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Dyes and Pigments 74 (2007) 578–584
DYES and PIGMENTS
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A facile synthesis of some new pyrazolo[1,5-*a*]pyrimidine heterocyclic disazo dyes and an evaluation of their solvatochromic behaviour

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Received 22 November 2005; received in revised form 11 January 2006; accepted 28 March 2006
Available online 6 June 2006

Abstract

Hetarylmalononitriles (thiazolylmalononitrile and benzothiazolylmalononitrile) were prepared by the coupling reaction of malononitrile with heterocyclic amines in nitrosyl sulfuric acid. 4-Hetarylazo-3,5-diaminopyrazole compounds were obtained by the reaction of hetarylmalononitriles with hydrazine hydrate (64%). Both compounds can react with arylazo- and hetarylazomalononitriles to give 3,6-di-(aryl or hetaryl)-azo-2,5,7-triaminopyrazolo[1,5-*a*]pyrimidine heterocyclic disazo dyes. These dyes were characterized by elemental and spectral analyses (IR, ^{1}H NMR and mass). The solvatochromic behaviour in various solvents was evaluated.

Keywords: Hetarylazopyrazole; Dihetarylazo-pyrazolo[1,5-*a*]pyrimidine; Disazo dyes; Solvents' effect

1. Introduction

In general the fused heterocyclic compound, pyrazolo[1,5-*a*] pyrimidine and its derivatives are known to possess pharmacological activity and anxiolytic properties. They are also used as intermediates in the dyestuff industry [1–13]. In our previous paper, we described the synthesis and solvatochromic properties of some symmetrical and asymmetrical 3,6-diaryl-2,5,7-triaminopyrazolo[1,5-*a*]pyrimidine disazo dyes, obtained by the cyclization of arylazomalononitriles with 4-arylazo-3,5-diaminopyrazole compounds. In continuation of our work, we report here the results of our new approaches into the reaction of malononitrile with heterocyclic amines. The study has resulted in the development of a novel procedure for the synthesis of 4-hetarylazo-3,5-diaminopyrazole compounds. It has been found that these compounds react easily with arylazo- and hetarylazomalononitrile to afford a number of new 3,6-disubstituted-azoyl-2,5,7-triaminopyrazolo[1,5-*a*]pyrimidine heterocyclic disazo dyes with different arylazo- and hetarylazo groups in 3,6-position, respectively. Their absorption properties in various solvents were also studied.

2. Results and discussion

In this paper, we report the synthesis and characterization of some new heterocyclic disazo dyes **III**, **IV** and **V**. A number of hetaryl (or aryl)-azomalononitriles **I** and 4-hetaryl(or aryl)-azo-3,5-diaminopyrazoles **II** were prepared as intermediates in the synthesis of the corresponding heterocyclic disazo dyes, as shown in Scheme 1. The intermediates **Ic–Ig** and **IIc–IIg** have previously been reported and are characterized by spectral analyses [5].

2.1. Preparation of 4-hetarylazo-3,5-diaminopyrazole intermediates *IIa* and *IIb*

Hetarylazomalononitriles **Ia–Ib** were prepared by diazotization of heterocyclic amines in nitrosyl sulfuric acid [14–16], followed by coupling with malononitrile [5,17]. **Ia–Ib** reacted then via cyclization with hydrazine hydrate in ethanol (95%) under reflux for 3–4 h to give **IIa–IIb** as yellow crystals in moderate yield. The physical data and elemental analyses of

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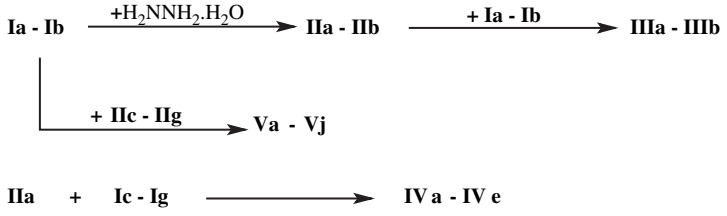
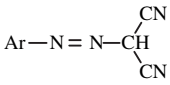
doi:10.1016/j.dyepig.2006.03.022





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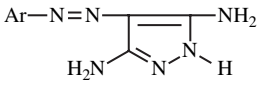
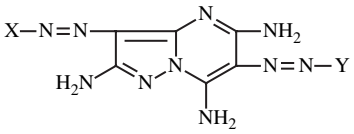


II

Compound	Ar	Compound	Ar
I a	Thiazolyl	**II a**	Thiazolyl
I b	Benzothiazolyl	**II b**	Benzothiazolyl
I c	C_6H_5	**II c**	C_6H_5
I d	C_6H_4Cl-2	**II d**	C_6H_4Cl-2
I e	$C_6H_4NO_2$-2	**II e**	$C_6H_4NO_2$-2
I f	C_6H_4Cl-4	**II f**	C_6H_4Cl-4
I g	$C_6H_4NO_2$-4	**II g**	$C_6H_4NO_2$-4



III, IV, V

Dye	X	Y	Dye	X	Y
III a	Thiazolyl	Thiazolyl	**V a**	C_6H_5	Thiazolyl
III b	Benzothiazolyl	Benzothiazolyl	**V b**	C_6H_5Cl-2	Thiazolyl
IV a	Thiazolyl	C_6H_5	**V c**	$C_6H_5NO_2$-2	Thiazolyl
IV b	Thiazolyl	C_6H_5Cl-2	**V d**	C_6H_5Cl-4	Thiazolyl
IV c	Thiazolyl	$C_6H_5NO_2$-2	**V e**	$C_6H_5NO_2$-4	Thiazolyl
IV d	Thiazolyl	C_6H_5Cl-4	**V f**	C_6H_5	Benzothiazolyl
IV e	Thiazolyl	$C_6H_5NO_2$-4	**V g**	C_6H_5Cl-2	Benzothiazolyl
			V h	$C_6H_5NO_2$-2	Benzothiazolyl
			V i	C_6H_5Cl-4	Benzothiazolyl
			V j	$C_6H_5NO_2$-4	Benzothiazolyl

Scheme 1.

Ia–**Ib** and **IIa**–**IIb** are summarized in Section 3 and their spectral characterizations are listed in Table 1.

2.2. Preparation of heterocyclic disazo dyes *III*, *IV* and *V*

The symmetrical heterocyclic disazo dyes 3,6-disubstituted hetarylazo-2,5,7-triaminopyrazolo[1,5-*a*]pyrimidine derivatives **IIIa**–**IIIb** were synthesized by cyclization, involving the reaction of **IIa**–**IIb** with equimolar amounts of **Ia**–**Ib** in ethanol (95%) under reflux for 3–4 h to give red-brown solids in moderate yield. Asymmetrical heterocyclic disazo dyes **IV** and **V** were synthesized by the same procedure. The disazo dyes **IVa**–**IVe** were synthesized by cyclization, involving the reaction of **IIa** with equimolar amounts of **Ic**–**Ig** [5,17–22] in ethanol under reflux for 3–4 h, in moderate yield. In contrast to **IV**, disazo dyes **Va**–**Ve** were obtained by the reaction of **Ia** with **IIc**–**IIg** in middle yield. Derivative **Ib** as intermediate reacted with **IIc**–**IIg** to give the heterocyclic disazo dyes **Vf**–**Vj** in low yield. These asymmetrical heterocyclic disazo dyes were in the range orange to brown solids of colour. The physical data and elemental analyses of **III**, **IV** and **V** are summarized in Section 3 and their spectral characterizations are listed in Table 1.

2.3. Electronic absorption properties of heterocyclic disazo dyes

Absorption spectra of some heterocyclic disazo dyes **IIIa**–**IIIb**, **IVa**–**IVe** and **Va**–**Vj** were recorded in various solvents at a concentration range of 10^{-6}–10^{-7} M, and the results are given in Table 2. We found that the electronic absorption spectra of these heterocyclic disazo dyes indicated a regular variation with the polarity of solvents, which did not change significantly. Apparently, these dyes did not exhibit a strong solvent dependence. The absorption maximum of these dyes

Table 1
Spectral data of dyes **II**, **III**, **IV** and **V**

Dye	MS (*m/e*, M^+)	IR (KBr) ν (cm^{-1})	^1H NMR[a] (DMSO-d_6) δ (ppm)
IIa	209	3388 (N–H), 1625 (C=N)	7.33 (1H, d, 5-thiazole-H), 7.63 (1H, d, 4-thiazole-H)
IIb	259	3389 (N–H), 1637 (C=N)	7.26–7.29 (1H, t, 6-benzothiazolyl-H), 7.37–7.40 (1H, t, 5-benzothiazolyl-H), 7.75 (1H, d, 4-benzothiazolyl-H), 7.86 (1H, d, 7-benzothiazolyl-H)
IIIa	386	3294 (N–H), 1608 (C=N)	7.49 (1H, d, 5-thiazole-H), 7.67 (1H, d, 4-thiazole-H), 7.78 (1H, d, 5-thiazole-H), 7.86 (1H, d, 4-thiazole-H)
IIIb	486	3279 (N–H), 1608 (C=N)	6.97 (2H, s, NH_2), 7.45–8.02 (8H, m, benzothiazolyl-H)
IVa	379	3268 (N–H), 1625 (C=N)	7.07 (2H, s, NH_2), 7.31–7.50 (5H, m, phenyl-H), 7.74 (1H, d, 5-thiazole-H), 8.05 (1H, d, 4-thiazole-H)
IVb	413	3285 (N–H), 1604 (C=N)	7.08 (2H, s, NH_2), 7.37–8.34 (4H, m, phenyl-H), 7.46 (1H, d, 5-thiazole-H), 7.77 (1H, d, 4-thiazole-H)
IVc	424	3306 (N–H), 1605 (C=N), 1504, 1344 (NO_2)	7.08 (2H, s, NH_2), 7.47 (1H, d, 5-thiazole-H), 7.77 (1H, d, 4-thiazole-H), 7.55–8.44 (4H, m, phenyl-H)
IVd	413	3270 (N–H), 1625 (C=N)	7.06 (2H, s, NH_2), 7.45–7.51 (4H, m, phenyl-H), 7.75 (1H, d, 5-thiazole-H), 8.10 (1H, d, 4-thiazole-H)
IVe	424	3276 (N–H), 1631 (C=N), 1514, 1337 (NO_2)	7.19 (2H, s, NH_2), 7.66 (1H, d, 5-thiazole-H), 7.88 (1H, d, t, thiazole-H), 7.86–8.34 (4H, m, phenyl-H)
Va	379	3271 (N–H), 1630 (C=N)	7.00 (2H, s, NH_2), 7.31–8.04 (5H, m, phenyl-H), 7.62 (1H, d, 5-thiazole-H), 7.83 (1H, d, 4-thiazole-H)
Vb	413	3272 (N–H), 1609 (C=N)	7.07 (2H, s, NH_2), 7.34–8.35 (4H, m, phenyl-H), 7.65 (1H, d, 5-thiazole-H), 7.85 (1H, d, 4-thiazole-H)
Vc	424	3257 (N–H), 1623 (C=N), 1513, 1345 (NO_2)	7.07 (2H, s, NH_2), 7.66 (1H, d, 5-thiazole-H), 7.86 (1H, d, 4-thiazole-H), 7.76–8.12 (4H, m, phenyl-H)
Vd	413	3282 (N–H), 1603 (C=N)	7.02 (2H, s, NH_2), 7.47–8.12 (4H, m, phenyl-H), 7.66 (1H, d, 5-thiazole-H), 7.86 (1H, d, 4-thiazole-H)
Ve	424	3291 (N–H), 1614 (C=N), 1511, 1321 (NO_2)	7.07 (2H, s, NH_2), 7.47 (1H, d, 5-thiazole-H), 7.77 (1H, d, 4-thiazole-H), 8.29 (4H, s, phenyl-H)
Vf	429	3271 (N–H), 1605 (C=N)	7.25 (2H, s, NH_2), 7.33–8.08 (9H, m, phenyl-H, benzothiazolyl-H)
Vg	463	3304 (N–H), 1623 (C=N)	7.25 (2H, s, NH_2), 7.66–7.99 (4H, m, benzothiazolyl-H), 7.48–8.29 (4H, m, phenyl-H)
Vh	474	3279 (N–H), 1615 (C=N), 1520, 1336 (NO_2)	7.10 (2H, s, NH_2), 7.34–7.86 (4H, m, benzothiazolyl-H), 8.01–8.45 (4H, m, phenyl-H)
Vi	463	3280 (N–H), 1615 (C=N)	7.24 (2H, s, NH_2), 7.32–7.99 (4H, m, benzothiazolyl-H), 7.73–8.12 (4H, m, phenyl-H)
Vj	474	3276 (N–H), 1616 (C=N) 1514, 1326 (NO_2)	7.23 (2H, s, NH_2), 7.33–8.00 (4H, m, benzothiazolyl-H), 8.24–8.33 (4H, m, phenyl-H)

[a] Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet.

shifted considerably in this order: DMF > acetone > ethyl acetate. The spectral shifts of dye **IVa** in various solvents are shown in Fig. 1. The absorption maximum of dye **IVa** showed bathochromic shift in DMF and acetone, with respect to the absorption maximum in ethyl acetate (e.g. λ_{max} is 485 nm in DMF, 476 nm in acetone and 470 nm in ethyl acetate). The same trends of absorption shifts in various solvents were observed for the entire series of dyes **IIIa–IIIb**, **IVa–IVe** and **Va–Vj**, as shown in Table 2. The substituents' effects of the heterocyclic disazo dyes **III**, **IV** and **V** on the 3,6-positions were evaluated. The spectral shifts of dyes **IIIa**, **IVa** and **Va** in acetone at a concentration range of 10^{-6}–10^{-7} M are given in Table 3. The absorption maxima of dyes **IIIa**, **IVa** and **Va** ranged from 476 nm to 499 nm are shown in Fig. 2. We found that dyes **IVa** and **Va** contain an electron donor group (phenyl) on the 6th- and 3rd-position of pyrazolo[1,5-*a*]pyrimidine ring, so that λ_{max} of dye **IVa** showed hypsochromic shift of −23 nm relative to dye **IIIa**, which contains an electron rich group (thiazole); λ_{max} of dye **Va** is −19 nm shorter than that of dye **IIIa** in acetone. The spectral shifts of dyes **IVa–IVe** and **Va–Vj** were recorded in acetone at

Table 2
Absorption spectra of dyes **III**, **IV** and **V** in various solvents

Compounds	DMF	Acetone	Ethyl acetate	log ε (acetone)
IIIa	506	499	497	4.44
IIIb	517	514	513	4.49
IVa	485	476	470	4.31
IVb	493	486	483	4.38
IVc	502	495	491	4.31
IVd	490	478	469	4.36
IVe	511	496	492	4.33
Va	485	480	479	4.34
Vb	495	489	486	4.35
Vc	501	490	489	4.24
Vd	491	485	480	4.25
Ve	515	504	499	4.41
Vf	494	489	486	4.28
Vg	506	498	496	4.39
Vh	512	504	502	4.32
Vi	500	494	492	4.22
Vj	518	510	508	4.35

The ε_r value of solvents: DMF = 36.7; acetone = 20.7; and ethyl acetate = 6.02.

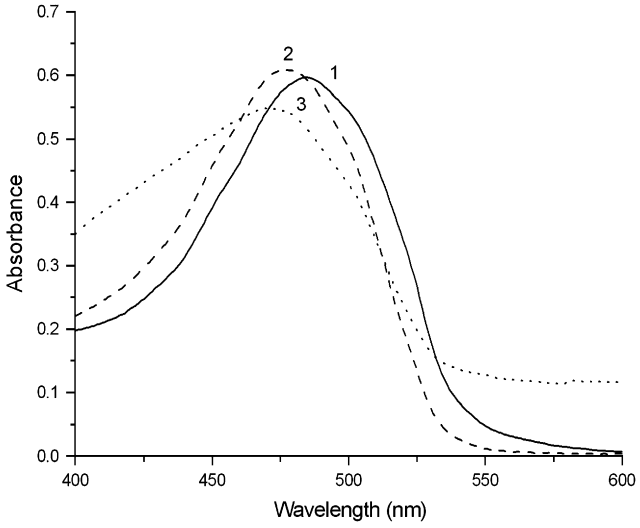
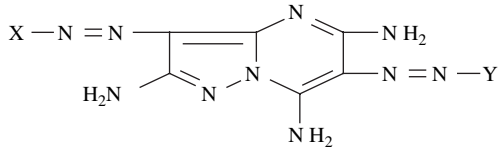


Fig. 1. Absorption spectra of dyes **IVa**: 1. DMF; 2. Acetone; 3. Ethyl acetate (conc.: 10^{-6}–10^{-7} mol/L).

Table 3
Substituent effect of dyes **IIIa**, **IVa**, **Va** in acetone



Compounds	λ_{max}	X	Y	$\Delta\lambda$[a]
IIIa	499	Thiazolyl	Thiazolyl	–
IVa	476	Thiazolyl	C_6H_5	−23
Va	480	C_6H_5	Thiazolyl	−19

[a] Relative to **IIIa**: X = Y = thiazolyl.

a concentration range of 10^{-6}–10^{-7} M, and the results are given in Table 4. The absorption maxima of dyes **Va**–**Ve** ranged from 480 nm to 504 nm are shown in Fig. 3. We found that dyes **Vc** and **Ve** contain a stronger electron acceptor of nitro group in the *para*- and *ortho*-position of phenylsubstituted on the 3rd-position of the pyrazolo[1,5-*a*]pyrimidine ring, so that the λ_{max} of dyes **Vc** and **Ve** showed bathochromic shift of +10 nm and +24 nm relative to dye **Va**, respectively; λ_{max} of dyes **Vb** and **Vd** is +9 nm and +5 nm longer than that of dye **Va**, due to weaker electron acceptor of chloro group in the *para*- and *ortho*-position of phenyl group on the 3rd-position of the pyrazolo[1,5-*a*]pyrimidine ring, respectively. Similar effects of the substituent were also observed in the absorption maxima of dyes **IVa**–**IVe** and **Va**–**Vj**, as shown in Table 4.

3. Experimental

All melting points are uncorrected and are in degree Celsius. The IR spectra were recorded on a JASCO FT-IR-3 spectrometer (KBr). The ^{1}H NMR spectra were obtained on a Joel-EX-400 MHz NMR spectrometer, and the chemical shifts are expressed in δ (ppm) using TMS as an internal standard. The

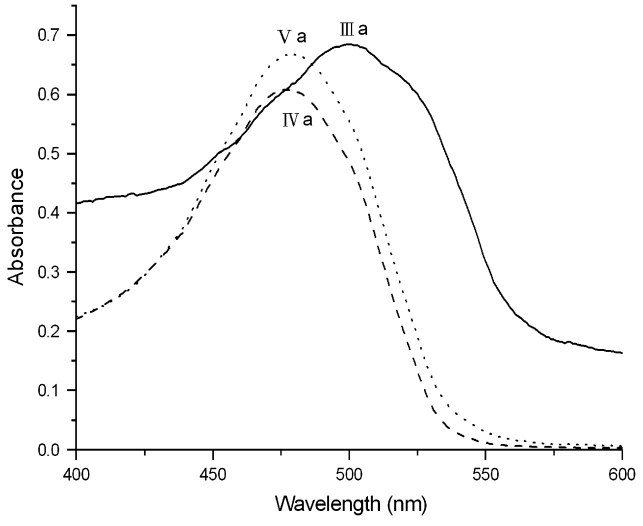
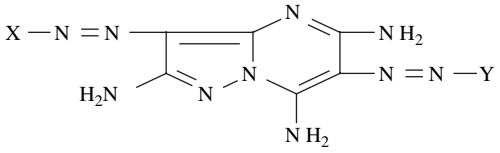


Fig. 2. Absorption spectra of dyes **IIIa**, **IVa**, **Va** in acetone (conc.: 10^{-6}–10^{-7} mol/L).

Table 4
Substituent effect of dyes **Va**–**Ve** in acetone



Compounds	λ_{max}	X	Y	$\Delta\lambda$[a]
IVa	476	Thiazolyl	C_6H_5	–
IVb	486	Thiazolyl	C_6H_5Cl-2	+10
IVc	495	Thiazolyl	$C_6H_5NO_2$-2	+19
IVd	478	Thiazolyl	C_6H_5Cl-4	+5
IVe	496	Thiazolyl	$C_6H_5NO_2$-2	+20
Compounds	λ_{max}	X	Y	$\Delta\lambda$[b]
Va	480	C_6H_5	Thiazolyl	–
Vb	489	C_6H_5Cl-2	Thiazolyl	+9
Vc	490	$C_6H_5NO_2$-2	Thiazolyl	+10
Vd	485	C_6H_5Cl-4	Thiazolyl	+5
Ve	504	$C_6H_5NO_2$-4	Thiazolyl	+24
Compounds	λ_{max}	X	Y	$\Delta\lambda$[c]
Vf	489	C_6H_5	Benzothiazolyl	–
Vg	498	C_6H_5Cl-2	Benzothiazolyl	+9
Vh	504	$C_6H_5NO_2$-2	Benzothiazolyl	+15
Vi	494	C_6H_5Cl-4	Benzothiazolyl	+5
Vj	510	$C_6H_5NO_2$-4	Benzothiazolyl	+21

[a] Relative to **IVa**: X = thiazolyl, Y = C_6H_5.
[b] Relative to **IVa**: X = C_6H_5, Y = thiazolyl.
[c] Relative to **IVa**: X = C_6H_5, Y = benzothiazolyl.

mass spectra were obtained from a Finnigan TSQ-700 GC/LC/MS spectrometer. Microanalyses for C, H and N were performed on a Perkin–Elmer 2400(II) elemental analyzer. Absorption spectra were recorded on a Heliosa UV1 in various solvents.

3.1. Preparation of malononitrile derivatives *Ia–Ig*

2-Arylazomalononitrile **Ic**–**Ig** were prepared by the method described in the literature [5,17–22].

The same procedures were used for the syntheses of compounds **Ia**–**Ib**, as represented by the preparation of compound **Ia** below.

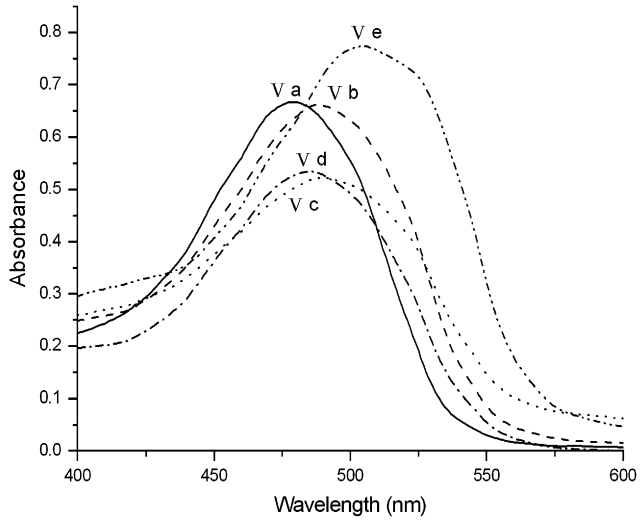


Fig. 3. Absorption spectra of dyes **Va**–**Ve** in acetone (conc.: 10^{-6}–10^{-7} mol/L).

*3.1.1. 2-Thiazolylazomalononitrile (**Ia**)*

A sulfuric acid solution (50%), 10 ml (hydrochloric acid can also be used) of 2-amino-thiazole (1.0 g, 0.01 mol) and an aqueous solution (3 ml) of sodium nitrite (0.72 g, 0.0105 mol) were mixed and stirred at 0 °C for 1 h, followed by the addition of an aqueous solution (10 ml) of the coupling component malononitrile (0.66 g, 0.01 mol) and stirring was continued at 0 °C for 2 h. The resulting product was filtered and the pre-cake was washed with water, dried, and recrystallized from ethanol to give **Ia** as yellow crystals (1.15 g, 65%), m.p. 231–234 °C; *m/e* 177.0 (M^+); FT-IR (KBr, cm^{-1}): 2214 ν (C≡N).

$C_6H_3N_5S$
Calcd: C, 40.67; H, 1.69; N, 39.54
Found: C, 40.64; H, 1.71; N, 39.42

*3.1.2. 2-Benzothiazoylazomalononitrile (**Ib**)*

This compound was obtained from 2-amino-benzothiazole and malononitrile as yellow crystals (1.1 g, 52%), m.p. 192–195 °C; *m/e* 227.0 (M^+); FT-IR (KBr, cm^{-1}): 2224 ν (C≡N).

$C_{10}H_5N_5S$
Calcd: C, 52.86; H, 2.19; N, 30.83
Found: C, 52.91; H, 2.17; N, 30.98

*3.2. Preparation of heterocyclic monoazo dyes **IIa–IIg***

4-Arylazo-3,5-diaminopyrazole **IIc**, **IIf** and **IIg** were prepared by the method described in the literature [5].

The syntheses of monoazo dyes **IIa**, **IIb**, **IId** and **IIe** were carried out by the same procedures, as described below for the preparation of dye **IIa**.

*3.2.1. 4-Thiazolylazo-3,5-diaminopyrazole (**IIa**)*

Hydrazine hydrate (0.59 g, 0.01 mol) was added to a solution of **Ia** (1.77 g, 0.01 mol) and pyridine (0.5 ml) in 30 ml ethanol. The reaction mixture was heated under reflux for 3–4 h, and then cooled to room temperature. The separated solid was filtered, washed with water, dried and recrystallized from ethanol to give **IIa** as orange solids (1.25 g, 60%), m.p. 265–267 °C.

$C_6H_7N_7S$
Calcd: C, 34.45; H, 3.35; N, 46.88
Found: C, 34.41; H, 3.32; N, 46.86

*3.2.2. 4-Benzothiazolylazo-3,5-diaminopyrazole (**IIb**)*

This compound was obtained from **Ib** and hydrazine hydrate as orange crystals (1.32 g, 51%), m.p. > 300 °C.

$C_{10}H_{11}N_7S$
Calcd: C, 46.33; H, 4.24; N, 37.83
Found: C, 46.52; H, 4.21; N, 37.75

*3.2.3. 4-(2-Chloro-phenylazo)-3,5-diaminopyrazole (**IId**)*

This compound was obtained from **Id** and hydrazine hydrate as yellow crystals (1.35 g, 57%), m.p. 270–272 °C.

$C_9H_9Cl\ N_6$
Calcd: C, 45.76; H, 3.81; N, 35.59
Found: C, 45.78; H, 3.83; N, 35.63

*3.2.4. 4-(2-Nitro-phenylazo)-3,5-diaminopyrazole (**IIe**)*

This compound was obtained from **Ie** and hydrazine hydrate as red-brown crystals (1.48 g, 60%), m.p. 255–257 °C.

$C_9H_9N_7O_2$
Calcd: C, 43.72; H, 3.64; N, 39.68
Found: C, 43.71; H, 3.65; N, 39.72

*3.3. Preparation of symmetrical and asymmetrical heterocyclic disazo dyes **IIIa–IIIb**, **IVa–IVe** and **Va–Vj***

*3.3.1. Preparation of symmetrical heterocyclic disazo dyes **IIIa–IIIb***

The syntheses of disazo dyes **IIIa–IIIb** followed the same procedures, as described below for the preparation of dye **IIIa**.

*3.3.1.1. 3,6-Dithiazolylazo-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**IIIa**).* To a solution of **IIa** (2.09 g, 0.01 mol) and pyridine (1 ml) in 30 ml ethanol was added compound **Ia** (1.7 g, 0.01 mol). The reaction mixture was heated under reflux for 3–4 h, and then cooled to room temperature. The separated solid was filtered, washed with hot ethanol, dried and recrystallized from DMF to give **IIIa** as red-brown solids (2.01 g, 52%), m.p. > 300 °C.

$C_{12}H_{10}N_{12}S_2$
Calcd: C, 31.08; H, 2.59; N, 43.52
Found: C, 31.12; H, 2.61; N, 43.41

*3.3.1.2. 3,6-Dibenzothiazolylazo-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**IIIb**).* This compound was obtained from **IIb** and **Ib** as red-brown crystals (2.07 g, 47%), m.p. > 300 °C.

$C_{20}H_{14}N_{12}S_2$
Calcd: C, 49.38; H, 2.88; N, 34.56
Found: C, 49.35; H, 2.89; N, 34.65

*3.3.2. Preparation of asymmetrical heterocyclic disazo dyes **IVa–IVe***

The syntheses of disazo dyes **IVa–IVe** followed the same procedures, as described below for the preparation of dye **IVa**.

*3.3.2.1. 3-Thiazolylazo-6-phenylazo-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**IVa**).* To a solution of **IIa** (2.09 g, 0.01 mol) and pyridine (1.0 ml) in 30 ml ethanol was added compound **Ic** (1.7 g, 0.01 mol). The reaction mixture was heated under reflux for 3–4 h, and then cooled to room temperature. The separated solid was filtered, washed with hot

ethanol, dried and recrystallized from DMF to give **IVa** as orange solids (1.44 g, 38%), m.p. > 300 °C.

$C_{15}H_{13}N_{11}S$
Calcd: C, 47.49; H, 3.43; N, 40.63
Found: C, 47.47; H, 3.44; N, 40.72

*3.3.2.2. 6-(2-Chloro-phenylazo)-3-thiazolylazo-2,5,7-triamino-pyrazolo[1,5-a]pyrimidine (**IVb**).* This compound was obtained from **IIa** and **Id** as orange crystals (1.82 g, 44%), m.p. > 300 °C.

$C_{15}H_{12}ClN_{11}S$
Calcd: C, 43.58; H, 2.91; N, 37.28
Found: C, 43.61; H, 2.89; N, 37.35

*3.3.2.3. 6-(2-Nitro-phenylazo)-3-thiazolylazo-2,5,7-triamino-pyrazolo[1,5-a]pyrimidine (**IVc**).* This compound was obtained from **IIa** and **Ie** as brown crystals (1.69 g, 40%), m.p. > 300 °C.

$C_{15}H_{12}N_{12}O_2S$
Calcd: C, 42.45; H, 2.83; N, 39.62
Found: C, 42.44; H, 2.81; N, 39.64

*3.3.2.4. 6-(4-Chloro-phenylazo)-3-thiazolylazo-2,5,7-triamino-pyrazolo[1,5-a]pyrimidine (**IVd**).* This compound was obtained from **IIa** and **If** as orange crystals (1.82 g, 44%), m.p. > 300 °C.

$C_{15}H_{12}ClN_{11}S$
Calcd: C, 43.58; H, 2.91; N, 37.28
Found: C, 43.60; H, 2.88; N, 37.33

*3.3.2.5. 6-(4-Nitro-phenylazo)-3-thiazolylazo-2,5,7-triamino-pyrazolo[1,5-a]pyrimidine (**IVe**).* This compound was obtained from **IIa** and **Ig** as red-brown crystals (1.69 g, 40%), m.p. > 300 °C.

$C_{15}H_{12}N_{12}O_2S$
Calcd: C, 42.45; H, 2.83; N, 39.62
Found: C, 42.42; H, 2.85; N, 39.65

*3.3.3. Preparation of asymmetrical heterocyclic disazo dyes **Va–Vj***

The syntheses of disazo dyes **Va–Vj** followed the same procedures, as described below for the preparation of dye **Va**.

*3.3.3.1. 3-Phenylazo-6-thiazolylazo-2,5,7-triaminopyrazolo [1,5-a]pyrimidine (**Va**).* To a solution of **Ia** (1.77 g, 0.01 mol) and pyridine (1.0 ml) in 30 ml ethanol was added compound **IIc** (2.02 g, 0.01 mol). The reaction mixture was heated under reflux for 3–4 h, and then cooled to room temperature. The separated solid was filtered, washed with hot ethanol, dried and recrystallized from DMF to give **Va** as red-brown solids (1.59 g, 42%), m.p. > 300 °C.

$C_{15}H_{13}N_{11}S$
Calcd: C, 47.49; H, 3.42; N, 40.63
Found: C, 47.51; H, 3.44; N, 40.58

*3.3.3.2. 3-(2-Chloro-phenylazo)-6-thiazolylazo-2,5,7-triamino-pyrazolo[1,5-a]pyrimidine (**Vb**).* This compound was obtained from **Ia** and **IId** as red-brown crystals (1.86 g, 45%), m.p. > 300 °C.

$C_{15}H_{12}ClN_{11}S$
Calcd: C, 43.58; H, 2.91; N, 37.29
Found: C, 43.56; H, 2.94; N, 37.35

*3.3.3.3. 3-(2-Nitro-phenylazo)-6-thiazolylazo-2,5,7-triamino-pyrazolo[1,5-a]pyrimidine (**Vc**).* This compound was obtained from **Ia** and **IIe** as brown crystals (1.95 g, 46%), m.p. > 300 °C.

$C_{15}H_{12}N_{12}O_2S$
Calcd: C, 42.45; H, 2.83; N, 39.62
Found: C, 42.43; H, 2.80; N, 39.66

*3.3.3.4. 3-(4-Chloro-phenylazo)-6-thiazolylazo-2,5,7-triamino-pyrazolo[1,5-a]pyrimidine (**Vd**).* This compound was obtained from **Ia** and **IIf** as red-brown crystals (1.78 g, 43%), m.p. > 300 °C.

$C_{15}H_{12}ClN_{11}S$
Calcd: C, 43.58; H, 2.91; N, 37.29
Found: C, 43.55; H, 2.93; N, 37.37

*3.3.3.5. 3-(4-Nitro-phenylazo)-6-thiazolylazo-2,5,7-triamino-pyrazolo[1,5-a]pyrimidine (**Ve**).* This compound was obtained from **Ia** and **IIg** as red-brown crystals (1.74 g, 41%), m.p. > 300 °C.

$C_{15}H_{12}N_{12}O_2S$
Calcd: C, 42.45; H, 2.83; N, 39.62
Found: C, 42.41; H, 2.81; N, 39.68

*3.3.3.6. 6-Benzothiazolylazo-3-phenylazo-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**Vf**).* This compound was obtained from **Ib** and **IIc** as red-brown crystals (1.72 g, 40%), m.p. > 300 °C.

$C_{19}H_{15}N_{11}S$
Calcd: C, 53.15; H, 3.49; N, 35.89
Found: C, 53.17; H, 3.50; N, 35.91

*3.3.3.7. 6-Benzothiazolylazo-3-(2-chloro-phenylazo)-2,5,7-triaminopyrazolo[1,5-a] -pyrimidine (**Vg**).* This compound was obtained from **Ib** and **IId** as orange crystals (1.71 g, 37%), m.p. > 300 °C.

$C_{19}H_{14}ClN_{11}S$
Calcd: C, 49.24; H, 3.02; N, 33.26
Found: C, 49.25; H, 3.03; N, 32.22

*3.3.3.8. 6-Benzothiazolylazo-3-(2-nitro-phenylazo)-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**Vh**).* This compound was obtained from **Ib** and **IIe** as brown crystals (1.61 g, 34%), m.p. > 300 °C.

$C_{19}H_{14}N_{12}O_2S$
Calcd: C, 48.11; H, 2.95; N, 35.44
Found: C, 48.13; H, 2.92; N, 35.48

*3.3.3.9. 6-Benzothiazolylazo-3-(4-chloro-phenylazo)-2,5,7-triaminopyrazolo[1,5-a]-pyrimidine (**Vi**).* This compound was obtained from **Ib** and **IIf** as red-brown crystals (1.76 g, 38%), m.p. > 300 °C.

$C_{19}H_{14}ClN_{11}S$
Calcd: C, 49.24; H, 3.02; N, 33.26
Found: C, 49.23; H, 3.01; N, 32.24

*3.3.3.10. 6-Benzothiazolylazo-3-(4-nitro-phenylazo)-2,5,7-triaminopyrazolo[1,5-a]-pyrimidine (**Vj**).* This compound was obtained from **Ib** and **IIg** as brown crystals (1.71 g, 36%), m.p. > 300 °C.

$C_{19}H_{14}N_{12}O_2S$
Calcd: C, 48.11; H, 2.95; N, 35.44
Found: C, 48.13; H, 2.94; N, 35.49

Acknowledgement

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

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