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Heterocyclic Monoazo Dyes Derived from 3-Cyano-2(1H)-Pyridinethione. Part 2: 2-[[4-(Arylazo)-3,5-Disubstituted-Pyrazol-1-yl]Carbonyl]-Thieno[2,3-*b*]Pyridine Derivatives

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ABSTRACT

*Acetylacetone and malononitrile were coupled with diazotised arylamines to give arylazoacetylacetones and arylazomalononitriles; these when refluxed with 3-amino-4,6-dimethyl-2-thieno[2,3-*b*]pyridine carbohydrazide in the presence of glacial acetic acid yielded the corresponding 2-[[4-(arylazo)-3,5-disubstituted-pyrazol-1-yl]carbonyl]-3-amino-4,6-dimethyl-thieno[2,3-*b*]pyridine dyes. The dyes were applied to polyester and polyamide fibres, and their spectral and fastness properties measured.*

1 INTRODUCTION

Some pyrazole derivatives possess anticancer properties[1,2] and biological activity[3–10] and also find application in photography[11,12] and as dyes.[13,14] We have previously reported the synthesis of 3-amino-4,6-dimethyl-2-ethoxycarbonyl-thieno[2,3-*b*]pyridine.[15] As a continuation of these studies, we report here the synthesis of some 2-[[4-(arylazo)-3,5-disubstituted-pyrazol-1-yl]carbonyl]-thieno[2,3-*b*]pyridine dyes from 3-amino-4,6-dimethyl-2-ethoxycarbonyl-thieno[2,3-*b*]pyridine and an evaluation of their properties on polyester and polyamide fibres.

2 RESULTS AND DISCUSSION

3-Amino-4,6-dimethyl-2-ethoxycarbonyl-thieno[2,3-*b*]pyridine[15] **3** was synthesized from 3-cyano-4,6-dimethyl-pyridinethione **1** and ethyl chloroacetate

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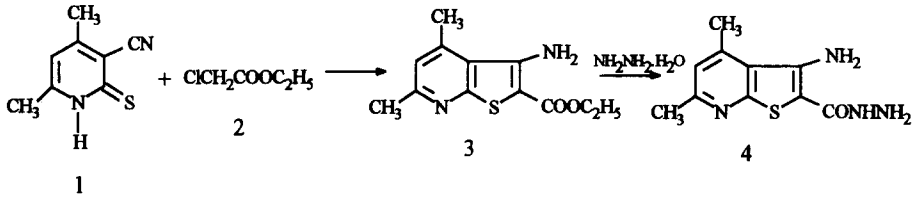


Scheme 1

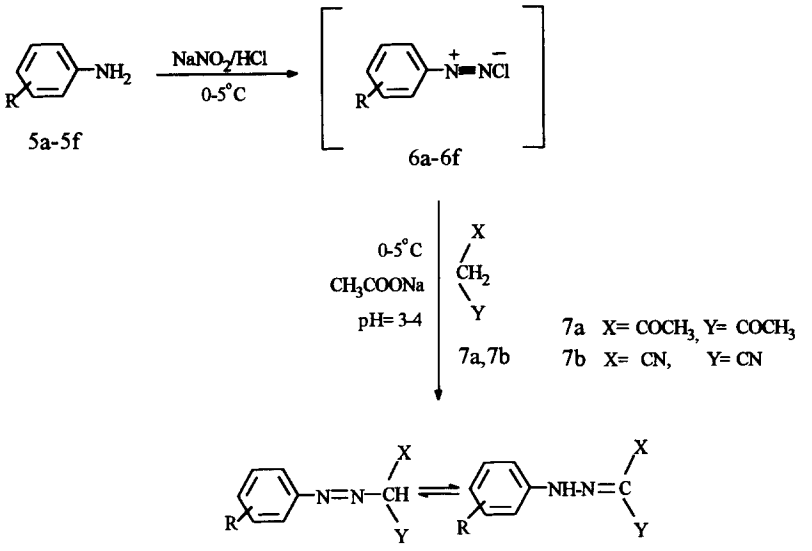
2 in DMF in the presence of excess anhydrous potassium carbonate at room temperature. Compound **3** reacted with 85% excess of hydrazine hydrate in refluxing ethanol to give 3-amino-4,6-dimethyl-2-thieno[2,3-*b*]pyridine carbohydrazide **4** (Scheme 1). The structure of compound **4** was confirmed by spectral data and elemental analysis.

Diazotised arylamines **5a–5f** coupled with active methylene compounds

TABLE 1
Characterisation Data for Arylazoacetylacetone and Arylazomalononitrile Derivatives **(8a–8l)**

Compound	*M.p.*[a] *(°C)*	*Yield (%)*	*Molecular formula*	*Elemental analysis (%) calcd/found*		
				C	*H*	*N*
8a	88	96	$C_{11}H_{12}N_2O_2$	64·71	5·88	13·73
				64·67	5·96	13·81
8b	124	95	$C_{12}H_{14}N_2O_2$	66·04	6·47	12·84
				66·15	6·51	12·83
8c	126	94	$C_{11}H_{11}ClN_2O_2$	55·35	4·61	11·74
				55·41	4·67	11·81
8d	173	97	$C_{12}H_{11}N_3O_2$	62·88	4·80	18·34
				62·81	4·83	18·32
8e	196	94	$C_{11}H_{11}N_3O_4$	53·01	4·45	16·86
				53·21	4·54	16·90
8f	230	92·5	$C_{13}H_{15}N_3O_3$	59·76	5·79	16·08
				60·01	5·83	16·44
8g	157	90·3	$C_9H_6N_4$	63·52	3·55	32·92
				63·51	3·50	32·98
8h	109	93·5	$C_{10}H_8N_4$	65·21	4·38	30·42
				65·25	4·41	30·38
8i	100	92	$C_9H_5ClN_4$	52·83	2·46	27·38
				52·78	2·51	27·40
8j	183	97·4	$C_{10}H_5N_5$	61·54	2·58	35·88
				61·56	2·61	35·90
8k	143	93	$C_9H_5N_5O_2$	50·24	2·34	32·55
				50·26	2·36	32·57
8l	227	90·2	$C_{11}H_9N_5O$	58·15	3·99	30·82
				58·45	3·96	30·88

[a] Solvent of recrystallization: $CHCl_3$.

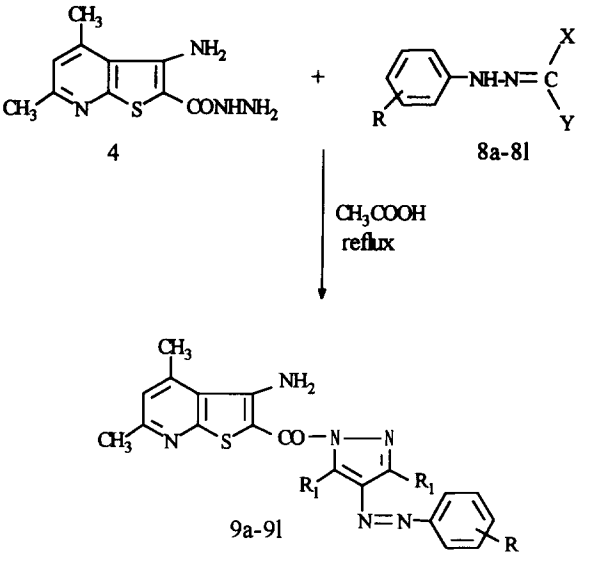


Compd.	R	X	Y	Compd.	R	X	Y
5a, 6a	H			8d	2-CN	$COCH_3$	$COCH_3$
5b, 6b	2-CH_3			8e	2-NO_2	$COCH_3$	$COCH_3$
5c, 6c	2-Cl			8f	4-$NHCOCH_3$	$COCH_3$	$COCH_3$
5d, 6d	2-CN			8g	H	CN	CN
5e, 6e	2-NO_2			8h	2-CH_3	CN	CN
5f, 6f	2-$NHCOCH_3$			8i	2-Cl	CN	CN
8a	H	$COCH_3$	$COCH_3$	8j	2-CN	CN	CN
8b	2-CH_3	$COCH_3$	$COCH_3$	8k	2-NO_2	CN	CN
8c	2-Cl	$COCH_3$	$COCH_3$	8l	4-$NHCOCH_3$	CN	CN

Scheme 2

such as acetylacetone **7a** and malononitrile **7b** in sodium acetate buffered solution to give the azobenzeneacetylacetone and azobenzenemalononitrile derivatives **8a–8f** and **8g–8l** in good yield, respectively (Scheme 2). Spectral data[16] for such compounds indicate them to have a hydrazone configuration;[17–19] characterisation and spectral data for compounds **8a–8l** are shown in Tables 1 and 2.

Compound **4**, when reacted with the azobenzeneacetylacetone derivatives **8a–8f** in glacial acetic acid yielded the 2-[[4-(arylazo)-3,5-dimethylpyrazol-1-yl]carbonyl]-3-amino-4,6-dimethyl-thieno[2,3-*b*]pyridine dyes **9a–9f** (Scheme 3). The reaction proceeds in two stages, viz., the initially formed



Dye	R	R_1	Dye	R	R_1
9a	H	CH_3	9g	H	NH_2
9b	2-CH_3	CH_3	9h	2-CH_3	NH_2
9c	2-Cl	CH_3	9i	2-Cl	NH_2
9d	2-CN	CH_3	9j	2-CN	NH_2
9e	2-NO_2	CH_3	9k	2-NO_2	NH_2
9f	4-$NHCOCH_3$	CH_3	9l	4-$NHCOCH_3$	NH_2

Scheme 3

hydroxypyrazoline subsequently loses water by an acid-catalysed reaction.[20-22] Compound **4** when reacted with azobenzenemalononitrile derivatives **8g–8l** in a similar manner gave the 2-[[4-(arylazo)-3,5-dicyanopyrazol-1-yl]carbonyl]-3-amino-4,6-dimethyl-thieno[2,3-*b*]pyridine dyes **9g–9l**. Characterisation and spectral data of compounds **9a–9l** are shown in Tables 3 and 4.

The absorption maxima of dyes **9a–9l** were recorded in DMF and are shown in Table 5. The absorption maxima of dyes **9a–9f** varied from 405 to 412 nm and those of dyes **9g–9l** from 414 to 430 nm. It was observed in general that dyes **9g–9l** derived from azobenzenemalononitrile derivatives **8g–8l** were bathochromic when compared with analogous dyes **9a–9f** derived from azobenzeneacetylacetone derivatives **8a–8f**. This bathochromic shift is attributed to the stronger electron-acceptor of the amino group with respect to the methyl group at the 3-, 5- position of the pyrazole ring, thus enhancing electron delocalisation in the dye molecule.[23]

TABLE 2
Spectral Data of Arylazoacetylacetone and Arylazomalononitrile Derivatives (**8a–8l**)

Compound	*MS* *(m/e M^+)*	*IR* *(KBr)* *ν (cm^{-1})*	*^1H NMR*[a] *($CDCl_3$)* *δ (ppm)*
8a	204	1678 (C=O)	2·45 (s, 3H, $COCH_3$), 2·56 (s, 3H, $COCH_3$), 7·37–7·15 (m, 5H, Aromatic-H), 14·70 (s, 1H, NH—N=)
8b	218	1666 (C=O)	2·33 (s, 3H, CH_3), 2·45 (s, 3H, $COCH_3$), 2·57 (s, 3H, $COCH_3$), 7·69–7·06 (m, 4H, Aromatic-H), 14·90 (s, 1H, NH—N=)
8c	238·5	1689 (C=O)	2·46 (s, 3H, $COCH_3$), 2·59 (s, 3H, $COCH_3$), 7·77–7·07 (m, 4H, Aromatic-H), 14·81 (s, 1H, NH—N=)
8d	229	2218 (C≡O), 1680 (C=O)	2·47 (s, 3H, $COCH_3$), 2·58 (s, 3H, $COCH_3$), 7·75–7·17 (m, 4H, Aromatic-H), 14·93 (s, 1H, NH—N=)
8e	249	1687 (C=O)	2·16 (s, 3H, $COCH_3$), 2·11 (s, 3H, $COCH_3$), 7·74–7·22 (m, 4H, Aromatic-H), 15·01 (s, 1H, NH—N=)[b]
8f	261	3332 (NH), 1681, 1651 (C=O)	2·18 (s, 3H, $NHCOCH_3$), 2·45 (s, 3H, $COCH_3$), 2·57 (s, 3H, $COCH_3$), 8·21 (s, 1H, NHCO), 7·96–7·73 (dd, 4H, Aromatic-H), 14·85 (s, 1H, NH—N=)[b]
8g	170	2230, 2215 (C≡N)	—
8h	184	2227 (C≡N)	—
8i	204·5	2231 (C≡N)	—
8j	195	2233 (C≡N)	—
8k	215	2235 (C≡N)	—
8l	227	2224 (C≡N)	—

[a] Abbreviations: s, single; d, doublet; m, multiplet.
[b] NMR in CF_3COOD.

These dyes were applied to polyester and polyamide fibres at 1% shade, and gave pale yellow to orange-yellow hues. Relevant fastness data for the dyes are given in Table 5. In general, the lightfastness of these dyes was good to very good (4–6) and the sublimation fastness of the dyes on polyester fibres was excellent (5).

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

TABLE 3

Characterisation Data for 2-[[4-(Arylazo)-3,5-disubstituted-pyrazol-1-yl]carbonyl]-3-amino-4,6-dimethyl-thieno[2,3-*b*]pyridine Derivatives (**9a–9l**)

Dye	*M.p.*[a] *(°C)*	*Yield (%)*	*Molecular formula*	*Elemental analysis (%) calcd/found*		
				C	*H*	*N*
9a	279	46·7	$C_{21}H_{20}N_6OS$	62·36	4·98	20·78
				62·34	5·04	20·76
9b	281	47	$C_{22}H_{22}N_6OS$	63·14	5·30	20·08
				63·22	5·38	20·03
9c	289	38·5	$C_{21}H_{19}ClN_6OS$	57·46	4·36	19·15
				57·46	4·41	19·20
9d	283	32	$C_{22}H_{19}N_7OS$	61·52	4·46	22·83
				61·54	4·49	22·91
9e	278	32·5	$C_{21}H_{19}N_7O_3S$	56·12	4·26	21·81
				56·10	4·29	21·88
9f	270	51	$C_{23}H_{23}N_7O_2S$	59·85	5·02	21·24
				59·81	5·01	21·22
9g	278	56	$C_{19}H_{18}NOS$	56·14	4·46	27·57
				56·11	4·50	27·51
9h	290	50·4	$C_{20}H_{20}N_8OS$	57·13	4·79	26·65
				57·18	4·81	26·57
9i	313	59·2	$C_{19}H_{17}ClN_8OS$	51·76	3·89	25·41
				51·79	3·91	25·49
9j	290	48	$C_{20}H_{17}N_9OS$	55·67	3·97	29·22
				55·77	4·01	29·31
9k	314	33	$C_{19}H_{17}N_9O_3S$	50·55	3·80	27·92
				50·68	3·85	27·86
9l	303	50·2	$C_{21}H_{21}N_9O_2S$	54·42	4·57	27·20
				54·41	4·59	27·25

[a] Solvent of recrystallization: DMF.

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^{-1}.

3.2 3-Amino-4,6-dimethyl-2-ethoxycarbonyl-thieno[2,3-*b*]pyridine (3)

To a solution of 3-cyano-4,6-dimethyl-2(1H)-pyridinethione **1** (1·64 g, 0·01 mole) in DMF (50 ml), potassium carbonate anhydrous (2·76 g, 0·02 mole) and ethyl chloroacetate **2** (1·23 g, 0·01 mole) were added. The reac-

TABLE 4

Spectral Data of 2-[[4-(Arylazo)-3,5-disubstituted-pyrazol-1-yl]carbonyl]-3-amino-4,6-dimethylthieno[2,3-*b*]pyridine Derivatives (**9a–9l**)

Dye	*MS* (*m/e* M^+)	*IR* (*KBr*) ν (cm^{-1})	^1H *NMR*[a] (CF_3COOD) δ (*ppm*)
9a	404	3445 (NH_2), 1640 (C=O)	2·80 (s, 6H, 3-,5-CH_3 of pyrazol), 2·93 (s, 3H, 4-CH_3), 2·95 (s, 3H, 6-CH_3), 7·62 (s, 1H, 5-H), 7·53–7·49, 7·89–7·87 (m, 5H, Aromatic-H).
9b	418	3472 (NH_2), 1665 (C=O)	2·69 (s, 3H, 2-CH_3 of Aromatic), 2·84–2·83 (s, 6H, 3-,5-CH_3 of pyrazol), 3·00–2·98 (s, 6H, 4-,6-CH_3), 7·68 (s, 1H, 5-H), 7·38–7·23 (m, 2H, 4-,5-H of Aromatic), 7·42 (d, 1H, 3-H of Aromatic), 7·69 (d, 1H, 6-H of Aromatic).
9c	438·5	3494 (NH_2), 1660 (C=O)	2·88 (s, 6H, 3-,5-CH_3 of pyrazol), 3·00 (s, 6H, 4-,6-CH_3), 7·70 (s, 1H, 5-H), 7·49–7·34 (m, 2H, 4-,5-H of Aromatic), 7·59 (d, 1H, 6-H of Aromatic), 7·80 (d, 1H, 3-H of Aromatic).
9d	429	3476 (NH_2), 2210 (C≡N) 1641 (C=O)	2·90 (s, 6H, 3-,5-CH_3 of pyrazol), 3·00 (s, 6H, 4-,6-CH_3), 7·69 (s, 1H, 5-H), 7·87–7·70 (m, 2H, 4-,5-H of Aromatic), 8·04–7·96 (dd, 2H, 3-,6-H of Aromatic).
9e	449	3476 (NH_2), 1665 (C=O)	2·86 (s, 6H, 3-,5-CH_3 of pyrazol), 3·03 (s, 6H, 4-,6-CH_3), 7·34 (s, 1H, 5-H), 8·08–7·75 (m, 4H, Aromatic-H).
9f	461	3473, 3456 (NH_2, NH), 1691, 1665 (C=O)	2·58 (s, 3H, $COCH_3$), 2·92 (s, 6H, 3-,5-CH_3 of pyrazol), 3·07 (s, 6H, 4-,6-CH_3), 7·74 (s, 1H, 5-H), 7·77 (d, 2H, 3-,5-H of Aromatic), 8·09–8·06 (d, 2H, 2-,6-H of Aromatic).
9g	406	3475 (NH_2), 1665 (C=O)	3·22 (s, 3H, 4-CH_3), 3·38 (s, 3H, 6-CH_3), 7·47 (s, 1H, 5-H), 8·06–7·64 (m, 5H, Aromatic-H).
9h	420	3475 (NH_2), 1665 (C=O)	2·56 (s, 3H, 2-CH_3 of Aromatic), 3·25 (s, 3H, 4-CH_3), 3·43 (s, 3H, 6-CH_3), 7·43 (s, 1H, 5-H), 7·99–7·56 (m, 5H, Aromatic-H).
9i	440·5	3427 (NH_2), 1641 (C=O)	3·40 (s, 3H, 4-CH_3), 3·51 (s, 3H, 6-CH_3), 7·87 (s, 1H, 5-H), 8·05–7·91 (m, 4H, Aromatic-H).
9j	431	3452 (NH_2), 2205 (C≡N) 1641 (C=O)	3·47 (s, 3H, 4-CH_3), 3·65 (s, 3H, 6-CH_3), 8·01 (s, 1H, 5-H), 8·45–8·10 (m, 4H, Aromatic-H).
9k	451	3473 (NH_2), 1659 (C=O)	3·45 (s, 3H, 4-CH_3), 3·63 (s, 3H, 6-CH_3), 8·10 (s, 1H, 5-H), 8·47–8·13 (dd, 2H, 4-,5-H of Aromatic), 8·83 (d, 1H, 6-H of Aromatic), 8·94 (d, 1H, 3-H of Aromatic).
9l	463	3474, 3450 (NH_2, NH), 1690 (C=O)	2·73 (s, 3H, $COCH_3$), 3·19 (s, 3H, 4-CH_3), 3·36 (s, 3H, 6-CH_3), 7·74 (s, 1H, 5-H), 8·44 (d, 2H, 3-,5-H of Aromatic), 8·72 (d, 2H, 2-,6-H of Aromatic), 8·04 (br, 1H, CONH).

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

TABLE 5
Absorption Spectra and Dyeing Properties of 2-[[4-(Arylazo)-3,5-disubstituted-pyrazol-1-yl]carbonyl]-3-amino-4,6-dimethyl-thieno[2,3-*b*]pyridine Dyes (**9a–9l**)

Dye	*Absorption* λ_{max} *in DMF (nm)*	*log ε*	*Lightfastness*		*Sublimation fastness (Polyester)*
			Polyester	*Polyamide*	
9a	405	4·23	5	5	5
9b	406	4·24	5	5	5
9c	408	4·26	5	5	5
9d	411	4·22	5	5	5
9e	412	4·27	4	4	5
9f	405	4·35	4	5	5
9g	414	4·38	4	4	5
9h	415	4·42	6	6	5
9i	420	4·63	4	5	5
9j	423	4·60	6	6	5
9k	430	4·43	5	6	5
9l	425	4·47	3	6	5

tion mixture was 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 ethyl acetate to give **3** (2·45 g, 98%); m.p. 159–161°C; IR (KBr): ν 3440, 3296 (NH_2), 1680 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 1·27 (3H, t, CH_3), 2·49 (3H, s, 4-CH_3), 2·69 (3H, s, 6-CH_3), 4·42 (2H, q, OCH_2), 6·75 (2H, br, NH_2), 7·03 (1H, s, 5-H); ms: M^+ 250.

Calcd for $C_{12}H_{14}N_2O_2S$: C, 57·60; H, 5·60; N, 11·20. Found: C, 57·75; H, 5·56; N, 11·06%.

3.3 3-Amino-4,6-dimethyl-2-thieno[2,3-*b*]pyridine carbohydrazide (4)

A mixture of **3** (2·50 g, 0·01 mole) and hydrazine hydrate (4 ml, 85% solution 0·04 mole) was refluxed in absolute ethanol (4 ml) for 24 h, cooled, and the pale yellow micro needles which separated were collected and washed with ethanol and water. Recrystallisation from benzene/ethanol gave 2·29 g (97%) of **4**; m.p. 220–224°C; IR (KBr): ν 3414–3199 (NH_2, NH), 1604 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 2·48 (3H, s, 4-CH_3), 2·69 (3H, s, 6-CH_3), 4·38 (2H, br, N—NH_2), 6·70 (2H, br, NH_2), 6·98 (1H, s, 5-H), 8·95 (1H, br, NH); ms: M^+ 236.

Calcd for $C_{10}H_{12}N_4OS$: C, 50·83; H, 5·12; N, 23·71. Found: C, 50·73; H, 5·31; N, 23·68%.

3.4 Azobenzeneacetylacetone derivatives (8a–8f): general procedure

The appropriate arylamine **5a–5f** (0·01 mole) was dissolved in aqueous hydrochloric acid (8 ml; 1:1) and cooled to 0–5°C, prior to addition of a cold solution of sodium nitrite (0·7 g in 3 ml water) whilst maintaining the temperature at 0–5°C.

The diazonium liquor was then added dropwise to a cooled and stirred mixture of acetylacetone **7a** (1·0 g, 0·01 mole) and sodium acetate (2·0 g, dissolved in 10 ml of 50% aqueous ethanol). Stirring was continued for 1·5 h and the resulting crystals collected, washed with water and recrystallised from chloroform. Physical and spectral data of the compounds are given in Tables 1 and 2.

3.5 Azobenzenemalononitrile derivatives (8g–8l)

The above procedures (Section 3.4) were repeated, except that acetylacetone **7a** was replaced by malononitrile **7b**. Physical and spectral data of the compounds are given in Tables 1 and 2.

3.6 2-[[4-(Arylazo)-3,5-dimethyl-pyrazol-1-yl]carbonyl]-3-amino-4,6-dimethyl-thieno[2,3-*b*]pyridines (9a–9f): general procedure

A mixture of 3-amino-4,6-dimethyl-2-thieno[2,3-*b*]pyridine carbohydrazide **4** (1·18 g, 0·005 moles) and the arylazoacetylacetone **8a–8f** (0·005 moles) was refluxed in glacial acetic acid (10 ml) with stirring for 6 h. The reaction mixture was cooled to room temperature and the separated solid was filtered, washed with water, dried and recrystallised from dimethylformamide. Physical and spectral data of the dyes are given in Tables 3 and 4.

3.7 2-[[4-(Arylazo)-3,5-diamino-pyrazol-1-yl]carbonyl]-3-amino-4,6-dimethyl-thieno[2,3-*b*]pyridines (9g–9l)

The above procedures (Section 3.6) were repeated, except that arylazoacetylacetone **8a–8f** was replaced by arylazomalononitrile **8g–8l**. Physical and spectral data of the compounds are given in Tables 3 and 4.

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