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Synthesis of some new azo pyrazolo[1,5-*a*]pyrimidine-thieno[2,3-*b*] pyridine derivatives and their application as disperse dyes

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Abstract

The 3-amino-4,6-disubstituted-thieno[2,3-*b*]pyridines were diazotized and coupled with 3-aminocrotononitrile to give the 3-(2-hydrozone-3-ketimino-butyronitrile)-4,6-disubstituted-thieno[2,3-*b*]pyridines which can react with 85% excess hydrazine hydrate to afford the corresponding 3-(5-amino-3-methyl-pyrazol-4-yl)-azo-4,6-disubstituted-thieno[2,3-*b*]pyridines. The 3-(2-methyl-5,7-disubstituted-pyrazolo[1,5-*a*]pyrimidine-3-yl)azo-4,6-disubstituted-thieno[2,3-*b*]pyridine dyes were obtained by the cyclocondensation reaction of 3-(5-amino-3-methyl-pyrazol-4-yl)-azo-4,6-disubstituted-thieno[2,3-*b*]pyridines with the appropriate 1,3-diketones under acidic condition. The dyes were applied to polyester fibers and their spectral characteristics and fastness properties measured.

Keywords: 3-Amino-4,6-disubstituted-thieno[2,3-*b*]pyridines; Azo pyrazolothieno-[2,3-*b*]pyridines; Azo pyrazolo[1,5-*a*]pyrimidine-thieno[2,3-*b*] pyridine dyes; Synthesis; Heterocyclic monoazo dyes; Fastness properties

1. Introduction

Pyrazole derivatives are important intermediates that possess biological and pharmacological activities [1–8] and also find application in photography [21,22] and as dyes [9,10]. We have previously reported the synthesis of novel heterocyclic systems such as 3-(aryl or hetaryl)azo-thieno[2,3-*b*]pyridines from 3-amino-4,6-disubstituted-thieno[2,3-*b*]pyridines [11] and 2-[[4-(arylazo)-3,5-disubstituted-pyrazol-1-yl]carbonyl]-thieno[2,3-*b*]pyridines from 3-amino-4,6-dimethyl-2-ethoxycarbonylthieno[2,3-*b*] pyridine [12] and their application to polyester and/or polyamide fibers as disperse dyes, which gave encouraging results. In continuation of our studies, we reported here the synthesis of some new azo pyrazolo [1,5-*a*]pyrimidine-thieno[2,3-*b*]pyridine dyes from 3-amino-4,6-disubstituted-thieno[2,3-*b*]pyridines; spectral characteristics and dyeing properties of the dyes are also discussed.

2. Results and discussion

2.1. Synthesis and spectral characteristics

The 3-amino-2-cyano-4,6-disubstituted-thieno[2,3-*b*] pyridines were diazotized with hydrochloric acid and solution nitrile, or with nitrosylsulfuric acid to afford the diazonium salts **1a** and **1b**, respectively. These, when coupled with 3-aminocrotononitrile **2** in sodium acetate buffered solution give the 2-cyano-3-(2-hydrozone-3-ketimino-butyronitrile)-4,6-disubstituted-thieno[2,3-*b*] pyridines **3a–b**, respectively (Scheme 1). Compounds **3a** and **3b**, when reacted with 85% excess of hydrazine hydrate **4** in refluxing ethanol give the corresponding 2-cyano-3-(5-amino-3-methyl-pyrazol-4-yl)azo-4,6-disubstituted-thieno[2,3-*b*]pyridines **5a** and **5b**, respectively

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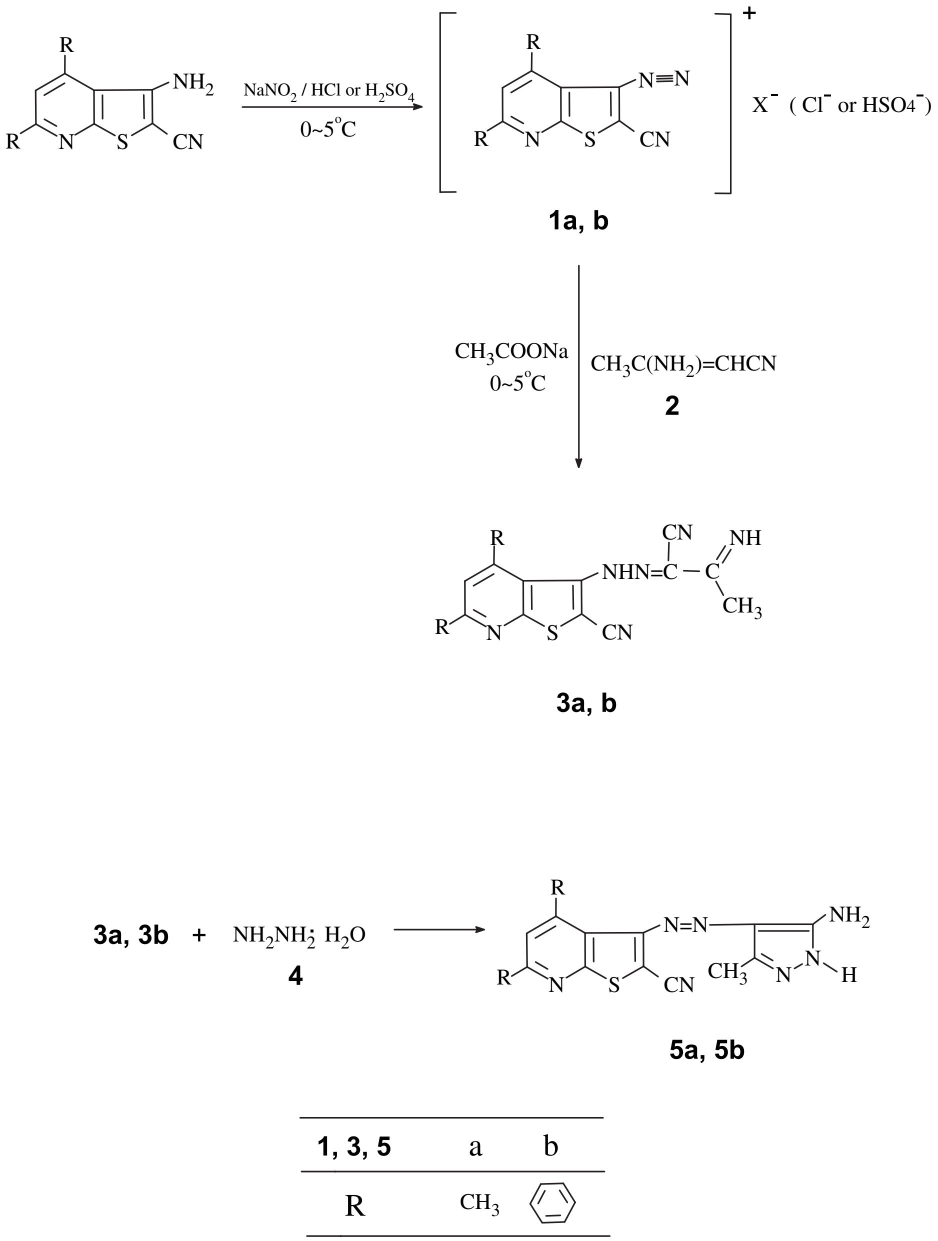
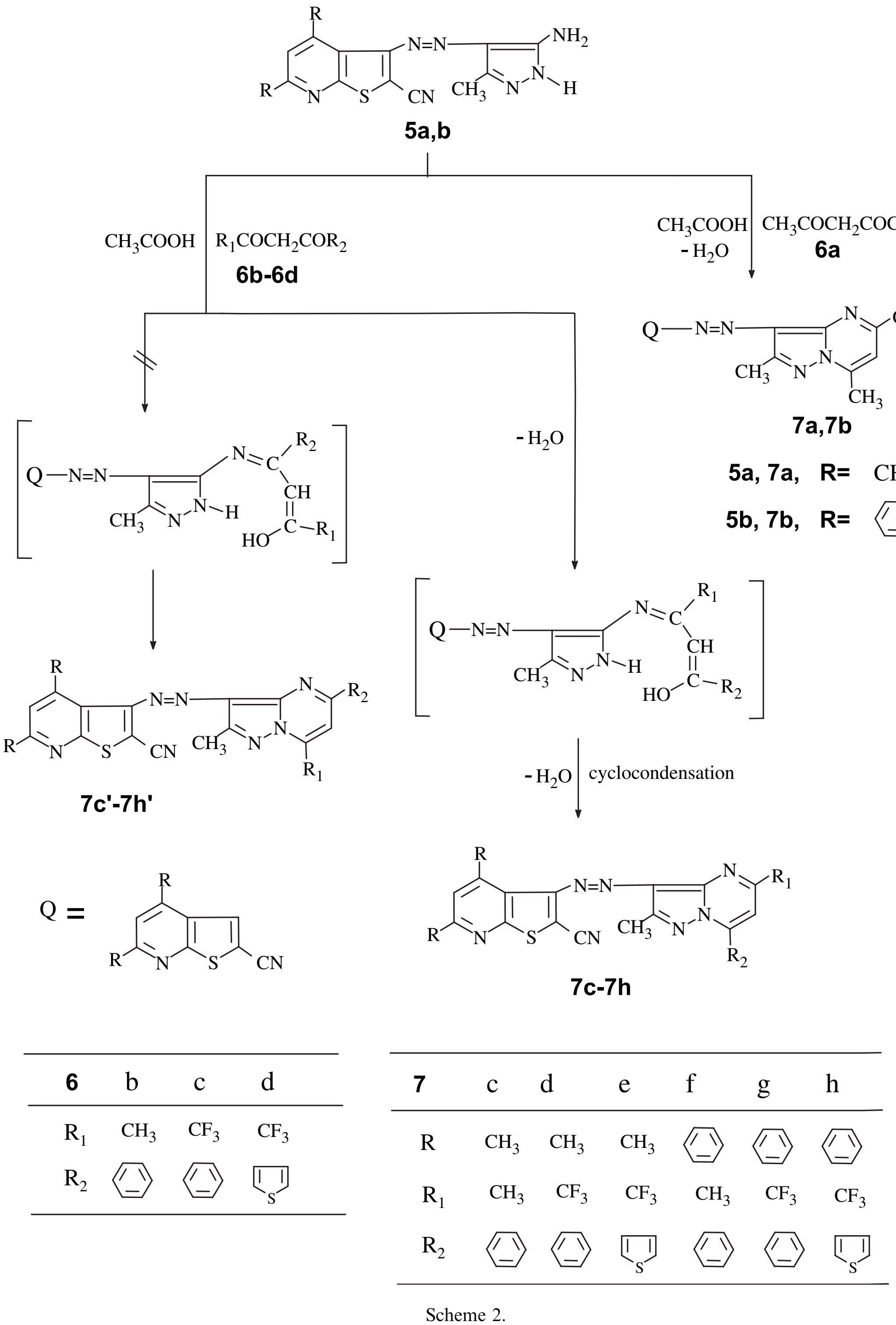


Scheme 1.

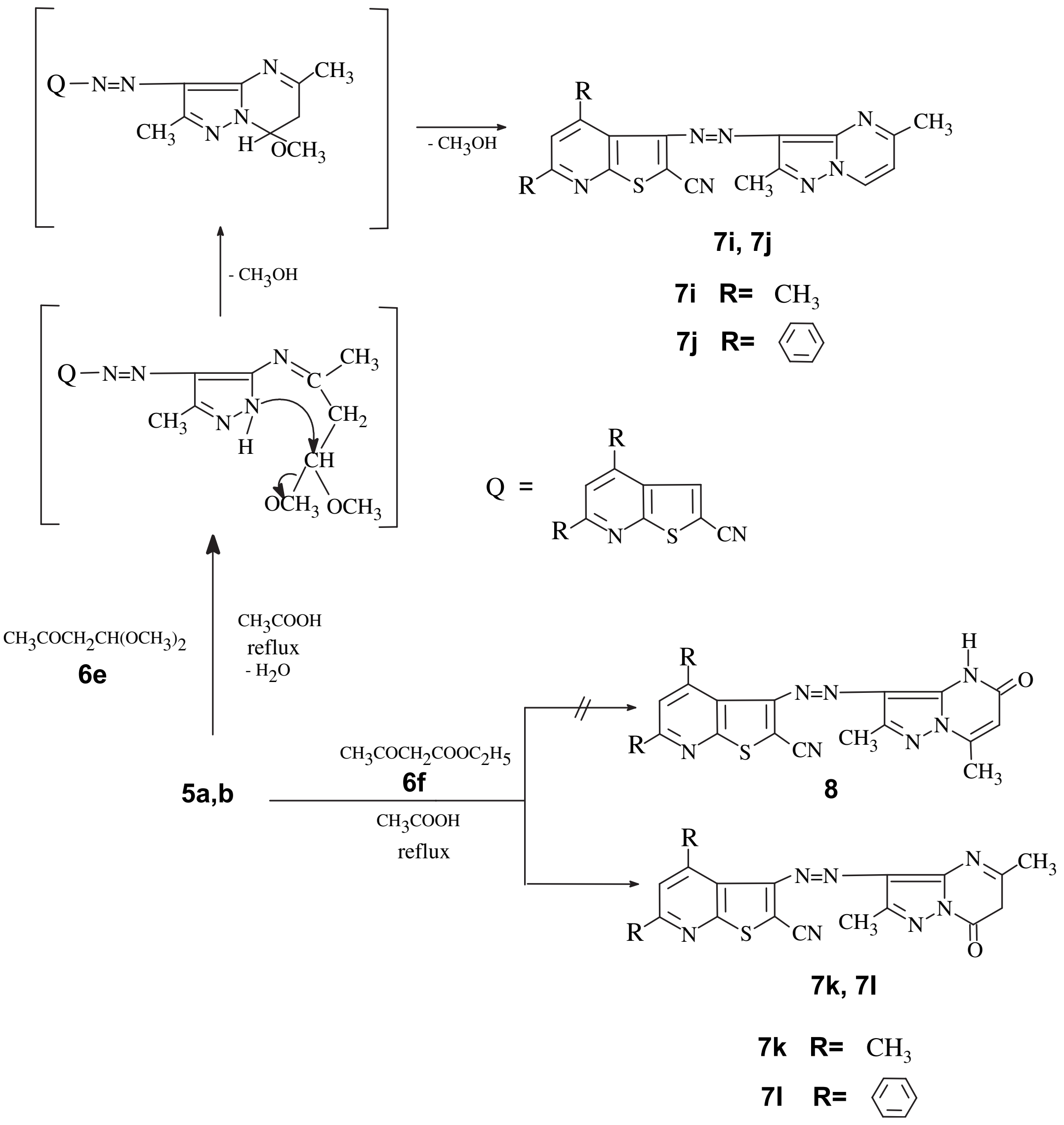
(Scheme 1). The IR spectra of compounds **5a** and **5b** showed the strong absorptions at 3447–3385 cm^{-1} for the amino group (NH$_2$), at 3240–3207 cm^{-1} for the imino group (NH) and at 2202–2200 cm^{-1} for the cyano group (C≡N). The ^{1}H NMR spectrum (CF$_3$COOD) of compounds **5a** and **5b** revealed a singlet at δ 3.00 (s, 3H) and 3.07 (s, 3H) assigned for the 3-CH$_3$ of pyrazole ring.

The reaction of compounds **5a** and **5b** with acetylacetone **6a**, in refluxing glacial acetic acid yield 2-cyano-3-(2,5,7-trimethyl-pyrazolo[1,5-*a*]pyrimidine-3-yl)-azo-4,6-disubstituted-thieno[2,3-*b*]pyridine dyes **7a** and **7b**, respectively (Scheme 2). Scheme 2 depicts the reaction of compounds **5a** and **5b** with appropriate unsymmetrical 1,3-diketones **6b**–**6d** such as 1-phenyl-1,3-butanedione **6b**, 4,4,4-trifluoro-1-phenyl-1,3-butanedione **6c** and 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione **6d**, under similar reaction conditions. The major products were 3-(2-methyl-5-R_1-7-R_2-pyrazolo[1,5-*a*]pyrimidine-3-yl)azo-4,6-dimethylthieno[2,3-*b*]pyridines **7c**–**7h** instead of the possible isomeric 3-(2-methyl-7-R_1-5-R_2-pyrazolo[1,5-*a*]-pyrimidine-3-yl)azo-4,6-dimethylthieno[2,3-*b*]pyridines **7c′**–**7h′**. The first step of the mechanism involves the condensation of the 5-NH$_2$ group of the pyrazole ring with the carbonyl group adjacent to the alkyl group, followed by dehydration, subsequent cyclization, with loss of water [13,14] (Scheme 2). Moreover, Barry [15] has reported an analogous reaction in his paper, indicating that the carbonyl group in ethyl



Scheme 2.

acetate, adjacent to the alkyl group, is relatively more reactive than the carbonyl group adjacent to the aryl (or hetaryl) ring which is in complete agreement with our observations and supports the formation of 3-(2-methyl-5-R_1-7-R_2-pyrazolo[1,5-*a*]pyrimidine-3-yl)azo-4,6-dimethylthieno[2,3-*b*]pyridines **7c**–**7h** rather than 3-(2-amino-7-R_1-5-R_2-pyrazolo[1,5-*a*]pyrimidine-3-yl)-azo-4,6-dimethylthieno[2,3-*b*]pyridines **7c′**–**7h′**. Under similar reaction conditions, condensation of compounds **5a** and **5b** with 1,1-dimethoxy-3-butanone **6e** afforded the 3-(2,5-dimethylpyrazolo[1,5-*a*]pyrimidine-3-yl)azo-4,6-disubstituted-thieno[2,3-*b*]pyridines **7i** and **7j**. The first step of the mechanism involves the condensation of the 5-NH_2 group of the pyrazole ring with the carbonyl



Scheme 3.

group, followed by dehydration, subsequent nucleophilic cyclization, with the loss of methanol [18,19] (Scheme 3). The structures of the new dyes **7a–7j** were established and confirmed on the basis of their elemental analysis, spectral data and mixed m.p. The IR spectra of dyes **7a–7j** showed the lack of the NH_2 and NH group of pyrazole moiety and the characteristic absorption band of the cyano group (C≡N) at 2220–2192 cm^{-1}. Moreover, ^1H NMR spectra (CF_3COOD) of dyes **7a–7h** revealed a singlet at δ 8.78–8.06 (s, 1H) assigned for the 6-H of pyrazolo[1,5-*a*]pyrimidine ring. The physical constants and spectral data of dyes **7a–7j** are recorded in Tables 1 and 2. The ^1H NMR spectra (CF_3COOD) revealed doublets at δ 9.32 (d, 1H) and 9.67 (d, 1H) for compound **7i**, at δ 9.23 (d, 1H) and 9.88 (d, 1H) for compound **7j**. These doublets were assigned to proton at the 6-,7-position of the pyrazolo[1,5-*a*]pyrimidine ring. On the other hand, compounds **5a** and **5b** also reacted with ethyl acetoacetate **6f** at refluxing glacial acetic acid for 10 h to yield a product for which structures **7k** and **7l** or possible isomeric **8** seemed probable (Scheme 3). Structures **7k** and **7l** were preferred on the basis of analogy to the well-established behavior of 5-aminopyrazoles toward β-ketoesters [15]. The IR spectrum of this reaction product provides further evidence for the proposed structure. Thus, its IR spectrum shows pyrimidine ring CO absorption at 1719–1711 cm^{-1}, almost identical with that reported for the pyrimidine ring absorption of 4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidines. If these compounds from **5a** and **5b** and ethyl acetoacetate **6f** is the isomeric **8**, it should present a downward shift of the frequency of the CO group due to conjugation of the CO with the $>C=C<$ [16].

Table 1
Characterization data for 2-cyano-3-(2-methyl-5,7-disubstituted-pyrazolo[1,5-*a*]-pyrimidine-3-yl)azo-4,6-disubstituted-thieno[2,3-*b*]pyridine derivatives (**7a**–**7l**)

Dye	M.p. (°C)	Yield (%)	Molecular formula	Elemental analysis (%) calcd./found		
				C	H	N
7a	276	82	$C_{19}H_{17}N_7S$	60.78	4.56	26.11
				60.34	4.41	26.36
7c	299	78	$C_{24}H_{19}N_7S$	65.89	4.38	22.41
				65.66	4.30	22.03
7d	296	68	$C_{24}H_{16}F_3N_7S$	55.06	3.08	18.74
				55.46	3.41	18.20
7e	261	91	$C_{22}H_{14}F_3N_7S_2$	53.11	2.84	19.72
				53.54	2.54	19.91
7i	294	82	$C_{18}H_{15}N_7S$	59.82	4.19	27.14
				59.81	4.09	27.22
7k	278	76	$C_{18}H_{15}N_7OS$	57.28	4.01	25.99
				57.65	4.29	25.88
7b	282	86	$C_{29}H_{21}N_7S$	69.72	4.24	19.64
				69.48	4.50	19.51
7f	145	84	$C_{34}H_{23}N_7S$	72.70	4.13	17.47
				72.89	4.45	17.57
7g	210	66	$C_{34}H_{20}F_3N_7S$	66.33	3.28	15.93
				66.79	3.49	15.49
7h	249	76	$C_{32}H_{18}F_3N_7S_2$	61.83	2.92	15.78
				61.91	3.01	15.31
7j	266	92	$C_{28}H_{19}N_7S$	69.26	3.95	20.20
				69.41	3.59	20.25
7l	244	79	$C_{28}H_{19}N_7OS$	67.05	3.82	19.56
				67.26	3.85	19.86

2.2. Absorption spectral characteristics

The absorption maxima of dyes **7a**–**7l** were recorded in DMF solution and are shown in Table 3. Their absorption maxima were in the range of 412–470 nm. The absorption maxima of dyes **7a**, **7c**–**7e**, **7i** and **7k** ranged from 424 to 470 nm and those of dyes **7b**, **7f**–**7h**, **7j** and **7l** from 412 to 451 nm. It was observed in general that dyes **7a**, **7c**–**7e**, **7i** and **7k** derived from compound **5a** were bathochromic when compared with analogous dyes **7b**, **7f**–**7h**, **7j** and **7l** derived from compound **5b**. The bathochromic shift accompanying methyl substitution of the 4,6-position results from hyperconjugation in which the σ-electrons of the methyl group are mobile enough to interact with the chromophoric group [11,24]. Color shifts are in accord with variations resultant from changes in substituents in the pyrazolo[1,5-*a*]pyrimidine ring observed in these dyes. The introduction of the trifluoromethyl group in dyes **7d** (λ_{max} 448 nm) and **7e** (λ_{max} 462 nm) resulted in bathochromic shifts of 8 and 22 nm, respectively, compared to dye **7a** (λ_{max} 440 nm). This bathochromic shift is attributed to the stronger electron-acceptor of the trifluoromethyl group with respect to the methyl group at the 5-position of the pyrazolo[1,5-*a*]pyrimidine ring, thus enhancing electron delocalisation in the dye molecule [23]. A similar behavior was apparent in dyes **7g** (λ_{max} 439 nm) and **7h** (λ_{max} 445 nm) which resulted in bathochromic shifts of 14 and 20 nm, respectively, compared to dye **7b** (λ_{max} 425 nm). On the other hand, the inductive influence of substituent in the carbonyl group at the 7-position of pyrazolo[1,5-*a*]pyrimidine ring gives greatest bathochromic shifts (**7k** and **7a**, $\Delta\lambda$, 30 nm; **7l** and **7b**, $\Delta\lambda$, 26 nm) relatable to polarisation effects [20].

2.3. Dyeing and fastness properties

The dyes **7a**–**7l** were applied to polyester fiber at 1% shade by high-temperature–pressure techniques and gave generally bright intense hues, ranging from pale yellow to orange. The fastness properties of the dyes are shown in Table 3. The lightness was determined using standard procedures [17]. For sublimation fastness determinations, the dyed polyester fibers were stitched between two pieces of undyed polyester fibers (stain cloth) and treated at 200 °C for 1 min. Any staining on the undyed piece, change in tone, or loss in depth was assessed on a 1 (poor) to 5 (very good) rating. Lightfastness of the dyeing was of a generally good order, the introduction of trifluoromethyl group in the pyrazolo[1,5-*a*]pyrimidine ring being particularly advantageous. Table 3 shows that the lightfastness of these dyes varied from 3–6, thus dye **7b** had poor lightfastness (3), dyes **7a**, **7c**, **7f** and **7j** had fair lightfastness (4), dyes **7i** and **7l** had good lightfastness (5) and dyes **7d**, **7e**, **7k**, **7g** and **7h** had very good lightfastness (6). The sublimation fastness of dyes **7a**–**7l** was in the range of

Table 2
Spectral data of 2-cyano-3-(2-methyl-5,7-disubstituted-pyrazolo[1,5-*a*]pyrimidine-3-yl)azo-4,6-disubstituted-thieno[2,3-*b*]pyridine derivatives (**7a–7l**)

Dye	MS (m/e M^+)	IR (KBr) ν (cm^{-1})	^1H NMR[a] (CF_3COOD) δ (ppm)
7a	375	2197 (C≡N)	3.16 (s, 3H, 4-CH_3), 3.26 (s, 3H, CH_3), 3.36 (s, 3H, 6-CH_3), 3.44 (s, 3H, CH_3), 3.66 (s, 3H, CH_3), 7.74 (s, 1H, 5-H), 8.06 (s, 1H, 6-H of pyrazolo[1,5-*a*]pyrimidinyl).
7c	437	2220 (C≡N)	3.14 (s, 3H, 4-CH_3), 3.25 (s, 3H, CH_3), 3.45 (s, 6H, 6-CH_3 and CH_3 of pyrazolo[1,5-*a*]pyrimidinyl), 8.06–7.94 (m, 5H, phenyl-H), 8.41 (s, 1H, 5-H), 8.43 (s, 1H, 6-H of pyrazolo[1,5-*a*]pyrimidinyl).
7d	523	2202 (C≡N)	3.46 (s, 3H, 4-CH_3), 3.75 (s, 3H, CH_3), 3.92 (s, 3H, 6-CH_3), 8.27 (m, 5H, phenyl-H), 8.41 (s, 1H, 5-H), 8.78 (s, 1H, 6-H of pyrazolo[1,5-*a*]pyrimidinyl).
7e	497	2200 (C≡N)	3.14 (s, 3H, 4-CH_3), 3.30 (s, 3H, CH_3), 3.43 (s, 3H, 6-CH_3), 7.56 (s, 1H, 5-H), 7.63 (dd, 1H, J = 1.6 and 2.0 Hz, 4-H of thienyl), 8.01 (d, 1H, J = 2.2 Hz, 3-H of thienyl), 8.23 (d, 1H, J = 1.6 Hz, 5-H of thienyl), 8.52 (s, 1H, 6-H of pyrazolo[1,5-*a*]pyrimidinyl).
7i	361	2200 (C≡N)	3.13 (s, 3H, 4-CH_3), 3.23 (s, 3H, CH_3), 3.39 (s, 3H, 6-CH_3), 3.41 (s, 3H, CH_3), 8.04 (s, 1H, 5-H), 9.32 (d, 1H, J = 1.0 Hz, 6-H of pyrazolo[1,5-*a*]pyrimidinyl), 9.67 (d, 1H, J = 2.2 Hz, 7-H of pyrazolo[1,5-*a*]pyrimidinyl).
7k	377	2192 (C≡N), 1711 (C=O)	2.98 (s, 3H, 4-CH_3), 3.32 (s, 3H, CH_3), 3.37 (s, 3H, 6-CH_3), 3.52 (s, 3H, CH_3), 8.03 (s, 1H, 5-H), 8.18 (s, 1H, 6-H of pyrazolo[1,5-*a*]pyrimidinyl).
7b	499	2210 (C≡N)	2.70 (s, 3H, CH_3), 2.93 (s, 3H, CH_3), 3.18 (s, 3H, CH_3), 7.56 (s, 1H, 5-H), 8.18–7.63 (m, 10H, phenyl-H), 8.44 (s, 1H, 6-H of pyrazolo[1,5-*a*]pyrimidinyl).
7f	561	2206 (C≡N)	2.80 (s, 3H, CH_3), 3.10 (s, 3H, CH_3), 8.46–7.72 (m, 16H, 5-H and phenyl-H), 8.56 (s, 1H, 6-H of pyrazolo[1,5-*a*]pyrimidinyl).
7g	615	2201 (C≡N)	3.01 (s, 3H, CH_3), 8.53–7.25 (m, 16H, 5-H and phenyl-H), 8.58 (s, 1H, 6-H of pyrazolo[1,5-*a*]pyrimidinyl).
7h	621	2217 (C≡N)	2.97 (s, 3H, CH_3), 7.93–7.78 (m, 11H, 4-H of thienyl and phenyl-H), 8.01 (s, 1H, 5-H), 8.21 (d, 1H, J = 2.1 Hz, 3-H of thienyl), 8.22 (d, 1H, J = 1.6 Hz, 5-H of thienyl), 8.43 (s, 1H, 6-H of pyrazolo[1,5-*a*]pyrimidinyl).
7j	485	2207 (C≡N)	3.07 (s, 3H, CH_3), 3.30 (s, 3H, CH_3), 8.84–8.05 (m, 11H, 5-H and phenyl-H), 9.23 (d, 1H, J = 1.0 Hz, 6-H of pyrazolo[1,5-*a*]pyrimidinyl), 9.88 (d, 1H, J = 2.0 Hz, 7-H of pyrazolo[1,5-*a*]pyrimidinyl).
7l	501	2201 (C≡N), 1719 (C=O)	2.49 (s, 3H, CH_3), 3.03 (s, 3H, CH_3), 8.27–7.84 (m, 11H, 5-H and phenyl-H), 8.49 (s, 1H, 6-H of pyrazolo[1,5-*a*]pyrimidinyl).

[a] Abbreviations: s, single; d, doublet; m, multiplet.

4–5, thus showed good sublimation fastness properties on polyester fibers.

3. Experimental

3.1. General

All melting points are uncorrected and in °C. IR spectra were recorded on a JASCO FTIR-3 spectrometer (KBr); ^1H NMR spectra were obtained on a Bruker AM-300 WB FI-NMR spectrometer, and chemical shifts are expressed in δ ppm using TMS as an internal standard. Electron impact mass spectra were obtained at 70 eV using a Fininigan Mat TSQ-46C spectrometer. Microanalyses for C, H, and N were performed on a Perkin–Elmer 240 elemental analyzer. Electronic spectra were recorded on a Shimadzu UV 240 from dye solutions in DMF at a concentration of 1×10^{-5} mol l^{-1}.

3.2. *2-Cyano-3-(2-hydrozone-3-ketimino-butyronitrile)-4,6-dimethyl-thieno[2,3-b]pyridine (**3a**)*

3-Amino-2-cyano-4,6-dimethylthieno[2,3-*b*]pyridine (2.03 g, 0.01 mol) was dissolved in hydrochloric acid (10 ml conc. hydrochloric acid in 10 ml water) by warming, and the solution was then cooled to 0–5 °C with stirring. Sodium nitrite (0.70 g, 0.01 mol) in water (5 ml) was gradually added to this solution over a 15 min period at 0–5 °C with stirring. The reaction mixture was stirred for an additional 30 min while maintaining a temperature of 0–5 °C. Excess nitrous acid was destroyed by the addition of urea, and the

Table 3
Absorption spectra and dyeing properties of 2-cyano-3-(2-methyl-5,7-disubstituted-pyrazolo[1,5-*a*]pyrimidine-3-yl)azo-4,6-disubstituted-thieno[2,3-*b*]pyridine derivatives (**7a–7l**)

Dye	Absorption λ_{max} in DMF (nm)	log ε	Lightfastness	Sublimation fastness
7a	440	4.71	4	4
7c	444	4.59	4	5
7d	448	4.80	6	5
7e	462	4.55	6	5
7i	424	4.72	5	5
7k	470	4.77	6	5
7b	425	4.69	3	4
7f	437	4.62	4	5
7g	439	4.45	5–6	5
7h	445	4.60	6	5
7j	412	4.96	4	5
7l	451	4.56	5	5

solution was filtered to obtain a clear diazonium salt solution **1a**.

The cold diazotized solution **1a** was then added dropwise to a well-cooled and stirred mixture of 3-aminocrotononitrile **2** (0.82 g, 0.01 mol) and sodium acetate (2.0 g dissolved in 10 ml of 50% aqueous ethanol). Stirring was continued for 4 h at 0–5 °C and the resulting crystals collected, washed with water and recrystallized from ethanol to give brown crystals (83% yield), m.p. 115 °C; IR (KBr): ν 3233 (NH), 2192 (C≡N) cm^{-1}; ^{1}H NMR (CF_3COOD): δ 2.82 (s, 3H, CH_3), 3.11 (s, 3H, 4-CH_3), 3.31 (s, 3H, 6-CH_3), 7.87 (s, 1H, 5-H); ms: M^+ 296.

Calcd. for $C_{14}H_{12}N_6S$: C, 56.74; H, 4.08; N, 26.36. Found: C, 56.48; H, 4.29; N, 26.88%.

3.3. *2-Cyano-3-(2-hydrozone-3-ketimino-butyronitrile)-4,6-diphenyl-thieno[2,3-b]pyridine (**3b**)*

3-Amino-2-cyano-4,6-diphenyl-thieno[2,3-*b*]pyridine (3.27 g, 0.01 mol) in glacial acetic acid (10 ml) was added in portions during 30 min to a cooled mixture of nitrosylhydrogensulfate prepared from sodium nitrite (0.70 g, 0.01 mol) and concentrated sulfuric acid (10 ml) at 0 °C. The mixture was stirred for an additional 30 min at 0 °C, then added to an ice–water mixture under stirring. Excess nitrous acid was destroyed by the addition of urea and the solution was filtered to obtain a clear diazonium salt solution **1b**.

The cold diazotized solution **1b** was then added dropwise to a well-cooled and stirred mixture of 3-aminocrotononitrile **2** (0.82 g, 0.01 mol) and sodium acetate (2.0 g dissolved in 10 ml of 50% aqueous ethanol). Stirring was continued for 4 h at 0–5 °C and the resulting crystals collected, washed with water and recrystallized from DMF to give yellow crystals (89% yield), m.p. 274 °C; IR (KBr): ν 3215 (NH), 2209 (C≡N) cm^{-1}; ^{1}H NMR (CF_3COOD): δ 2.95 (s, 3H, CH_3), 8.45–7.97 (m, 10H, phenyl-H), 8.47 (s, 1H, 5-H); ms: M^+ 420.

Calcd. for $C_{24}H_{16}N_6S$: C, 68.55; H, 3.84; N, 19.99. Found: C, 68.32; H, 3.99; N, 20.11%.

3.4. *2-Cyano-3-(5-amino-3-methyl-pyrazol-4-yl)azo-4,6-dimethyl-thieno[2,3-b]pyridine (**5a**)*

A solution of 2-cyano-3-(2-hydrozone-3-ketimino-butyronitrile)-4,6-dimethyl-thieno[2,3-*b*]pyridine **3a** (4.4 g, 0.015 mol) and 85% excess of hydrazine hydrate (10 ml) in ethanol (10 ml) was refluxed for 4 h. After cooling, the precipitate was filtered and recrystallized from acetic acid to give orange needles (81% yield), m.p. 275 °C; IR (KBr): ν 3425, 3385 (NH_2), 3240 (NH), 2200 (C≡N) cm^{-1}; ^{1}H NMR (CF_3COOD): δ 3.00 (s, 3H, 3-CH_3 of pyrazol), 3.17 (s, 3H, 4-CH_3), 3.30 (s, 3H, 6-CH_3), 7.95 (s, 1H, 5-H); ms: M^+ 311.

Calcd. for $C_{14}H_{13}N_7S$: C, 54.01; H, 4.21; N, 31.49. Found: C, 54.33; H, 4.29; N, 31.55%.

The above procedure was also used to synthesize compound **5b**.

3.5. *2-Cyano-3-(5-amino-3-methyl-pyrazol-4-yl)azo-4,6-diphenyl-thieno[2,3-b]pyridine (**5b**)*

Crystallized from acetic acid as orange-red needles (79%); m.p. 254 °C; IR (KBr): ν 3447, 3401 (NH_2), 3207 (NH), 2202 (C≡N) cm^{-1}; ^{1}H NMR (CF_3COOD): δ 3.07 (s, 3H, 3-CH_3 of pyrazol), 8.32–7.87 (m, 10H, phenyl-H), 8.53 (s, 1H, 5-H); ms: M^+ 435.

Calcd. for $C_{24}H_{17}N_7S$: C, 66.19; H, 3.93; N, 22.51. Found: C, 66.32; H, 3.99; N, 22.11%.

3.6. *2-Cyano-3-(2-methyl-5,7-disubstituted-pyrazolo[1,5-a]pyrimidine-3-yl)azo-4,6-disubstituted-thieno[2,3-b]pyridines (**7a**–**7h**): general procedure*

A solution of 2-cyano-3-(5-amino-3-methyl-pyrazol-4-yl)azo-4,6-disubstituted-thieno[2,3-*b*]pyridine **5a**–**b** (1.6 mmol) and the 1,3-diketones **6a**–**6d** (1.6 mmol) in glacial acetic acid (10 ml) was refluxed for 4 h. After cooling, the precipitate was filtered and recrystallized from DMF/H_2O. Physical and spectral data of the dyes **7a**–**7h** are given in Tables 1 and 2.

3.7. *2-Cyano-3-(2,5-dimethyl-7-oxo-6,7-dihydropyrazolo[1,5-a]pyrimidine-3-yl)-azo-4,6-disubstituted-thieno[2,3-b]pyridines (**7i**–**7l**): general procedure*

A solution of 2-cyano-3-(5-amino-3-methyl-pyrazol-4-yl)azo-4,6-disubstituted-thieno[2,3-*b*]pyridine **5a**–**b** (1.6 mmol) with the ethyl acetoacetate **6e** and 1,1-dimethoxy-3-butanone **6f** (1.6 mmol) in glacial acetic acid (10 ml) was refluxed for 10 h. After the solvent was removed in vacuo and the residue was triturated with water. The solid formed was recrystallized from acetic acid. Physical and spectral data of the dyes **7i**–**7l** are given in Tables 1 and 2.

4. Conclusions

The 3-(2-methyl-5,7-disubstituted-pyrazolo[1,5-*a*]pyrimidine-3-yl)azo-4,6-disubstituted-thieno[2,3-*b*]pyridine derivatives were synthesized from 3-amino-4,6-disubstituted-thieno[2,3-*b*]pyridines and were applied as disperse dyes. These dyes showed good fastness properties on polyester fibers.

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