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Review

Synthesis and solvatochromic properties of 3,6-bis-hetarylazo dyes derived from pyrazolo[1,5-*a*]pyrimidine

Pi Chen Tsai, Ing Jing Wang*

Department of Polymer Engineering, National Taiwan University of Science and Technology, Taipei 10772, Taiwan

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Abstract

Novel, symmetrical and asymmetrical, 3,6-bis-hetarylazo-2,5,7-triaminopyrazolo[1,5-*a*]pyrimidine heterocyclic disazo dyes were synthesized via cyclization from substituted hetarylazomalononitrile precursors with various substituted hetarylazopyrazole compounds. The synthesized heterocyclic disazo dyes were characterized using FT-IR, ^{1}H NMR, mass spectroscopy and elemental analysis. The solvatochromic effects of the dyes in various organic solvents were studied.

Keywords: Hetarylazopyrazole; Bis-hetarylazopyrazolo[1,5-*a*]pyrimidine; Disazo dyes; Solvents effect

1. Introduction

In recent years, substituted pyrazole and pyrazolo[1,5-*a*]-pyrimidine derivatives have proved to be useful synthetic intermediates in the dye industry and they have also been utilized in non-textile applications such as biodegradable agrochemicals, pharmaceuticals and photographic technology [1–17]. In previous work, we reported the synthesis of heterocyclic disazo dyes such as 3,6-bis-arylazopyrazolo[1,5-*a*]-pyrimidine, 3-arylazo-6-hetarylazo-pyrazolo[1,5-*a*]pyrimidine and 3-hetarylazo-6-arylazo-pyrazolo[1,5-*a*]pyrimidine and their solvatochromic properties [18,19]. It was found that λ_{max} of the disazo dyes containing a hetarylazo group at either the 3- or 6-position of the pyrazolo[1,5-*a*]pyrimidine ring occurred at longer wavelengths than the corresponding disazo dyes containing an arylazo group in the same position. In a continuation of these studies, we decided to investigate the synthesis and evaluation of novel, substituted 3,6-bis-hetarylazopyrazolo[1,5-*a*]pyrimidine heterocyclic disazo dyes which contained a variety of heterocyclens in the heterocyclic pyrazolo[1,5-*a*]pyrimidine ring system.

2. Results and discussion

2.1. Preparation of disazo dyes

The synthesis of substituted hetarylazopyrazole compounds **II** are outlined in Scheme 1. Hetaryl amines were diazotized [19–21] and coupled with malononitrile [18,19,22] to give the hetarylazomalononitrile precursors **I** and subsequent cyclization of **I** with an excess of hydrazine hydrate (65%) in ethanol (95%) under reflux for 3–4 h. The 3,5-diamino-4-hetarylazo-1H-pyrazole intermediates **II** were orange solids obtained in moderate yield. Several, symmetrical and asymmetrical 3,6-bis-hetarylazo-2,5,7-triaminopyrazolo[1,5-*a*]-pyrimidine heterocyclic disazo dyes **III**, **IV**, **V** and **VI** were prepared, as shown in Scheme 2. The symmetrical 3,6-bis-hetarylazo heterocyclic disazo dyes **IIIa–IIId** were synthesized, either by the cyclization of **Ia–Id** with hydrazine hydrate (65%) in the molar ratio 2:1 in ethanol (95%) under reflux for 3–4 h or by the reaction of **IIa–IId** with equimolar amounts of **Ia–Id**, being obtained as red-brown to purple

* Corresponding author.
E-mail address: iwang@tx.ntust.edu.tw (I.J. Wang).

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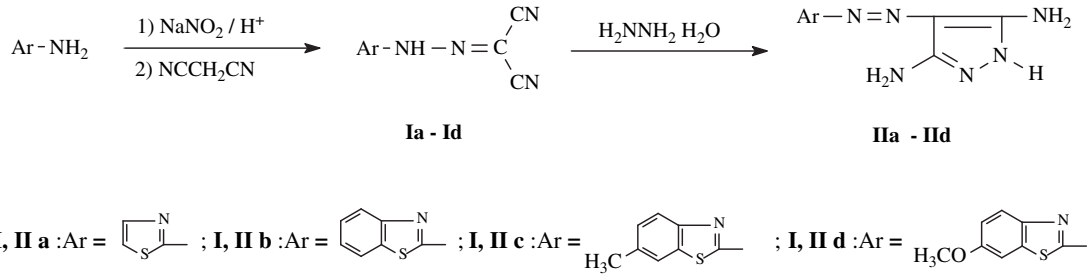
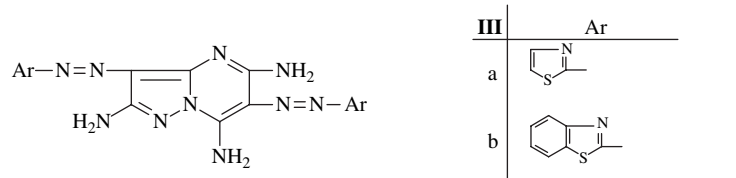


Scheme 1.

solids in low to moderate yield. The asymmetrical 3,6-bis-hetarylazoyl heterocyclic disazo dyes **IVa**–**IVc**, **Va**–**Vc** and **VIa**–**VIf** were obtained by reaction of **IIa**–**IId** with a variety of **Ia**–**Id** under similar conditions, yielding red-brown or purple solids, respectively. The relevant physical and spectral data of the disazo dyes are summarized in Section 3.

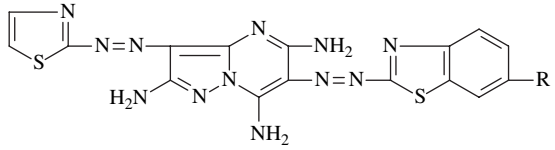
2.2. Solvatochromic properties of disazo dyes

The solvatochromic behaviour of disazo dyes **III**, **IV**, **V** and **VI** was systematically investigated in various solvents, namely, dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF) and acetone. The electronic spectra of the dyes were recorded at a concentration range of 10^{-6}–10^{-7} M (Table 1). It is evident that the absorption of the disazo dyes clearly depended on the properties of solvents. Generally, bathochromicity of absorption increased with increasing polarity of the solvents in the order: acetone < dimethylformamide < dimethyl sulfoxide. However, the λ_{max} of the dyes in all solvents did not change significantly. As shown in Fig. 1, the absorption spectra of dye **IIIa** in all solvents shifted bathochromically with respect to the absorption spectra in acetone (e.g. for dye **IIIa**



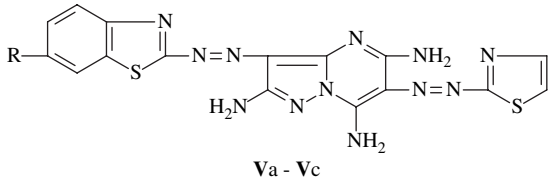
IIIa - **III**d

III	Ar
a	
b	
c	H_3C
d	H_3CO



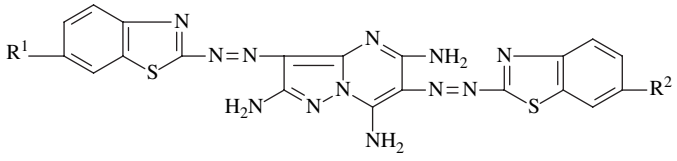
IVa - **IV**c

IVa R=H
b R=CH_3
c R=OCH_3



Va - **V**c

Va R=H
b R=CH_3
c R=OCH_3



VIa - **VI**f

VI	R^1	R^2
a	H	CH_3
b	H	OCH_3
c	CH_3	H
d	CH_3	OCH_3
e	OCH_3	H
f	OCH_3	CH_3

Scheme 2.

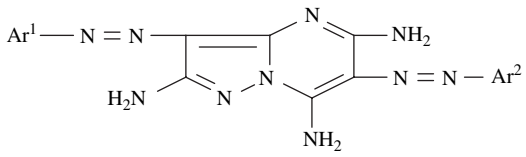
Table 1
Absorption spectra of dyes **III**, **IV**, **V** and **VI** in various solvents

Compounds	DMSO	DMF	Acetone	log ε (DMSO)
IIIa	511	506	499	4.54
IIIb	531	517	514	4.58
IIIc	542	538	534	4.52
IIId	551	546	542	4.66
IVa	525	519	512	4.46
IVb	527	523	516	4.51
IVc	532	528	521	4.56
Va	521	514	509	4.42
Vb	519	516	513	4.49
Vc	529	523	520	4.62
VIa	534	531	525	4.52
VIb	542	536	530	4.37
VIc	535	530	524	4.53
VId	544	540	535	4.68
VIe	539	537	532	4.53
VIf	550	546	540	4.58

The ε_r value of solvents: DMSO = 48.9; DMF = 36.7; acetone = 20.7.

λ_{max} was 511 nm in DMSO, 506 nm in DMF and 499 nm in acetone). Similar absorption shifts in all solvents were also found for the entire series of both the symmetrical dyes **III** and the asymmetrical disazo dyes **IV**, **V** and **VI**. Table 2 shows that disazo dyes **IIIa**, **IIIb**, **IVa** and **Va** had absorption maxima in the range 499–514 nm in acetone. The symmetrical disazo dye **IIIa**, possessing a thiazole residue in the 3,6-position of the pyrazolo[1,5-*a*]pyrimidine ring, adsorbed at shorter wavelengths in acetone than dyes **IIIb**, **IVa** and **Va** bearing a benzothiazolyl moiety in the 3 or 6-position of pyrazolo[1,5-*a*]-pyrimidine ring (Fig. 2). Replacement of a thiazolyl residue in dye **IIIa** by a benzothiazolyl residue at 6- or 3-position of heterocyclic pyrazolo[1,5-*a*]pyrimidine ring, as in dye **IVa** or **Va**, displaced the absorption maxima at 512 nm or 509 nm in acetone, so that the $\Delta\lambda_{max}$ value of **IVa** and **Va** showed bathochromic shifts of +13 nm and +10 nm, respectively, relative to dye **IIIa** due to the fact that the benzothiazole moiety possessed greater electron density than the thiazole moiety.

Table 2
Substituent effect of dyes **IIIa**, **IIIb**, **IVa** and **Va** in acetone



Compounds	λ_{max}	Ar^1	Ar^2	$\Delta\lambda$[a]
IIIa	499	Thiazolyl	Thiazolyl	–
IIIb	514	Benzothiazolyl	Benzothiazolyl	+15
IVa	512	Thiazolyl	Benzothiazolyl	+13
Va	509	Benzothiazolyl	Thiazolyl	+10

[a] Relative to (**IIIa**: $Ar^1 = Ar^2$ = Thiazolyl).

The influence on the absorption maxima of heterocyclic disazo dyes **III**, **IV**, **V** and **VI** of the introduction of substituents at the 6-position of the benzothiazole residue in the 3, 6-position of the pyrazolo[1,5-*a*]pyrimidine ring was systematically evaluated. As shown in Table 1, the absorption maxima of dyes **IIIb**–**IIId** were in the range 514–542 nm in acetone, 517–546 nm in DMF and 531–551 nm in DMSO, respectively. The introduction of electron donating methyl and methoxy groups into dye **IIIb** at the 6-position of the unsubstituted benzothiazole residue in the 3,6-position of pyrazolo[1,5-*a*]pyrimidine ring resulted in bathochromic shifts in all solvents. Dye **IIIc** exhibited bathochromic shifts of +11 nm (DMSO), +21 nm (DMF) and +20 nm (acetone) relative to dye **IIIb**, whereas **IIId** gave further shifts of +20 nm (DMSO), +29 nm (DMF) and +28 nm (acetone) relative to **IIIb**. It is evident that the presence of the electron donating methyl and methoxy groups imparted significant change to the absorption maxima in all solvents of dyes **IIIc** and **IIId**. From Table 3, it is apparent that the absorption maxima of dyes **IVa**–**IVc** were in the range 512–521 nm in acetone, whereas the similar dyes **Va**–**Vc** had absorption

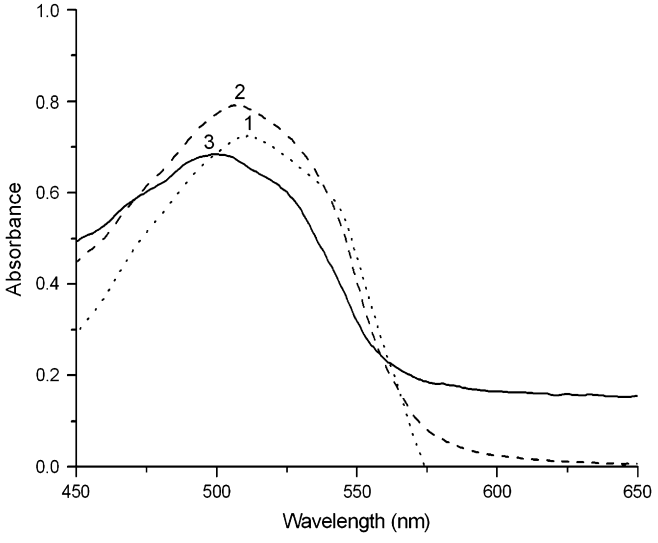


Fig. 1. Absorption spectra of dye **IIIa**: 1. DMSO; 2. DMF; 3. Acetone (conc.: 10^{-6}–10^{-7} mol/l).

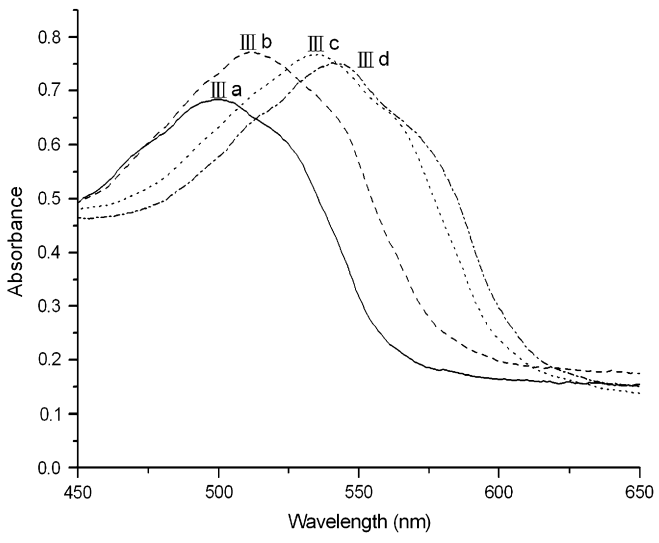
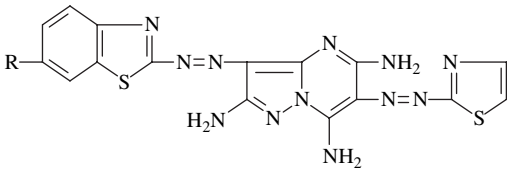
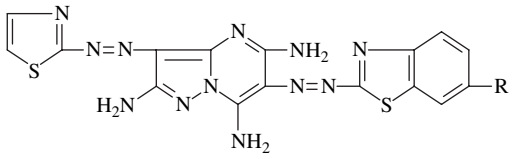


Fig. 2. Absorption spectra of dyes **IIIa**, **IIIb**, **IIIc** and **IIId** in acetone (conc.: 10^{-6}–10^{-7} mol/l).

Table 3
Substituent effect of dyes **IV** and **V** in acetone





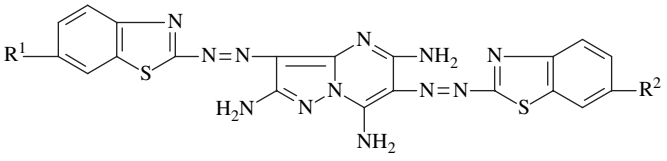
Compounds	λ_{max}	R	$\Delta\lambda$[a]	Compounds	λ_{max}	R	$\Delta\lambda$[b]	$\Delta\lambda$[c]
IVa	512	H	–	**Va**	509	H	–	+3
IVb	516	CH_3	+4	**Vb**	513	CH_3	+4	+3
IVc	521	OCH_3	+9	**Vc**	520	OCH_3	+11	+1

[a] Relative to (**IVa**: R = H).
[b] Relative to (**Vb**: R = H).
[c] Relative to λ_{max} (**IV**)−λ_{max} (**V**).

maxima in the range 509–520 nm in the same solvent. The introduction of electron donating methyl and methoxy groups into dye **IVa** at the 6-position of the unsubstituted benzothiazole residue resulted in bathochromic shifts in acetone, so that for dye **IVb** the $\Delta\lambda_{max}$ value was +4 nm relative to dye **IVa** and for dye **IVc** the $\Delta\lambda_{max}$ value was +9 nm relative to dye **IVa**. It was also observed that dyes **Vb**–**Vc** adsorbed bathochromically compared to dye **Va**. The $\Delta\lambda_{max}$ value of dye **Vb** was +4 nm in acetone compared to dye **V**a and the $\Delta\lambda_{max}$ of dye **Vc** was + 11 nm longer than **Va** in the same solvent. Additionally, the λ_{max} of **IVa**–**IVc** showed slight spectral shifts of between 1 and 3 nm in acetone relative to dyes **Va**–**Vc**, as shown in Table 3. It can be concluded that the introduction of an electron donating group (methyl or methoxy) at the 6-position of the unsubstituted benzothiazole residue in the 3- or 6-position of the pyrazolo[1,5-*a*]pyrimidine ring results only in a slight bathochromic shift in acetone. It is also observed that the λ_{max} of dyes **IV** and **V** did not change significantly in polar aprotic solvents DMSO and DMF, as shown in Table 1.

The effect of substituents in dye **VI** compared to dyes **IIIb**–**IIId** in acetone was also evaluated. It was found (Table 4) that the introduction of an electron donating group (methyl or methoxy) into dye **IIIb** at the 6-position of the benzothiazolyl group at the 3- or 6-position of the pyrazolo[1,5-*a*]-pyrimidine ring resulted in bathochromic shifts in acetone (e.g. for dye **VIa** $\Delta\lambda_{max} = +11$ nm, for **VIb** $\Delta\lambda_{max} = +16$ nm, for dye **VIc** $\Delta\lambda_{max} = +10$ nm, and for dye **VIe** $\Delta\lambda_{max} = +18$ nm

Table 4
Substituent effect of dyes **IIIb**–**IIId**, and **VIa**–**VIe** in acetone



Compounds	λ_{max}	R^1	R^2	$\Delta\lambda$
IIIb	514	H	H	–[a]
VIa	525	H	CH_3	+11[a]
VIb	530	H	OCH_3	+16[a]
VIc	524	CH_3	H	+10[a]
VIe	532	OCH_3	H	+18[a]
IIIc	534	CH_3	CH_3	–[b]
VIc	524	CH_3	H	−10[b]
VId	535	CH_3	OCH_3	+1[b]
VIa	525	H	CH_3	−9[b]
VIf	540	OCH_3	CH_3	+6[b]
IIId	542	OCH_3	OCH_3	–[c]
VIe	532	OCH_3	H	−20[c]
VIf	540	OCH_3	CH_3	−2[c]
VIb	530	H	OCH_3	−12[c]
VId	535	CH_3	OCH_3	−7[c]

[a] Relative to (**IIIb**: $R^1 = H$, $R^2 = H$).
[b] Relative to (**IIIc**: $R^1 = CH_3$, $R^2 = CH_3$).
[c] Relative to (**IIId**: $R^1 = OCH_3$, $R^2 = OCH_3$).

relative to dye **IIIb**). Interestingly, it was observed that the absorption spectra of dye **VI** resulted in different spectral shifts compared to dye **IIIc**. The disazo dyes **VIa** and **VIc** exhibited hypsochromic shifts of −10 nm and −9 nm, relative to dye **IIIc**, whereas dyes **VId** and **VIf** exhibited a bathochromic shift of +1 nm and +6 nm relative to **IIIc**. It was also observed that the absorption maxima of **VI** shifted hypsochromically with respect to **IIId** (e.g. for dye **VIe** $\Delta\lambda_{max} = -20$ nm, for dye **VIf** $\Delta\lambda_{max} = -2$ nm, for dye **VIb** $\Delta\lambda_{max} = -12$ nm and for dye **VId** $\Delta\lambda_{max} = -7$ nm relative to **IIId**).

3. Experimental

All melting points were uncorrected and in °C. IR spectra were recorded on a JASCO FT-IR-3 spectrophotometer (KBr); ^{1}H NMR spectra were obtained on a Joel-EX-400 MHz NMR spectrophotometer and chemical shifts are expressed in δ ppm using TMS as internal standard. 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 spectrophotometer.

*3.1. Preparation of 2-hetarylazo-malononitrile derivatives **Ia–Id***

The 2-hetarylazo-malononitrile compounds, **Ia–Ib**, were prepared according to the procedure described in the literature [19]. The same procedures were used for the syntheses of compounds **Ic–Id**, as represented by the preparation of compound **I**c below.

*3.1.1. 2-(6-Methylbenzothiazolylazo)-malononitrile (**Ic**)*

A sulfuric acid solution (50%; 10 ml) of 2-amino-6-methylbenzothiazole (1.64 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, to which was added an aqueous solution (10 ml) of malononitrile (0.66 g, 0.01 mol) and stirring was continued at 0 °C for 2 h. The resulting product was filtered, washed with water, dried and recrystallized from ethanol to give **Ic** as yellow crystals (1.32 g, 55%), m.p. 156–159 °C; *m/e* 241.0 (M^+); FT-IR (KBr, cm^{-1}): 2229 ν (C≡N); $C_{11}H_7N_5S$ Calcd: C, 54.71; H, 2.91; N, 29.05; Found: C, 54.81; H, 2.88; N, 29.11.

*3.1.2. 2-(6-Methoxybenzothiazolylazo)-malononitrile (**Id**)*

Yield of crude product 52%, yellow crystals purified by recrystallization from ethanol; m.p. 211–213 °C; *m/e* 257.0 (M^+); FT-IR (KBr, cm^{-1}): 2222 ν (C≡N); $C_{11}H_7N_5OS$ Calcd: C, 51.36; H, 2.72; N, 27.24; Found: C, 51.32; H, 2.74; N, 27.38.

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

The 4-hetarylazo-3,5-diaminopyrazole compounds **IIa** and **IIb** were prepared according to the procedure described in the literature [19]. The syntheses of the monoazo dyes **IIc** and **IId** were carried out by the same procedures, as described below for the preparation of dye **IIc**.

*3.2.1. 4-(6-Methylbenzothiazolylazo)-3,5-diaminopyrazole (**IIc**)*

Hydrazine hydrate (0.59 g, 0.01 mol) was added to a solution of **Ic** (2.41 g, 0.01 mol) in 30 ml of ethanol (95%) together with 0.5 ml of pyridine. The reaction mixture was heated under reflux for 3–4 h and cooled to room temperature. The precipitate was filtered, dried and recrystallized from ethanol to give **IIc** as orange solids (1.36 g, 50%), m.p. >300 °C; *m/e* 273.1 (M^+); FT-IR (KBr, cm^{-1}): 3391 ν (N-H), 1623 ν (C=N); ^{1}H NMR (DMSO-d_6) δ, ppm: 2.36 (3H, s, CH_3), 7.19–7.68 (3H, m, benzothiazolyl-H); $C_{11}H_{11}N_7S$ Calcd: C, 48.35; H, 4.01; N, 35.89; Found: C, 48.37; H, 3.98; N, 35.98.

*3.2.2. 4-(6-Methoxybenzothiazolylazo)-3,5-diaminopyrazole (**IId**)*

This compound was obtained from **Id** and hydrazine hydrate as orange crystals purified by recrystallization from ethanol; yield of crude product 49%; m.p. >300 °C; *m/e* 289.0 (M^+); FT-IR (KBr, cm^{-1}): 3390 ν (N-H), 1635 ν (C=N); ^{1}H NMR (DMSO-d_6) δ, ppm: 3.81 (3H, s, OCH_3), 7.00–7.67 (3H, m, benzothiazolyl-H); $C_{11}H_{11}N_7OS$ Calcd: C, 45.67; H, 3.81; N, 33.91; Found: C, 45.71; H, 3.83; N, 33.79.

*3.3. Preparation of symmetrical and asymmetric heterocyclic disazo dyes **III**, **IV**, **V** and **VI***

These disazo dyes were prepared by the cyclization of **Ia–Id** with **IIa–IId**.

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

The 3,6-bis-hetarylazo-3,5-diaminopyrazole compounds **IIIa–IIIb** were prepared according to the procedure described in the literature [19]. The syntheses of disazo dye **IIIa–IIId** 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**) [19]. Method A:* To a solution of **Ia** (3.54 g, 0.02 mol) in 30 ml of ethanol (95%) was added 1 ml of pyridine hydrazine hydrate (0.59 g, 0.01 mol). The reaction mixture was heated under reflux for 3–4 h and then cooled to room temperature. The resulting product was filtered, washed with hot ethanol, dried and recrystallized from DMF to give a pale red-brown solid 3,6-dithiazolylazo-2,5,7-triaminopyrazolo[1,5-*a*]pyrimidine (**IIIa**) (1.93 g, 50%), m.p. >300 °C; *m/e* 386.0 (M^+); FT-IR (KBr, cm^{-1}): 3294 ν (N-H), 1608 ν (C=N); ^{1}H NMR (DMSO-d_6) δ, ppm: 7.33 (1H, d, 5-thiazole-H), 7.63 (1H, d, 4-thiazole-H); $C_{12}H_{10}N_{12}S_2$ Calcd: C, 31.08; H, 2.59; N, 43.52; Found: C, 31.12; H, 2.61; N, 43.41.

Method B: To a solution of **IIa** (2.09 g, 0.01 mol) in 30 ml ethanol (95%) was added 0.5 ml of pyridine compound **Ia** (1.77 g, 0.01 mol). The reaction mixture was heated under reflux for 3–4 h and cooled to room temperature. The resulting

product was filtered, washed with hot ethanol, dried and recrystallized from DMF to give a pale red-brown solid **IIIa** (2.01 g, 52%), m.p. >300 °C.

*3.3.1.2. 3,6-Dibenzothiazolylazo-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**IIIb**) [19]. Method A:* The compound was obtained from **Ib** and hydrazine hydrate as red-brown crystals purified by recrystallization from DMF; the yield of the crude product was 43%; m.p. >300 °C; *m/e* 486.0 (M^+); FT-IR (KBr, cm^{-1}): 3279 ν (N-H), 1608 ν (C=N); ^1H NMR (DMSO-d_6) δ, ppm: 6.97 (2H, s, NH_2), 7.45–8.02 (8H, m, benzothiazolyl-H); $C_{20}H_{14}N_{12}S_2$ Calcd: C, 49.38; H, 2.88; N, 34.56; Found: C, 49.35; H, 2.89; N, 34.65.

Method B: The compound was obtained from **Ib** and **IIb**; yield of crude product 47%; m.p. >300 °C.

*3.3.1.3. 3,6-Di-(6-methylbenzothiazolylazo)-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**IIIc**). Method A:* The compound was obtained from **Ic** and hydrazine hydrate as purple crystals purified by recrystallization from DMF; yield of crude product 45%; m.p. >300 °C; *m/e* 514.0 (M^+); FT-IR (KBr, cm^{-1}): 3420 ν (N-H), 1616 ν (C=N); ^1H NMR (DMSO-d_6) δ, ppm: 2.39 (6H, s, CH_3), 7.17–7.93 (6H, m, benzothiazolyl-H); $C_{22}H_{18}N_{12}S_2$ Calcd: C, 51.36; H, 3.50; N, 32.68; Found: C, 51.37; H, 3.48; N, 32.75.

Method B: This compound was obtained from **Ic** and **IIc**; yield of crude product 46%; m.p. >300 °C.

*3.3.1.4. 3,6-Di-(6-methoxybenzothiazolylazo)-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**IIId**). Method A:* The compound was obtained from **Id** and hydrazine hydrate as purple crystals purified by recrystallization from DMF; yield of crude product 42%; m.p. >300 °C; *m/e* 546.0 (M^+); FT-IR (KBr, cm^{-1}): 3279 ν (N-H), 1608 ν (C=N); ^1H NMR (DMSO-d_6) δ, ppm: 3.81 (6H, s, OCH_3), 7.21 (2H, s, NH_2), 6.98–7.79 (6H, m, benzothiazolyl-H); $C_{22}H_{18}N_{12}O_2S_2$ Calcd: C, 48.35; H, 3.29; N, 30.77; Found: C, 48.33; H, 3.31; N, 30.85.

Method B: The compound was obtained from **Id** and **IId**; yield of crude product 44%; m.p. >300 °C.

*3.3.2. Preparation of asymmetric heterocyclic disazo dyes **IV**, **V** and **VI***

The syntheses of disazo dyes **IV**, **V** and **VI** followed the same procedures as described below for the preparation of dye **IIIa** (*Method B*).

*3.3.2.1. 6-Benzothiazolylazo-3-thiazolylazo-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**IVa**).* The compound was obtained from **Ib** and **IIa** as purple crystals purified by recrystallization from DMF; yield of crude product 56%; m.p. >300 °C; *m/e* 436.2 (M^+); FT-IR (KBr, cm^{-1}): 3257 ν (N-H), 1601 ν (C=N); ^1H NMR (DMSO-d_6) δ, ppm: 7.09–7.81 (4H, m, benzothiazolyl-H), 7.95 (1H, d, 5-thiazolyl-H), 8.01 (1H, d, 4-thiazolyl-H); $C_{16}H_{12}N_{12}S_2$ Calcd: C, 44.04; H, 2.75; N, 38.53; Found: C, 44.08; H, 2.63; N, 38.61.

*3.3.2.2. 6-(6-Methylbenzothiazolylazo)-3-thiazolylazo-2,5,7-triaminopyrazolo-[1,5-a]pyrimidine (**IVb**).* The compound was obtained from **Ic** and **IIa** as red-brown crystals purified by recrystallization from DMF; yield of crude product 54%; m.p. >300 °C; *m/e* 450.1 (M^+); FT-IR (KBr, cm^{-1}): 3420 ν (N-H), 1631 ν (C=N); ^1H NMR (DMSO-d_6) δ, ppm: 2.42 (3H, s, CH_3), 7.31–7.52 (3H, m, benzothiazolyl-H), 7.82 (1H, d, 5-thiazolyl-H), 7.98 (1H, d, 4-thiazolyl-H); $C_{17}H_{14}N_{12}S_2$ Calcd: C, 45.33; H, 3.11; N, 37.33; Found: C, 45.29; H, 3.15; N, 37.31.

*3.3.2.3. 6-(6-Methoxybenzothiazolylazo)-3-thiazolylazo-2,5,7-triaminopyrazolo-[1,5-a]pyrimidine (**IVc**).* The compound was obtained from **Id** and **IIa** as red-brown crystals purified by recrystallization from DMF; yield of crude product 55%; m.p. >300 °C; *m/e* 466.0 (M^+); FT-IR (KBr, cm^{-1}): 3279 ν (N-H), 1602 ν (C=N); ^1H NMR (DMSO-d_6) δ, ppm: 3.85 (3H, s, OCH_3), 7.10–7.57 (3H, m, benzothiazolyl-H), 7.79 (1H, d, 5-thiazolyl-H), 8.01 (1H, d, 4-thiazolyl-H); $C_{17}H_{14}N_{12}OS_2$ Calcd: C, 43.78; H, 3.01; N, 36.05; Found: C, 43.72; H, 3.07; N, 36.01.

*3.3.2.4. 3-Benzothiazolylazo-6-thiazolylazo-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**Va**).* The compound was obtained from **Ia** and **IIb** as red-brown crystals purified by recrystallization from DMF; yield of crude product 54%; m.p. >300 °C; *m/e* 436.1.0 (M^+); FT-IR (KBr, cm^{-1}): 3427 ν (N-H), 1594 ν (C=N); ^1H NMR (DMSO-d_6) δ, ppm: 7.28–7.91 (4H, m, benzothiazolyl-H), 7.45 (1H, d, 5-thiazolyl-H), 7.70 (1H, d, 4-thiazolyl-H); $C_{16}H_{12}N_{12}S_2$ Calcd: C, 44.04; H, 2.75; N, 38.53; Found: C, 43.99; H, 2.70; N, 38.59.

*3.3.2.5. 3-(6-Methylbenzothiazolylazo)-6-thiazolylazo-2,5,7-triaminopyrazolo-[1,5-a]pyrimidine (**Vb**).* The compound was obtained from **Ia** and **IIc** as red-brown crystals purified by recrystallization from DMF; yield of crude product 55%; m.p. >300 °C; *m/e* 450.1 (M^+); FT-IR (KBr, cm^{-1}): 3154 ν (N-H), 1601 ν (C=N); ^1H NMR (DMSO-d_6) δ, ppm: 2.42 (3H, s, CH_3), 7.26 (1H, d, 5-thiazolyl-H), 7.26–7.89 (3H, m, benzothiazolyl-H), 7.79 (1H, d, 4-thiazolyl-H); $C_{17}H_{14}N_{12}S_2$ Calcd: C, 45.33; H, 3.11; N, 37.33; Found: C, 45.28; H, 3.05; N, 37.39.

*3.3.2.6. 3-(6-Methoxybenzothiazolylazo)-6-thiazolylazo-2,5,7-triaminopyrazolo-[1,5-a]pyrimidine (**Vc**).* The compound was obtained from **Ia** and **IId** as red-brown crystals purified by recrystallization from DMF; yield of crude product 43%; m.p. >300 °C; *m/e* 466.0 (M^+); FT-IR (KBr, cm^{-1}): 3390 ν (N-H), 1608 ν (C=N); ^1H NMR (DMSO-d_6) δ, ppm: 3.84 (3H, s, OCH_3), 7.04–7.69 (3H, m, benzothiazolyl-H), 7.19 (1H, d, 5-thiazolyl-H), 7.88 (1H, d, 4-thiazolyl-H); $C_{17}H_{14}N_{12}OS_2$ Calcd: C, 43.78; H, 3.01; N, 36.05; Found: C, 43.73; H, 3.06; N, 36.11.

*3.3.2.7. 3-Benzothiazolylazo-6-(6-methylbenzothiazolylazo)-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**VIa**).* The compound was obtained from **Ic** and **IIb** as red-brown crystals purified by recrystallization from DMF; yield of crude product 45%; m.p. >300 °C; *m/e* 500.3 (M^+); FT-IR (KBr, cm^{-1}): 3360 ν

(N-H), 1623 ν (C=N); ^{1}H NMR (DMSO-d_6) δ, ppm: 2.36 (3H, s, CH_3), 7.26–7.89 (7H, m, benzothiazolyl-H); $C_{21}H_{16}N_{12}S_2$ Calcd: C, 50.4; H, 3.2; N, 33.6; Found: C, 50.33; H, 3.27; N, 33.64.

*3.3.2.8. 3-Benzothiazolylazo-6-(6-methoxybenzothiazolylazo)-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**VIb**).* The compound was obtained from **Id** and **IIb** as red-brown crystals purified by recrystallization from DMF; yield of crude product 44%; m.p. >300 °C; *m/e* 516.1 (M^+); FT-IR (KBr, cm^{-1}): 3176 ν (N-H), 1601 ν (C=N); ^{1}H NMR (DMSO-d_6) δ, ppm: 3.86 (3H, s, OCH_3), 7.10–7.98 (7H, m, benzothiazolyl-H); $C_{21}H_{16}N_{12}OS_2$ Calcd: C, 48.84; H, 3.1; N, 32.56; Found: C, 48.79; H, 3.12; N, 36.51.

*3.3.2.9. 6-Benzothiazolylazo-3-(6-methylbenzothiazolylazo)-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**VIc**).* The compound was obtained from **Ib** and **IIc** as red-brown crystals purified by recrystallization from DMF; yield of crude product 44%; m.p. >300 °C; *m/e* 500.2 (M^+); FT-IR (KBr, cm^{-1}): 3265 ν (N-H), 1616 ν (C=N); ^{1}H NMR (DMSO-d_6) δ, ppm: 2.50 (3H, s, CH_3), 7.05–7.87 (7H, m, benzothiazolyl-H); $C_{21}H_{16}N_{12}S_2$ Calcd: C, 50.4; H, 3.2; N, 33.6; Found: C, 50.46; H, 3.21; N, 33.51.

*3.3.2.10. 3-(6-Methylbenzothiazolylazo)-6-(6-methoxybenzothiazolylazo)-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**VId**).* The compound was obtained from **Id** and **IIc** as purple crystals purified by recrystallization from DMF; yield of crude product 42%; m.p. >300 °C; *m/e* 530.1 (M^+); FT-IR (KBr, cm^{-1}): 3427 ν (N-H), 1608 ν (C=N); ^{1}H NMR (DMSO-d_6) δ, ppm: 2.35 (3H, s, CH_3), 3.79 (3H, s, OCH_3), 6.98–8.11 (6H, m, benzothiazolyl-H); $C_{22}H_{18}N_{12}OS_2$ Calcd: C, 49.81; H, 3.39; N, 31.7; Found: C, 49.77; H, 3.42; N, 31.63.

*3.3.2.11. 6-Benzothiazolylazo-3-(6-methoxybenzothiazolylazo)-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**VIe**).* The compound was obtained from **Ib** and **IId** as purple crystals purified by recrystallization from DMF; yield of crude product 44%; m.p. >300 °C; *m/e* 516.2 (M^+); FT-IR (KBr, cm^{-1}): 3413 ν (N-H), 1601 ν (C=N); ^{1}H NMR (DMSO-d_6) δ, ppm: 3.81 (3H, s, OCH_3), 7.02–7.67 (7H, m, benzothiazolyl-H); $C_{21}H_{16}N_{12}OS_2$ Calcd: C, 48.84; H, 3.1; N, 32.56; Found: C, 48.76; H, 3.17; N, 36.45.

*3.3.2.12. 3-(6-Methoxybenzothiazolylazo)-6-(6-methylbenzothiazolylazo)-2,5,7-triaminopyrazolo[1,5-a]pyrimidine (**VIf**).* The compound was obtained from **Ic** and **IId** as purple crystals purified by recrystallization from DMF; yield of crude product 40%; m.p. >300 °C; *m/e* 530.0 (M^+); FT-IR (KBr, cm^{-1}): 3327 ν (N-H), 1602 ν (C=N); ^{1}H NMR (DMSO-d_6) δ, ppm: 2.41 (3H, s, CH_3), 3.82 (3H, s, OCH_3), 7.01–7.93 (6H, m, benzothiazolyl-H); $C_{22}H_{18}N_{12}OS_2$ Calcd: C, 49.81; H, 3.39; N, 31.7; Found: C, 49.83; H, 3.42; N, 31.61.

4. Conclusions

New 3,6-bis-hetarylazo-2,5,7-triaminopyrazolo[1,5-*a*]-pyrimidine heterocyclic disazo dyes were synthesized by the reaction of substituted hetarylazomalononitrile precursors with various substituted hetarylazopyrazole compounds. In the cases of dyes **III**, **IV**, **V** and **VI**, bathochromicity of absorption increased with increasing polarity of the solvents in the order: DMSO > DMF > acetone. The results of substituent effects on the various positions of dyes (**III**, **IV**, **V** and **VI**) indicated that the absorption maxima of dyes were only slightly influenced by substituents.

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References

[1] Masoud MS, Khalil EA, Hindawy AM, Ali AE, Mohamed EF. Spectrochimica Acta. Part A: Molecular and Biomolecular Spectroscopy 2004; 60:2807.
[2] Nasr MR. Spectrochimica Acta. Part A: Molecular and Biomolecular Spectroscopy 2004;60:1917.
[3] Nag JK, Santra PK, Sinha C, Liao FL, Lu TH. Polyhedron 2001;20:2253.
[4] Santra PK, Ray U, Pal S, Sinha C. Inorganic Chemistry Communications 2001;4:269.
[5] Elnagdi MH, Fahmy SM, Zayed EM, Ilias MAM. Zeitschrift fur Naturforschung B 1976;31:795.
[6] Auzzi G, Bruni F, Costanzo A, Vettori LP, Pirsino R, Corrias M, et al. Journal of Medicinal Chemistry 1983;26:1706.
[7] Robins R, O'Brien DE, Novinson T, Springer RH. German Patent 2 257 547; 1972 (Chemical Abstract 1973;79:78840).
[8] Zeng H, Lin Zp, Sartorelli AC. Biochemical Pharmacology 2004;68:911.
[9] Sharma P, Rane N, Gurram VK. Bioorganic and Medicinal Chemistry Letters 2004;14:4185.
[10] Huang CQ, Wilcoxen KM, Grigoriadis DM, McCarthy JR, Chen C. Bioorganic and Medicinal Chemistry Letters 2004;14:3943.
[11] Dhavale DD, Matin MM, Sharma T, Sabharwal SG. Bioorganic and Medicinal Chemistry Letters 2004;12:4039.
[12] West TP. Microbiological Research 2004;29:159.
[13] Devesa I, Alcaraz MJ, Riguera R, Ferrandiz ML. European Journal of Pharmacology 2004;488:225.
[14] David DR. British Patent, 1491604; 1977.
[15] Brooker, White. US Patent, 2646409; 1953.
[16] HO YW. Dyes and Pigments 2005;64:223.
[17] Karcı F, Demirçalı A. Dyes and Pigments 2007;74:288.
[18] Tsai PC, Wang IJ. Dyes and Pigments 2005;64:259.
[19] Tsai PC, Wang IJ. Dyes and Pigments 2007;74:578.
[20] Yen MS, Wang IJ. Dyes and Pigments 2004;61:243.
[21] Yen MS, Wang IJ. Dyes and Pigments 2004;63:1.
[22] Ho YW, Wang IJ. Dyes and Pigments 1995;29:181.