (**6e**, $C_{19}H_{16}ClN_3O_3S$)

Yield 72%; red crystals, mp >300°C (*Et*OH:DMF = 2:1); IR (KBr): $\bar{\nu} = 3251$ (OH), 1641 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.35$ (t, CH_3), 4.30 (q, OCH_2), 7.10–7.60 (m, *Ar*′H), 11.10 (s, OH), 13.60 (s, NH) ppm.

2-Cyano-3-hydroxy-4-phenylazo-5-anilinothiophene (**7a**, $C_{17}H_{12}N_4OS$)

Yield 68%; red crystals, mp 178–179°C (*Et*OH); IR (KBr): $\bar{\nu} = 3170$ (OH), 2204 (C≡N) cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): $\delta = 7.20$–7.80 (m, *Ar*′H), 12.10 (s, OH), 13.60 (s, NH) ppm; MS ($M^+ + H$, CI *iso*-butane): m/z (%) = 321 (100).

2-Cyano-3-hydroxy-4-(p-tolylazo)-5-anilinothiophene (**7b**, $C_{18}H_{14}N_4OS$)

Yield 77%; red crystals, mp 190–192°C (*Et*OH); IR (KBr): $\bar{\nu} = 3188$ (OH), 2202 (C≡N) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.40$ (s, CH_3), 7.20–7.65 (m, *Ar*′H), 11.90 (s, OH), 13.85 (s, NH) ppm; MS ($M^+ + H$, CI *iso*-butane): m/z (%) = 335 (100).

2-Cyano-3-hydroxy-4-(p-anisylazo)-5-anilinothiophene (**7c**, $C_{18}H_{14}N_4O_2S$)

Yield 79%; red crystals, mp 195–196°C (*Et*OH); IR (KBr): $\bar{\nu} = 3214$ (OH), 2194 (C≡N) cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): $\delta = 3.80$ (s, OCH_3), 6.80–7.70 (m, *Ar*′H), 12.20 (s, OH), 13.60 (s, NH) ppm; MS ($M^+ + H$, CI *iso*-butane): m/z (%) = 351 (100).

4.1.19 2-Cyano-3-hydroxy-4-(p-nitrophenylazo)-5-anilinothiophene (**7d**, $C_{17}H_{11}N_5O_3S$)

Yield 82%; violet crystals, mp 233–234°C (*Et*OH); IR (KBr): $\bar{\nu} = 3196$ (OH), 2198 (C≡N) cm^{-1}; ^{1}H NMR ($CDCl_3/CF_3COOD$): $\delta = 7.20$–8.10 (m, *Ar*′H) ppm.

2-Cyano-3-hydroxy-4-(p-chlorophenylazo)-5-anilinothiophene (**7e**, $C_{17}H_{11}ClN_4OS$)

Yield 89%; orange crystals, mp 200–201°C (*Et*OH); IR (KBr): $\bar{\nu} = 3204$ (OH), 2194 (C≡N) cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): $\delta = 7.20$–7.70 (m, *Ar*′H), 11.60 (s, OH), 13.80 (s, NH) ppm.

Dyebath preparation and dyeing

A dispersion of the dye was produced by dissolving the appropriate amount of dye (2% o.m.f. shade) in 1 cm^3 acetone and then added to the dyebath (liquor ratio 20:1) containing 1% Avolan IS (Bayer AG, Germany) as a dispersing agent. The *pH* of the dyebath was adjusted to 4–4.5 with aqueous acetic acid and the wetted-out polyester fabric was added. Dyeing was performed by raising the dyebath temperature from 60 to 130°C at 1.5°C/min, holding at this temperature for 60 min, and rapidly cooling to 70°C. The dyeings were rinsed with cold water and reduction cleared (1 g dm^{-3} sodium hydroxide, 1 g dm^{-3} sodium hydrosulfite, 10 min, 80°C). The samples were rinsed with hot and cold water and finally air-dried.

Color fastness tests

The results are listed in Table 1. The color fastness of dyeings was evaluated using standard methods [17]:

(i) *Washing fastness.* The dyed fabrics were tested according to the standard ISO C06 C2S wash test, using an ECE detergent and steel balls were employed during washing. The staining of adjacent cotton fabrics was assessed using the grey scale: 1 – poor, 2 – fair, 3 – moderate, 4 – good, 5 – excellent.

(ii) *Perspiration fastness.* A composite sample was sandwiched on each side by the undyed cotton, all of equal length, and then immersed in the acid or alkaline solution for 30 min. The staining on the undyed adjacent fabric was assessed according to the grey scale: 1 – poor, 2 – fair, 3 – moderate, 4 – good, 5 – excellent. The acid solution (*pH* = 3.5) contained sodium chloride (10 g dm^{-3}), lactic acid (1 g dm^{-3}), disodium orthophosphate (1 g dm^{-3}), and histidine monohydrochloride (0.25 g dm^{-3}). The alkaline solution (*pH* = 8) contained sodium chloride (10 g dm^{-3}), ammonium chloride (4 g dm^{-3}), disodium orthophosphate (1 g dm^{-3}), and histidine monohydrochloride (0.25 g dm^{-3}).

(iii) *Rubbing fastness.* The test is designed to determine the amount of color transferred from the surface of colored fabrics to another surface by rubbing. The rubbing test is carried out using the AATCC crockmeter, a square of white testing cloth was allowed to slide on the tested fabric back and forth twenty times by making ten complete turns of the crank. Both dry and wet rubbing fastness tests were carried out. The staining on the white testing cloth was assessed according to the grey scale: 1 – poor, 2 – fair, 3 – moderate, 4 – good, 5 – excellent.

(iv) *Sublimation fastness.* Sublimation fastness was measured with an iron tester (Yasuda no. 138). The dyes samples were stitching between two pieces of undyed polyester, all of equal length, and then treated at 180 and 210°C each for 1 min. Any staining on the undyed adjacent fabric was assessed on the grey scale: 1 – poor, 2 – fair, 3 – moderate, 4 – good, 5 – excellent.

(v) *Light fastness.* Light fastness was determined using a Xenon test 150 (Original Hanau, chamber temperature 25–30°C, black panel temperature 60°C, relative humidity

50–60%, dark glass (UV filter system) for 40 h. The changes in color were assessed according to the blue scale: 1 – poor, 3 – moderate, 5 – good, 8 – very good.

Color assessment

The color parameters of the dyed fabric (Table 2) were determined on a spectro multichannel photo detector (model MCPD-110A), equipped with a D65/10° source and $BaSO_4$ as a standard blank. The color of the dyed fabric was assessed in terms of tristimulus colorimetry. The values of the chromaticity coordinates, luminance factor and the positions of colors in the CIELAB color solid are reported.

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References

1. Town AD (1999) Dyes Pigm 42:3
2. Annen O, Egli R, Hasler R, Henzi B, Jakob H, Matzinger P (1987) Rev Prog Color 17:72
3. Egli R (1999) In: Peters AT, Freeman HS (eds) Colour chemistry. The design and synthesis of organic dyes and pigments. Elsevier, London, Chapter 1
4. Ho YW, Yao WH (2006) Dyes Pigm 70:60
5. Ho YW (2005) Dyes Pigm 64:223
6. Maradiya HR, Patel VS (2002) Chem Heterocycl Comp 38:1324
7. Hallas G, Towns AD (1997) Dyes Pigm 35:219
8. Hallas G, Towns AD (1997) Dyes Pigm 33:319
9. Hallas G, Towns AD (1996) Dyes Pigm 32:135
10. Hallas G, Choi J-H (1999) Dyes Pigm 40:99
11. Hallas G, Choi J-H (1999) Dyes Pigm 40:119
12. Hallas G, Choi J-H (1999) Dyes Pigm 42:249
13. Metwally MA, Abdel-latif E, Amer FA (2003) Sulfur Lett 26:119
14. Harhash AH, Amer FA, Eldin MAN, Awad ML (1976) Z Naturforsch 31B:846
15. Silverstein RM, Bassler GC, Morrill TC (1981) Spectrometric identification of organic compounds, 4th edn. John Wiley and Sons, New York, p 311
16. Gordon PF, Gregory P (1983) Organic chemistry in colour. Springer, Berlin, p 289
17. Anon (1990) Standard methods for the determination of the color fastness of textiles and leather, 5th edn. Society of Dyes and Colorists Publication, Bradford, England