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Substituted 5-Antipyrinylazo-4-phenyl-2-aminothiazoles as Disperse Dyes for Dyeing Polyester Fabrics

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Summary. A series of some new substituted 5-antipyrinylazo-4-phenyl-2-aminothiazole disperse dyes was synthesized by diazocoupling of 4-antipyrinyldiazonium chloride with aminothiazole derivatives. The synthesized dyes were characterized by UV-Vis absorption, IR, ^{1}H NMR, and MS spectroscopy. The dyes gave orange to reddish-violet shades with very good depth and levelness when applied to polyester fabrics as disperse dyes and their fastness properties were evaluated on polyester fibers. Also the position of color in CIELAB coordinates (L^*, a^*, b^*, H^*, and C^*) was assessed.

Keywords. Antipyrine; Thiazole; Disperse dyes; Polyester fabrics; Fastness properties.

Introduction

In recent years, efforts have been made to replace certain anthraquinone dyes with technically equivalent azo dyes, for both environmental and economic reasons [1]. In this regard, azo dyes based on heterocyclic amines have been developed, and the resultant dyes have higher tinctorial strength and give brighter dyeings than those derived from aniline-based diazo components. For instance, amino-substituted thiazole, isothiazole, thiophene, and pyrazole compounds afford very electronegative diazo components and, consequently, provide a pronounced bathochromic effect compared to the corresponding benzenoid compounds [2–4].

The aminopyrazole compounds are very useful as precursors for the synthesis of fused heterocyclic ring systems, which play an important role in biological and pharmacological activities [5–7], and they can also be used as intermediates in the dyestuff industry [8, 9]. In continuation of our previous work [10–13] on the synthesis of disperse dyes for dyeing polyester fabrics, the present work describes the synthesis of several new antipyrinylazothiazole derivatives and their applications as azo-disperse dyes for dyeing polyester fabrics.

Results and Discussion

Synthesis of Substituted 5-Antipyrinylazo-4-phenyl-2-aminothiazole Dyes

4-Aminoantipyrine was reacted with sodium nitrite and hydrochloric acid to give the corresponding 4-antipyrinyldiazonium chloride **1**. The synthetic potential of **1** was investigated in the present study through its reactions with several diazocoupling components. Thus, a series of 2-amino-5-antipyrinylazothiazole dyes **4** and **5** was prepared through diazocoupling of 4-antipyrinyldiazonium chloride **1** with 2-aminothiazole derivatives **2**. The diazocoupling reaction proceeds under slightly basic condition in ethanol buffered with sodium acetate. The structure of the highly functionalized 5-antipyrinylazothiazole dyes **4** and **5** was assigned on the basis of spectral data. The IR spectrum of dye **4** exhibited bands at 3421, 3270 cm^{-1} corresponding to an NH$_2$ group, and at 1639 cm^{-1} corresponding to a CO group (pyrazole ring). The ^{1}H NMR spectrum of **4**

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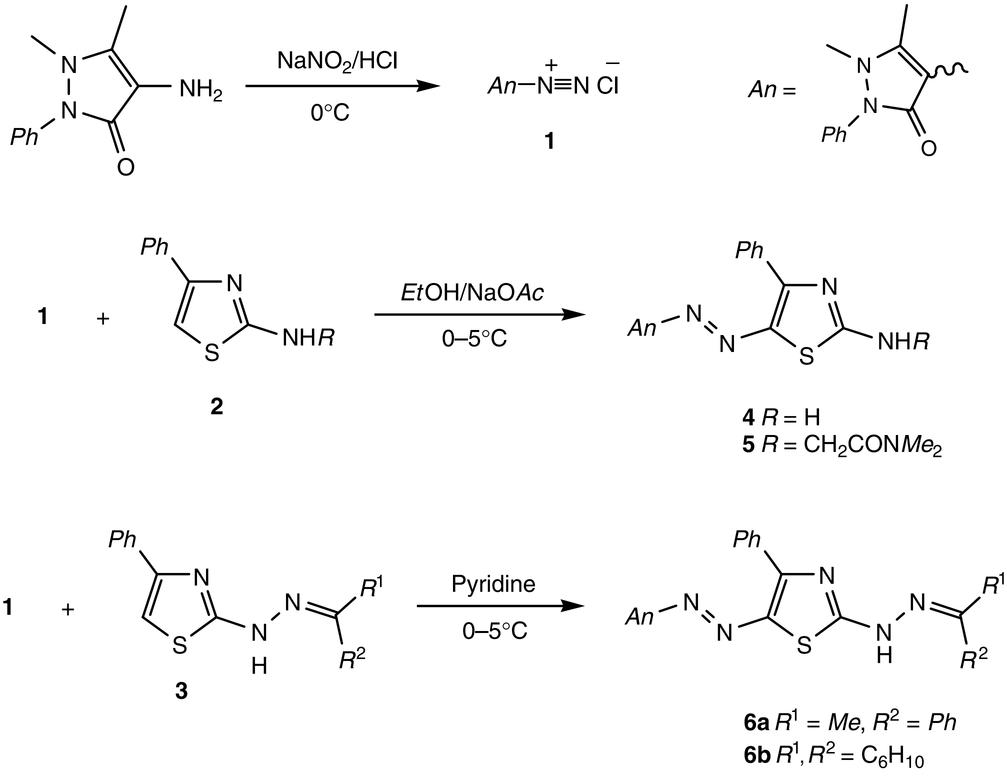


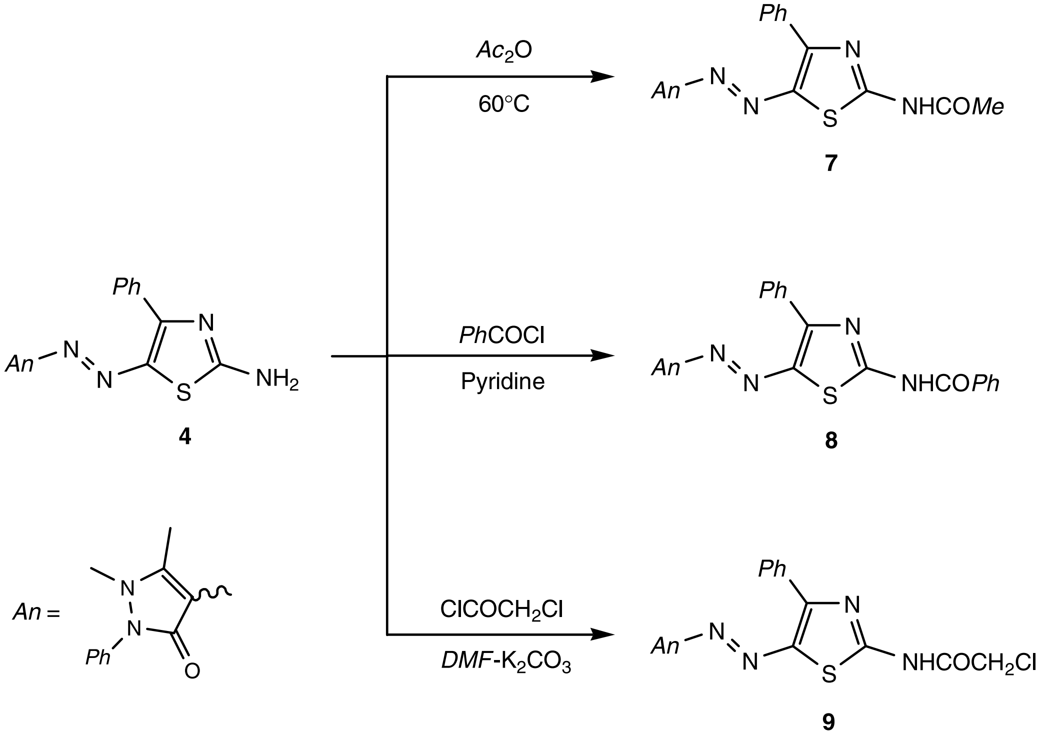
Scheme 1

displayed a singlet signal at $\delta = 2.50$ ppm due to the methyl protons (CH_3–C=C), a singlet signal at $\delta = 3.30$ ppm due to the methyl protons (CH_3–N), a multiplet signal in the region $\delta = 7.35$–7.85 ppm due to the aromatic protons, and a doublet signal at $\delta = 8.45$ ppm due to the amino protons (NH_2).

The thiazole C-5 position in 4-phenyl-2-thiazolylhydrazone derivatives **3** [14, 15] is highly reactive to diazocoupling with the antipyrinyldiazonium chloride **1** and furnishes the corresponding antipyrinylazothiazole dyes **6** (Scheme 1). The structure of the highly functionalized thiazolyl dyes **6** was assigned on the basis of spectral data. The IR spectra of dyes **6** clearly indicate the presence of an NH absorption band at 3154–3135 cm^{-1} and a CO absorption band at 1664–1649 cm^{-1}. The ^1H NMR spectrum of **6a** revealed the presence of singlet signals at $\delta = 2.40$, 2.60, and 3.30 ppm for the methyl protons, a multiplet signal at $\delta = 7.10$–7.80 ppm due to the aromatic protons, and a singlet at $\delta = 8.25$ ppm due to the NH proton.

2-(Acetylamino)-5-(antipyrinylazo)-4-phenylthiazole **7** was synthesized by treatment of the corresponding 2-amino-5-antipyrinylazothiazole **4** with acetic anhydride at 60°C. The spectral data of the antipyrinylazothiazole derivative **7** were consistent with the assigned structure. The IR spectrum of **7** revealed intense bands at 3443 cm^{-1} (NH, amide), 1690 cm^{-1} (CO, amide), and 1637 cm^{-1} (CO, pyrazole ring). The ^1H NMR spectrum of **7** displayed a singlet signal at $\delta = 1.75$ ppm due to the methyl protons (CH_3CO), a singlet signal at $\delta = 2.65$ ppm due to the methyl protons (CH_3–C=C), a singlet signal at $\delta = 3.10$ ppm due to the methyl protons (CH_3–N), a multiplet signal in the region $\delta = 7.25$–7.90 ppm due to the aromatic protons, and a singlet signal at $\delta = 12.50$ ppm due to the imino proton (NH).

2-Amino-5-antiyrinylazothiazole **4** was treated with benzoyl chloride in dry pyridine (*Schotten-Baumann* method) to give the corresponding 2-(benzoylamino)-5-antipyrinylazothiazole **8** as a highly colored compound. Assignment of the product was based on its spectral data. The IR spectrum of the antipyrinylazothiazole derivative **8** is characterized by the presence of a strong absorption band of the NH group at 3434 cm^{-1} and a strong broad absorption band of the carbonyl groups at 1660 cm^{-1}. The ^1H NMR spectrum of **8** revealed a singlet signal at $\delta = 2.65$ ppm for the methyl protons (CH_3–C=C), a singlet signal at $\delta = 2.90$ ppm for the methyl protons



Scheme 2

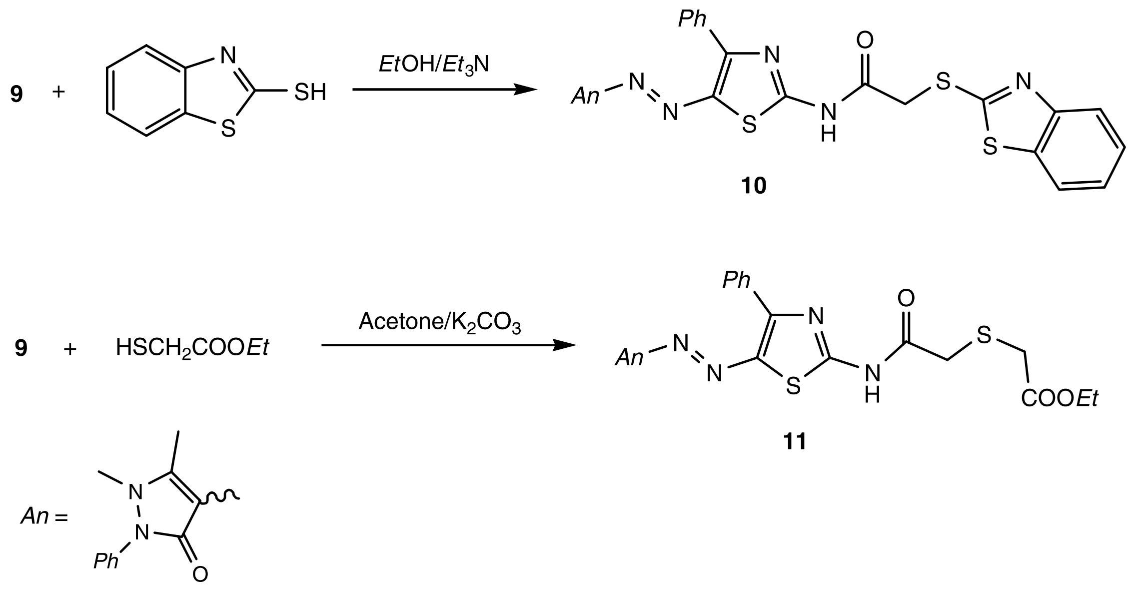
(CH_3–N), a multiplet in the region $\delta = 7.30$–8.15 ppm for the aromatic protons, and a singlet signal for the imino proton (NH) at $\delta = 12.80$ ppm.

2-Amino-5-antiyrinylazothiazole **4** was reacted with chloroacetyl chloride in *DMF* containing drops of triethylamine to give the corresponding 2-[(chloroacetyl)amino]-5-antiyrinylazothiazole **9**. The structure of the synthesized compound was secured on the basis of spectral data (IR and NMR spectra). The infrared spectrum revealed absorption bands at 3500 cm^{-1} assignable to the NH stretching, 1713 cm^{-1} assignable to the carbonyl stretching (CO, amide), and 1636 cm^{-1} assignable to the carbonyl stretching (CO, pyrazole ring). The ^1H NMR spectrum of **9** showed two singlet signals at $\delta = 2.50$ and 3.30 ppm for the two methyl protons ($2CH_3$, pyrazole ring), a singlet signal at $\delta = 4.40$ ppm for the methylene protons, a multiplet at $\delta = 7.40$–7.60 ppm for the aromatic protons, and a singlet signal at $\delta = 12.70$ ppm for the imine proton (CONH).

The highly versatile 2-[(chloroacetyl)amino]thiazole **9** was used as a precursor for the synthesis of several new azo dyes through chemical modification. Thus a series of sulfide derivatives were prepared through the reaction of **9** with a variety of thiol derivatives. The 2-[(chloroacetyl)amino]thiazole **9** was reacted with 2-mercaptobenzothiazole in the presence of ethanol containing a few drops of triethylamine to afford the sulfide compound **10**. In addition, the reaction of **9** with ethyl thioglycolate in acetone and anhydrous potassium carbonate furnished the corresponding sulfide **11**.

The structure of the sulfide products **10** and **11** was established *via* inspection of their analytical and spectral data. The IR spectrum of **11** clearly indicates the appearance of an ester carbonyl group absorption band at 1725 cm^{-1}. The ^1H NMR spectrum of **10** revealed two singlet signals at $\delta = 2.60$ and 3.30 ppm for the two methyl protons ($2CH_3$, pyrazole ring), a singlet signal at $\delta = 4.18$ ppm for the methylene protons, a multiplet at $\delta = 7.30$–8.50 ppm for the aromatic protons, and a singlet signal at $\delta =$ 12.05 ppm for the imine proton (CONH).

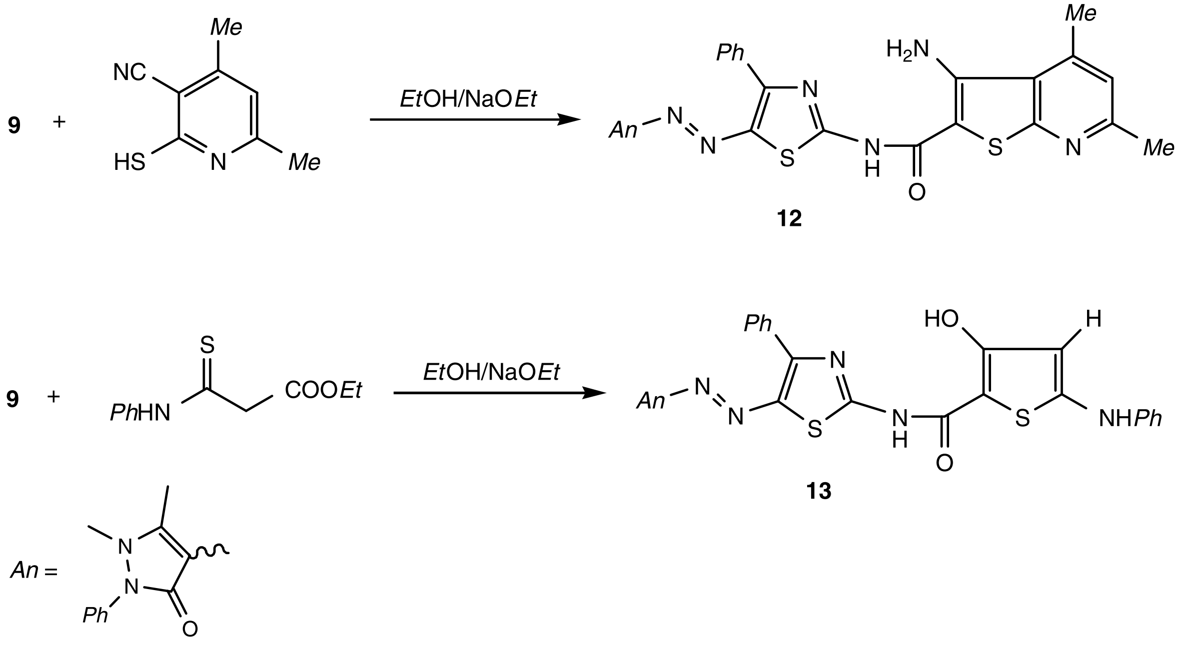
Moreover, the highly versatile 2-[(chloroacetyl)-amino]-5-antiyrinylazothiazole **9** was reacted with 4,6-dimethyl-2-mercaptonicotinonitrile by heating in a solution of ethanol containing sodium ethoxide to afford the corresponding thieno[2,3-*b*]pyridine derivative **12**. The chemical structure of **12** was established on the basis of its spectral data. The IR spectrum clearly indicated the lack of a cyano absorption band and revealed the characteristics of



Scheme 3

NH_2 and NH absorption bands at 3487, 3396, and 3309 cm^{-1} in addition to the carbonyl absorption bands at 1665 cm^{-1} (CO, amide) and 1642 cm^{-1} (CO, pyrazole ring). The ^{1}H NMR spectrum of **12** revealed the presence of singlet signals at $\delta = 2.40$, 2.70, and 3.30 ppm due to the methyl protons, a singlet signal at $\delta = 7.20$ ppm due to the pyridine C-5 proton, and the multiplet signal at $\delta = 7.40$–7.90 ppm due to the aromatic protons.

In a similar manner, the reaction of **9** with ethyl 2-phenylthiocarbamoylacetate [16] in a hot solution of ethanol containing sodium ethoxide afforded the corresponding thiophene derivative **13**. The IR spectrum of the dye **13** clearly indicates the presence of NH and OH absorption bands at 3308 and 3170 cm^{-1}. The ^{1}H NMR spectrum of **13** (in $CDCl_3$/CF_3COOD) revealed the presence of singlet signals at $\delta = 2.60$ and 3.25 ppm for the methyl protons, a



Scheme 4

singlet at $\delta = 6.55$ ppm due to the thiophene C-4 proton, and a multiplet signal at $\delta = 7.25$–7.80 ppm due to the aromatic protons.

Absorption Spectroscopic Characteristics

Absorption maxima of the synthesized dyes **4–13** were measured in chloroform and are listed in Table 2. Generally, variation in color of these dyes results from the alternation in coupling components. The absorption maxima of the dyes (412–494 nm) tend to give the following results: (i) The introduction of a $-CH_2CON(CH_3)_2$ group into the coupling component of the dye **4** ($\lambda_{max} = 444$) causes bathochromic shift in the dye **5** ($\lambda_{max} = 466$) by 22 nm. (ii) The dye **6a** ($\lambda_{max} = 494$) substituted with a phenylethylidene group absorbs maximally at longer wavelength than the corresponding dye with a cyclohexylidene group **6b** ($\lambda_{max} = 460$). (iii) The introduction of acetyl, benzoyl, or chloroacetyl groups into the coupling component of dye **4** ($\lambda_{max} = 444$) results in hypsochromic shift in the dyes **7** ($\lambda_{max} = 412$), **8** ($\lambda_{max} = 436$), and **9** ($\lambda_{max} = 428$).

Dyeing and Fastness Properties

The functionalized 4-antipyrinylazothiazole disperse dyes **4–13** were applied to polyester fabrics at 2% shade by high-temperature pressure technique (130°C) and gave generally deep and bright hues, ranging from orange to reddish-violet. The dyeings on polyester fabrics were evaluated in terms of their fastness properties using standard methods [17]. The results are given in Table 1 and revealed that these dyes have good fastness properties to washing, perspiration, rubbing, and sublimation with little variation in the moderate to good light fastness.

Table 1. Fastness properties of the dyes **4–13** on polyester fabrics

Dye	Washing	Perspiration		Rubbing		Sublimation fastness		Light (40 h)
		Acid	Alkali	Dry	Wet	Staining at 180°C	Staining at 210°C	
4	4–5	4–5	4–5	4	4–5	4–5	4–5	3
5	4–5	4–5	4–5	4	4	4–5	4–5	3
6	4–5	4–5	4–5	2–3	2–3	4–5	4–5	2–3
6b	4–5	4	4	2–3	2–3	3	3	2–3
7	4–5	4–5	4–5	4–5	4–5	4–5	4–5	3–4
8	4–5	4–5	4–5	2	3–4	4–5	4–5	3–4
9	4–5	4–5	4–5	4	4	4–5	4–5	5–6
10	4–5	4–5	4	2	2–3	4–5	2–3	5
11	4–5	4–5	4–5	4	4	4–5	4	3
12	4	4–5	4	3	4–5	4–5	4–5	2–3
13	4–5	4–5	4	2	2–3	4–5	4–5	2–3

Table 2. UV-Vis spectroscopic data and color coordinates of the dyes **4–13** (light source = D65/10° observer)

Dye	λ_{max}/nm	Color coordinates					K/S
		L*	C*	H*	a*	b*	
4	444	69.70	65.70	69.10	23.50	61.40	3.23
5	466	73.30	49.50	62.10	23.20	43.80	1.32
6	494	58.20	9.90	46.80	6.80	7.20	0.66
6b	460	54.40	43.90	70.20	14.9	41.30	3.70
7	412	58.40	32.20	91.80	−0.99	32.20	0.37
8	436	80.40	45.40	76.80	10.40	44.20	0.71
9	428	78.60	56.80	75.00	14.70	54.90	1.19
10	426	76.50	43.50	66.20	17.50	39.80	0.73
11	440	75.50	70.90	73.70	19.90	77.00	2.39
12	456	84.10	25.00	77.30	5.50	24.40	0.22
13	440	67.00	53.50	67.60	20.40	49.50	2.16

Color Assessment

The color of a dyeing on polyester fibers is expressed in terms of CIELAB values (Table 2) and the following CIELAB coordinates are measured, lightness (L^*), chroma (C^*), hue angle from 0° to 360° (H), a^* value represents the degree of redness (positive) and greenness (negative) and b^* represents the degree of yellowness (positive) and blueness (negative).

A reflectance spectrophotometer (*Gretag Macbeth* CE 7000a) was used for the colorimetric measurements on the dyed samples. K/S values given by the reflectance spectrometer are calculated at $\lambda_{\max}$ and are directly correlated with the dye concentration on the dye substrate according to the *Kubelka–Munk* equation: $K/S = (1-R)^2/2R$, where K = absorbance coefficient, S = scattering coefficient, R = reflectance ratio.

The color coordinates (Table 2) indicate that the dyes have good affinity to polyester fabrics and tend to give the following conclusions: (i) The dyes under investigation showed good affinity towards polyester fabrics at high temperature (130°C) and gave generally deep and bright intense hues, ranging from orange to reddish violet. (ii) The color hues of the dyes under investigation on polyester fabrics are shifted to the yellowish direction on the yellow–blue axis according to the positive values of b^*. (iii) The color hue of dye **7** on polyester fabrics is shifted to the greenish direction on the red–green axis as indicated from the negative value of a^* (-0.99). (iv) The color hues of the other synthesized dyes on polyester fabrics are shifted to the reddish direction on the red–green axis as according to the positive values of a^* for these dyes.

In conclusion, a set of eleven useful disperse dyes **4**–**13** was synthesized by azocoupling of 4-antipyrinyldiazonium chloride with a variety of aminothiazole derivatives. The dyes were investigated for their dyeing characteristics on polyester and showed good washing, perspiration, rubbing, and sublimation fastness properties, with little variation in the moderate to good light fastness.

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 chloroform as a 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 (electron impact: 70 eV). 4-Aminoantipyrine and 4,6-dimethyl-2-mercaptonicotinonitrile were purchased from Fluka and used without purification. Ethyl 2-phenylthiocarbamoylacetate [16] was prepared according to the reported method.

2-Amino-5-antipyrinylazo-4-phenylthiazoles ***4*** *and* ***5***

The antipyrinyldiazonium chloride **1** was prepared by adding cold sodium nitrite solution (0.7 g in 10 cm^3 H_2O) to a cold suspension of 0.01 mol 4-aminoantipyrine in 3 cm^3 concentrated HCl with stirring. The freshly prepared antipyrinyldiazonium chloride **1** solution was added with continuous stirring to a cold solution (0–5°C) of 0.01 mol 2-amino-4-phenylthiazole derivatives **2** in 50 cm^3 ethanol and 4.0 g sodium acetate. The reaction mixture was allowed to stand in cold for 2 h, diluted with water, and then filtered. 2-Amino-5-antipyrinylazothiazoles **4** and **5** thus obtained were dried and recrystallized from ethanol.

2-Amino-5-antipyrinylazo-4-phenylthiazole (**4**, $C_{20}H_{18}N_6OS$)

Yield 92%; mp 270–271°C (*Et*OH); IR (KBr): $\bar{\nu}$ = 3421, 3270 (NH_2), 1639 (CO) cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): δ = 2.50 (s, CH_3), 3.30 (s, CH_3), 7.35–7.85 (m, *Ar*′H), 8.45 (d, NH_2) ppm.

2-(5-Antipyrinylazo-4-phenylthiazol-2-ylamino)-N,N-dimethylacetamide (**5**, $C_{24}H_{25}N_7O_2S$)

Yield 82%; mp 265–266°C (*Et*OH:*DMF* = 2:1); IR (KBr): $\bar{\nu}$ = 3312 (NH), 1664 (CO), 1642 (CO) cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): δ = 2.40 (s, CH_3), 3.00 (s, 2CH_3), 3.20 (s, CH_3), 4.20 (s, CH_2), 6.90 (s, NH), 7.20–7.80 (m, *Ar*′H) ppm.

N-(4-Substituted 5-Antipyrinylazothiazol-2-yl)-N′-(1-aryl-ethylidene)hydrazine Dyes ***6***

To a cold solution (0–5°C) of 5 mmol thiazole derivatives **3** in 30 cm^3 pyridine, a cold solution of 5 mmol freshly prepared antipyrinyldiazonium chloride **1** was added with continuous stirring. The reaction mixture was allowed to stand in cold for 2 h, diluted with water, and then filtered. The antipyrinylazothiazole dyes **6** thus obtained were dried and recrystallized from ethanol.

N-(5-Antipyrinylazo-4-phenylthiazol-2-yl)-N′-(1-phenyl-ethylidene)hydrazine (**6a**, $C_{28}H_{25}N_7OS$)

Yield 71%; mp 270–271°C (*Et*OH:*DMF* = 2:1); IR (KBr): $\bar{\nu}$ = 3140 (NH), 1650 (CO) cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): δ = 2.40 (s, CH_3), 2.60 (s, CH_3), 3.30 (s, CH_3), 7.10–7.80 (m, *Ar*′H), 8.25 (s, NH) ppm; MS (M^+): m/z (%) = 507 (87).

N-(Cyclohexylidene)-N′-(5-antipyrinylazo-4-phenylthiazol-2-yl)hydrazine (**6b**, $C_{26}H_{27}N_7OS$)

Yield 73%; mp 231–232°C (*Et*OH); IR (KBr): $\bar{\nu}$ = 3154 (NH), 1649 (CO) cm^{-1}.

Synthesis of 2-Acetylamino-5-antipyrinylazo-4-phenylthiazole (**7**, $C_{22}H_{20}N_6O_2S$)

A mixture of 3 mmol 2-amino-5-antipyrinylazothiazole (**4**) and 3 cm^3 acetic anhydride was heated in an oil bath at 60–65°C for 1 h. The reaction mixture was allowed to cool at room temperature and then recrystallized from ethanol. Yield 77%; mp 233–235°C; IR (KBr): $\bar{\nu} = 3443$ (NH), 1690 (CO), 1637 (CO) cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): $\delta =$ 1.75 (s, CH_3), 2.65 (s, CH_3), 3.10 (s, CH_3), 7.25–7.90 (m, *Ar'*H), 12.50 (s, NH) ppm.

2-Benzoylamino-5-antipyrinylazo-4-phenylthiazole (**8**, $C_{27}H_{22}N_6O_2S$)

A mixture of 3 mmol 2-amino-5-antipyrinylazothiazole (**4**) and 0.45 cm^3 benzoyl chloride (4 mmol) was stirred in 15 cm^3 pyridine at room temperature. The reaction mixture was diluted by a solution of sodium acetate and then filtered. The 2-benzoylamino-5-antipyrinylazothiazole thus obtained was dried and recrystallized from ethanol:*DMF* mixture (2:1). Yield 71%; mp 260–262°C; IR (KBr): $\bar{\nu} = 3434$ (NH), 1660 (broad, 2 CO) cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): $\delta = 2.65$ (s, CH_3), 2.90 (s, CH_3), 7.30–8.15 (m, *Ar'*H), 12.80 (s, NH) ppm.

2-[N-(Chloroacetyl)amino]-5-antipyrinylazo-4-phenylthiazole (**9**, $C_{22}H_{19}ClN_6O_2S$)

To a solution of 0.01 mol 2-amino-5-antipyrinylazothiazole (**4**) in 25 cm^3 *DMF* containing 0.5 cm^3 triethylamine, 0.015 mol chloroacetyl chloride was added dropwise with stirring at room temperature. Stirring was continued for 2 h and the reaction mixture was poured into ice-cooled water. The precipitate which formed was collected by filtration, dried, and recrystallized from ethanol. Yield 74%; mp 205–206°C; IR (KBr): $\bar{\nu} = 3500$ (NH), 1713 (CO), 1636 (CO) cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): $\delta = 2.50$ (s, CH_3), 3.30 (s, CH_3), 4.40 (s, CH_2), 7.40–7.60 (m, *Ar'*H), 12.70 (s, NH) ppm.

2-(Benzothiazol-2-ylsulfanyl)-N-(5-antipyrinylazo-4-phenylthiazol-2-yl)acetamide (**10**, $C_{29}H_{23}N_7O_2S_3$)

A mixture of 3 mmol 2-chloroacetylamino-5-antipyrinylazothiazole (**9**) and 3 mmol 2-mercaptobenzothiazole was refluxed for 3 h in 50 cm^3 ethanol containing drops of triethylamine. The solid product that separated on cooling was filtered off and crystallized from ethanol:*DMF* mixture (2:1). Yield 83%; mp 165–167°C; IR (KBr): $\bar{\nu} = 3164$ (NH), 1677 (CO), 1644 (CO) cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): $\delta = 2.60$ (s, CH_3), 3.30 (s, CH_3), 4.18 (s, CH_2), 7.30–8.50 (m, *Ar'*H), 12.05 (s, NH) ppm.

Ethyl [(5-antipyrinylazo-4-phenylthiazol-2-ylcarbamoyl)-methylsulfanyl]acetate (**11**, $C_{26}H_{26}N_6O_4S_2$)

A mixture of 3 mmol 2-chloroacetylamino-5-antipyrinylazothiazole (**9**), 3 mmol ethyl thioglycolate, and 3 mmol anhydrous K_2CO_3 in 30 cm^3 acetone was refluxed for 2 h. The excess acetone was evaporated under reduced pressure. The residue was washed with water and recrystallized from ethanol to afford **11** as red crystals. Yield 64%; mp 195–196°C; IR (KBr): $\bar{\nu} = 3177$ (NH), 1726 (CO), 1657 (broad, 2CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.30$ (t, CH_3), 2.50 (s, CH_3), 3.20 (s, CH_3), 4.20 (s, CH_2), 4.35 (q, CH_2), 4.65 (s, CH_2), 7.20–7.60 (m, *Ar'*H), 11.65 (s, NH) ppm.

3-Amino-4,6-dimethyl-N-(4-phenyl-5-antipyrinylazo-2-thiazolyl)thieno[2,3-b]pyridine-2-carboxamide (**12**, $C_{30}H_{26}N_8O_2S_2$)

A mixture of 5 mmol 2-chloroacetylamino-5-antipyrinylazothiazole (**9**) and 5 mmol 4,6-dimethyl-2-mercaptonicotinonitrile was refluxed in sodium ethoxide solution (prepared from 0.12 g Na metal in 30 cm^3 absolute ethanol). The solution was refluxed for 2 h, left to cool, and diluted with 50 cm^3 cold water. The solid obtained was filtered off and recrystallized from ethanol. Yield 91%; mp >300°C; IR (KBr): $\bar{\nu} =$ 3487, 3396, 3309 (NH_2 and NH), 1665 (CO), 1642 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3/CF_3COOD$): $\delta = 2.40$ (s, CH_3), 2.70 (s, $2CH_3$), 3.30 (s, CH_3), 7.20 (s, pyridine H-5), 7.40–7.90 (m, *Ar'*H) ppm; MS (M^+): m/z (%) = 595 (52).

3-Hydroxy-5-anilino-N-(4-phenyl-5-antipyrinylazo-2-thiazolyl)thiophene-2-carboxamide (**13**, $C_{31}H_{25}N_7O_3S_2$)

A mixture of 5 mmol 2-chloroacetylamino-5-antipyrinylazothiazole (**9**) and 5 mmol ethyl 2-phenylthiocarbamoylacetate was refluxed in sodium ethoxide solution (prepared from 0.12 g Na metal in 30 cm^3 absolute ethanol). The solution was refluxed for 2 h, left to cool, and diluted with 50 cm^3 cooled water. The solid obtained was filtered off and recrystallized from ethanol. Yield 63%; mp 229–231°C; IR (KBr): $\bar{\nu} = 3308$ (NH), 3170 (OH), 1653 (broad, 2CO) cm^{-1}; ^{1}H NMR ($CDCl_3/CF_3COOD$): $\delta = 2.60$ (s, CH_3), 3.25 (s, CH_3), 6.55 (s, thiophene H-4), 7.25–7.80 (m, *Ar'*H) ppm.

Dyeing Procedure

A dispersion of the dye was produced by dissolving the appropriate amount of dye (2% shade) in 1 cm^3 acetone and then added dropwise with stirring to the dyebath (liquor ratio 20:1) containing 1% Setamol WS (sodium salt of a condensation product of naphthalenesulfonic acid and formaldehyde) as anionic dispersing agent of BASF. The *pH* of the dyebath was adjusted to 5.5 using aqueous acetic acid and the wetted-out polyester fibers were added. Dyeing was performed by raising the dyebath temperature to 130°C at a rate of 3°C/min, holding at this temperature for 60 min, and rapidly cooling to 50°C. The dyed fibers was 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 collected in Table 1.

(i) *Fastness to Washing.* A specimen of dyed polyester sample was stitched between two pieces of undyed cotton and polyester fabrics (10 cm × 4 cm), all of equal weight and then washed at 50°C for 30 min. The staining of adjacent fabrics was assessed using the grey scale: 1 – poor, 2 – fair, 3 – moderate, 4 – good, 5 – excellent.

(ii) *Fastness to Perspiration.* 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 fabrics 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 ($10\,\mathrm{g\,dm^{-3}}$), lactic acid ($1\,\mathrm{g\,dm^{-3}}$), disodium orthophosphate ($1\,\mathrm{g\,dm^{-3}}$), and histidine monohydrochloride ($0.25\,\mathrm{g\,dm^{-3}}$). The alkaline solution ($pH = 8$) contained sodium chloride ($10\,\mathrm{g\,dm^{-3}}$), ammonium chloride ($4\,\mathrm{g\,dm^{-3}}$), disodium orthophosphate ($1\,\mathrm{g\,dm^{-3}}$), and histidine monohydrochloride ($0.25\,\mathrm{g\,dm^{-3}}$).

(iii) *Fastness to Rubbing.* The dyed polyester fibers were placed on the base of Crockmeter, so that it rested flat on the abrasive cloth with its long dimension in the direction of rubbing. A square of white testing cloth was mount over the end of the finger which protects downward on the dry specimen sliding back and forth twenty times by making ten complete turns of the crank at the rate of one turn per second. For wet rubbing test, the testing squares were thoroughly wet in distilled water and squeezed between filter papers through hand wringer under standard conditions. The rest of the procedure is the same as the dry crocking test.

(iv) *Fastness to Sublimation.* Sublimation fastness was measured with an iron tester (*Yasuda* no. 138). The dyes samples were stitched between two pieces of undyed polyester, all of equal length, and then treated at 180 and 210°C each for 1 min.

(v) *Fastness to Light.* 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 hours. The changes in color were assessed according to the blue scale: 1 – poor, 3 – moderate, 5 – good, 8 – very good.

Color Assessment

The colorimetric parameters (Table 2) of the dyed polyester fibers were determined on a reflectance spectrophotometer (*GretagMacbeth* CE 7000a), equipped with a D65/10° source and barium sulfate as standard blank, UV excluded, specular component included, and three repeated measurements average settings.

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