Dyes and Pigments, Vol. 29, No. 2, pp. 117–129, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0143-7208/95 $9.50 + 0.00

ELSEVIER 0143-7208(95)00037-2

Heterocyclic Monoazo Dyes Derived from 3-Cyano-2(1H)-Pyridinethiones. Part 1: 3-(Aryl or Hetaryl)azo-Thieno[2,3-*b*]pyridine Derivatives

Yuh Wen Ho & Ing Jing Wang*

Department of Textile and Polymer Engineering,
National Taiwan Institute of Technology, Taipei, Taiwan

(Received 8 March 1995; accepted 12 April 1995)

ABSTRACT

*The reaction of cyanothioacetamide with appropriate ketones afforded 2-cyano-4,6-disubstituted-2(1H)-pyridinethiones. 3-Amino-2-cyano-4,6-disubstituted-thieno[2,3-*b*]pyridines were synthesized by cyclization of 3-cyano-4,6-disubstituted-2(1H)-pyridinethiones with chloroacetonitrile. The 3-amino-thieno[2,3-*b*]pyridine derivatives were diazotized and coupled with a variety of coupling components to give new azo dyes. The dyes were applied to polyester; their spectral and dyeing properties are reported.*

1 INTRODUCTION

3-Cyano-2(1H)-pyridinethiones are of interest due to use as intermediates for the synthesis of the biologically active deazafolic acid and for deazaaminopterin ring synthesis;[1–2] they are also useful as central nerve depressants and in application in dyes.[3–8]

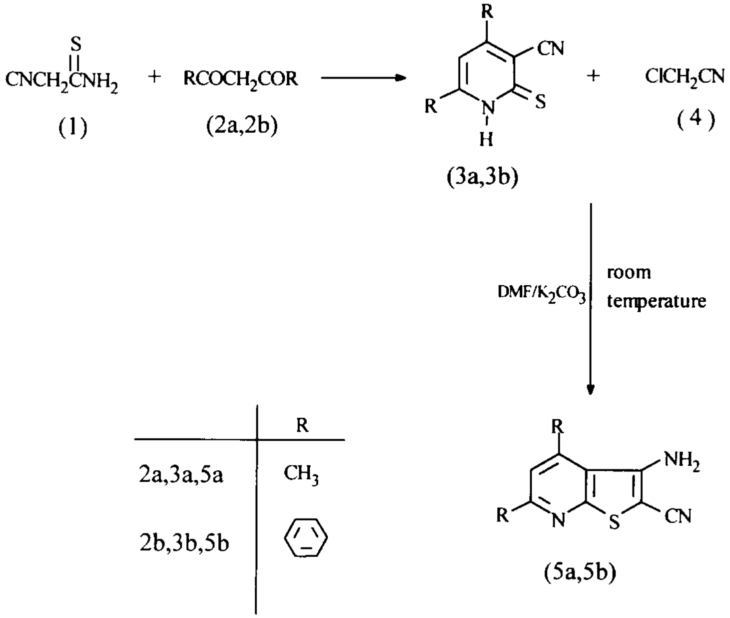
In the present study, we report the synthesis of some azo dyes derived from 3-cyano-2(1H)-pyridinethione derivatives; spectral characteristics and dyeing properties of the dyes are also discussed.

2 RESULTS AND DISCUSSION

The general route used for the synthesis of 3-amino-2-cyano-thieno[2,3-*b*]pyridines is outlined in Scheme 1. Reaction of 2-cyanothioacetamide **1**

---

* To whom correspondence should be addressed.

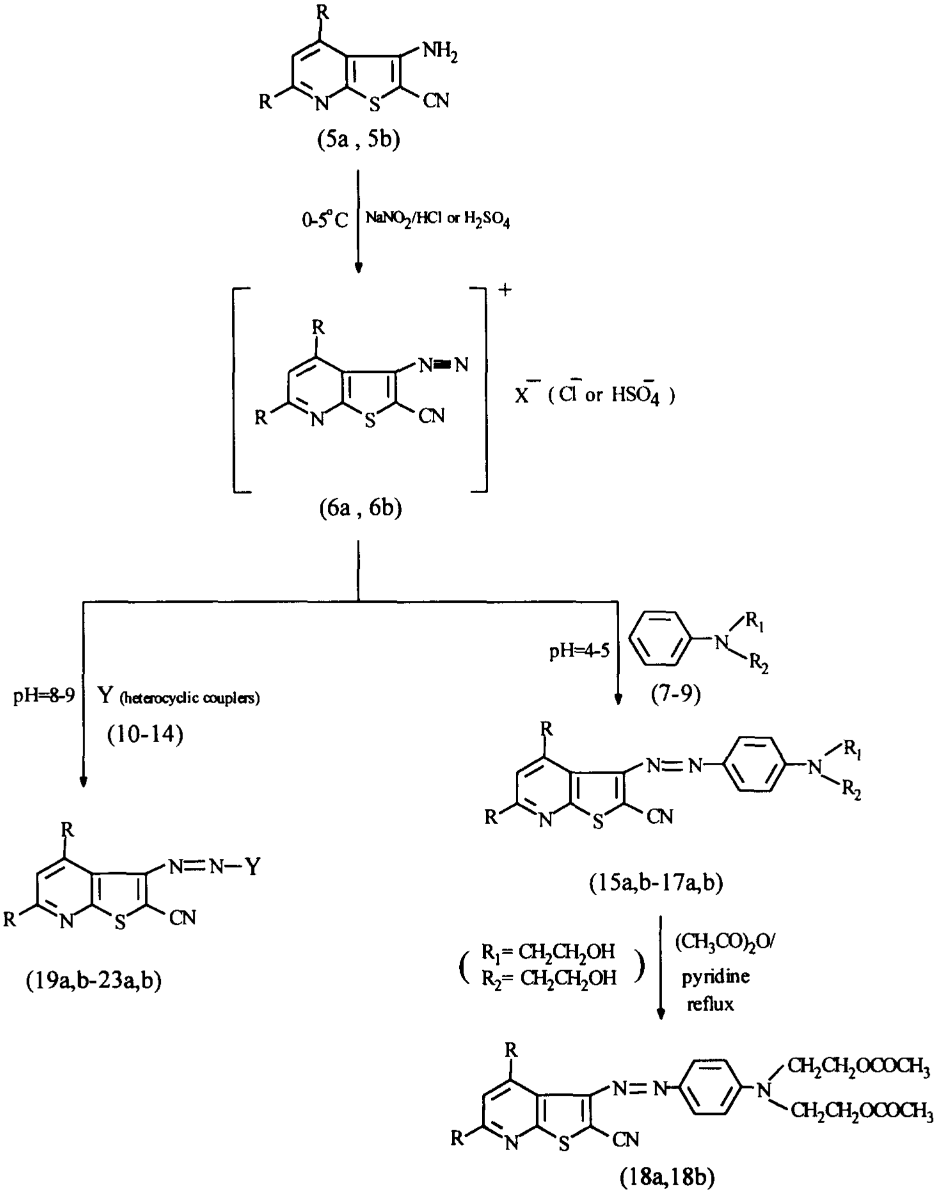


Scheme 1

with ketones such as acetylacetone **2a** or 1,3-diphenyl-1,3-propanedione **2b** in absolute ethanol in the presence of a basic catalyst yielded the 2-cyano-4,6-disubstituted-2(1H)-pyridinethione derivatives **3a** and **3b**, which were then cyclized with chloroacetonitrile **4** in DMF in the presence of anhydrous potassium carbonate to give the corresponding 3-amino-2-cyano-4,6-disubstituted-thieno[2,3-*b*]pyridines **5a** and **5b** in good yield.

The IR spectra of **3a** and **3b** showed absorptions at 3352–3150 cm^{-1} for the NH group, at 2230–2220 cm^{-1} for the C≡N group, and at 1210–1205 cm^{-1} for the C═S group. In the ^{1}H-NMR spectrum (DMSO-d$_6$) of compounds **3a** and **3b**, broad singlets were observed at δ 13·80 ppm and 13·85 ppm respectively, for the NH proton; these were absent after the cyclization reaction with chloroacetonitrile. The NH$_2$ protons of compounds **5a** and **5b** appeared at δ 6·46 ppm and 5·63 ppm, respectively. The IR spectra of compounds **5a** and **5b** showed no typical NH and C═S bands; amino bands were at 3433, 3296 cm^{-1} and 3462, 3212 cm^{-1}, in the form of two bands due to intramolecular association between the 3-NH$_2$ and 2-C≡N group of compounds **5a** and **5b**.

The 3-amino-2-cyano-thieno[2,3-*b*]pyridines **5a** and **5b** were diazotized with hydrochloric acid and solution nitrite, or with nitrosylsulfuric acid to afford the diazonium salts **6a** and **6b**, respectively (Scheme 2). These, when coupled with a variety of aromatic couplers such as *N*,*N*-dimethylaniline **7**, *N*-(2-cyanoethyl)-*N*-(2-hydroxyethyl)aniline **8**, *N*,*N*-bis(hydroxy-



Scheme 2

ethyl)aniline **9** in acidic medium at pH 4–5, yielded the 3-arylazo-2-cyano-4,6-disubstituted-thieno[2,3-*b*]pyridines **15a**, **b**–**17a**, **b**. The use of heterocyclic couplers such as 1-phenyl-3-methyl-5-hydroxypyrazole **10**, 4-hydroxy-1-methylquinoline-2-one **11**, 3-cyano-6-hydroxy-4-methyl-pyridone **12**, β-naphthol **13** and barbituric acid **14** at pH 8–9, yielded the 3-hetarylazo-2-cyano-4,6-disubstituted-thieno[2,3-*b*]pyridines **19a**, **b**–**23a**, **b**. Acetyla-

TABLE 1
Characterisation Data of 3-Azo-thieno[2,3-*b*]pyridine Derivatives (**15a**–**23a**, **15b**–**23b**)

Dye	*MS* *(m/e M⁺)*	*IR* *(KBr)* *ν (cm⁻¹)*	*1H-NMR*[a] *(CDCl$_3$)* *δ (ppm)*
15a	335	2208 (C≡N)	2·62 (s, 3H, 4—CH$_3$), 2·78 (s, 3H, 6-CH$_3$), 3·12 (s, 6H, N(CH$_3$)$_2$), 7·10 (s, 1H, 5—H), 6·78–6·72 (d, 2H, 3—H, 5—H of phenyl), 7·94–7·87 (d, 2H, 2—H, 6—H of phenyl).
16a	404	3498 (OH), 2208 (C≡N)	2·59–2·57 (t, 2H, N—CH$_2\underline{CH_2}$CN), 2·90–2·84 (t, 2H, N—CH$_2\underline{CH_2}$OH), 2·65 (s, 3H, 4—CH$_3$), 2·77 (s, 3—H, 6—CH$_3$), 3·54–3·50 (t, 2H, N—$\underline{CH_2}$CH$_2$CN), 3·90–3·86 (t, 2H, N—$\underline{CH_2}$CH$_2$OH), 7·11 (s, 1H, 5—H), 6·80–6·77 (d, 2H, 3—H, 5—H of phenyl), 7·95–7·92 (d, 2H, 2—H, 6—H of phenyl).
17a	395	3452 (OH), 2206 (C≡N)	2·63 (s, 3H, 4—CH$_3$), 2·81 (s, 3—H, 6—CH$_3$), 3·75–3·72 (m, 4H, N (CH$_2\underline{CH_2}$OH)$_2$), 3·97–3·93 (m, 4H, N($\underline{CH_2}$CH$_2$OH)$_2$), 7·09 (s, 1H, 5—H), 6·77–6·74 (d, 2H, 3—H, 5—H of phenyl), 7·90–7·87 (d, 2H, 2—H, 6—H of phenyl).
18a	448	2200 (C≡N), 1739 (C=O)	2·06 (s, 6H, (—COCH$_3$)$_2$), 2·69 (s, 3H, 4—CH$_3$), 2·81 (s, 3H, 6—CH$_3$), 3·76–3·63 (m, 4H, N(CH$_2\underline{CH_2}$OCOCH$_3$)$_2$), 4·32–4·22 (m, 4H, N($\underline{CH_2}$CH$_2$OCOCH$_3$)$_2$), 6·88–6·78 (d, 2H, 3—H, 5—H of phenyl), 7·15 (s, 1H, 5—H), 7·95–7·92 (d, 2H, 2—H, 6—H of phenyl).
19a	388	3467 (OH), 2209 (C≡N)	2·25 (br, 1H, OH) 2·96 (s, 3H, 3—CH$_3$ of pyrazol), 3·00 (s, 3H, 4—CH$_3$), 3·18 (s, 3H, 6—CH$_3$), 7·84–7·35 (m, 6H, 5—H and phenyl-H).[b]
20a	389	3477 (OH), 2207 (C≡N), 1666 (C=O)	2·69 (s, 3H, N—CH$_3$), 2·95 (s, 3H, 4—CH$_3$), 3·48 (s, 3H, 6—CH$_3$), 7·50 (s, 1H, 5—H), 7·24–7·13 (dd, 2H, 6—H, 7—H of quinolinyl), 7·63–7·60 (d, 1H, 5—H of quinolinyl), 8·07–8·04 (d, 1H, 8—H of quinolinyl).[b]
21a	364	3468 (OH), 3154 (NH), 2213 (C≡N), 1702 (C=O)	2·53 (s, 3H, 4—CH$_3$ of pyridone), 2·58 (s, 3H, 4—CH$_3$), 2·84 (s, 3—H, 6—CH$_3$), 7·34 (s, 1H, 5—H), 12·28 (br, 1H, NH).[c]
22a	358	3495 (OH), 2200 (C≡N)	2·62 (s, 3H, 4—CH$_3$), 2·93 (s, 3—H, 6—CH$_3$), 7·06 (s, 1H, 5—H), 6·76, 7·28–7·24, and 8·74–8·70 (m, 6H, β-naphthyl-H).
23a	—	3472, 3375 (OH, NH), 2213 (C≡N), 1724 (C=O)	3·08 (s, 3H, 4—CH$_3$), 3·21 (s, 3H, 6—CH$_3$), 7·24 (s, 1H, 5—H), 7·62, 7·67–7·64 (br, 3H, OH).[b]
15b	460	2213 (C≡N)	3·12 (s, 6H, N(CH$_3$)$_2$), 7·32 (s, 1H, 5—H), 6·97–6·94 (d, 2H, 3—H, 5—H of N-phenyl), 7·60–7·35 (m, 10H, 4,6-phenyl-H), 8·17–8·14 (d, 2H, 2—H, 6—H of N-phenyl).

TABLE 1—*contd.*

Dye	*MS* (*m/e* M^+)	*IR* (*KBr*) ν (cm^{-1})	*1H-NMR*[a] ($CDCl_3$) δ (*ppm*)
16b	529	3476 (OH), 2208 (C≡N)	3·74–2·69 (t, 2H, N—$\mathrm{CH_2\underline{CH_2}CN}$), 3·69–3·65 (t, 2H, N—$\mathrm{CH_2\underline{CH_2}OH}$), 3·90–3·81 (m, 4H, N—$\mathrm{\underline{CH_2}CH_2OH}$, N—$\mathrm{\underline{CH_2}CH_2}$—CN, 6·60–6·56 (d, 2H, 3—H, 5—H of N-phenyl), 7·82 (s, 1H, 5—H), 8·16 (d, 2H, 2—H, 6—H of N-phenyl), 7·57–7·43 8·14–8·07 (m, 10H, 4,6-phenyl-H).
17b	520	3449 (OH), 2204 (C≡N)	4·79–4·66 (m, 4H, N—$\mathrm{(CH_2\underline{CH_2}OH)_2}$), 5·39–5·34 (m, 4H, N—$\mathrm{(\underline{CH_2}CH_2OH)_2}$), 8·05 (s, 1H, 5—H), 8·89–8·28 (m, 14H, N-phenyl-H and 4,6-phenyl-H).[b]
18b	572	2203 (C≡N), 1738 (C=O)	2·06 (s, 6H, (—$\mathrm{COCH_3)_2}$), 3·72–3·68 (t, 4H, N—$\mathrm{(CH_2\underline{CH_2}OCOCH_3)_2}$), 4·29–4·25 (t, 4H, N—$\mathrm{(\underline{CH_2}CH_2OCOCH_3)_2}$), 6·66–6·63 (d, 2H, 3—H, 5—H of N-phenyl), 7·50–7·24 (m, 10H, 4,6-phenyl-H), 7·81 (s, 1H, 5—H), 8·16–8·13 (d, 2H, 2—H, 6—H of N-phenyl).
19b	512	3477 (OH), 2207 (C≡N)	2·35 (s, 3H, CH_3 of pyrazol), 2·59 (br, 1H, OH), 7·58–7·30 (m, 5H, N-phenyl-H), 8·26–7·75 (m, 11H, 5—H and 4,6-phenyl-H).[b]
20b	513	3475 (OH), 2213 (C≡N), 1665 (C=O)	2·71 (s, 3H, N—CH_3), 6·64–6·61 (dd, 2H, 6—H, 7—H of quinolinyl), 7·03–6·80 (m, 11H, 5—H and 4,6-phenyl-H), 7·24–7·18 (d, 1H, 5—H of quinolinyl), 7·53–7·50 (d, 1H, 8—H of quinolinyl).[c]
21b	488	3473 (OH), 3291 (NH), 2208 (C≡N), 1704 (C=O)	3·41 (s, 3H, CH_3 of pyridone), 3·85 (br, 1H, OH), 8·82 (s, 1H, 5—H), 8·66–8·23 (m, 10H, 4,6-phenyl-H), 12·63 (br, 1H, NH).[b]
22b	482	3473 (OH), 2201 (C≡N)	6·55–6·52 (d, 1H, 8—H of β-naphthol), 7·76 (s, 1H, 5—H), 8·16–8·13, 7·63–7·37 (m, 14H, 4,6-phenyl-H and 4, 5, 6, 7—H of β-naphthol).
23b	466	3472, 3343 (OH, NH), 2212 (C≡N), 1723 (C=O)	9·06–8·47 (m, 11H, 5—H and 4,6-phenyl-H), 9·60, 9·72 (br, 3H, OH).[b]

[a] Abbreviations: s, single; t, triplet; m, multiplet; br, broad.
[b] NMR in CF_3COOD.
[c] NMR in DMSO-d_6.

tion of dyes **17a** and **17b** with acetic anhydride in the presence of pyridine afforded the corresponding dyes **18a** and **18b** (Scheme 2). IR, ^{1}H-NMR and mass spectra data of **15a**, **b**–**23a**, **b** are given in Table 1.

The absorption maxima of dyes **15a**, **b**–**23a**, **b** were recorded in DMF and are shown in Table 2. The absorption maxima of dyes **15a**–**23a** ranged from 430 to 522 nm and those of dyes **15b**–**23b** from 420 to 513 nm.

TABLE 2
Adsorption Spectra and Dyeing Properties of 3-Azo-thieno[2,3-*b*]pyridines (**15a–23a**, **15b–23b**)

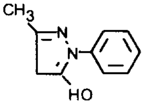
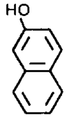
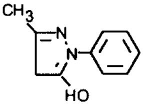
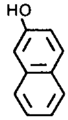
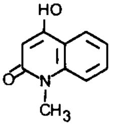
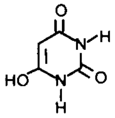
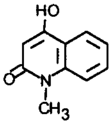
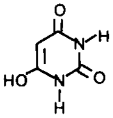
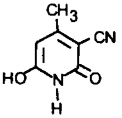
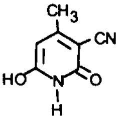
Dye	*Colour on dyed polyester fibres*	*Absorption maximum* λ_{max} *nm (in DMF)*	*log* ε	*Light fastness*	*Sublimation fastness*
15a	Deep red	510	4·30	3	3–4
16a	Deep red	500	4·53	3	5
17a	Red-violet	520	4·46	3	4–5
18a	Very bright orange-red	491	4·35	6	5
19a	Very bright yellow	430	3·86	6	5
20a	Yellow-orange	445	4·10	5	5
21a	Yellow-orange	480	4·62	3–4	5
22a	Red	522	4·32	2	5
23a	Very bright yellow	442	4·05	6	5
15b	Deep red	500	4·15	5	5
16b	Deep red	492	4·29	6	5
17b	Red-violet	513	4·48	4	5
18b	Very bright orange-red	490	4·45	5	5
19b	Yellow	420	4·40	5	5
20b	Yellow-orange	430	3·39	3–4	5
21b	Yellow-red	460	4·35	5	5
22b	Very bright pink	498	3·94	3	5
23b	Very bright yellow	435	3·96	5	5

It was observed in general that dyes **15a–23a** derived from the diazo component **5a** were bathochromic when compared with analogous dyes **15b–23b** derived from the diazo component **5b**. The bathochromic shift accompanying methyl subsitution results from a hyperconjugation effect in which the σ-electrons of the methyl group are mobile enough to interact with the chromophoric group.[12]

Acetylation of the terminal hydroxy group in dyes based on hydroxyethylated couplers leads to hypsochromic shifts, in accordance with the increased polarization effect.[10] The effect of acetylation is apparent in dyes **17a–18a** and **17b–18b**, in which bis-acetylation induces hypsochromic shifts of 29 nm and 23 nm, respectively.

The dyes **15a, b–23a, b** were dyed on polyester fibers at 1% shade by high-temperature–pressure techniques and gave generally deep and bright intense hues, ranging from yellow to red-violet. The fastness properties of the dyes are shown in Table 2. The lightfastness was determined using standard procedures.[11] For sublimation fastness determinations, the dyed polyester fibers were stitched between two pieces of undyed polyester

Dye	R	R_1	R_2
15a	CH_3	CH_3	CH_3
15b	C_6H_5	CH_3	CH_3
16a	CH_3	C_2H_4OH	C_2H_4CN
16b	C_6H_5	C_2H_4OH	C_2H_4CN
17a	CH_3	C_2H_4OH	C_2H_4OH
17b	C_6H_5	C_2H_4OH	C_2H_4OH

Dye	R	Y	Dye	R	Y
19a	CH_3		22a	CH_3	
19b			22b		
20a	CH_3		23a	CH_3	
20b			23b		
21a	CH_3				
21b					

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.

Table 2 shows that the lightfastness of the majority of the dyes was moderate to excellent (3–6), with only dye **22a** showing poor lightfastness (2). In general, sublimation fastness ranged from good to very good (4–5) for all dyes.

3 EXPERIMENTAL

3.1 General

All melting points are uncorrected and in °C. IR spectra were recorded on a JASCO FTIR-3 spectrometer (KBr); ^{1}H-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 Finnigan 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/litre.

3.2 Synthesis of 3-amino-2-cyano-thieno[2,3-*b*]pyridine derivatives

*3.2.1 2-Cyano-4,6-dimethyl-2(1H)-pyridinethione (**3a**)*

This compound was prepared by the reported method.[9] m.p. 264°C. IR (KBr): ν 3352 (NH), 2230 (C≡N), 1210 (C=S) cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 2·29 (s, 3H, 4-CH_3), 2·32 (s, 3H, 6-CH_3), 6·67 (s, 1H, 5-H), 13·8 (br, 1H, NH); Calculated for $C_8H_8N_2S$: C, 58·54; H, 4·88; N, 17·07%. Found: C, 58·66; H, 4·90; N, 17·25%.

*3.2.2 2-Cyano-4,6-diphenyl-2(1H)-pyridinethione (**3b**)*

To a mixture of 1,3-diphenyl-1,3-propanedione **2b** (9·00 g, 0·04 mol) and cyanothioacetamide **1** (4·00 g, 0·004 mol) in absolute ethanol (10 ml), a few drops of piperidine and 2-mercaptoethanol (0·47 g, 0·006 mol) were added sequentially. The reaction mixture was refluxed for 24 h. After cooling, the precipitate was filtered, washed, and recrystallized from acetic acid to give 8 g (69%) of yellow crystals; m.p. 233°C. Mass spectrum *m/z*: 288; IR (KBr): ν 3150 (NH), 2220 (C≡N), 1205 (C=S) cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 6·9 (s, 1H, 5-H), 7·8–7·2 (m, 10H, 4-,6-phenyl-H), 14·2–13·5 (br, 1H, NH); Calculated for $C_{18}H_{12}N_2S$: C, 74·97; H, 4·19; N, 9·71%. Found: C, 75·0; H, 4·17; N, 9·72%.

*3.2.3 3-Amino-2-cyano-4,6-dimethyl-thieno[2,3-*b*]pyridine (**5a**)*

Anhydrous potassium carbonate (2·76 g, 0·02 mol) was added to a solution of 2-cyano-4,6-dimethyl-2(1H)-pyridinethione **3a** (1·64 g, 0·01 mol) in DMF (50 ml) and the reaction mixture stirred at room temperature for 4 h and then diluted with cold water (50 ml). The resulting product was filtered, washed with water, and recrystallized from ethylacetate to give 2·0 g (98·5%) of pale yellow needles; m.p. 243°C. Mass spectrum *m/z*: 203; IR (KBr): ν 3433, 3296 (NH_2), 2220 (C≡N) cm^{-1}; ^{1}H-NMR (DMSO-

d_6): δ 2·49 (s, 3H, 4-CH_3), 2·69 (s, 3H, 6-CH_3), 6·46 (br, 2H, NH_2) 7·08 (s, 1H, 5-H); Calculated for $C_{10}H_9N_3S$: C, 59·11; H, 4·43; N, 20·68%. Found: C, 59·31; H, 4·44; N, 19·89%.

*3.2.4 3-Amino-2-cyano-4,6-diphenyl-thieno[2,3-*b*]pyridine (**5b**)*

This compound was synthesized from 2-cyano-4,6-diphenyl-2(1H)-pyridinethione **3b** and chloroacetonitrile **4** in a manner similar to that described for the preparation of compound **5a**; it was crystallized from ethylacetate as pale yellow needles (98·3%), m.p. 237°C. Mass spectrum *m/z*: 327; IR (KBr): ν 3462, 3212 (NH_2), 2204 (C≡N) cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 5·36 (br, 2H, NH_2), 8·42–7·50 (m, 10H, 4-,6-phenyl-H); Calculated for $C_{20}H_{13}N_3S$: C, 73·38; H, 4·01; N, 12·84%. Found: C, 73·39; H, 3·97; N, 12·84%.

3.3 Preparation of dyes

*3.3.1 3-[4-(Dimethylamino)phenylazo]-2-cyano-4,6-dimethyl-thieno[2,3-*b*]-pyridine (**15a**)*

3-Amino-2-cyano-4,6-dimethyl-thieno[2,3-*b*]pyridine **5a** (2·03 g, 0·01 mol) was dissolved in warm conc. hydrochloric acid (10 ml) and water (10 ml) 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 15 min at 0–5°C with stirring. The reaction mixture was then stirred for 30 min while maintaining 0–5°C. Excess nitrous acid was destroyed by the addition of urea, and the solution was filtered to obtain a clear diazonium salt solution **6a**.

N,N-Dimethylaniline **7** (1·21 g, 0·01 mol) was dissolved in sulfuric acid (1·1 g conc. sulfuric acid in 5 ml water) and the solution cooled to 0–5°C. To the cooled solution, the diazonium salt **6a** was added slowly so that the temperature did not rise above 5°C, while maintaining pH at 4–5 by addition of sodium acetate. The mixture was then stirred for 4 h at 0–5°C, filtered, and the presscake washed with water, dried, and recrystallized from acetone as red-violet crystals (60·6%), m.p. 171°C. Calculated for $C_{18}H_{17}N_5S$: C, 64·45; H, 5·11; N, 20·88%. Found: C, 64·12; H, 5·08; N, 20·93%.

The above procedure was also used to synthesize dyes **16a** and **17a**.

*3.3.2 3-[[4-(*N*-2-Cyanoethyl)-(*N*-2-hydroxyethyl)amino]phenylazo]-2-cyano-4,6-dimethyl-thieno[2,3-*b*]pyridine (**16a**)*

Crystallized from ethyl acetate as red-violet needles (67%); m.p. 166°C. Calculated for $C_{21}H_{20}N_6OS$: C, 62·38; H, 4·95; N, 20·97%. Found: C, 62·54; H, 5·01; N, 20·99%.

*3.3.3 3-[4-[Bis(2-hydroxyethyl)amino]phenylazo]-2-cyano-4,6-dimethylthieno[2,3-*b*]pyridine (**17a**)*

Crystallized from ethyl acetate as red-violet needles (71·3%); m.p. 170°C. Calculated for $C_{20}H_{21}N_5O_2S$: C, 60·59; H, 5·59; N, 17·66%. Found: C, 60·58; H, 5·33; N, 17·86%.

*3.3.4 3-[4-[Bis(2-acetoxyethyl)amino]phenylazo]-2-cyano-4,6-dimethylthieno[2,3-*b*]pyridine (**18a**)*

A mixture of dye **17a** (1·00 g, 0·0025 mol), pyridine (0·20 g, 0·0025 mol), and acetic anhydride (5 ml) was refluxed on a water bath for 5 h. The cooled solution was poured into 250 ml of water/acetone 2:1. The mixture was stirred overnight, and the resulting product was filtered and recrystallized from ethyl acetate as red violet crystals (74·4%); m.p. 97°C. Calculated for $C_{24}H_{26}N_5O_2S$: C, 64·26; H, 5·84; N, 15·61%. Found: C, 64·34; H, 5·80; N, 15·68%.

*3.3.5 3-[(5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)azo]-2-cyano-4,6-dimethyl-thieno[2,3-*b*]pyridine (**19a**)*

3-Methyl-1-phenyl-1H-pyrazol-5-ol **10** (1·74 g, 0·01 mol) was dissolved in dilute sodium bicarbonate and the solution cooled to 0–5°C. To this solution, the diazonium salt **6a** was added slowly so that the temperature did not rise above 5°C, while maintaining the pH at 8–9 by addition of sodium carbonate. The mixture was further stirred for 4 h at 0–5°C and the partially separated dye was completely precipitated by neutralizing with dilute hydrochloric acid (5%). It was filtered, washed with water, dried, and recrystallized from DMF/ethanol as orange-yellow needles crystals (83%); m.p. 227°C. Calculated for $C_{20}H_{16}N_6OS$: C, 61·84; H, 4·15; N, 21·36%. Found: C, 61·66; H, 4·12; N, 21·70%.

The above procedure was also used to synthesize dyes **20a**–**23a**.

*3.3.6 3-[(4-Hydroxy-1-methylquinolin-2-one-3-yl)azo]-2-cyano-4,6-dimethylthieno[2,3-*b*]pyridine (**20a**)*

Crystallized from DMF/ethanol as orange crystals (91·5%); m.p. 224°C. Calculated for $C_{20}H_{15}N_5O_2S$: C, 61·68; H, 3·88; N, 17·98%. Found: C, 61·79; H, 3·92; N, 17·91%.

*3.3.7 3-[(Cyano-6-hydroxy-4-methyl-pyridone)azo]-2-cyano-4,6-dimethylthieno[2,3-*b*-]pyridine (**21a**)*

Crystallized from DMF/ethanol as orange-yellow crystals (81·2%); m.p. 337°C. Calculated for $C_{17}H_{12}N_6O_2S$: C, 56·04; H, 3·32; N, 23·06%. Found: C, 56·11; H, 3·43; N, 23·15%.

*3.3.8 3-[(2-Hydroxynaphthyl-1-yl)azo]-2-cyano-4,6-dimethyl-thieno[2,3-*b*]pyridine (**22a**)*

Crystallized from DMF/ethanol as red-brown crystals (70·3%); m.p. 271°C. Calculated for $C_{20}H_{14}N_4OS$: C, 67·02; H, 3·94; N, 15·63%. Found: C, 67·09; H, 3·89; N, 15·70%.

*3.3.9 3-[(2,4,6-Trihydroxy-5-pyrimidinyl)azo]-2-cyano-4,6-dimethyl-thieno-[2,3-*b*]pyridine (**23a**)*

Crystallized from DMF/ethanol as yellow crystals (70%); m.p. >340°C. Calculated for $C_{14}H_{10}N_6O_3S$: C, 49·12; H, 2·94; N, 24·55%. Found: C, 49·53; H, 2·98; N, 24·67%.

*3.3.10 3-[4-(Dimethylamino)phenylazo]-2-cyano-4,6-diphenyl-thieno[2,3-*b*]pyridine (**15b**)*

3-Amino-2-cyano-4,6-diphenyl-thieno[2,3-*b*]pyridine **5b** (3·27 g, 0·01 mol) in glacial acetic acid (10 ml) was added in portions during 30 min to a cooled mixture of nitrosyl sulfuric acid prepared from sodium nitrite (0·70 g, 0·01 mol) and concentrated sulfuric acid (10 ml) at 0°C. The mixture was stirred for 30 min at 0°C and then stirred into an ice–water mixture. Excess nitrous acid was destroyed by the addition of urea and the solution was filtered to obtain a clear diazonium salt solution **6b**.

N,*N*-Dimethylaniline **7** (1·21 g, 0·01 mol) was dissolved in sulfuric acid (1·1 g sulfuric acid in 5 ml water). The solution was cooled to 0–5°C and the diazonium salt **6b** was then added slowly so that the temperature did not rise above 5°C, while maintaining the pH at 4–5 by addition of sodium carbonate. The mixture was stirred for 4 h at 0–5°C and filtered, and the presscake washed with water, dried and recrystallized from acetone, giving red-violet crystals (84·5%), m.p. 125°C. Calculated for $C_{28}H_{22}N_5S$: C, 73·02; H, 4·81; N, 15·21%. Found: C, 73·12; H, 4·90; N, 15·19%.

The above procedure was also used to synthesize dyes **16b** and **17b**.

*3.3.11 3-[[4-(*N*-2-Cyanoethyl)-(*N*-2-hydroxyethyl)amino]phenylazo]-2-cyano-4,6-diphenyl-thieno[2,3-*b*]pyridine (**16b**)*

Crystallized from ethyl acetate as red-brown needles (71·9%); m.p. 166°C. Calculated for $C_{31}H_{25}N_6OS$: C, 70·30; H, 4·76; N, 15·87%. Found: C, 70·25; H, 4·81; N, 15·88%.

*3.3.12 3-[4-[Bis(2-hydroxyethyl)amino]phenylazo]-2-cyano-4,6-diphenyl-thieno[2,3-*b*]pyridine (**17b**)*

Crystallized from ethyl acetate as red-violet needles (84·7%); m.p. 201°C. Calculated for $C_{30}H_{26}N_5O_2S$: C, 69·21; H, 5·03; N, 13·45%. Found: C, 69·31; H, 5·08; N, 13·50%.

*3.3.13 3-[4-[Bis(2-acetoxyethyl)amino]phenylazo]-2-cyano-4,6-diphenyl-thieno[2,3-*b*]pyridine (**18b**)*

Dye **18b** was synthesized from dye **17b** (1·30 g, 0·0025 mol), pyridine (0·20 g, 0·0025 mol) and acetic anhydride (5 ml) in a manner similar to that described for the preparation of dye **18a**; it was crystallized from ethyl acetate in red-violet needles (72·6%); m.p. 155°C. Calculated for $C_{34}H_{20}N_5O_2S$: C, 71·31; H, 5·28; N, 12·23%. Found: C, 71·35; H, 5·30; N, 12·26%.

*3.3.14 3-[(5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)azo]-2-cyano-4,6-diphenyl-thieno[2,3-*b*]pyridine (**19b**)*

Dye **19b** was synthesized from 3-methyl-1-phenyl-1H-pyrazol-5-ol (1·74 g, 0·01 mol) and the diazonium salt **6b** in a manner similar to that described for the preparation of dye **19a**. Crystallization from benzene gave orange-yellow crystals (84·4%); m.p. 169°C. Calculated for $C_{30}H_{20}N_6OS$: C, 70·30; H, 3·39; N, 14·64%. Found: C, 70·32; H, 3·98; N, 16·45%.

The above procedure was also used to synthesize dyes **20b–23b**.

*3.3.15 3-[(4-Hydroxy-1-methylquinolin-2-one-3-yl)azo]-2-cyano-4,6-diphenyl-thieno[2,3-*b*]pyridine (**20b**)*

Crystallized from benzene/acetone as orange crystals (84·5%); m.p. 159°C. Calculated for $C_{30}H_{19}N_5O_2S$: C, 70·16; H, 3·73; N, 13·64%. Found: C, 70·21; H, 3·80; N, 13·68%.

*3.3.16 3-[(3-Cyano-6-hydroxy-4-methyl-pyridone)azo]-2-cyano-4,6-diphenyl-thieno[2,3-*b*]pyridine (**21b**)*

Crystallized from DMF/benzene as orange crystals (93·3%); m.p. 300°C. Calculated for $C_{27}H_{16}N_6O_2S$: C, 66·38; H, 3·30; N, 17·20%. Found: C, 66·49; H, 3·38; N, 17·68%.

*3.3.17 3-[(2-Hydroxynaphthyl-1-yl)azo]-2-cyano-4,6-diphenyl-thieno[2,3-*b*]pyridine (**22b**)*

Crystallized from benzene as red-brown crystals (89·1%); m.p. 225°C. Calculated for $C_{30}H_{18}N_4OS$: C, 74·76; H, 3·76; N, 11·61%. Found: C, 74·88; H, 3·81; N, 11·64%.

*3.3.18 3-[(2,4,6-Trihydroxy-5-pyrimidinyl)azo]-2-cyano-4,6-diphenyl-thieno-[2,3-*b*]pyridine (**23b**)*

Crystallized from DMF/pyridine as golden yellow crystals (91·4%); m.p. 279°C. Calculated for $C_{24}H_{14}N_6O_3S$: C, 61·80; H, 3·03; N, 18·02%. Found: C, 61·89; H, 3·08; N, 18·10%.

ACKNOWLEDGEMENTS

The authors are grateful to the National Science Council of Taiwan for their financial support.

REFERENCES

1. Taylor, E. C., Palmer, D. C., George, T. J., Fletcher, S. R., Tseng, C. P., Harrington, P. J. & Beardsley, G. P., *J. Org. Chem.*, **48** (1983) 4852.
2. Gangill, A., Devraj, R. & Lin, F., *J. Heterocyclic Chem.*, **28** (1991) 1747.
3. Sharanin, Y. A. & Promonenkov, V. K., *Znform. Ser. Khim. Sredstva ZaschRast.*, *NIITEKhim*, Moscow 28 (1981).
4. Japanese Patent 70 39263 (1970); *Chem. Abstr.*, **74** (1971) 87836.
5. Japanese Patent 70 39264 (1970); *Chem. Abstr.*, **74** (1971) 125459.
6. U.S. Patent 3965107 (1976).
7. Hagen, H., Hansen, G. & Niess, R., BASF, German Patent 2507187 (1976).
8. Guerrera, F., Siracusa, M. & Tornetta, B., *Farm. Ed. Sci.*, **31** (1976) 21.
9. Schmidt, U. & Kubitzek, H., *Chem. Ber.*, 1559 (1960).
10. Peters, A. T. & Gbadamosi, N. M. A., *Dyes and Pigments*, **18** (1992) 115.
11. *Standard Methods for the Determination of the Colour Fastness of Textiles*, 3rd edn. The Society of Dyes and Colourists, Bradford, 1962.
12. Silverstein, R. M., Bassler, G. C. & Morrill, T. C., *Spectrometric Identification of Organic Compounds*, 4th edn (1981) p. 311.